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TESIS DOCTORAL

Vinylic addition polynorbornene as catalyst support: Applications in organocatalysis and palladium-catalyzed C-C coupling reactions.

Presentada por Jesús Ángel Molina de la Torre para
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Dirigida por:
Ana Carmen Albéniz Jiménez

AUTORIZACIÓN DE LA DIRECTORA DE TESIS

Ana Carmen Albéniz Jiménez, Catedrática de Química Inorgánica de la Universidad de Valladolid e investigadora del I. U. CINQUIMA

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Jesús A. Molina de la Torre y Ana C. Albéniz.
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A mi familia y a Ana

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Preface

Preface

Supported catalysis is a powerful tool which comprises interesting and advantageous properties from heterogeneous catalysts (reusability, easy separation…) and homogenous systems (selectivity, capability to modify electronic or steric features…). As far as sustainability is concerned this is a good solution to reduce wastes and costs in some processes. Among the many different solid supports used, polymers have an increasing interest due to the improvement in their syntheses. New functionalizations and better control over their real composition make them a good choice in this regard.

Our group has previously developed new vinylic addition polynorbornenes with different functional groups such as ω-halogen alkyl chains or tin derivatives proving their applicability as support of reagents in the Stille reaction. We considered that this kind of polymer can be also effective as support of some catalysts because of its attractive properties such as high thermal stability and robustness. Its structure only contains single C-C and C-H bonds; there are no heteroatoms, multiple bonds, aromatic rings or benzylic positions, susceptible of undergoing side reactions that could degrade the polymer backbone.

The work presented in this thesis is focused on the development of different catalysts supported on vinylic addition polynorbornenes and their application in several useful reactions. It is divided in five chapters. *Chapter 1* is a general introduction about supported catalysis and the different types of polynorbornene. The remaining four chapters are subdivided in four sections: introduction, results and discussion, conclusions and experimental part.

Chapter 2 and *Chapter 3* describe the results obtained when supporting N-Heterocyclic Carbenes onto the polymer. The first one contains the different routes used to synthesized polymer-supported imidazolium salts and the application of the corresponding free carbenes as organocatalysts in some organic transformations. The second one describes the outcome of our work in the synthesis of supported Pd-NHC complexes and their uses in organometallic catalysis, namely, C-C cross coupling reactions.

Chapter 5 is dedicated to the use of vinylic addition polynorbornenes as scaffold in the synthesis of Pd-diimine complexes. Different approaches are commented and the results of the use of these complexes in catalysis are described.

Chapter 4 includes a study of the behavior of different solvents in the presence of palladium complexes and their possible risks. Although, not fully related with the central goal of this thesis, some results observed during our main research led us to consider the interest in having a better knowledge of these risks.

This dissertation contains an appendix with the abbreviations used and an index of the compounds described which are numbered in order of appearance. Every reference appears at the foot of the page where it is cited and additionally in the appendix to ease the search of cross references. This thesis is presented to obtain the International Ph.D. degree and, as part of the doctoral training, it was chosen to write this dissertation in English. To comply with the current regulations of the UVa, it includes a brief summary of the results in Spanish, with its own bibliography, as well as an index and the general conclusions.

Chapter 1

1. General Introduction.

1.1 Relevance of catalysis

On looking for a sustainable world, modern chemistry is deeply focused on the accomplishment of the objectives of the so-called green chemistry.[1]

Enhancement of known processes, development of greener methodologies or upgrading of equipment must concentrate the efforts in both academic and industrial chemistry. Furthermore, from an industrial point of view, it would be desired to decrease, not only direct costs from energy and raw materials, but also resulting costs from waste treatment in many interesting synthetic processes. Among the multiple choices to fulfil these objectives, catalysis is one of the most convenient and conventional routes to minimize times and energy expenses. Additionally, easy-recoverable catalysts able to be reused contribute to raise even further the advantages of the catalysis.[2]

Nowadays, catalysis is involved in more than 85% of the world's chemical processes.[3] A vast majority of this production is centered in bulk chemicals (products largely manufactured with low complexity), for example, sulfuric acid, ammonia or petroleum

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[1] (a) Anastas, P. T.; Warner, J. C. *Green Chemistry: Theory and Practice*; Oxford University Press*:* New York, **1998**. (b) Winterton, N. *Green Chem.* **2001**, *3*, G73-G75. (c) Horvath, I. T.; Anastas, P. T. *Chem. Rev*. **2007**, *107*, 2169-2173.

[2] (a) Descorme, C.; Gallezot, P.; Geantet, C.; George, C. *ChemCatChem*, **2012**, *4*, 1897-1906. (b) de Jong, K. P. In *Synthesis of solid catalysts*; de Jong, K. P. Ed.; Wiley-VCH: Weinheim, **2009**, ch 1.

[3] (a) Fechete, I.; Wang, Y.; Védrine, J. C. *Catal. Today*, **2012**, 2-27. (b) Dumesic, J. A.; Huber, G. W.; Boudart, M. In *Handbook of heterogeneous catalysis*; Ertl, G.; Knözinger, H.; Schüth, F.; Weitkamp, J., Eds.; Wiley-VCH: Weinheim, **2008**, Vol. 1, ch 1.1.

cracking products like ethylene and propylene.[4] In all these cases heterogeneous catalysis (vanadium oxide on silica, iron or zeolites) is successfully applied. Traditionally, most of the heterogeneous catalysts are metal-based systems which carry out the catalytic reactions on their surfaces. Although quite effective, their performance usually is accompanied by a lack of knowledge of the reaction mechanisms because of the complexity and diversity of the interactions between surfaces and reagents. An irregular surface implies different types of coordination spheres for the atoms in the surface (Figure 1.1). It can be challenging to discover the true active site of the catalyst.

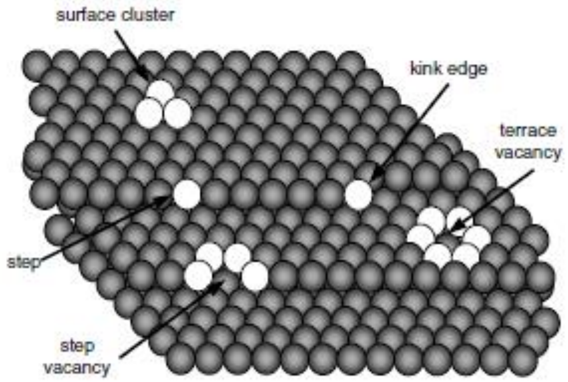

Figure 1.1: Schematic representation of a solid catalyst crystal surface.

On the other hand, in order to produce fine chemicals (substances with higher complexity and high added value), such as pharmaceutical or agrochemical products, more specific systems with better control over the reaction pathways are often required. In this case well-defined catalysts are commonly used in one or more of the reactions needed to make the product (Scheme 1.1). It is well known that transition-metal complexes or organic molecules are used as catalysts in countless homogeneous reactions with outstanding results.[5] However, most of these processes imply the loss of the catalyst after the reaction due to its difficult recovery.[6] This shortcoming entails two major problems. From an

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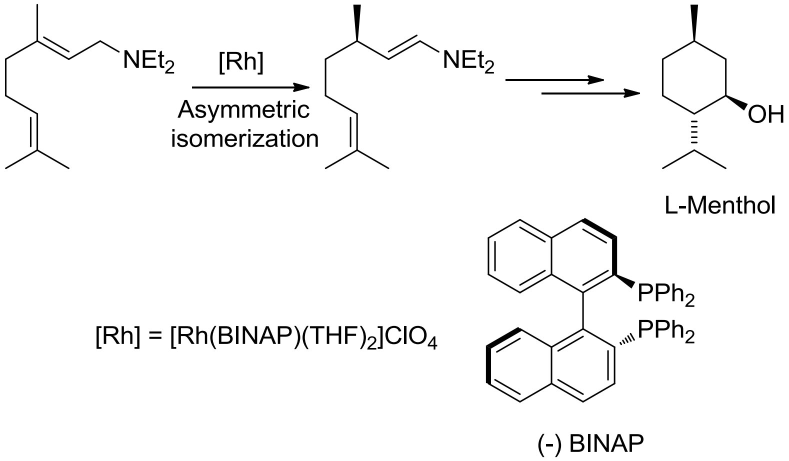
[4] McCoy, M.; Reisch, M.; Tullo, A. H. *Chem. Eng. News*, **2006**, *84* (28), 59-68.

[5] van Leeuwen, P. W. N. M. *Homogeneous Catalysis: Understanding the Art*; Kluwer Academic Publishers: Dordrecht, **2004**.

[6] (a) Welch, C. J.; Albaneze-Walker, J.; Leonard, W. R.; Biba, M.; DaSilva, J.; Henderson, D.; Laing, B.; Mathre, D. J.; Spencer, S.; Bu, X.; Wang, T. *Org. Process Res. Dev.* **2005**, *9*, 198-205. (b) Garrett, C. E.; Prasad, K. *Adv. Synth. Catal.* **2004**, *346*, 889-900. (c) Pagliaro, M.; Pandarus, V.; Ciriminna, R.; Béland, F.; Carà, P. D. *ChemCatChem*, **2012**, *4*, 432-445.

economical point of view, the loss of precious metals or complex organic molecules hard and expensive to synthesize implies higher overall costs of the processes. From an ecological perspective, the toxicity levels of these residues, especially in pharmaceutical or food products, must be carefully considered and additional steps to remove toxic wastes are usually necessary.



Scheme 1.1: Rhodium-catalyzed asymmetric isomerization of alkenes in the synthesis of L-Menthol.[7]

1.2 Supported catalysis

Among the different possibilities to achieve the recycling and reutilization of the catalysts in those reactions,[8] many efforts are being made to anchor the active species onto solid supports. The main objective of this technique is to obtain single-site heterogeneous catalysts which keep the reactivity of their homogeneous analogues. These “immobilized molecular catalysts” present combined characteristics of well-defined highly-tunable homogeneous species and easy-recoverable heterogeneous systems. In this regard, one of the likely options is the covalent binding of the catalyst or, in the event of transition metal complexes, some of their ligands, in some solid support. Among the different inorganic

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[7] Inoue, S. I.; Takaya, H.; Tani, K.; Otsuka, S.; Sato, T.; Noyori, R. *J. Am. Chem. Soc.* **1990**, *112*, 4897-4905.

[8] (a) Cole-Hamilton, D. *Science*, **2003**, *299*, 1702-1706. (b) Gladysz, J. A. *Chem. Rev.* **2002**, *102*, 3215-3216. (c) Gladysz J. A. In *Recoverable and Recyclable Catalysts*; Benaglia, M. Ed.; John Wiley & Sons, Ltd.: Chichester, **2009**, ch 1.

solids described, magnetic nanoparticles[9] or clays[10] can be found. Nevertheless, SiO_2 (amorphous and mesoporous) is by large the most used.[11] Sometimes these supports are developed like hybrids with organic molecules or with another inorganic solid like in the case of organometallic complexes supported on silica-coated magnetic nanoparticles (Figure 1.2).

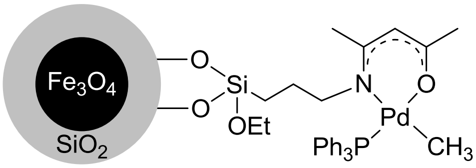

Figure 1.2: Magnetic nanoparticle-supported (β-oxoiminato)(phosphanyl) palladium complex reported by Jin.[12]

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[9] (a) Shylesh, S.; Schünemann, V.; Thiel, W. R. *Angew. Chem. Int. Ed.* **2010**, *49*, 3428-3459. (b) Polshettiwar, V.; Luque, R.; Fihri, A.; Zhu, H.; Bouhrara, M.; Basset, J. M. *Chem. Rev.* **2011**, *111*, 3036-3075. (c) Wang, D.; Astruc, D. *Chem. Rev.* **2014**, *114*, 6949-6985. (d) Gawande, M. B.; Branco, P. S.; Varma, R. S. *Chem. Soc. Rev.* **2013**, *42*, 3371-3393. (e) Xu, H. J.; Wan, X.; Geng, Y.; Xu, X. L. *Curr. Org. Chem.* **2013**, *17*, 1034-1050. (f) Pereira, C.; Pereira, A. M.; Quaresma, P.; Tavares, P. B.; Pereira, E.; Araújo, J. P.; Freire, C. *Dalton Trans.* **2010**, *39*, 2842-2854. (g) Rossi, L. M.; Costa, N. J. S.; Silva, F. P.; Wojcieszak, R. *Green Chem.* **2014**, *16*, 2906-2933. (h) Kainz, Q. M.; Reiser, O. *Acc. Chem. Res.* **2014**, *47*, 667-677.

[10] (a) Kuźniarska-Biernacka, I.; Silva, A. R.; Carvalho, A. P.; Pires, J; Freire, C. *Langmuir*, **2005**, *21*, 10825-10834. (b) Pereira, C.; Silva, A. R.; Carvalho, A. P.; Pires, J.; Freire, C. *J. Mol. Catal. A: Chem.* **2008**, *283*, 5-14. (c) Pereira, C.; Patrício, S.; Silva, A. R.; Magalhães, A. L.; Carvalho, A. P.; Pires, J.; Freire, C. *J. Colloid Interface Sci.* **2007**, *316*, 570-579. (d) Fariasa, M.; Martinelli, M.; Rolim, G. K. *Appl. Catal. A*, **2011**, *403*, 119-127.

[11] (a) McMorn, P.; Hutchings, G. J. *Chem. Soc. Rev.* **2004**, *33*, 108-122. (b) Thomas, J. M.; Raja, R.; Lewis, D. W. *Angew. Chem. Int. Ed.* **2005**, *44*, 6456-6482. (c) Corma, A.; Garcia, H. *Adv. Synth. Catal.* **2006**, *348*, 1391-1412. (d) Polshettiwara, V.; Molnár, A. *Tetrahedron*, **2007**, *63*, 6949-6976. (e) Margelefsky, E. L.; Zeidan, R. K.; Davis, M. E. *Chem. Soc. Rev.* **2008**, *37*, 1118-1126. (f) Basset, J. M.; Candy, J. P.; Copéret, C. In *Comprehensive Organometallic Chemistry III*; Crabtree, R. H.; Mingos, D. M. P., Eds.; Elsevier Ltd.: Amsterdam, **2007**, *Vol. 12*, ch 12.10. (g) Rendón, N.; Blanc, F.; Copéret, C. *Coord. Chem. Rev.* **2009**, *253*, 2015-2020. (h) Minakata, S.; Komatsu, M. *Chem. Rev.* **2009**, *109*, 711-724. (i) Polshettiwara, V.; Len C.; Fihri, A. *Coord. Chem. Rev.* **2009**, *253*, 2599-2626. (j) Camposa, J. M; Lourenço, J. P.; Cramail, H.; Ribeiro, M. R. *Prog. Polym. Sci.* **2012**, *37*, 1764-1804. (k) Díaz, U.; Brunel, D.; Corma, A. *Chem. Soc. Rev.* **2013**, *42*, 4083-4097. (l) Liang, Y.; Anwander, R. *Dalton Trans.* **2013**, *42*, 12521-12545. (m) Balcar, H.; Čejka, J. *Coord. Chem. Rev.* **2013**, *257*, 3107-3124. (n) Conley, M. P.; Copéret, C.; Thieuleux, C. *ACS Catal.* **2014**, *4*, 1458-1469. (o) Rostamnia, S.; Doustkhah, E. *RSC Adv.* **2014**, *4*, 28238-28248. (p) Molnár, A. In *Palladium-Catalyzed Coupling Reactions*; Molnár, A. Eds.; Wiley-VCH Verlag GmbH & Co. KGaA.: Weinheim, **2013**, ch 4.

[12] Jin, M. J.; Lee, D. H. *Angew. Chem. Int. Ed.* **2010**, *49*, 1119 –1122.

1.3 Polymer-supported catalysts

An alternative approach is the use of polymers as organic supports. Over the last decades there has been an increasing control over the polymerization techniques and post-functionalization reactions of the polymers. Many a different polymer has been described in the literature as support for both organic and organometallic catalysts.[13] It must be commented that some polymers are soluble in the reaction solvents so that the reaction is not performed in a heterogeneous way, but the option of recovering these supports by straightforward filtration after a simple change of the solvent makes them to be considered as heterogeneous-like recoverable systems.[14]

In the event of organocatalysis some useful organic molecules, for instance, prolines (along with prolineamides and diarylprolinols), cinchona alkaloids or imidazolidinones (Figure 1.3) have been attached to polystyrenes, poly (ethylene glycol) or other types of polymers.[14f,15] Some reactions performed by these polymer-supported catalysts have shown excellent yields as well as high enantioselectivities when chirality is concerned. Nitrogen Heterocyclic Carbenes (NHCs) have also demonstrated their value as organocatalysts in heterogeneous catalysis and they will be closely analyzed in chapter 2.

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[13] (a) Haag, R.; Roller, S. *Top. Curr. Chem.* **2004**, *242*, 1-42. (b) Dioos, B. M. L.; Vankelecom, I. F. J.; Jacobs, P. A. *Adv. Synth. Catal.* **2006**, *348*, 1413-1446. (c) Lu, J.; Toy, P. H. *Chem. Rev.* **2009**, *109*, 815-838. (d) Buchmeiser, M. R. *Polymeric Materials in Organic Synthesis and Catalysis*; Wiley-VCH Verlag GmbH & Co. KGaA.: Weinheim, **2003**.

[14] (a) Bergbreiter, D. E. *Chem. Rev.* **2002**, *102*, 3345-3384. (b) Dickerson, T. J.; Reed, N. N.; Janda, K. D. *Chem. Rev.* **2002**, *102*, 3325-3344. (c) Bergbreiter, D. E.; Sung, S. D. *Adv. Synth. Catal.* **2006**, *348*, 1352-1366. (d) Chinnusamy, T.; Hilgers, P.; Reiser, O. In *Recoverable and Recyclable Catalysts*; Benaglia, M. Eds.; John Wiley & Sons, Ltd.: Chichester, **2009**, ch. 4. (e) Bergbreiter, D. E.; Tian, J.; Hongfa, C. *Chem. Rev.* **2009**, *109*, 530-582. (f) Bergbreiter, D. E.; Yang, Y. C. *Pure Appl. Chem.* **2013**, *85*, 493-509.

[15] (a) Benaglia, M.; Puglisi, A.; Cozzi, F. *Chem. Rev.* **2003**, *103*, 3401-3429. (b) Kristensen, T. E.; Hansen, T. *Eur. J. Org. Chem.* **2010**, 3179-3204. (c) Itsuno, S.; Parvez, M.; Haraguchi, N. *Polym. Chem.* **2011**, *2*, 1942-1949. (d) Haraguchi, N.; Itsuno, S. In *Polymeric Chiral Catalyst Design and Chiral Polymer Synthesis*; Itsuno, S. Ed.; John Wiley & Sons, Inc.: Hoboken, **2011**, ch. 2. (e) Lu, J.; Toy, P. H. *Pure Appl. Chem.* **2013**, *85*, 543-556.

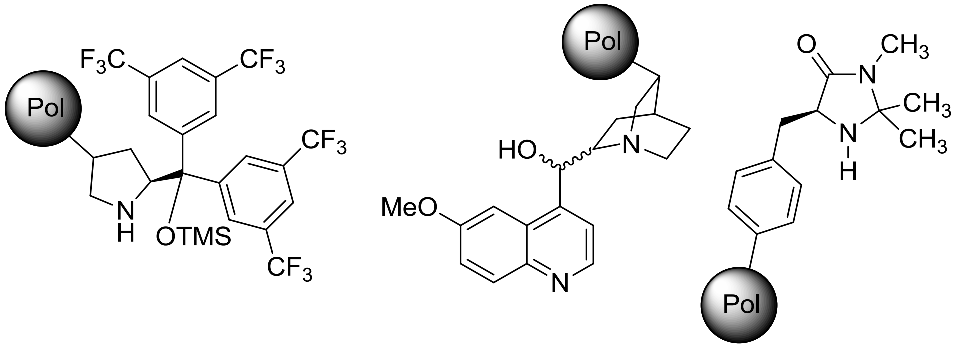

Figure 1.3: Polymer-supported organocatalysts.

Many metals have also been supported on polymers to be used in catalysis.[16] Cross-coupling reactions catalyzed by palladium[17], metathesis reactions with ruthenium or molybdenum[18] or polymerization of alkenes with metallocenes[19] are some interesting reactions performed by polymer-supported catalysts.

A particular family of polymers is the coordination polymers. In this group the metal is forming part of the main chain, coordinated to polidentate ligands that extend the structure. These self-supported catalysts can be linear or multidimensional depending on the organic linkers (ligands) employed to obtain them (Figure 1.4).[20] When they are displayed in a tridimensional way a mesoporous structure is formed and these polymers are also known

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[16] (a) Leadbeater, N. E.; Marco, M. *Chem. Rev*. **2002**, *102*, 3217-3274. (b) Kann, N. *Molecules*, **2010**, *15*, 6306-6331.

[17] (a) Uozumi, Y. *Top. Curr. Chem*. **2004**, *242*, 77-112. (b) Albéniz, A. C.; Carrera, N. *Eur. J. Inorg. Chem*. **2011**, 2347-2360. (c) Karimi, B.; Abedi, S.; Zamani, A. In *Palladium-Catalyzed Coupling Reactions;* Molnár, A. Ed.; Wiley-VCH Verlag GmbH & Co. KGaA.: Weinheim, **2013**, ch 5.

[18] (a) Copéret, C.; Basset, J. M. *Adv. Synth. Catal*. **2007**, *349*, 78-92. (b) Buchmeiser, M. R. *Chem. Rev*. **2009**, *109*, 303-321. (c) Kingsbury, J. S.; Hoveyda, A. H. In *Polymeric Materials in Organic Synthesis and Catalysis*; Buchmeiser, M. R. Ed.; Wiley-VCH Verlag GmbH & Co. KGaA.: Weinheim, **2003**, ch 11.

[19] (a) Zhang, J.; Wang, X.; Jin, G. X. *Coord. Chem. Rev*. **2006**, *250*, 95-109. (b) Heurtefeu, B.; Bouilhac, C.; Cloutet, E.; Taton, D.; Deffieux, A.; Cramail, H. *Prog. Polym. Sci*. **2001**, *36*, 89-126.

[20] (a) Ding, K.; Wang, Z.; Wang, X.; Liang, Y.; Wang, X. *Chem. Eur. J.* **2006**, *12*, 5188-5197. (b) Ding, K.; Wang, Z.; Shi, L. *Pure Appl. Chem*. **2007**, *79*, 1531-1540. (c) Wang, Z.; Chen, G.; Ding, K. *Chem. Rev*. **2009**, *109*, 322-359. (d) Lee, J.; Farha, O. K.; Roberts, J.; Scheidt, K: A.; Nguyen, S. T.; Hupp, J. T. *Chem. Soc. Rev*. **2009**, *38*, 1450-1459.

as Porous Coordination Polymers (PCPs) or Metal Organic Frameworks (MOFs).[21] Coordination polymers have been applied in many different processes. Taking advantage of their porosity (as it happens in the case of zeolites or other mesoporous materials) they have been utilized like adsorbing agents. Moreover, these polymers have been used in some catalytic organic transformations where, either the metal which is forming part of the main structure or another metal supported, is responsible of the catalysis.

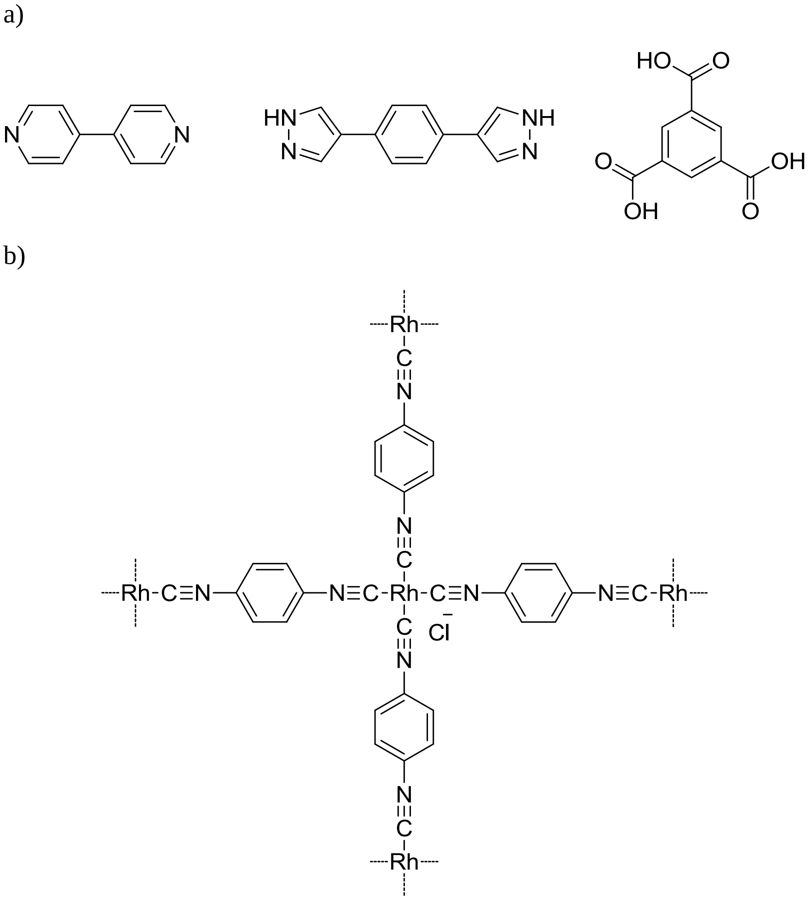

Figure 1.4: a) Some multitopic ligands used in coordination polymers. b) Example of a coordination polymer.

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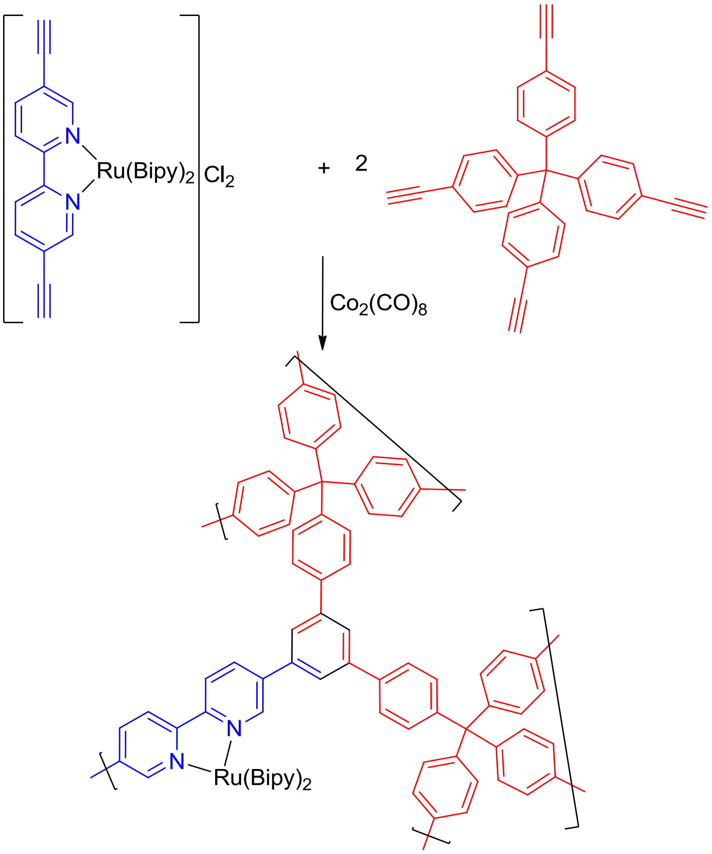
[21] (a) Corma, A.; García, H.; Llabrés i Xamena, F. X. *Chem. Rev.* **2010**, *110*, 4606-4655. (b) Yoon, M.; Srirambalaji, R.; Kim, K. *Chem. Rev.* **2012**, *112*, 1196-1231. (c) Nakagaki, S.; Ferreira, G. K. B.; Ucoski, G. M.; Castro, K. A. D. d. F. *Molecules*, **2013**, *18*, 7279-7308. (d) Liu, J.; Chen, L.; Cui, H.; Zhang, J.; Zhang, L.; Su, C. Y. *Chem. Soc. Rev.* **2014**, *43*, 6011-6061. (e) Llabrés i Xamena, F. X.; Gascon, J. *Metal Organic Frameworks as Heterogeneous Catalysts*; RSC Publishing: Cambridge, **2013**.

Related to the last type, but slightly different, are the so called Covalent or Elemental Organic Frameworks (COFs or EOFs). This kind of polymers presents a microporous structure too, but there are no metals in the main chain. Their synthesis is generally based on condensations or C-C coupling reactions between highly symmetrical organic molecules (Scheme 1.2). Although there is no metal in the main structure, some metals have been introduced via some ligand, as shown in Scheme 1.2, or as nanoparticles into the pores and have been used as heterogeneous catalysts.[22]



Scheme 1.2: Synthesis of porous cross-linked polymer by alkyne trimerization reported by Lin et al.[23]

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[22] (a) Zhang, Y.; Riduan, S. N. *Chem. Soc. Rev.* **2012**, *41*, 2083-2094. (b) Rose, M. *ChemCatChem*, **2014**, *6*, 1166-1182. (c) Rose, M.; Palkovits, R. In *Metal Organic Frameworks as Heterogeneous Catalysts;* Llabrés i Xamena, F. X.; Gascon, J. Eds.; RSC Publishing: Cambridge, **2013**, ch. 13.

[23] Xie, Z.; Wang, C.; deKrafft, K. E.; Lin, W. *J. Am. Chem. Soc.* **2011**, *133*, 2056-2059.

One of the most common routes to obtain polymer–supported catalysts analogous to homogeneous complexes involves the anchorage of the metal through some polymer-bound ligands. Some of the most common ligands in organometallic chemistry are phosphines and many works involving their attachment to polymers have been reviewed.[16a,24] From straight triphenylphosphine to more complicated chiral species have successfully been supported and used in catalysis (Figure 1.5.a). Other species frequently reported are Salen ligands and different metals have been anchored to a polymer via these ligands (Figure 1.5.b).[25] Probably, the type of ligands which has the widest horizon is Nitrogen Heterocyclic Carbenes (NHCs). A lot of polymers have been utilized as solid support in order to prove their activity in heterogeneous catalysis and their role in organometallic catalysis will be addressed in chapter 3.

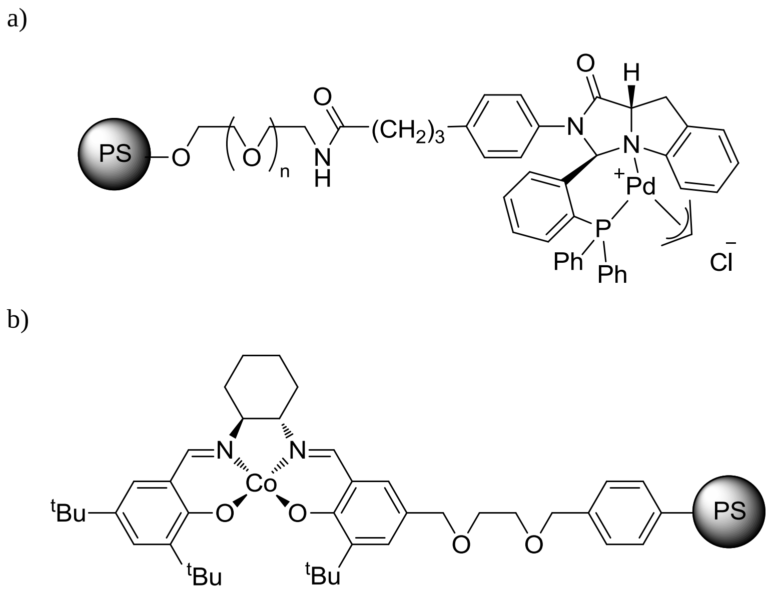

Figure 1.5: Polystyrene supported: a) phosphine ligand; b) Salen ligand.

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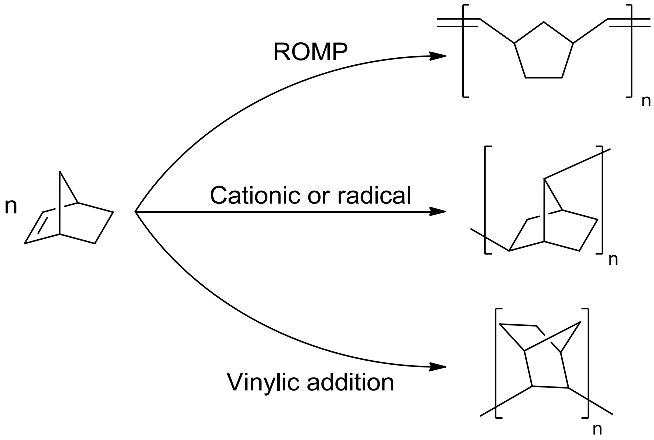
[24] Guinó, M.; Hii, K. K. *Chem. Soc. Rev*. **2007**, *36*, 608-617.

[25] (a) Kleij, A. W. *Eur. J. Inorg. Chem*. **2009**, 193-205. (b) Gupta, K. C.; Sutar, A. K.; Lin, C. C. *Coord. Chem. Rev*. **2009**, *253*, 1926-1946.

1.4 Polynorbornenes

In recent years, our group has been working in the development of functionalized polynorbornenes (PNBs) as supports of reagents and catalysts. Norbornene (bicyclo[2.2.1]hept-2-ene) and its derivatives can be polymerized by diverse procedures affording polymers with different structures and properties (Scheme 1.3).[26]



Scheme 1.3: Different types of norbornene polymerization.

1.4.1 Ring Opening Metathesis Polymerization (ROMP)

Ring Opening Metathesis Polymerization (ROMP) is probably the most used method to polymerize norbornene. This type of polymerization produces unsaturated backbones with double bonds in the main chain forming ethylene groups between cyclopentane rings. This unsaturation can be a problem in catalysis due to the fact that they are reactive centers which can coordinate to palladium or other metal slowing down the reaction or even reacting with the catalyst. ROMP-PNB have some interesting applications such as absorption of oils, fuels or solvents useful in case of spill or in the waste treatment. In this regard, Norsorex® was the first polynorbornene commercially available in 1976

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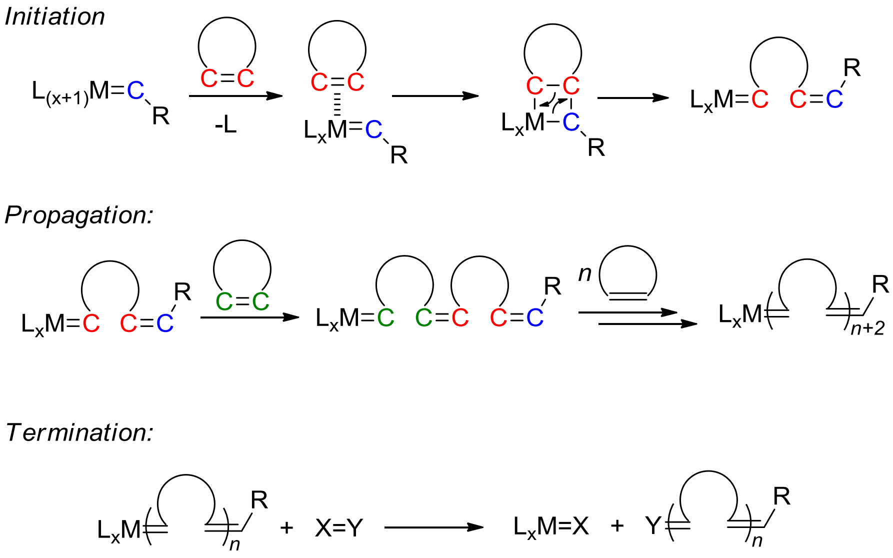
[26] (a) Janiak. C.; Lassahn P. G. *Macromol. Rapid Commun.* **2001**, *22*, 479-492. b) Janiak, C.; Lassahn, P. G. *J. Mol. Catal. A: Chem.* **2001**, *166*, 193-209.

obtained by ROMP of norbornene with $RuCl_3$/HCl in butanol.[27] Nowadays, there are some other commercially available hydrogenated ROMP-PNBs such as Zeonex® or Zeonor®. Undoubtedly, this is by far the type of polynorbornene most commonly employed as scaffold for catalysis and numerous examples of supported ruthenium, molybdenum or palladium complexes have been reported in the literature.[18b,28]

The reaction mechanism of this polymerization is based in olefin metathesis between cyclic or bicyclic alkenes catalyzed by a transition metal complex. Chauvin in 1971 proposed a plausible reaction pathway with three different stages (Scheme 1.4).[29]



Scheme 1.4: Ring opening metathesis polymerization mechanism.

The initiation step starts with the coordination of the cycloalkene to a metal alkylidene complex. A [2+2] cycloaddition affords a metallacyclobutane intermediate which results in a new metal alkylidene complex after opening. During the second stage the polymer chain grows due to subsequent coordination, cycloaddition and opening steps. Since ROMP is consider as “living polymerization”, which means the system is active while

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[27] (a) Mol, J. C. *J. Mol. Cat. A: Chem.* **2004**, *213*, 39-45. (b) Yamazaki, M. *J. Mol. Catal. A*, **2004**, *213*, 81-87. (c) Trimmer, M. S. In *Handbook of Metathesis*; Grubbs, R. H. Ed.; Wiley-VCH Verlag GmbH & Co. KGaA.: Weinheim, **2003**, *Vol 3*, ch. 12.

[28] (a) Buchmeiser, M. R. In *Polymeric Materials in Organic Synthesis and Catalysis*; Buchmeiser, M. R. Ed.; Wiley-VCH Verlag GmbH & Co. KGaA.: Weinheim, **2003**, ch. 8.

[29] Hérisson, J. L.; Chauvin, Y. *Makromol. Chem*. **1971**, *141*, 161-176.

the monomer concentration is high enough, addition of a chain transfer agent (CTA) to suppress the propagation step is necessary. Depending on the catalyst used in the polymerization, different CTA can be used in the termination step. The most common reagents used are ethyl vinyl ether in the case of a ruthenium catalyst or benzaldehydes when molybdenum or tungsten is the metal used.[30]

This type of polymerization has been tried with a lot of catalysts based in many different transition metals such as titanium,[31] zirconium,[31c] vanadium,[32] niobium,[33] tantalum,[33,34] molybdenum,[35] tungsten,[36] osmium,[37] ruthenium[38] or rhenium.[39] Group 9 metals such as cobalt[40] or iridium[41] have shown activity as catalyst in either ROMP or vinylic-addition polymerization depending on the amount of cocatalyst (MAO) added.

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[30] Hilf, S.; Kilbinger, A. F. M. *Nat. Chem.* **2009**, *1*, 537-546.

[31] (a) Gilliom, L. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 733-742. (b) Zhang, D.; Huang, J.; Qian, Y.; Chan, A. *J. Mol. Catal. A: Chem.* **1998**, *133*, 131-133. (c) Eisch, J. J.; Adeosun, A. A. *Eur. J. Org. Chem.* **2005**, 993-997.

[32] (a) Nomura, K.; Sagara, A.; Imanishi, Y. *Macromolecules*, **2002**, *35*, 1583-1590. (b) Yamada, J.; Fujiki, M.; Nomura K. *Organometallics*, **2005**, *24*, 2248-2250.

[33] Nakayama, Y.; Tanimoto, M.; Shiono, T. *Macrom. Rapid Commun.* **2007**, *28*, 646-650.

[34] (a) Wallace, K. C.; Liu, A. H.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1988**, *110*, 4964-4977. (b) Rietveld, M. H. P.; Lohner, P.; Nijkamp, M. G.; Grove, D. M.; Veldman, N.; Spek, A. L.; Pfeffer, M.; van Koten, G. *Chem. Eur. J.* **1997**, *3*, 817-822. (c) Rietveld, M. H. P.; Teunissen, W.; Hagen, H.; van der Water, L.; Grove, D. M.; Veldman, N.; Spek, A. L.; van Koten, G. *Organometallics*, **1997**, *16*, 1674-1684.

[35] (a) Murdzek, J. S.; Schrock, R. R. *Organometallics* **1987**, *6*, 1373-1374. (b) Murdzek, J. S.; Schrock, R. R. *Macromolecules* **1987**, *20*, 2640-2642. (c) Bazan, G. C.; Schrock, R. R.; Cho, H. N.; Gibson, V. C. *Macromolecules*, **1991**, *24*, 4495-4502. (d) Hiya, K.; Nakayama, Y.; Yasuda, H. *Macromolecules*, **2003**, *36*, 7916-7922. (e) Yuan, J.; Schrock, R. R.; Gerber, L.; Müller, P.; Smith, S. *Organometallics* **2013**, *32*, 2983−2992.

[36] (a) Kress, J.; Osborn, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 6346-6347. (b)Schaverien, C. J.; Dewan, J. C.; Schrock, R.R. *J. Am. Chem. Soc.* **1986**, *108*, 2771-2773. (c) Schrock, R. R.; Feldman, J.; Canizzo, L. F.; Grubbs, R. H. *Macromolecules* **1987**, *20*, 1169-1172. (d) Kress, J.; Osborn, J. A.; Greene, R. M. E.; Ivin, K. J.; Rooney, J. J. *J. Am. Chem. Soc.* **1987**, *109*, 899-901. (e) Lehtonen, A.; Sillanpää, R. *Inorg. Chem. Commun.* **2002**, *5*, 267-268. (f) Hakala, J.; Hänninen, M. M.; Lehtonen, A. *Inorg. Chem. Commun.* **2011**, *14*, 1362-1364.

[37] (a) Burmaghim, J. L.; Girolami, G. S. *Organometallics*, **1999**, *18*, 1923-1929. (b) Malosh, T. J.; Shapley, J. R. *J. Organomet. Chem.* **2010**, *695*, 1776-1786.

[38] (a) Schwab, P.; France, M. B:; Ziller, J. W.; Grubbs, R. H. *Angew. Chem. Int. Ed.* **1995**, *34*, 2039-2041. (b) Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100-110. (c) Castarlenas, R.; Sémeril, D.; Noels, A. F.; Demonceau, A.; Dixneuf, P. H. *J. Organomet. Chem.* **2002**, *663*, 235-238. (d) Bernechea, M.; Lugan, N.; Gil, B.; Lalinde, E.; Lavigne, G. *Organometallics*, **2006**, *25*, 684-692. (e) Silva S. J. L.; Nascimento, E. S. P.; Fonseca, L. R.; Lima-Neto, B. S. *J. Appl. Polym. Sci.* **2013**, *127*, 3578-3585.

[39] Frech, C. M.; Blacque, O.; Schmalle, H. W.; Berke, H.; Adlhart, C.; Chen, P. *Chem. Eur. J.* **2006**, *12*, 3325-3338.

[40] Bao, F.; Lu, X.-Q.; Gao, H.; Gui, G.; Wu, Q. *J. Polym. Sci. A: Polym. Chem.* **2005**, *43*, 5535-5544.

[41] Meng, X.; Tang, G.-R.; Jin, G.-X. *Chem. Commun.* **2008**, 3178-3180.

Among all those examples were the works of R. R. Schrock and R. H. Grubbs which unquestionably meant a breakthrough in this field. Their contribution in olefin metathesis together with the former explanation of the mechanism by Y. Chauvin's afforded them the 2005 Nobel Prize in Chemistry. Both authors achieved great results with alkylidene-complexes of molybdenum or ruthenium (Figure 1.6). Schrock-type molybdenum-catalyst, bearing two alkoxides, a bulky-imido group and an alkylidene moiety, showed high activity in the polymerization of cyclic olefins but exhibited little functional group tolerance.[35a-c,42] On the contrary, first generation Grubbs catalyst with ruthenium showed larger tolerance but lower activities.[38a-b,43] This drawback was overcome with the second generation Grubbs catalyst obtained by changing one of the phosphine ligands for an imidazolidinylidene moiety.[44]

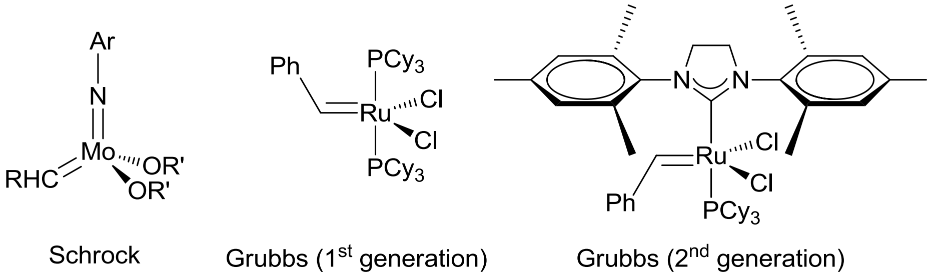

Figure 1.6: Successful ROMP catalysts.

1.4.2 Radical or cationic polymerization

Polymers obtained by cationic or radical polymerization of norbornene present 2-7 connectivity between monomers (Scheme 1.3). The most common catalyst used in cationic polymerization is $AlCl_2Et$.[45] In the case of radical polymerization, azobisisobutyronitrile (AIBN), di-sec-butyl percarbonate (DsBPDC), tert-butyl perpivalate (tBPP) or tert-butyl

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[42] (a) Schrock, R. R.; Hoveyda, A. H. *Angew. Chem. Int. Ed.* **2003**, *42*, 4592-4633. (b) Schrock, R. R. In *Handbook of Metathesis*; Grubbs, R. H.; Ed Wiley-VCH Verlag GmbH & Co. KGaA.: Weinheim, **2003**, *Vol 1*, ch. 3.

[43] (a) Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18-29. (b) Nguyen, S. T.; Trnka, T. M. In *Handbook of Metathesis*; Grubbs, R. H.; Ed Wiley-VCH Verlag GmbH & Co. KGaA.: Weinheim, **2003**, *Vol 1*, ch. 7.

[44] (a) Scholl, M.; Ding, S.; Lee, C. W.; Grubbs, R. H. *Org. Lett.* **1999**, *1*, 953-956. (b) Bielawski, C. W.; Grubbs, R. H. *Angew. Chem. Int. Ed.* **2000**, *39*, 2903-2906.

[45] Kennedy, J. P.; Makowski, H. S. *J. Macromol. Sci. Chem.* **1967**, *A1*, 345-370.

peracetate (tBPA) are radical initiators traditionally used.[46] Although showing completely saturated backbones, these polymers have low molecular weights.

1.4.3 Vinylic addition polymerization (VA)

The third possibility is the vinylic addition polymerization of norbornene which can be catalyzed by many different transition metal complexes.[26b,47] In this case, nickel[48] and palladium[49] complexes are more commonly used than other metals such as iron, chromium or cobalt,[50] or group 4 elements titanium or zirconium.[51] Polymers synthesized by this method can be roughly described as linear chains of norbornane units linked by positions

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[46] (a) Gaylord, N. G.; Mandal, B. M.; Martan, M. *J. Polym. Sci. Polym. Lett. Ed.* **1976**, *14*, 555-559. (b) Gaylord, N. G.; Deshpande, A. B.; Mandal, B. M.; Martan, M. *J. Macromol. Sci. Chem.* **1977**, *A11*, 1053-1070.

[47] (a) Janiak. C.; Lassahn P. G. *Macromol. Rapid Commun.* **2001**, *22*, 479-492. (b) Janiak, C.; Lassahn, P. G.; Lozan, V. *Macromol. Symp.* **2006**, *236*, 88-99. (c) Blank, F.; Janiak, C. *Coord. Chem. Rev.* **2009**, *253*, 827-861. (d) Ma, R.; Hou, Y.; Gao, J.; Bao, F. *J. Macromol. Sci.-Pol. R.* **2009**, 49, 249-287.

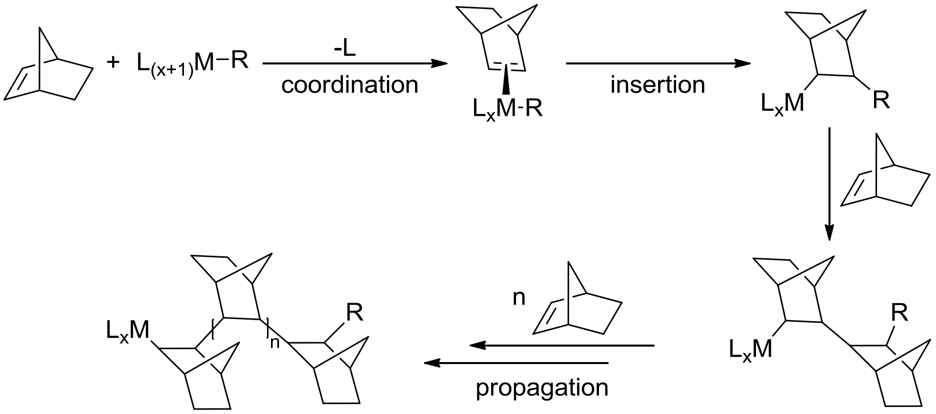
[48] (a) Deming, T. J.; Novak, B. M. *Macromolecules*, **1993**, *26*, 7089-7091. (b) Benedikt, G. M.; Elce, E.; Goodall, B. L.; Kalamarides, H. A.; McIntosh, L. H.; Rhodes, L. F.; Selvy, K. T.; Andes, C.; Oyler, K.; Sen, A. *Macromolecules* **2002**, *35*, 8978-8988. (c) Barnes, D. A.; Benedikt, G. M.; Goodall, B. L.; Huang, S. S.; Kalamarides, H. A.; Lenhard, S.; McIntosh, L. H.; Selvy, K. T.; Shick, R. A.; Rhodes, L. F. *Macromolecules* **2003**, *36*, 2623-2632. (d) Shi, Q.; Jie, S.; Zhang, S.; Yang, H.; Sun, W. H. *Macromol. Symp.* **2007**, *260*, 74-79. (e) He, F.; Chen, Y.; He, X.; Chen, M.; Zhou, W.; Wu, Q. *J. Polym. Sci. A: Polym. Chem.* **2009**, *47*, 3990-4000. (f) Niu, Y. P.; Wang, X. W.; Zheng, Z. W.; Ma, X. F.; Cai, J. Q.; Zhang, J. K.; Cheng, J. L. *Appl. Organometal. Chem.* **2014**, *28*, 688-695. (g) Hao, Z.; Yang, N.; Gao, W.; Xin, L.; Luo, X.; Mu, Y. *J. Organomet. Chem.* **2014**, *749*, 350-355.

[49] (a) Hennis, A. D.; Polley, J. D.; Long, G. S.; Sen, A.; Yandulov, D.; Lipian, J.; Benedikt, G. M.; Rhodes, L. F.; Huffman, J. *Organometallics*, **2001**, *20*, 2802-2812. (b) Lipian, J.; Mimna, R. A.; Fondran, J. C.; Yandulov, D.; Shick, R. A.; Goodall, B. L.; Rhodes, L. F.; Huffman, J. *Macromolecules*, **2002**, *35*, 8969-8977. (c) Liu, B.; Li, Y.; Shin, B. G.; Yoon, D. Y.; Kim, I.; Zhang, L.; Yang, W. *J. Polym. Sci. A: Polym. Chem.* **2007**, *45*, 3391-3399. (d) Walter, M. D.; Moorhouse, R. A.; Urbin, S. A.; White, P. S.; Brookhart, M. *J. Am. Chem. Soc*. **2009**, *131*, 9055-9069. (e) Deng, J.; Gao, H.; Zhu, F.; Wu, Q. *Organometallics*, **2013**, *32*, 4507-4515. (f) Dang, L.; Song, H.; Wang, B. *Organometallics*, **2014**, *33*, 6812-6818. (g) Huo, P.; Liu, W.; He, X.; Wei, Z.; Chen, Y. *Polym. Chem.* **2014**, *5*, 1210-1218.

[50] (a) Sato, Y.; Nakayama, Y.; Yasuda, H. *J. Organomet. Chem.* **2004**, *689*, 744-750. (b) Chen, J.; Huang, Y.; Li, Z.; Zhang, Z.; Wie, C.; Lan, T.; Zhang, W. *J. Mol. Catal. A*, **2006**, *259*, 133-141. (c) Ricci, G.; Boglia, A.; Boccia, A. C.; Zetta, L. *Macromol. Symp.* **2007**, *260*, 172-178. (d) Leone, G.; Boglia, A.; Boccia, A. C.; Scafati, S. T.; Bertini, F.; Ricci, G. *Macromolecules*, **2009**, *42*, 9231-9237. (e) Benade, L. L.; Ojwach, S. O.; Obuah, C.; Guzei, I. A.; Darkwa, J. *Polyhedron*, **2011**, *30*, 2878-2883.

[51] (a) Kaminsky, W.; Noll, A. *Polym. Bull.* **1993**, *31*, 175-182. (b) Mi, X.; Xu, D.; Yan, W.; Guo, C.; Ke, Y.; Hu, Y. *Polym. Bull*. **2002**, *47*, 521-527. (c) Hasan, T.; Ikeda, T.; Takeshi, S. T. *Macromolecules,* **2004**, *37*, 7432-7436. (d) Nishizawa, O.; Misaka, H.; Sakai, R.; Kakuchi, T.; Satoh, T. *J. Polym. Sci. A: Polym. Chem.* **2008**, *46*, 7411-7418. (e) Ricci, G.; Leone, G.; Rapallo, A.; Biagini, P.; Guglielmetti, G.; Porri, L. *Polymer*, **2011**, *52*, 5708-5715.

2-3 with moderate to high molecular weights.[52] The formation of this structure can be explained with a coordination-insertion mechanism (Scheme 1.5).



Scheme 1.5: Vinylic-addition polymerization mechanism.

In a first step norbornene is coordinated to the metal by the double bond in a vacant position left by the displacement of a labile ligand. A later insertion of the olefin in the metal-carbon bond generates a new vacant which is occupied by another molecule of norbornene. Subsequent steps during the propagation of the chain afford the polymer with the bicyclic moiety unaltered. This structure endows the polymer some interesting properties like good thermal stability, transparency to UV-V light or low moisture absorption.[49c] Furthrmore, since this structure is completely saturated, there are no double bonds unlike ROMP-PNBs and therefore this scaffold is likely to be more suitable for catalysis.

VA-Polymerization of norbornene derivatives and VA-copolymerization of these monomers with norbornene are much more challenging, and most catalyst active for the polymerization of norbornene fail to do that. Only a few examples can be found in the

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[52] There are also some examples, especially in the case of zirconium metallocenes, with more complicated structures where a recurrent σ-bond metathesis yields polynorbornenes with conectivities 2-3 and 2-7. (a) Karafilidis, C.; Hermann, H.; Rufińska, A.; Gabor, B.; Mynott, R. J.; Breitenbruch, G.; Weidenthaler, C.; Rust, J.; Joppek, W.; Brookhart, M. S.; Thiel, W.; Fink, G. *Angew. Chem. Int. Ed.* **2004**, *43*, 2444-2446. (b) Karafilidis, C.; Angermund, B. G.; Rufińska, A.; Mynott, R. J.; Breitenbruch, G.; Thiel, W.; Fink, G. *Angew. Chem. Int. Ed.* **2007**, *46*, 3745-3749.

literature where good yields and incorporations of both monomers in the copolymer have been achieved.[48e,53]

In this matter, our group has been using a nickel complex [Ni(C_6F_5)$_2$($SbPh_3$)$_2$].[54] It has two aryl ligands and two labile ligands and it is able to copolymerize norbornene and some functionalized norbornenes with good results without the need of adding a cocatalyst.[55] Copolymers obtained with this procedure do not contain any further functionality except those intentionally added as part of the functionalized monomer, which means a robust and inert scaffold is obtained. This interesting property must be added to those aforementioned. It is noteworthy that a family of haloalkyl-substituted vinylic addition polynorbornenes (VA-PNBs) has been developed in our group and this is a convenient starting material for the synthesis of other functionalized VA-PNBs, in a similar fashion to some commercial halo-substituted resins (polystyrene or poly (ethylene glycol) as examples).[55b]

Previous works have shown the applicability of VA-PNBs as supports of tin reagents and their utilization in the Stille reaction with good results and recyclabilities affording an alternative route to address the problem of tin toxic waste (Figure 1.7).[56] More recently, in collaboration with Pericàs' group, these polymers have also been used as a support of prolines and have been applied for the asymmetric direct aldol reaction of benzaldehydes with ketones.[57]

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[53] (a) Goodall, B. L.; Benedikt, G. M.; McIntosh, L. H.; Barnes, D. A.; Rhodes, L. F. U.S. 5,569,730, **1996**. (b) Rhodes, L. F.; Bell, A.; Jayaraman, S.; Lipian, J. H.; Goodall, B. L.; Shick, R. A. U.S. 6,232,417 B1, **2001**. (c) Yamashita, M.; Takamiya, I.; Jin, K.; Nozaki, K. *Organometallics*, **2006**, *25*, 4588-4595. (d) Kaita, S.; Matsushita, K.; Tobita, M.; Maruyama, Y.; Wakatsuki, Y. *Macromol. Rapid Commun.* **2006**, *27*, 1752-1756. (e) Wang, L. Y.; Li, Y. F.; Zhu, F. M.; Wu, Q. *Eur. Polym. J.* **2006**, *42*, 322-327.

[54] Arcas, A.; Royo, P. *Inorg. Chim. Acta*, **1978**, *30*, 205-207.

[55] (a) Casares, J. A.; Espinet, P.; Martín-Alvarez, J. M.; Martínez-Ilarduya, J. M.; Salas, G. *Eur. J. Inorg. Chem.* **2005**, *19*, 3825-3831. (b) Martínez-Arranz, S.; Albéniz, A. C.; Espinet, P. *Macromolecules*, **2010**, 4*3*, 7482-7487.

[56] (a) Carrera, N.; Gutiérrez, E.; Benavente, R.; Villavieja, M. M.; Albéniz, A. C.; Espinet, P. *Chem. Eur. J.* **2008**, *14*, 10141-10148; (b) Meana, I.; Albéniz, A. C.; Espinet, P. *Adv. Synth. Catal.*, **2010**, *352*, 2887-2891; c) Martínez-Arranz, S.; Carrera, N.; Albéniz, A. C.; Espinet, P.; Vidal-Moya, A. *Adv. Synth. Catal.* **2012**, *354*, 3551-3560. d) Albéniz, A. C.; Martínez-Arranz, S; Espinet, P.; WO2012/160228 A1, **2012**.

[57] Sagamanova, I. K.; Sayalero, S.; Martínez-Arranz, S.; Albéniz A. C.; Pericàs, M. A. *Catal. Sci. Technol.* **2015**, *5*, 754-764.

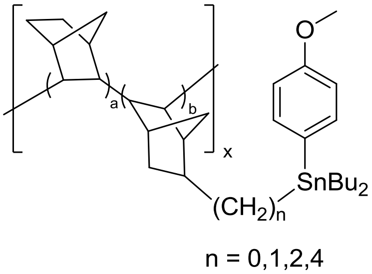

Figure 1.7: VA-PNB-supported tin reagent used in the Stille reaction.

The work described here is devoted to the development of a new family of polymer-supported catalysts, based on the vinylic addition polynorbornene skeleton, with two different types of functional groups. On one hand, VA-PNBs with tethered Nitrogen Heterocyclic Carbenes (NHCs) have been applied both as organocatalysts and as ligands of palladium complexes active in catalysis. On the other hand, polymers with α-diimines forming part of the norbornene structure have been employed as ligands to form different palladium complexes. More detailed information about these specific types of functional groups and their use in catalysis can be found in the introduction of each chapter.

Chapter 2

2. N-Heterocyclic Carbenes supported on vinylic addition polynorbornenes. Uses in organocatalysis.

2.1 INTRODUCTION

2.1.1 Non supported N-Heterocyclic Carbenes

N-Heterocyclic carbenes (NHCs) have got a significant role in modern catalysis. They exhibit especial prominence in those systems with metals acting as active centers where NHCs behave as important ligands responsible for the most part of the success of the reaction. But they have also become interesting alternatives in metal-free catalysis due to their nucleophilic behavior. Although they were initially described independently by Wanzlick[58] and Ofele[59] in 1968 and in spite of the subsequent work in organometallic carbenes by Lappert and coworkers[60], there was no full interest in their applicability until

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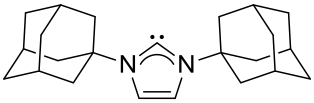
[58] (a) Wanzlick, H. W.; Schönherr, H. J. *Angew. Chem.* **1968**, *80*, 154; *Angew. Chem. Int. Ed. Engl.* **1968**, *7*, 141-142. (b) Schönherr, H. J.; Wanzlick, H. W. *Chem. Ber.* **1970**, *103*, 1037-1046.

[59] Öfele, K. *J. Organomet. Chem.* **1968**, *12*, P42-P43.

[60] Lappert, M. F. *J. Organomet. Chem.* **2005**, *690*, 5467-5473.

the early 90s when Arduengo[61] succeeded in the isolation as stable carbenes (Figure 2.1). A vast new horizon had just been discovered and soon several works proved the wide offer of types of carbenes and their good results in both transition–metal[62] and organic catalysis.[63] Several studies in the following years afforded a better knowledge about their electronic and steric characteristics,[64] allowing the synthesis and exploitation of many carbenes with enhanced properties.



IAd

Figure 2.1: First "bottle-able" N-Heterocyclic Carbene.

Free carbenes can act as catalysts in different organic reactions. Among the best known transformations it is imperative to cite: umpolung (processes where there is an inversion of the innate reactivity of a functional group) such as the benzoin condensation or the Stetter reaction (mainly with aldehydes), transesterifications, polymerizations or ring–opening reactions (Scheme 2.1).[65]

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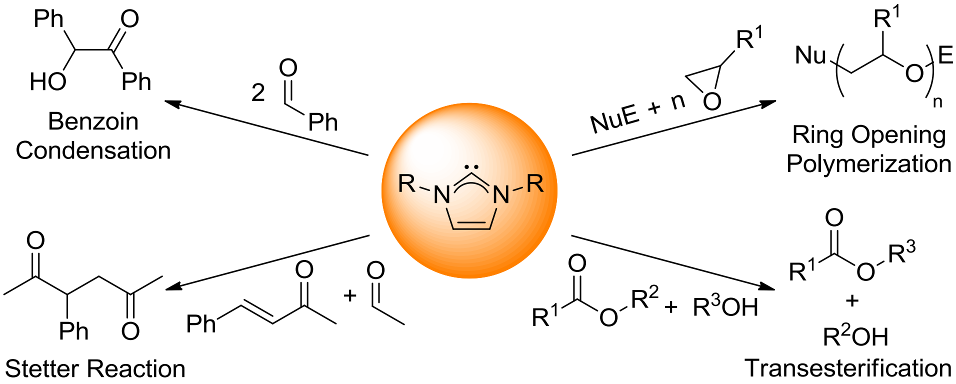
[61] (a) Arduengo III, A. J.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361-363. (b) Arduengo III, A. J.; Rasika Dias, H. V.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1992**, *114*, 5530-5534.

[62] (a) Herrmann, W. A.; Elison, M.; Fischer, J.; Köchter, C.; Arthus, G. R. J. *Angew. Chem*. **1995**, *107*, 2602-2605; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2371-2373. (b) Çetinkaya, B.; Özdemir, I.; Dixneuf, P. H. *J. Organomet. Chem.* **1997**, *534*, 153-158.

[63] Teles, J. H.; Melder, J. P.; Ebel, K.; Schneider, R.; Gehrer, E.; Harder, W.; Brode, S.; Enders, D.; Breuer, K.; Raabe, G. *Helv. Chim. Acta*, **1996**, *79*, 61-83.

[64] (a) Kühl, O. *Chem. Soc. Rev*. **2007**, *36*, 592-607. (b) Díez-González, S.; Nolan, S. P. *Coord. Chem. Rev*. **2007**, *251*, 874-883. (c) Hahn, F. E.; Jahnke, M. C. *Angew. Chem. Int. Ed*. **2008**, *47*, 3122-3172. (d) Jahnke, M. C.; Hahn, F. E. In *N-Heterocyclic Carbenes*; Díez-González, S. Ed.; RSC Publishing: Cambridge, **2011**, ch. 1. (e) Nelson, D. J.; Nolan, S. P. *Chem. Soc. Rev*. **2013**, *42*, 6723-6753.

[65] (a) Nair, V.; Bindu, S.; Sreekumar, V. *Angew. Chem. Int. Ed.* **2004**, *43*, 5130-5135; *Angew. Chem.* **2004**, *116*, 5240-5245. (b) Enders, D.; Niemeier, O.; Henseler, A. *Chem. Rev*. **2007**, *107*, 5606-5655. (c) Díez-González, S.; Nolan, S. P.; Marion, N. *Angew. Chem. Int. Ed.* **2007**, *46*, 2988-3000; *Angew. Chem*. **2007**, *119*, 3046-3058. (d) Fuchter, M. J. *Chem. Eur. J.* **2010**, *16*, 12286-12294. (e) Kiesewetter, M. K.; Shin, E. J.; Hedrick, J. L.; Waymouth, R. M. *Macromolecules*, **2010**, *43*, 2093-2107. (f) Chiang, P. C.;Bode, J. W. In *N-Heterocyclic Carbenes*; Díez-González, S. Ed.; RSC Publishing: Cambridge, **2011**, ch. 14. (g) Bugaut, X.; Glorius, F. *Chem. Soc. Rev*. **2012**, *41*, 3511-3522. (h) Fèvre, M.; Pinaud, J.; Gnanou, Y.; Vignolle, J.; Taton, D. *Chem. Soc. Rev*. **2013**, *42*, 2142-2172. (i) Hopkinson, M. N.; Richter, C.; Schedler, M.; Glorius, F. *Nature* **2014**, *510*, 485-496.



Scheme 2.1.

2.1.2 Polymer-supported NHCs in organocatalysis

Due to their exceptional behavior in catalysis either as ligands or catalysts there is an increasing interest in managing the anchorage of NHCs onto solid supports in order to avoid their loss and consequent drawbacks previously commented. In this regard, our attention is focused on the use of polymers, considered useful tools for this goal. Different methodologies to obtain polymer-supported NHCs can be found in the literature.

In the event of organocatalysis there are a few examples of polymers with NHCs. Probably, the easiest approach is the use of commercially available polymers. Polystyrene resins have been modified by direct nucleophilic substitution of some halide present in the polymer[66] and poly(ethylene glycol) (PEG) has been functionalized using click-chemistry with alkyne substituted azolium salts (Figure 2.2).[67] However, they show moderate results and their recyclability is strongly dependent on the reaction conditions in the case of PEG or exhibits a fall of 10% yield after every cycle when polystyrene-supported NHCs are employed. Other cases with polystyrenes are those with thiazolium functionalities[68]. They have shown good behavior in a continuous flow system, although if they come to a halt they cannot be reused.

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[66] Storey, M. D.; Williamson, C. *Tetrahedron Lett.* **2005**, *46*, 7337-7339.

[67] Zeitler, K.; Mager, I. *Adv. Synth. Catal.* **2007**, *349*, 1851-1857.

[68] (a) van den Berg, H. J.; Challa, G.; Pandit, U. K. *React. Polym.* **1989**, *11*, 127-134. (b) Bortolini, O.; Cavazzini, A.; Dambruoso, P.; Giovannini, P. P.; Caciolli, L.; Massi, A.; Pacifico, S.; Ragno, D. *Green Chem.* **2013**, *15*, 2981-2992.

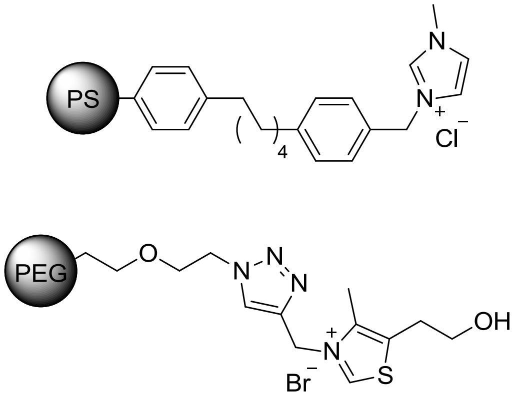

Figure 2.2.

A different strategy entails a previous synthesis of some monomers which have imidazolium substituents[69-71] or CO_2-protected NHCs.[72] These monomers have been polymerized by a radical mechanism in the cases of the work of Taton and Chung whereas Barret and Buchmeiser used a ROMP methodology (Figure 2.3). Most of these examples exhibit high activities in the organic reactions performed but some of them have no data about recyclability or show poor results in this respect, with the exception of Seo and Chung, which got better results in their recent work.[70]

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[69] (a) Pinaud, J.; Vignolle, J.; Gnanou, Y.; Taton, D. *Macromolecules*, **2011**, *44*, 1900-1908. (b) Coupillaud, P.; Pinaud, J.; Guidolin, N.; Vignolle, J.; Fèvre, M.; Veaudecrenne, E.; Mecerreyes, D.; Taton, D. *J. Polym. Sci. Part A*, **2013**, *51*, 4530-4540. (c) Kuzmicz, D.; Coupillaud, P.; Men, Y.; Vignolle, J.; Vendraminetto, G.; Ambrogi, M.; Taton, D.; Yuan, J: *Polymer*, **2014**, *55*, 3423-3430.

[70] (a) Seo, U. R.; Chung, Y. K. *RSC Adv*. **2014**, *4*, 32371-32374. (b) Seo, U. R.; Chung, Y. K. *Adv. Synth. Catal.* **2014**, *356*, 1955-1961.

[71] Barrett, A. G. M.; Love, A. C.; Tedeschi, L. *Org. Lett*. **2004**, *6*, 3377-3380.

[72] Pawar, G. M.; Buchmeiser, M. R. *Adv. Synth. Catal*. **2010**, *352*, 917-928.

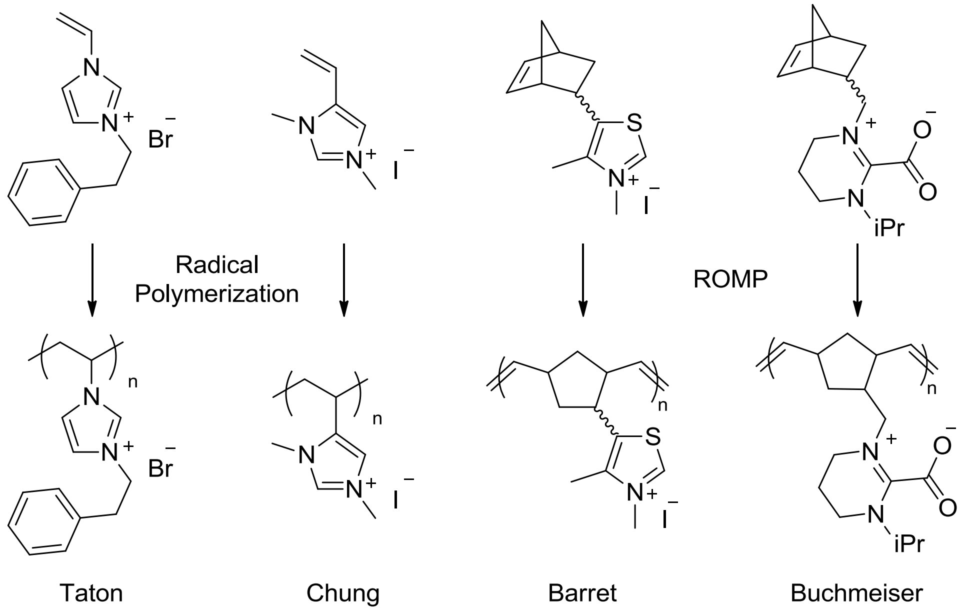

Figure 2.3: Polymerization of imidazolium salts for their use as organocatalyst precursor.

Polymeric frameworks with NHCs within the structure have performed organocatalytic reactions with high yields and good results as far as recyclability is concerned. They are solid supports with symmetric NHCs that can be formed through polymerization of specific monomers obtained with a several-step synthesis. In some cases that polymerization is produced by concomitant Suzuki couplings[73] (Scheme 2.2.a) and in other example the polymer is formed by condensation processes based on nucleophilic attack (Scheme 2.2.b).[74] Nevertheless, any modification in the carbene moiety means the synthesis of a new polymeric framework from scratch.

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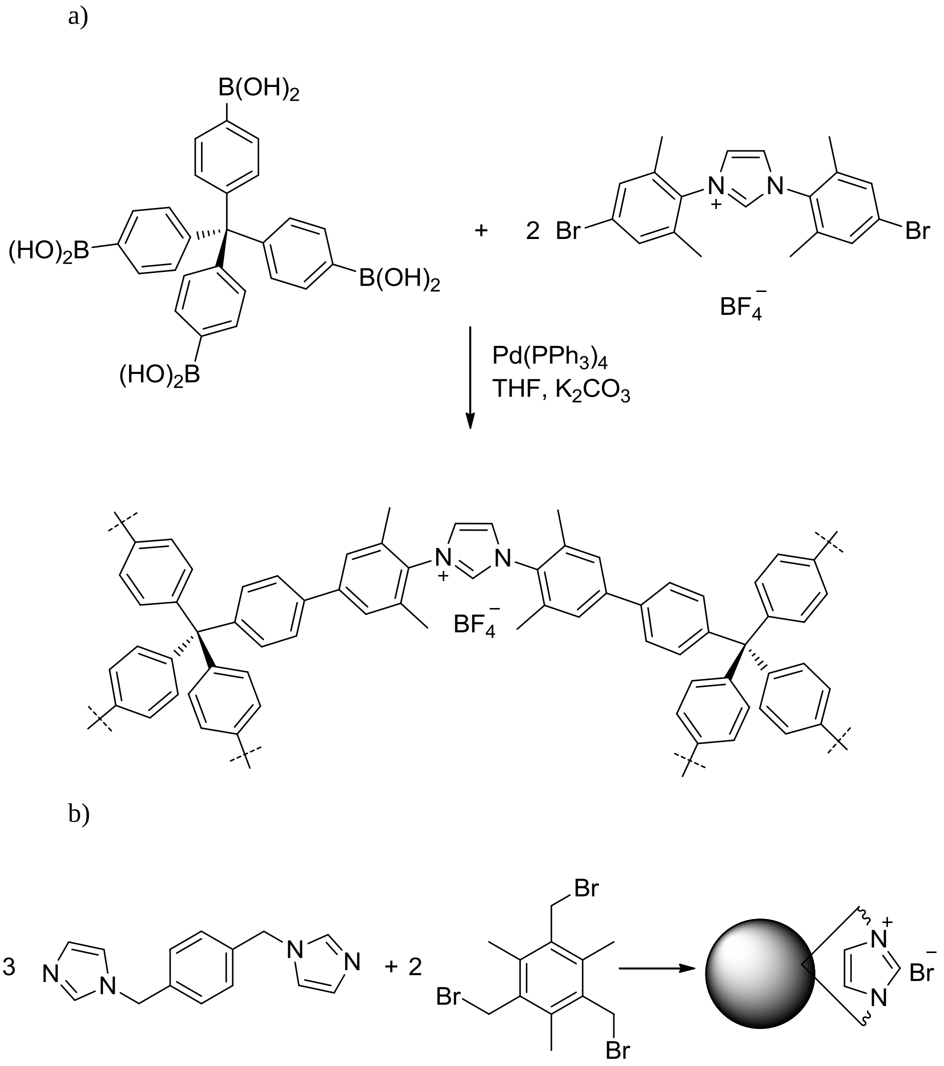
[73] (a) Rose, M.; Notzon, A.; Heitbaum, M.; Nickerl, G.; Paasch, S.; Brunner, E.; Glorius, F.; Kaskel, S. *Chem. Commun*. **2011**, *47*, 4814-4816. (b) Powell, A. B.; Suzuki, Y.; Ueda, M.; Bielawski, C. W.; Cowley, A. H. *J. Am. Chem. Soc*. **2011**, *133*, 5218-5220.

[74] Tan, M.; Zhang, Y.; Ying, J. Y. *Adv. Synth. Catal*. **2009**, *351*, 1390-1394.



Scheme 2.2: Synthesis of polymeric frameworks with azolium salts in the main chain.

Peptides have also been used as supports of NHCs showing a decrease of conversion after every recycling run.[75] Finally, an alternative route to obtain reusable organocatalysts has described the use of supported anionic bases to retain thiazolium cations, but the initial good yields cannot be reproduced after two runs.

No previous examples of NHCs supported on vinylic addition polynorbornenes have been found. Considering the interesting properties of this type of polymer cited in

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[75] Gondo, C. A.; Bode, J. W. *Synlett*, **2013**, *24*, 1205-1210.

chapter 1 (thermal stability, non-reactive backbone...) we decided to develop a new family of polymer-supported NHCs and test their organocatalytic activity in some organic transformations.

2.2 RESULTS AND DISCUSSION

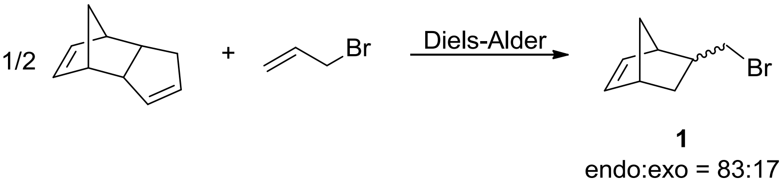
2.2.1 Synthesis of VA-polynorbornene supported imidazolium salts

The easiest protocol to get NHCs is by deprotonation of the corresponding azolium salt. In our particular case we have been working with imidazole derivatives, so any reference to NHCs from now on will stand for these particular heterocycles.

In order to obtain VA-PNBs with tethered imidazolium salts we planned two different synthetic routes. Primarily, we tried the polymerization of imidazole-substituted norbornenes. Alternatively, we chose the introduction of the heterocycle into a previously synthesized polymer.

2.2.1.1 Synthesis of functionalized norbornenes

The first step of this approach was the synthesis of norbornyl methylene bromide. This molecule had been described by Dolman and coworkers via Diels-Alder reaction of dicyclopentadiene and allylbromide (Scheme 2.3).[76] We followed the same route and the product was obtained as a mixture of isomers endo:exo = 83:17.



Scheme 2.3: Synthesis of norbornyl methylene bromide.

Nucleophilic substitution of the bromide atom by 1-methylimidazole produces the imidazolium bromide (Equation 2.1). This reaction was carried out heating the reagents in toluene for 3 days. The imidazolium salt **2** was obtained with the same isomeric ratio than **1**.

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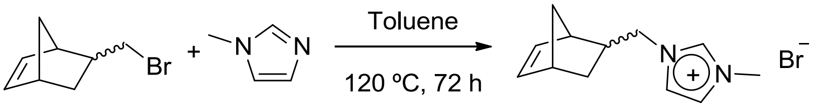
[76] Dolman, S. J.; Hultzsh, K. C.; Pezet, F.; Teng, X.; Hoveyda, A. H.; Schrock, R. R. *J. Am. Chem. Soc.* **2004**, *126*, 10945-10953.

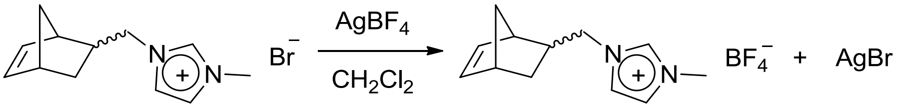


(2.1)

1
exo:endo = 15:85

2

Once the monomer was synthesized we tried its copolymerization with norbornene using the nickel complex [Ni(C_6F_5)$_2$(SbPh$_3$)$_2$] (**3**) as catalyst. As mentioned in chapter 1, this neutral complex had satisfactorily been used in norbornene polymerization and copolymerization with different norbornene derivatives.[55] Nevertheless, in our case no polymer was obtained, not even the homopolymer of the norbornene in the reaction mixture. This absolute lack of activity suggested that the catalyst had been deactivated by **2**. Since the imidazolium salt possesses a bromide, we considered that this coordinating anion could be responsible of the formation of a new inactive nickel complex. To avoid this problem we chose to interchange the bromide for a less coordinating anion like tetrafluoroborate (Equation 2.2).



(2.2)

2

4

Imidazolium salt **4** can be synthesized using other sources of tetrafluoroborate than $AgBF_4$, such as $NaBF_4$ or HBF_4 but longer reaction times are required and yields are poorer in any case.

Although **2** and **4** are ionic salts with the same cation, it is noteworthy that they have notable differences in their ^{1}H-NMR spectra. When recorded in $CDCl_3$, where both monomers are soluble, the signals that belong to the proton between nitrogen atoms show a chemical shift at 10.3 and 8.8 ppm respectively. This dissimilarity, larger than 1 ppm, between these two identical imidazole moieties is consequence of the strength of the ionic pairs formed in a solvent with a low dielectric constant. Furthermore, former studies involving imidazolium salts reported the existence of hydrogen bonds between every proton of the heterocycle and the corresponding anion.[77] Logically, the more acidic is the hydrogen the more effective is the influence of the anion. In our case, we observed differences around 0.2 ppm in the signals of the methyl group, methylene bridge and both methine groups.

Copolymerization of **4** with norbornene catalyzed by **3** yielded poorly (6 %) and with no incorporation of imidazolium tetrafluoroborate. When we tried to homopolymerize **4** in the same reaction conditions no polymer was obtained. These results led us to consider the possibility that at the beginning of the reaction the imidazolium salt could be interacting with the catalyst forming a nickel-carbene complex inactive in the polymerization of norbornene and derivatives. Then we decided to synthesize a palladium-carbene complex so that, on the one hand we could test the ability of our norbornene-substituted imidazole to form metal-complexes, and on the other hand we would try the polymerization of this complex, where no carbene ligand is available to the nickel catalyst, to obtain polynorbornene-supported palladium-carbene complexes.

Imidazolium salt **4** was deprotonated with tetrabutylammonium hydroxide and the resulting carbene was added to a solution of $[PdCl_2(AsPh_3)_2]$ (Equation 2.3). Complex **5** was successfully obtained as a yellow solid and characterized by ^{1}H, ^{13}C and ^{19}F NMR. ^{19}F NMR spectra showed a signal corresponding to tetrafluoroborate indicating the ionic nature of the complex. The integration value of the signals associated with the phenyl groups in ^{1}H NMR revealed the presence of two arsine ligands. Since no crystallographic analysis was carried out, a cis or trans configuration could not be unequivocally determined. However, we propose a trans arrangement due to the fact that the ^{13}C NMR showed a unique type of signals for the phenyl groups of the ligands. In a cis complex both ligands would show some difference, especially for the carbon at the ipso position.

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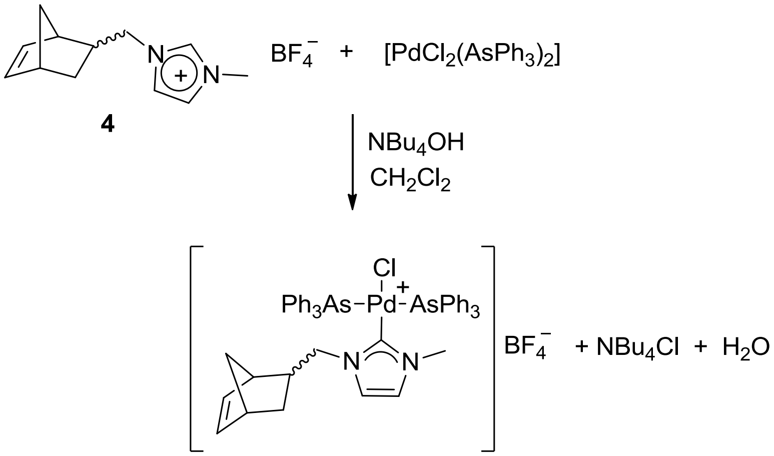
[77] Suarez, P. A. Z.; Einloft, S.; Dullius, J. E. L.; de Souza, R. F.; Dupont, J. *J. Chim. Phys*. **1998**, *95*, 1626-1639



4

5

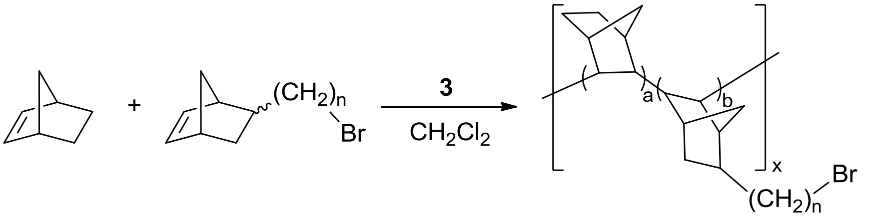
(2.3)

When copolymerization of complex **5** with norbornene was attempted very low yield was obtained again, without incorporation of the functionalized monomer.

Considering that the polymerization of neither the imidazolium salts nor the complex was possible, we decided to try the introduction of imidazole moieties into preformed polymers.

2.2.1.2 Derivatization of VA-polynorbornenes

In recent years our group has developed a family of VA-PNBs which have an alkyl chain with a terminal halogen.[55b] Therefore, we decided to use some of these polymers as raw material to anchor some imidazole groups by simple, one step nucleophilic substitution. These polymers are obtained by direct copolymerization of norbornene with the halogen substituted norbornene produced by a Diels-Alder reaction alike to that showed in scheme 2.3. In these examples nickel complex **3** affords excellent yields after optimizing reaction conditions (Scheme 2.4). These polymers are soluble and can be easily characterized by NMR spectroscopy.



n = 1, **6** = VA-CopNBNB(CH_2)–Br
n = 4, **7** = VA-CopNBNB($(CH_2)_4$–Br

Scheme 2.4: Vinylic-addition copolymerization of norbornene with haloalkylnorbornenes.

As shown in scheme 2.4, we chose polymers containing a bromo atom linked to the norbornene by a methylene (**6**) or butylene (**7**) bridge. These copolymers are richer in norbornene, so this contributes to a larger separation of the bromo substituents in the main chain. The composition of the copolymers show an average ratio of monomers of a/b = 1.96 (2.691 mmol Br/g copolymer) for **6** and a/b = 2.73 (2.055 mmol Br/g copolymer) for **7**. The structure shown in Scheme 2.4 is a simplified one, since VA-PNBs have a very complex morphology.[26b,48c,78] Also, they are generally quite polydisperse with molecular weights around $M_w = 10^5$ ($M_w/M_n \approx 1.7$) for **6** and $M_w \geq 10^6$ ($M_w/M_n \approx 2$) for **7**.[55b] We got excellent results in the nucleophilic substitution of polymer **7** with 1-methylimidazole, but unfortunately, polymer **6** did not react by either microwave irradiation or conventional thermal heating (Scheme 2.5). The different behavior of both polymers in identical reaction conditions suggests the relevance of the length of the alkyl chain tethering the halogen. The steric hindrance of the polymer backbone might be preventing the substitution in the polymer with the shortest pendant chain.

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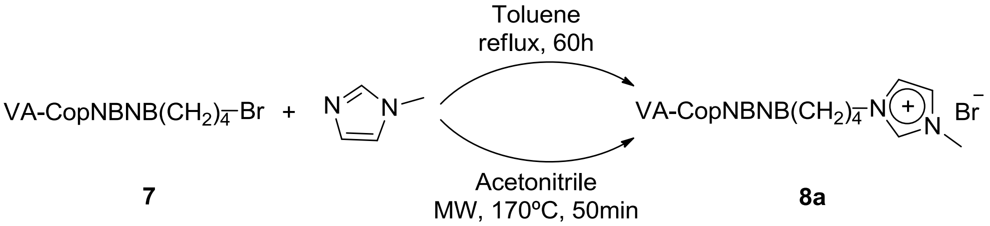
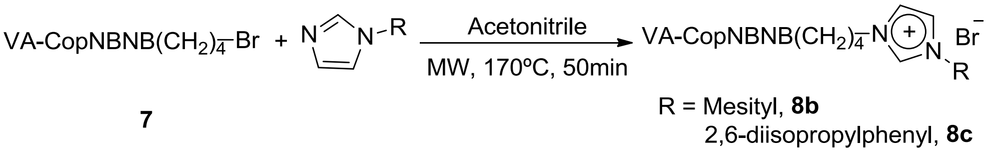
[78] (a) Ahmed, S.; Bidstrup, S. A.; Kohl, P.; Ludovice, P. *Macromol. Symp.* **1998**, *133*, 1-10. (b) Huang, W. J.; Chang, F. C.; Chu, P. P. *J. Polym. Sci. B: Polym. Phys.* **2000**, *38*, 2554-2563.



Scheme 2.5: Alternative routes used for the nucleophilic substitution of **7** with 1-methylimidazole.

Two more imidazoles were tested with polymer **7** (Scheme 2.6). In this case both heterocycles have a bulkier substituent than methyl and unlike the 1-methylimidazole, for these reactions only microwave heating was useful.



Scheme 2.6: Nucleophilic substitution of **7** with bulkier imidazoles.

Among the three polymers obtained only **8a** swells in methanol forming a viscous solution, whereas **8b** and **8c** are insoluble in most common solvents. The ^{1}H NMR spectrum of **8a** in deuterated methanol showed clearly the appearance of the signals corresponding to the methyl and methylene groups bound to the two nitrogen atoms as well as the signals of the double bond of the imidazole. However, no signal could be associated with the proton in the carbon between both nitrogen atoms. This can be explained attending to the high acidity of this proton and considering a fast exchange between it and the deuterium of the solvent.

All the polymer-bound imidazolium salts were characterized in the solid state by ^{13}C CP-MAS NMR and IR spectroscopy. The ν(C-Br) IR absorption band at 562 cm^{-1} in polymer **7** disappeared completely after the reaction. Furthermore, representative ν(C=N) bands were found in a range between 1570 to 1540 cm^{-1} for polymers **8**. In addition, quantitative bromide and nitrogen analysis confirms the complete substitution of the halogen in the alkyl chain by imidazole in every case. The unreacted excess of imidazole employed can be easily recovered by evaporation of the solution after the filtration of the polymer. This is rather important due to the fact that a lot of interesting 1-substituted imidazoles are not commercially available, like those used in **8b** and **8c** and have to be synthesized in a several-step procedure. Moreover, most of those imidazoles which can be purchased are usually quite expensive.

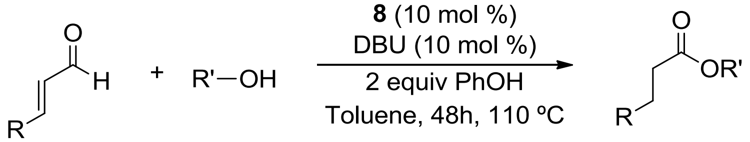
This methodology allows the introduction of different imidazole moieties into a polymeric support without the need of making a new polymer each time a new imidazole group wants to be tested.

2.2.2 Use of VA-polynorbornene-supported imidazolium salts as organocatalysts

Two different reactions were chosen in order to check the activity of our polymers as heterogeneous organocatalysts. Both processes were umpolung reactions with α,β-unsaturated aldehydes catalyzed by NHCs. The nucleophilic behavior of the catalyst is responsible of the performance of the aldehydes in a similar fashion to that of homoenolates.

2.2.2.1 Conversion of α,β-unsaturated aldehydes into saturated esters

The first reaction tested was the synthesis of saturated esters from α,β-unsaturated aldehydes (Scheme 2.7).[79] In this transformation an alcohol acts as nucleophile and a proton as electrophile.



R = Ph, R' = $PhCH_2$,**9**
R = Ph, R' = Ph, **10**
R = nPr, R' = $PhCH_2$, **11**
R = nPr, R' = Ph, **12**

Scheme 2.7.

The first step was the synthesis of the carbene from the imidazolium salt by treatment of the starting polymers **8** with a base. In our case the active species were formed stirring the polymers at room temperature for 30 minutes with an equivalent amount of

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[79] Chan, A.; Scheidt, K. A. *Org. Lett.* **2005**, *7*, 905-908

1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). As mentioned before, the starting imidazolium salts are insoluble in common solvents including toluene. Additionally, swelling measures in this solvent showed no increase of the volume. Even when the polymers were soaked in a solution of DBU in toluene, the polymer-supported carbenes presented negligible solubility and swelling.

After the formation of the carbene the reaction follows using the conditions described by Chan and Scheidt.[79] To a suspension of 10 %mol of the carbene in toluene the α,β-unsaturated aldehyde was added with a twofold molar amount of phenol (acting as source of protons responsible of the electrophillic attack), and a fivefold molar amount of the alcohol responsible of the nucleophilic attack. After heating the mixture for 48 hours at 110 ºC the reaction was cooled down and the yields were determined by ^{1}H NMR.

Table 2.1 shows the results obtained for the three different imidazolium salts used. In a standard reaction, cinammaldehyde and benzyl alcohol were used in the conditions described in Scheme 2.7 to form ester **9**. Polymer **8a** gave a lower yield compared to those achieved by the polymers with an aryl substituent. Between **8b** and **8c** no differences could be observed since quantitative yields were reached in both cases. These results indicate that the presence of a bulky group in the carbene is evidently positive for the organocatalysis.

Table 2.1. Comparison of the activities of the imidazolium salts **8** as organocatalysts in the synthesis of **9**.[a]

Entry	Catalyst	**9**, Yield (%)[b]
1	**8a**	73
2	**8b**	99
3	**8c**	99

a) Reaction conditions shown in Scheme 2.7. Reactions performed with 5 equiv of benzyl alcohol. b) Crude yields determined by ^{1}H NMR.

As mentioned above, the aryl-substituted imidazoles used in the functionalization of the polymers had to be prepared since they are not commercially available. The synthesis of the molecule with a mesityl group is more convenient and, in our hands, afforded higher yields than that with 2,6-diisopropylphenyl; therefore we decided to use polymer **8b** in the subsequent experiments.

Given the good results achieved with the heterogeneous organocatalyst, several recycling tests were performed. After the end of the reaction, polymer **8b** was filtered and washed with toluene under a nitrogen atmosphere and reused without further treatment. The excellent yields were reproduced for at least five times (Table 2.2, entries 2-5). After these experiments the imidazolium salt was recovered by treatment of the polymer with an acid, namely tetrafluoroboric acid in diethyl ether. This new imidazolium salt was exposed to the air, stored several days and reused later in the same reaction conditions used previously affording again quantitative yields (Table 2.2, entry 6). A moderate yield was obtained when phenol was used both as electrophile source and nucleophile to form **10** (Table 2.2, entry 7).

Table 2.2. Catalytic results on the conversion of cinnamaldehyde into saturated esters by **8b**.[a]

Entry	Cycle	Alcohol	Yield (%)[b]
1	1	$PhCH_2OH$	**9** (99)
2	2	$PhCH_2OH$	**9** (97)
3	3	$PhCH_2OH$	**9** (94)
4	4	$PhCH_2OH$	**9** (99)
5	5	$PhCH_2OH$	**9** (99)
6[c]	6	$PhCH_2OH$	**9** (99)
7	1	PhOH	**10** (53)
8[d]	1	$PhCH_2OH$	**9** (0)
9[e]	1	$PhCH_2OH$	**9** (0)

a) Reaction conditions shown in Scheme 2.7. Reactions performed with 5 equiv of alcohol (R'OH). b) Crude yields determined by ^1H NMR. c) Catalyst recovered by protonation after cycle 5, stored for days in the air and reused. d) Without DBU. e) Without polymer **8b**.

A good yield of **11** was also achieved with *trans*-2-hexenal when benzyl alcohol was used as nucleophile (Table 2.3, entry 1). These results can be maintained for at least four recycling experiments without loss of activity (Table 2.3, entries 2-5). However when this β-alkyl-enal was made react with phenol as nucleophile no formation of **12** was observed (Table 2.3, entry 6).

Table 2.3. Catalytic results on the conversion of *trans*-2-hexenal into saturated esters by **8b**.[a]

Entry	Cycle	Alcohol	Yield (%)[b]
1	1	$PhCH_2OH$	**11** (80)
2	2	$PhCH_2OH$	**11** (82)
3	3	$PhCH_2OH$	**11** (92)
4	4	$PhCH_2OH$	**11** (87)
5	5	$PhCH_2OH$	**11** (85)
6	1	PhOH	**12** (0)

a) Reaction conditions shown in Scheme 2.7. Reactions performed with 5 equiv of alcohol (R'OH). b) Crude yields determined by ^{1}H NMR.

Some additional experiments were done to assure the role of the heterogeneous carbene as organocatalyst. When the experiment with cinnamaldehyde and benzyl alcohol to give **9** was performed in the presence of the polymer-supported imidazolium salt **8b** but without addition of base no reaction was observed (Table 2.2, entry 8). The same result was obtained when DBU was added but the polymer was not (Table 2.2, entry 9). These results clearly point out to the carbene formed as the active species in the organocatalysis. Furthermore, a filtration test was carried out to discard the presence of homogeneous species responsible of the catalysis. In an experiment similar to that described in Table 2.1, entry 2, the reaction was cooled after 12 hours and checked by ^{1}H NMR observing that **9** had been formed in a 20.6% yield. The polymer was then filtered under nitrogen and the filtrate was kept in the same reaction conditions for an additional 12 hours. After this time the yield remained almost identical (20.7 %). This data supports the consideration that the carbene formed from **8b** stays on the polymer and acts as a heterogeneous catalyst.

In order to have a better knowledge of our polymer, scanning electron microscopy images of it were taken before and after its use. Originally, polymer **8b** has a granular texture with small pores (Figure 2.4a). After 5 uses and the recovery of the imidazolium salt by treatment with tetrafluoroboric acid in diethyl ether, the polymer presents a smoother and less porous surface (Figure 2.4b). Since the polymer showed a very low swelling effect with the solvent, this seem to indicate that the polymeric matrix exposes enough active centers on the outer surface to guarantee a high catalytic activity.

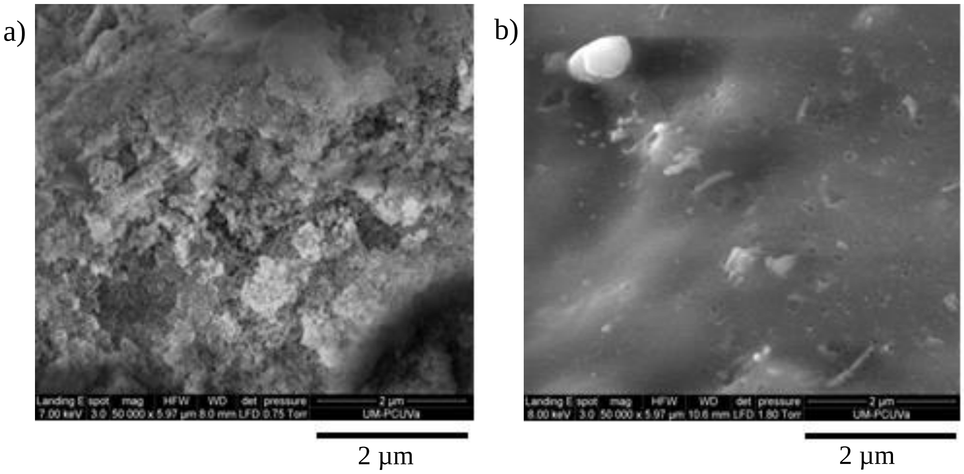

Figure 2.4: SEM images of polymer **8b**: a) before use; b) after five uses in the synthesis of saturated esters.

When comparing our results with those reported by Chan and Scheidt, where a non-supported benzimidazolium salt was used as precatalyst,[79] it is worthwhile mentioning that, although our system requires longer times (48 hours for **8b** versus 2-6 hours for the benzimidazole derivative), in the same reaction conditions (base, solvent and temperature) similar yields are achieved and the reusability of our polymer largely compensates that drawback.

2.2.2.2 Synthesis of γ-butyrolactones

The second organic reaction tested with our polymer **8b** was the synthesis of a γ-butyrolactone from cinnamaldehyde and a fluorinated ketone (Scheme 2.8).[80] In this transformation the role of the electrophile is played by the ketone leading to the cyclization product.

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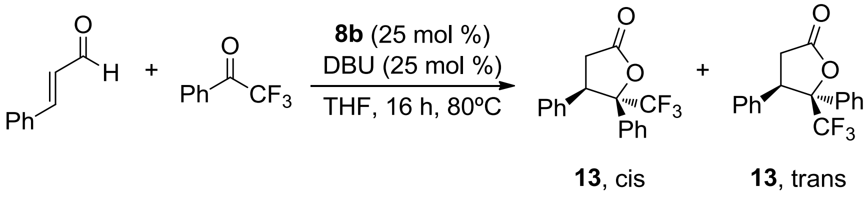
[80] (a) Burstein, C.; Glorius, F. *Angew. Chem. Int. Ed*. **2004**, *43*, 6205-6208; *Angew. Chem*. **2004**, *116*, 6331-6334. (b) Sohn, S S.; Rose, E. L.; Bode, J. W. *J. Am. Chem. Soc*. **2004**, *126*, 14370-14371. (c) Ye, W.; Cai, G.; Zhuang, Z.; Jia, X.; Zhai, H. *Org. Lett*. **2005**, *7*, 3769-3771.



Scheme 2.8.

Table 2.4. Results of the synthesis of butyrolactones catalyzed by **8b**.[a]

Cycle	**13**, Yield (%)[b]	dr (*cis*/*trans*)[b]
1	58	2.22
2	56	2.22
3	59	2.17
4	60	2.26
5	61	2.14
6[c]	60	2.15
7[d]	0	-
8[e]	0	-

a) Reaction conditions shown in Scheme 2.8. Reactions performed with 3 equiv of ketone. b) Crude yields and diateromeric ratios determined by ^{19}F NMR. c) Catalyst stored in THF under a nitrogen atmosphere after cycle 5 for 3 months and reused. d) Without DBU. e) Without polymer **8b**.

As it happened in the synthesis of saturated esters, the first step was the formation of the carbene form **8b** with the same procedure described above. In this case the reactions were performed in THF and the results of the swelling measurements of the imidazolium salt and the carbene were analogous to those observed in toluene. After that cinnamaldehyde and 2,2,2-trifluoroacetophenone were added to a suspension of 25 % mol of the preformed carbene and heated at 80 ºC for 16 hours. After cooling, the reaction was checked by ^{19}F NMR and the polymer was filtered under a nitrogen atmosphere, washed with THF and recovered for its reutilization. After five uses the yields and diasteromeric ratios remained constants (Table 2.4, entries 1-5). After these experiments the polymer was kept under THF and reused three months later affording again good yields (Table 2.4, entry 6). As it occurred with the conversion of α,β-unsaturated aldehydes into saturated esters no reaction was observed when either **8b** or DBU were absent.

Comparing our polymer with other catalytic systems used in the synthesis of γ-butyrolactones, **8b** requires higher temperatures (80 ºC for **8b** versus room temperature) but similar reaction times than non-supported carbene precursors. However the need of higher temperature has also been observed in the only example found in the literature where this reaction was catalyzed by a main chain polymeric carbene shown in scheme 2.2,a.[73a]

2.3 CONCLUSIONS

We have developed a new family of VA-PNBs containing imidazole moieties (**8**). They are the first examples of NHCs anchored in this type of support. The polymer backbone is a robust and inert vinyl-type polynorbornene with no functionalities except those introduced at will. That implies a high tolerance to harsh reaction conditions.

Starting from a ω-bromoalkyl-substituted polynorbornene, direct nucleophilic substitution of the Br with an imidazole allows a straightforward synthesis of several imidazolium salts. Depending on the imidazole unit to be introduced thermal heating (**8a**) or microwave irradiation (**8b**, **8c**) is required. This procedure allows the introduction of different functionalities into the support without the necessity of polymerizing specific monomers in every case. This type of polymer cannot be obtained by direct polymerization of norbornene derivatives with imidazole moieties in their structure.

These imidazolium salts can be used as precursors of carbenes active in different organocatalysis. After treatment with a base the polymer-supported NHCs obtained have been used in the conversion of α,β-unsaturated aldehydes into saturated esters and the synthesis of γ-butyrolactones with good results even after several recycling cycles. Treatment of the NHCs with an acid after the reaction allows the regeneration of the imidazolium salt which can be stored without special precautions for further use.

2.4 EXPERIMENTAL PART

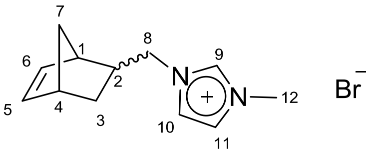
2.4.1 General Methods

^{1}H, ^{13}C and ^{19}F NMR spectra were recorded using Bruker AV-400 and Agilent MR-500 instruments. Chemical shifts (δ) are reported in ppm and referenced to Me_4Si (^{1}H, ^{13}C) or $CFCl_3$ (^{19}F). All of the NMR spectra were acquired at 293 K. The NMR spectra were recorded in deuterated solvents such as $CDCl_3$ or CD_3OD or, in the case of the catalytic reactions, in protic solvents using an acetone-d6 capillary. The solid state NMR spectra were recorded at 293 K under magic angle spinning (MAS) in a Bruker AV-400 spectrometer using a Bruker BL-4 probe with 4mm diameter zirconia rotors spinning at 8 kHz. ^{13}C CP MAS NMR spectra were measured at 100.61 MHz and recorded with proton decoupling (tppm), with a 90° pulse length of 4.5 µs and a contact time of 3 ms and recycle delay of 3 s. The ^{13}C NMR spectra were referred to glycine (CO signal at 176.1 ppm). IR spectra were recorded on a Perkin-Elmer FT/IR SPECTRUM FRONTIER spectrophotometer with CsI + ATR diamond accessory. Scanning Electron Microscopy (SEM) measurements have been carried out at the *Unidad de Microscopía Avanzada of the Parque Científico UVa* by means of an Environmental Scanning Electron Microscope (ESEM), model FEI-Quanta 200FEG provided with a Schottky-Field Emission filament. The SEM analyses were performed at Low Vacuum Mode using water vapour as auxiliary gas. This imaging mode allows working with non-conductive samples without any specific preparation or metallic coatings. The measurements were performed at a working pressure in the chamber ranging between 0.6 - 1 Torr [80 - 133 Pa] and an accelerating voltage of 7kV. The Secondary Electron SEM images were acquired with a Large Field Detector (LFD) which is the suitable one for working at Low Vacuum Mode. Microwave-promoted experiments were carried out with a CEM Discover 300W single-mode microwave instrument, with simultaneous cooling with compressed air. The reaction mixtures were prepared in 10 mL special glass reaction tubes with self-sealing septa with a pressure sensor on top of the vial. The temperature was monitored through a noncontact infrared sensor centrally located beneath the cavity floor. Magnetic stirring was provided to ensure complete mixing of the reagents. The power applied was 300 W with a ramp time of 10 min. The halogen content in the polymers was determined by oxygen-flask combustion of a sample and analysis of the residue by mercurimetric titration of the bromide.[81] Solvents were dried prior to use and stored under nitrogen. The reagents used in the synthesis of the monomers and organocatalytic reactions were purchased from Aldrich, Alfa-Aesar and Acros. Bromomethylnorbornene (**1**),[76] [$Ni(C_6F_5)_2(SbPh_3)_2$] (**3**),[54,55a] [$PdCl_2(AsPh_3)_2$],[82] vinylic addition polynorbornenes (**6** and **7**),[55b] 1-mesitylimidazole and 1-(2,6-diisopropylphenyl)imidazole,[83] were prepared according to the literature procedures.

2.4.2 Synthesis of norbornene monomers bearing imidazole moieties

Synthesis of [$NBCH_2IMe$]Br (2) (IMe = 1-methylimidazole)

1-Methylimidazole (1.18 g, 14.3 mmol) was added to a solution of **1** (2.68 g, 14.3 mmol) in toluene (30.0 mL) and heated at reflux for 72 h. After that time was two immiscible liquid phases were formed. Toluene was evaporated and the oily phase remaining was washed with THF (5 x 20.0 mL) in order to remove unreacted 1-methylimidazole. The mixture was then evaporated to eliminate the residual THF and the product was obtained as pale orange oil (2.27 g, 58.7% yield). **2** was obtained as a mixture of isomers in a ratio endo:exo = 83:17.



2 endo: ^1H NMR (400.13 MHz, $CDCl_3$) δ: 10.26 (br, 1H, H^9), 7.62 (dd, $J_{11-10,\ 11-9}$ = 1.8, 1.7 Hz, 1H, H^{11}), 7.40 (dd, $J_{10-11,\ 10-9}$ = 1.8, 1.7 Hz, 1H, H^{10}), 6.25 (dd, $J_{5-6,\ 5-4}$ = 5.7, 3.1 Hz, 1H, H^5), 6.10 (dd, $J_{6-5,\ 6-1}$ = 5.7, 2.6 Hz, 1H, H^6), 4.12 (s, 3H, H^{12}), 3.97 (dd, $J_{8-8',\ 8-2}$ = 13.2, 7.0 Hz, 1H, H^8), 3.90 (dd, $J_{8'-8,\ 8'-2}$ = 13.2, 8.8 Hz, 1H, $H^{8'}$), 2.84 (br, 1H, H^1), 2.72 (br, 1H, H^4), 2.65 (m, 1H, H^2), 1.94 (ddd, $J_{3-3',\ 3-2,\ 3-4}$ = 11.9, 8.7, 4.0 Hz, 1H, H^3), 1.45 (m, $J_{7-7',\ 7-3'}$ = 8.5, 2.6 Hz, 1H, H^7), 1.27 (m, $J_{7'-7}$ = 8.5 Hz, 1H, $H^{7'}$), 0.63 (ddd, $J_{3'-3,\ 3'-2,\ 3'-7}$ = 11.9, 4.0, 2.6 Hz, $H^{3'}$). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$) δ: 138.8 (s, C^5), 136.6 (s, C^9), 131.2 (s, C^6), 123.8

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[81] White, D. C. *Mikrochim. Acta*, **1961**, 449-456.

[82] Usón, R.; Royo, P.; Forniés, J.; Martínez, F. *J. Organomet. Chem.* **1975**, *90*, 367-374.

[83] Liu, J.; Chen, J.; Zhao, J.; Zhao, Y.; Li, L.; Zhang, H. *Synthesis*, **2003**, *17*, 2661-2666.

(s, C^{11}), 122.2 (s, C^{10}), 53.6 (s, C^{8}), 49.2 (s, C^{7}), 43.7 (s, C^{4}), 42.1 (s, C^{1}), 39.6 (s, C^{2}), 36.5 (s, C^{12}), 29.7 (s, C^{3}).

2 exo: ^{1}H NMR (400.13 MHz, $CDCl_3$) δ: 10.30 (br, 1H, H^{9}), 7.63 (dd, $J_{11-10,\ 11-9}$ = 1.8, 1.7 Hz,1H, H^{11}), 7.48 (dd, $J_{10-11,\ 10-9}$ = 1.8, 1.7 Hz, 1H, H^{10}), 6.06 (dd, $J_{5-6,\ 5-4}$ = 5.7, 3.1 Hz, 1H, H^{5}), 6.02 (dd, $J_{6-5,\ 6-1}$ = 5.7, 3.1 Hz, 1H, H^{6}), 4.39 (dd, $J_{8-8',\ 8-2}$ = 13.8, 8.1 Hz, 1H, H^{8}), 4.30 (dd, $J_{8'-8,\ 8'-2}$ = 13.8, 9.2 Hz, 1H, $H^{8'}$), 2.86 (br, 1H, H^{4}), 2.55 (br, 1H, H^{1}). * $^{13}C\{^{1}H\}$ NMR (100.6 MHz, $CDCl_3$) δ: 137.2 (s, C^{5}), 135.4 (s, C^{6}), 135.0 (s, C^{9}), 122.4 (s, C^{11}), 120.4 (s, C^{10}), 54.3 (s, C^{8}), 45.0 (s, C^{7}), 43.8 (s, C^{4}), 42.1 (s, C^{1}), 39.6 (s, C^{2}), 36.0 (s, C^{12}), 30.4 (s, C^{3}).

*Some signals of the exo isomer cannot be observed because they are overlapped by signals of the endo isomer.

Synthesis of [$NBCH_2IMe$]BF_4 (4)

In a round-bottom flask protected from light, **2** (0.965 g, 3.58 mmol) was disolved in CH_2Cl_2 (20.0 mL). Silver tetrafluoroborate (0.698 g, 3.58 mmol) was then added and the mixture was stirred at room temperature for 3 h. After removing the precipitate by filtration the solvent was evaporated and the product was obtained as a yellow oil (0.823 g, 83.2% yield). **4** was obtained as a mixture of isomers in a ratio endo:exo = 83:17 that parallel the starting material (**2**).

4 endo: ^{1}H NMR (400.13 MHz, $CDCl_3$) δ: 8.82 (br, 1H, H^{9}), 7.40 (dd, $J_{11-10,\ 11-9}$ = 1.5, 1.2 Hz, 1H, H^{11}), 7.31 (dd, $J_{10-11,\ 10-9}$ = 1.5, 1.2 Hz, 1H, H^{10}), 6.27 (dd, $J_{5-6,\ 5-4}$ = 6.0, 3.0 Hz,1H, H^{5}), 6.05 (dd, $J_{6-5,\ 6-1}$ = 6.0, 3.2 Hz, 1H, H^{6}), 3.96 (s, 3H, H^{12}), 3.89 (dd, $J_{8-8',\ 8-2}$ = 13.8, 7.6 Hz, 1H, H^{8}), 3.85 (dd, $J_{8'-8,\ 8'-2}$ = 13.8, 8.4 Hz, 1H, $H^{8'}$), 2.86 (br, 1H, H^{1}), 2.73 (br, 1H, H^{4}), 2.60 (m, 1H, H^{2}), 1.94 (ddd, $J_{3-3',\ 3-2,\ 3-4}$ = 11.8, 9.2, 3.60 Hz, 1H, H^{3}), 1.47 (m, $J_{7-7',\ 7-3'}$ = 8.4, 2.2 Hz, 1H, H^{7}), 1.29 (m, $J_{7'-7}$ = 8.4 Hz, 1H, $H^{7'}$), 0.63 (ddd, $J_{3'-3,\ 3'-2,\ 3'-7}$ = 11.8, 4.0, 2.2 Hz, $H^{3'}$). $^{13}C\{^{1}H\}$ NMR (100.6 MHz, $CDCl_3$) δ: 139.1 (s, C^{5}), 135.8 (s, C^{9}), 131.3 (s, C^{6}), 123.8 (s, C^{11}), 122.4 (s, C^{10}), 53.8 (s, C^{8}), 49.5 (s, C^{7}), 44.0 (s, C^{4}), 42.4 (s, C^{1}), 39.7 (s, C^{2}), 36.2 (s, C^{12}), 29.9 (s, C^{3}).

4 exo: ^{1}H NMR (400.13 MHz, $CDCl_3$) δ: 8.87 (br, 1H, H^{9}), 7.36 (dd, $J_{10-11,\ 10-9}$ = 1.5, 1.2 Hz, 1H, H^{10}), 6.08 (dd, $J_{5-6,\ 5-4}$ = 5.6, 3.2 Hz, 1H, H^{5}), 4.23 (dd, $J_{8-8',\ 8-2}$ = 13.9, 8.0 Hz, 1H, H^{8}), 4.17 (dd, $J_{8'-8,\ 8'-2}$ = 13.9, 8.4 Hz, 1H, $H^{8'}$), 2.89 (br, 1H, H^{1}). * $^{13}C\{^{1}H\}$ NMR (100.6 MHz, $CDCl_3$) δ: 54.6 (s, C^{8}), 44.9 (s, C^{7}), 41.9 (s, C^{1}), 30.7 (s, C^{3}).*

*Many signals of the exo isomer cannot be observed because they are overlapped by signals of the endo isomer.

^{19}F NMR (376.5 MHz, $CDCl_3$) δ: -151.11 (s, 4F, B*F*4).

Synthesis of [PdCl(NBCH$_2$IMe)(AsPh$_3$)$_2$]BF$_4$ (5)

NBu_4OH (0.351 g, solution in MeOH, 40% wt, 1.35 mmol) was added to a solution of **4** (0.374 g, 1.35 mmol) in CH_2Cl_2 (20.0 mL). After 10 min a solution of [PdCl$_2$(AsPh$_3$)$_2$] (1.07 g, 1.35 mmol) in CH_2Cl_2 (50.0 mL) was added to the carbene solution and the mixture was stirred at room temperature for 16 h. After drying over magnesium sulfate the solvent was partially removed. Then MeOH (15.0 mL) was added and a yellow solid precipitated. The solid was filtered, washed with cold MeOH (3 x 5.0 mL) and air-dried. The complex was a light yellow powder (0.996 g, 71.5% yield). **5** was obtained as a mixture of isomers in a ratio endo:exo = 83:17 that parallel the starting material (**4**).

5 endo: ^{1}H NMR (400.13 MHz, $CDCl_3$) δ: 7.6-7.3 (m, 30 H, $AsC_6\mathit{H}_5$), 7.10 (d, $J_{11\text{-}10}$ = 2.0 Hz, 1H, H^{11}), 6.71 (d, $J_{10\text{-}11}$ = 2.0 Hz, 1H, H^{10}), 6.10 (dd, $J_{5\text{-}6,\ 5\text{-}4}$ = 5.9, 2.9 Hz, 1H, H^5), 5.77 (dd, $J_{6\text{-}5,\ 6\text{-}1}$ = 5.9, 2.9 Hz, 1H, H^6), 3.42 (dd, $J_{8\text{-}8',\ 8\text{-}2}$ = 13.6, 7.8 Hz, 1H, H^8), 3.22 (s, 3H, H^{12}), 3.21 (dd, $J_{8'\text{-}8,\ 8'\text{-}2}$ = 13.6, 7.3 Hz, 1H, $H^{8'}$), 2.61 (br, 1H, H^1), 2.38 (br, 1H, H^4), 1.97 (m, 1H, H^2), 1.51 (ddd, $J_{3\text{-}3',\ 3\text{-}2,\ 3\text{-}4}$ = 11.2, 9.2, 3.9 Hz, 1H, H^3) 1.25 (m, $J_{7\text{-}7',\ J7\text{-}3'}$ = 8.6, 2.4 Hz, 1H, H^7), 0.66 (m, $J_{7'\text{-}7}$ = 8.6 Hz, 1H, $H^{7'}$), 0.34 (ddd, $J_{3'\text{-}3,\ 3'\text{-}2,\ 3'\text{-}7}$ = 11.2, 3.9, 2.4 Hz, 1H, $H^{3'}$). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) δ: 153.0 (s, C^9), 138.9 (s, C^5), 133.1, 131.3, 129.7 (3 s, C_{ortho}, C_{meta}, C_{para}), 130.9 (s, C^6), 130.6 (s, C_{ipso}), 126.7 (s, C^{11}), 124.2 (s, C^{10}), 55.4 (s, C^8), 49.4 (s, C^7), 44.6 (s, C^4), 42.3 (s, C^1), 39.5 (s, C^2), 37.4 (s, C^{12}), 30.8 (s, C^3).

5 exo: ^{1}H NMR (400.13 MHz, $CDCl_3$) δ: 7.6-7.3 (m, 30 H, $AsC_6\mathit{H}_5$), 7.03 (d, $J_{11\text{-}10}$ = 2.0 Hz, 1H, H^{11}), 6.81 (d, $J_{10\text{-}11}$ = 2.0 Hz, 1H, H^{10}), 5.52 (dd, $J_{6\text{-}5,\ 6\text{-}1}$ = 5.4, 2.9 Hz, 1H, H^6), 3.71 (dd, $J_{8\text{-}8',\ 8\text{-}2}$ = 13.4, 7.4 Hz, 1H, H^8), 3.52 (dd, $J_{8'\text{-}8,\ 8'\text{-}2}$ = 13.4, 8.3 Hz, 1H, $H^{8'}$), 2.66 (br, 1H, H^1), 2.33 (br, 1H, H^4). * ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) δ: 153.3 (s, C^9), 137.1 (s, C^5), 134.8 (s, C^6), 126.3 (s, C^{11}), 124.7 (s, C^{10}), 56.4 (s, C^8), 44.9 (s, C^7), 44.6 (s, C^4), 41.8 (s, C^1), 39.6 (s, C^2), 37.4 (s, C^{12}), 31.4 (s, C^3).*

*Some signals of isomer the exo isomer cannot be observed because they are overlapped by signals of the endo isomer.

^{19}F NMR (376.5 MHz, $CDCl_3$) δ: -153.42 (s, 4F, B*F*4).

2.4.3 Synthesis of imidazolium salts supported on VA-PNBs

Synthesis of [VA-CopNBNB(CH_2)$_4$IMe]Br (8a) (IMe = 1-methylimidazole)

In a round-bottom flask copolymer VA-CopNBNB(CH_2)$_4$Br (**7,** 0.2000 g, 0.4113 mmol of Br) and 1-methylimidazole (0.1689 g, 2.057 mmol) were stirred in toluene (30 mL) at reflux for 60 hours. The solvent was partially removed to c.a. 15 mL, the mixture was then poured into acetone (40 mL) and stirred for 7 hours at room temperature. The polymer was filtered, washed with acetone (5 x 10 mL) and air-dried. A white solid was obtained (0.2301 g, 98% yield). Elemental analysis: calcd for $[(C_7H_{10})_x\{C_7H_9(CH_2)_4(C_4H_6N_2)\}_y]Br$ (x/y = 2.73): 140.6 mg Br/g (14.06%), N 4.93%; found: Br 141.2 mg Br/g (14.12%), N 4.86%. IR (neat), cm^{-1}: 1567 ν(C=N). ^{1}H NMR (400.15 MHz, δ, CD_3OD): 7.8-7.4 (br, 2H, N-C*H*=C*H*-N), 4.2 (br, 2H, -CH_2-N), 3.9 (br, 3H, N-CH_3), 2.8-0.3 (br, 25H). ^{13}C CP-MAS NMR (100.6 MHz): 143-134 (br, N*C*HN), 130-117 (br, N*C*H=*C*HN), 67-16 (br, polyNB, Me).

Synthesis of [VA-CopNBNB(CH_2)$_4$IMes]Br (8b) (IMes = 1-mesitylimidazole)

Copolymer VA-CopNBNB(CH_2)$_4$Br **7** (0.2000 g, 0.4113 mmol Br), 1-mesitylimidazol (0.3831 g, 2.057 mmol) and CH_3CN (2 mL) were placed in a 10 mL microwave reaction vessel. The mixture was heated to 170 ºC and stirred for 50 minutes in the microwave oven using a maximum power of 300 W. The reaction mixture was poured into Et_2O (30 mL) and stirred for four hours. The solid was filtered, washed with Et_2O (5 x 10 mL) and air-dried. The product was obtained as a white solid (0.2760 g, 99% yield). This procedure can be scaled to obtain a larger amount (4.120 g, 99% yield). Elemental analyses: calcd for $[(C_7H_{10})_x\{C_7H_9(CH_2)_4(C_{12}H_{14}N_2)\}_y]Br$ (x/y = 2.73): 118.8 mg Br/g (11.88%), N 4.17%; found: Br 118.2 mg Br/g (11.82%), N 4.39%. IR (neat), cm^{-1}: 1544 ν(C=N). ^{13}C CP-MAS NMR (100.61 MHz): 150-120 (br, aromatic, N*C*HN, N*C*H=*C*HN), 70-24 (br, polyNB), 24-15 (br, Me).

Synthesis of [VA-CopNBNB(CH_2)$_4$IPr]Br (8c) (IPr = 1-(2,6-diisopropyl-phenyl)-imidazole)

Copolymer VA-CopNBNB(CH_2)$_4$Br **1** (0.2000 g, 0.4113 mmol Br), 1-(2,6-diisopropylphenyl)-imidazol (0.4700 g, 2.057 mmol) and CH_3CN (2 mL) were placed in a 10 mL microwave reaction vessel. The mixture was heated to 170 ºC and stirred for 50 minutes in the microwave oven using a maximum power of 300 W. The reaction mixture was poured into CH_3CN (30 mL) and stirred for four hours. The solid was filtered, washed with CH_3CN (5 x 10 mL) and air-dried. The product was obtained as a white solid (0.2861 g, 97% yield). Elemental analyses: calcd for $[(C_7H_{10})_x\{C_7H_9(CH_2)_4(C_{15}H_{20}N_2)\}_y]Br$ (x/y = 2.73): 111.8 mg Br/g (11.18%), N 3.92%; found: Br 109.2 mg Br/g (10.92%), N 3.67 IR (neat), cm^{-1}: 1541 ν(C=N). ^{13}C CP-MAS NMR (100.61 MHz): 151-143 (br, N*C*HN, C_{ortho}), 142-137 (br, C_{ipso}), 136-129 (br, $(CH_2)_4$N*C*H=CHN, C_{para}), 128-119 (br, $(CH_2)_4$NCH=*C*HN, C_{meta}), 70-10 (br, polyNB, ^{i}Pr).

2.4.4 Standard procedure for conversion of α,β-unsaturated aldehydes into saturated esters. Synthesis of 9

To a suspension of **8b** (7.4 mg, 0.011 mmol of IMes) in 2 mL of dry toluene, DBU (1.52 mg, 0.01 mmol) was added. After stirring for 30 minutes at room temperature cinnamaldehyde (13.2 mg, 0.1 mmol), benzylic alcohol (54.1 mg, 0.5 mmol) and phenol (18.8 mg 0.2 mmol) were added. The reaction mixture was stirred at 110 ºC for 48 h and then checked by ^{1}H NMR (crude yield 99%). The mixture was filtered under nitrogen and the polymer was washed (4 x 5 mL toluene) and stored under 2 mL of dry toluene to be recycled. The filtrate was evaporated and purified by silica gel chromatography (hexane/ether 10:1) affording the ester **9** as a light yellow oil (22.9 mg, 95%). The other experiments collected in Table 2.2 and Table 2.3 were carried out in the same way. The identity of the products was confirmed by comparison of the characterization data with those found in the literature: **9**,[84] **10**[85] and **11**.[86]

2.4.5 Standard procedure for synthesis of γ-butyrolactone 13

In a Schlenk tube under a nitrogen atmosphere 10 mL of dry THF, copolymer **8b** (74.0 mg, 0.11 mmol of IMes) and DBU (15.2 mg, 0.10 mmol) were added. The mixture was stirred at room temperature for 30 minutes. Then cinnamaldehyde (52.9 mg, 0.40 mmol) and

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[84] Black, P. J.; Cami-Kobeci, G.; Edwards, M. G.; Slatford, P. A.; Whittlesey, M. K.; Williams, J. M. J. *Org. Biomol. Chem.* **2006**, *4*, 116-125.

[85] Barton, P.; Laws, A. P.; Page, M. I. *J. Chem. Soc. Perkin Trans. 2*, **1994**, *9*, 2021-2030.

[86] Peterson, P.E.; Stepanian, M. *J. Org. Chem*. **1988**, *53*, 1903-1907.

2,2,2-trifluoroacetophenone (208.9 mg, 1.2 mmol) were added and the reaction mixture was heated for 16 hours at 80 ºC. The reaction was checked by ^{1}H and ^{19}F NMR (crude yield 58%). The mixture was filtered and the polymer was washed (4 x 5 mL of THF) and stored under 10 mL of dry THF in order to be recycled. The filtrate was evaporated and the product was purified by silica gel chromatography (hexane/ethyl acetate 20:1) to obtain a yellowish oil (69.6 mg, 56.8%). The identity of the products **13** was confirmed by comparison of the characterization data with those found in the literature.[80a]

2.4.6 Protonation of the carbene with acid

After being used in the catalytic processes described above, a suspension of **8b** (0.011 mmol of IMes) in toluene was treated with $HBF_4.Et_2O$ (0.0027 mL, 0.02 mmol). It was stirred at room temperature for 1 hour and the polymer was filtered, washed with toluene (4 x 5 mL) and air dried. The polymer can be stored for an indefinite period of time.

Chapter 3

3. NHC-Pd complexes supported on vinylic addition polynorbornenes. Uses in C-C cross-coupling reactions.

3.1 INTRODUCTION

3.1.1 Non supported NHC-metal complexes

Although NHCs have allowed great advances in organocatalysis, the paramount progress can be found in organometallic chemistry where the coordinative ability of NHCs to metal centers has been extensively considered. Since the beginning, they were seen as alternatives to phosphines. NHCs are ligands capable to form strong bonds and with no tendency to oxidation which make them optimal choices in many cases.[64,87] Over the last two decades there has been a singular interest in this discipline and complexes of almost every single metallic element along the periodic table have been described in some

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[87] Jacobsen, H.; Correa, A.; Poater, A.; Costabile, C.; Cavallo, L. *Coord. Chem. Rev*. **2009**, *253*, 687-703.

occasion: main group elements,[88] early transition metals,[88d,89] late transition metals[90] and rare earth elements.[89b,91] From a catalytic point of view, not all of them have been tested or show good results but there has been a remarkable progress in the synthesis and application of some specific transition metals. Organometallic complexes of gold with NHCs have shown great results in C-H bond activation, cycloisomerization, propargylic ester activation or hydration reactions.[92] Also in group 11, NHC-complexes of copper are attracting interest quickly due to their activity in cycloaddition reactions, conjugate addition processes or fluorine chemistry.[92c,93] Another metal with outstanding results when coordinated with heterocyclic carbenes is ruthenium. As mentioned in chapter 1, the second generation Grubbs catalyst was an astonishing contribution to olefin metathesis, especially ROMP.[94]

But the largest application of NHCs can be found in palladium-chemistry. Within organometallic chemistry and catalysis, palladium complexes have played a main role for several decades and the use of NHCs as ancillary ligands, especially imidazole-2-ylidenes, has become a common practice. Their high activity even in harsh reaction conditions makes them appropriate catalysts in a lot of processes. There are many examples of these

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[88] (a) Kuhn, N.; Al-Sheikh, A. *Coord. Chem. Rev*. **2005**, *249*, 829-857. (b) Fliedel, C.; Schnee, G.; Avilés, T.; Dagorne, S. *Coord. Chem. Rev*. **2014**, *275*, 63-86. (c) Prabusankar, G.; Sathyanarayana, A.; Suresh, P.; Babu, C. N.; Srinivas, K.; Metla, B. P. R. *Coord. Chem. Rev*. **2014**, *269*, 96-133. (d) Bellemin-Laponnaz, S.; Dagorne, S. *Chem. Rev*. **2014**, *114*, 8747-8774.

[89] (a) Wang, Z.; Jiang, L.; Mohamed, D. K. B.; Zhao, J.; Hor, T. S. A. *Coord. Chem. Rev*. **2015**, *293-294*, 292-126. (b) Schaper, L. A.; Tosh, E.; Herrmann, W. A. In *N-Heterocyclic Carbenes*; Díez-González, S. Ed.; RSC Publishing: Cambridge, **2011**, ch. 6.

[90] (a) Díez-González, S.; Marion, N.; Nolan, S. P. *Chem. Rev*. **2009**, *109*, 3612-3676. (b) Lin, J. C. Y.; Huang, R. T. W.; Lee, C. S.; Bhattacharyya, A.; Hwang, W. S.; Lin, I. J. B. *Chem. Rev*., **2009**, *109*, 3561-3598. (c) Delaude, L.; Demonceau, A. In *N-Heterocyclic Carbenes*; Díez-González, S. Ed.; RSC Publishing: Cambridge, **2011**, ch. 7. (d) César, V.; Gade, L. H.; Bellemin-Laponnaz, S. In *N-Heterocyclic Carbenes*; Díez-González, S. Ed.; RSC Publishing: Cambridge, **2011**, ch. 8. (e) Fort, Y.; Comoy, C. In *N-Heterocyclic Carbenes*; Díez-González, S. Ed.; RSC Publishing: Cambridge, **2011**, ch. 10. (f) Marion, N. In *N-Heterocyclic Carbenes*; Díez-González, S. Ed.; RSC Publishing: Cambridge, **2011**, ch. 11.

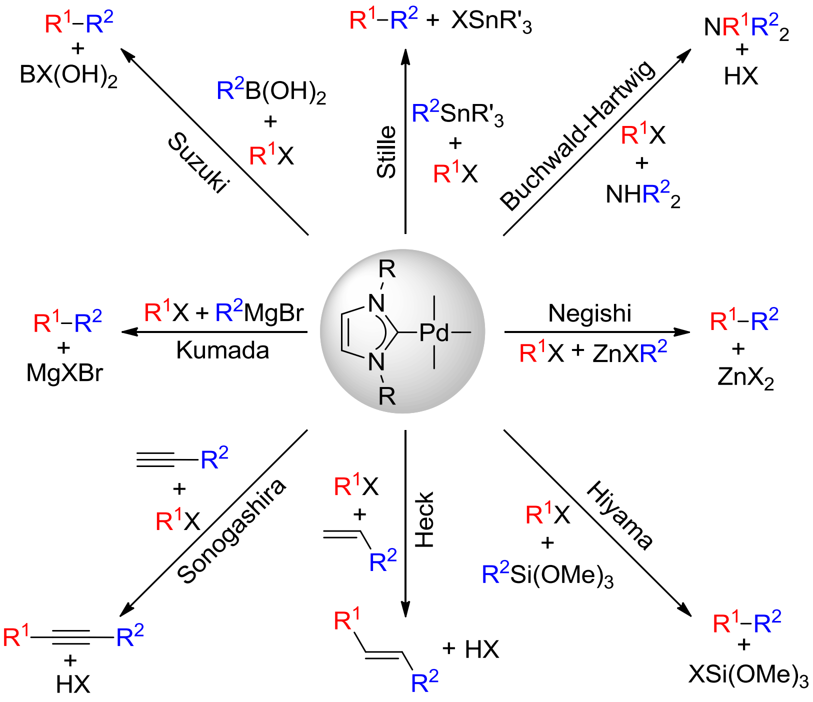
[91] Arnold, P. L.; Casely, I. J. *Chem. Rev*. **2009**, *109*, 3599-3611.

[92] (a) Marion, N.; Nolan, S. P. *Chem. Soc. Rev*. **2008**, 37, 1776-1782. (b) Nolan, S. P. *Acc. Chem. Res*. **2011**, 44, 91-100. (c) Gaillard, S.; Cazin, C. S. J.; Nolan, S. P. *Acc. Chem. Res*. **2012**, 45, 778-787.

[93] (a) Douthwaite, R. E. *Coord. Chem. Rev*. **2007**, *251*, 702-717. (b) Egbert, J. D.; Cazin, C. S. J.; Nolan, S. P. *Catal. Sci. Technol*. **2013**, *3*, 912-926. (c) Lazreg, F.; Nahra, F.; Cazin, C. S. J. *Coord. Chem. Rev*. **2015**, *293-294*, 48-79.

[94] (a) Samojłowicz, C.; Bieniek, M.; Grela, K. *Chem. Rev*. **2009**, *109*, 3708-3742. (b) Vougioukalakis, G. C.; Grubbs, R. H. *Chem. Rev*. **2010**, *110*, 1746-1787.

complexes in C-C cross-coupling reactions as well as in aminations and other reactions (Scheme 3.1).[93a,95]



Scheme 3.1.

3.1.2 Polymer-supported Pd-NHC complexes

As it happens in the case of NHCs used in organocatalysis, there have been a lot of efforts to anchor NHC-Pd complexes onto solid supports. In this case not only the carbene but also the metal is an expensive material and an increasing interest to avoid their loss can be witnessed. Moreover, the bond between palladium and carbene possesses high dissociation energy, higher than the phosphorus-metal bond, and therefore is more resistant to its cleavage. As a consequence of the stability of the Pd-C bond, NHCs are, in principle,

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[95] (a) Kantchev, E. A. B.; O'Brien, C. J.; Organ, M. G. *Angew. Chem. Int. Ed*. **2007**, *46*, 2768-2813. (b) Marion, N.; Nolan, S. P. *Acc. Chem. Res*. **2008**, 41, 1440-1449. (c) Fortman, G. C.; Nolan, S. P. *Chem. Soc. Rev*. **2011**, 40, 5151-5169. (d) Normand, A. T.; Cavell, K. J. In *N-Heterocyclic Carbenes*; Díez-González, S. Ed.; RSC Publishing: Cambridge, **2011**, ch. 9. (e) Valente, C.; Çalimsiz, S.; Hoi, K. H.; Mallik, B.; Sayah, M.; Organ, M. G. *Angew. Chem. Int. Ed*. **2012**, *51*, 3314-3332.

suitable ligands to be attached to a solid support, so they can become the anchor of the metal to it. Over the last decade many a different polymer has been used for this purpose, including some commercially available, like those collected in Figure 3.1.

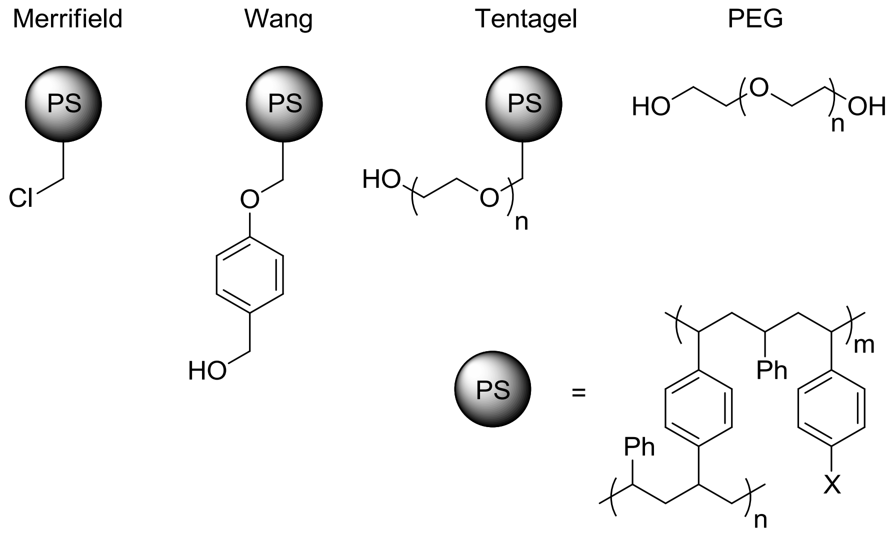

Figure 3.1: Some common commercially available resins.

Usually, the supported Pd-NHCs have been assessed in the Suzuki, Sonogashira or Heck reactions. Although a lot of publications involving supported catalysis report good results, in most cases direct comparison between systems cannot be made because of the many different conditions used (reagents, reaction times, catalyst loading,…) and the unlike way of presenting data. Also, the operating mechanism in reactions using supported catalysts should not be assumed without a careful look at how the system works. A crucial point is to determine if the catalytic reaction actually occurs on the support or if this is a mere palladium reservoir, the real catalytic species being homogeneous and formed under catalytic conditions. Some reviews have addressed this subject.[96] Their authors emphasize that work concerning reusability must be cautious with the results reported. To get the best knowledge of every system they recommend doing heterogeneity tests, leaching quantification or rigorous measures of the reaction times. For instance, some studies about reusability of supported catalysts show the results obtained for the first experiment after

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[96] (a) Gladysz, J. A. *Pure Appl. Chem*. **2001**, *73*, 1319-1324. (b) Molnár, A. *Chem. Rev*. **2011**, *111*, 2251-2320. (c) Crabtree, R. H. *Chem. Rev*. **2012**, *112*, 1536-1554.

some time (hours generally) without considering the possibility that the reaction finishes in shorter times. When this is the case and complete conversion is reached long before, subsequent runs with the same reaction time may not show the actual decrease in the yields whether the catalyst suffers partial loss or decomposition with every cycle. The characterization of the supported palladium NHC complexes is usually less straightforward than the determination of the structure of the non-supported analogues, especially when insoluble polymers are used. Thus, in many reports, the nature of the metal species attached to a polymer, used as catalysts precursors, is frequently unknown o poorly determined. This adds some uncertainty to the way the catalysis works. Taking all this into account, here follows the most representative examples reported in the literature of polymer-supported palladium NHC complexes and their use in C-C cross-coupling reactions. For convenience, they are mentioned according to the type of polymer support they use. Often, just the precursor imidazolium salts are represented in the schemes and figures that follow since, in many cases, the supported palladium complexes are not well characterized.

Undoubtedly the type of polymer more frequently reported is polystyrene. Most of the cases describe carbene precursors being attached to purchased polystyrenes, normally Merrifield or Wang resins. Fewer examples can be found where the polymer is specifically prepared. Lee and coworkers described the synthesis of styrene-substituted imidazolium salts able to be polymerized in a suspension copolymerization with divinylbenzene (DVB), and styrene (Scheme 3.2). In this polymer the imidazole moieties are on the surface of the beads. Upon reaction with palladium acetate, a dark green polymer was obtained which was formulated by the authors as shown in scheme 3.2, based on quantitative analysis of the Pd content and energy-dispersive X-ray spectroscopy which located the Pd atoms in the proximity of the NHC region. These polymers were used in Suzuki, Heck or copper-free Sonogashira reactions with good yields and recyclability data.[97]

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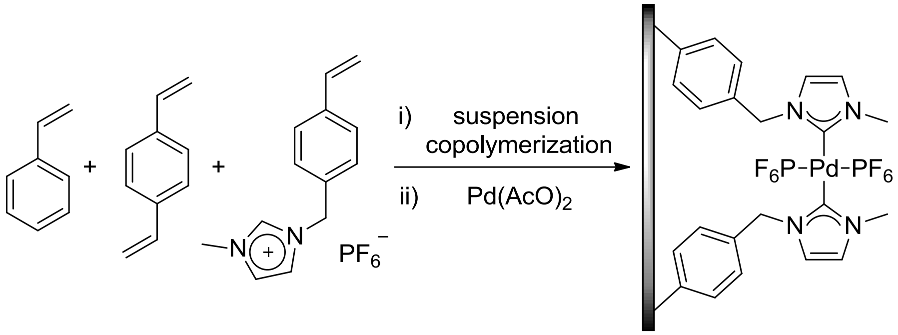
[97] (a) Kim, J. H.; Jun, B. H.; Byun, J. W.; Lee, Y. S. *Tetrahedron Lett*. **2004**, *45*, 5827-5831. (b) Kim, J. H.; Kim, J. W.; Shokouhimehr, M.; Lee, Y. S. *J. Org. Chem.* **2005**, *70*, 6714-6720. (c) Shokouhimehr, M.; Kim, J. H.; Lee, Y. S. *Synlett*, **2006**, 618-620. (d) Kim, J. H.; Lee, D. H.; Jun, B. H.; Lee, Y. S. *Tetrahedron Lett*. **2007**, *48*, 7079-7084.



Scheme 3.2.

Lee´s group has also published additional results in Suzuki cross-coupling reactions with commercially available polystyrene. When they used macroporous polystyrene to support an NHC-Pd complex they achieved good performance of the catalyst and they could reuse it five times in the reaction of bromoarenes.[98]

Direct nucleophilic substitution of chlorine in Merrifield resins by 1-methylimidazolium affords polymer-supported imidazolium salts. NHC-Pd complexes by reaction of the former polymeric salts with palladium acetate have been tested in Suzuki reactions with poor behavior[99] and in Heck reactions with good results in specific conditions.[100] The best performance of this system has been reported by Bhanage and coworkers in different types of carbonylative coupling processes or reduction reactions.[101] There are some reports on similar catalysts where non-commercial chloromethylated-polystyrene was used, specifically prepared for this purpose.[102]

Merrifield-type polystyrene has also been used to attach bisimidazolium salts which have been used as precursors of NHC-Pd complexes. Parallel works were published by the

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[98] Lee, D. H.; Kim, J. H.; Jun, B. H.; Kang, H.; Park, J.; Lee, Y. S. *Org. Lett.* **2008**, *10*, 1609-1612.

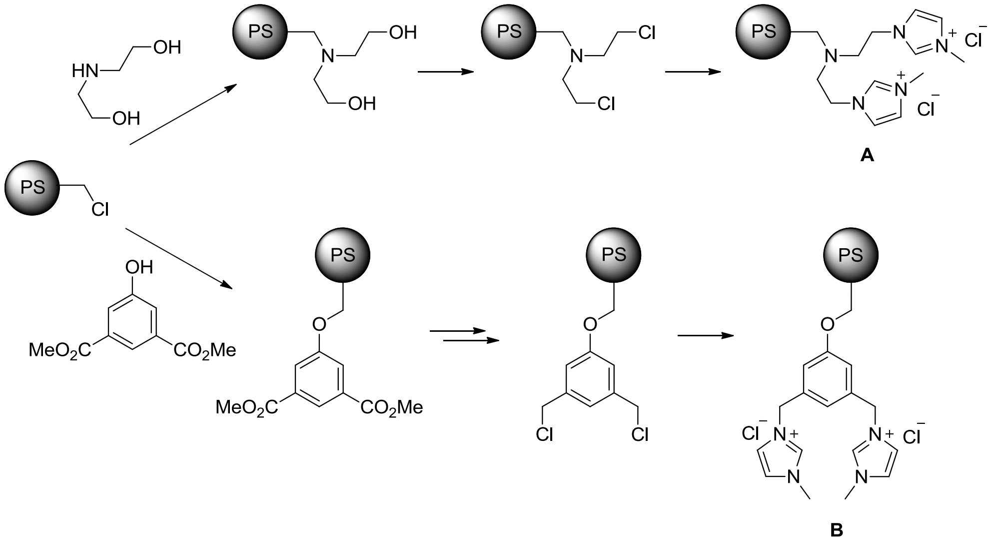
[99] Byun, J. W.; Lee, Y. S. *Tetrahedron Lett.* **2004**, *45*, 1837-1840.

[100] Burguete, M. I.; García-Verdugo, E.; Garcia-Villar, I.; Gelat, F.; Licence, P.; Luis, S. V.; Sans. V. *J. Catal.* **2010**, *269*, 150-160.

[101] (a) Qureshi, Z. S.; Deshmukh, K. M.; Tambade, P. J.; Bhanage, B. M. *Synthesis*, **2011**, 243-250. (b) Bagal, D. B.; Qureshi, Z. S.; Dhake, K. P.; Khan, S. R.; Bhanage, B. M. *Green Chem.* **2011**, *13*, 1490-1494. (c) Qureshi, Z. S.; Revankar, S. A.; Khedkar, M. V.; Bhanage, B. M. *Catal. Today*, **2012**, *198*, 148-153. (d) Khedkar, M. V.; Khan, S. R.; Dhake, K. P.; Bhanage, B. M. *Synthesis* **2012**, *44*, 2623-2629. (e) Bagal, D. B.; Watile, R. A.; Khedkar, M. V.; Dhake, K. P.; Bhanage, B. M. *Catal. Sci. Technol.* **2012**, *2*, 354–358. (f) Khairnar, B. J.; Bhanage, B. M. *Synthesis*, **2014**, *46*, 1236-1242.

[102] (a) Zeng, X.; Zhang, T.; Qin, Y.; Wei, Z.; Luo, M. *Dalton Trans.* **2009**, 8341-8348. (b) Gömann, A.; Deverell, J. A.; Munting, K. F.; Jones, R. C.; Rodemann, T.; Canty, A. J.; Smith, J. A.; Guijt, R. M. *Tetrahedron Lett.* **2009**, *65*, 1450-1454.

groups of Luis and Luo showing two different approaches. In Luis' proposal chloromethyl polystyrenes were functionalized by reaction with a molecule with two reactive groups (diethanolamine or dimethyl-5-hydroxyisophtalate) which were transformed into di(alkylhalides) useful to introduce two imidazole derivatives (Scheme 3.3). The palladium species supported on these polymers by reaction with $Pd(OAc)_2$ catalyze Heck reactions with good results. Ligand A afforded the highest activity but had poor recyclability. On the contrary B had lower activity but showed good behavior for at least five cycles.[103]



Scheme 3.3.

In Luo's methodology, both imidazolium salts were linked via the terminal carbon atoms of an isopropyl alcohol fragment. Nucleophilic substitution of the halogen of the resin with the alcohol in basic reaction conditions afforded the supported-imidazolium salts through the ether group formed (Scheme 3.4). $Pd(OAc)_2$ was used as palladium source. There are no experimental data to confirm whether one carbene or both are bound to the metal. This polymer with $Pd(OAc)_2$ as palladium source has been used in Suzuki reactions

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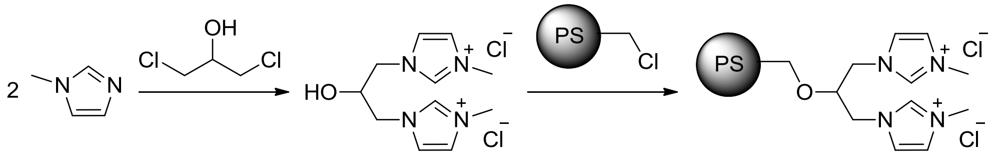
[103] (a) Altava, B.; Burguete, M. I.; García-Verdugo, E.; Karbass, N.; Luis, S. V.; Puzary, A.; Sans. V. *Tetrahedron Lett*. **2006**, *47*, 2311-2314. (b) Sans, V.; Gelat, F.; Burguete, M. I.; García-Verdugo, E.; Luis, S. V. *Catal. Today*, **2012**, *196*, 137-147.

with arylhalides, arylsulfonyl chlorides, aryltriazennes or arenediazonium salts with high yields even after several runs.[104]



Scheme 3.4.

Wang resin has been used by Herrmann and coworkers to anchor bisimidazoles. In a first example they reported the introduction of a methylene-bridged biscarbene-palladium complex through one side of the dimer (Figure 3.2.a). When this catalyst was tested in Heck reactions showed good activity and great recyclability particularly with activated haloarenes.[105] Another work was based in the same procedure followed by Luo, although with a palladium dibromide complex (Figure 3.2.b). In this case the catalyst used in Suzuki reactions presented very low activity.[106] Recently, they published a work where benzoyl chloride-functionalized polystyrene was connected to a bisimidazole group by the methylene bridge (Figure 3.2.c). Yields obtained as well as reusability show a great performance of the catalyst.[107]

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[104] (a) Kang, T.; Feng, Q.; Luo, M. *Synlett* **2005**, 2305–2308. (b) Zhang, S.; Zeng, X.; Wei, Z.; Zhao, D.; Kang, T.; Zhang, W.; Yan, M.; Luo, M. *Synlett* **2006**, 1891–1894. (c) Qin, Y.; Wei, W.; Luo, M. *Synlett* **2007**, 2410–2414. (d) Nan, G.; Ren, F.; Luo, M. *Beilstein J. Org. Chem.* **2010,** *6,* No. 70.

[105] Schwarz, J.; Böhm, V. P. W.; Gardiner, M. G.; Grosche, M.; Herrmann, W. A.; Hieringer, W.; Raudaschl-Sieber, G. *Chem. Eur. J.* **2000**, *6*, 1773-1780.

[106] Jokíc, N. B.; Straubinger, C. S.; Goh, S. L. M.; Herdtweck, E.; Herrmann, W. A.; Kühn, F. E. *Inorg. Chim. Acta*, **2010**, *363*, 4181-4188.

[107] Zhong, R.; Pöthig, A.; Haslinger, S.; Hofmann, B.; Raudaschl-Sieber, G.; Herdtweck, E.; Herrmann, W. A.; Kühn, F. E. *ChemPlusChem*, **2014**, *79*, 1294-1303.

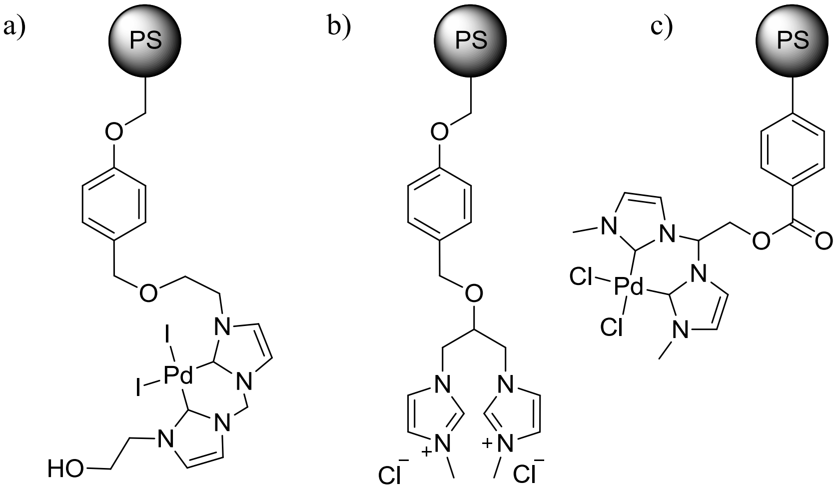

Figure 3.2.

Buchmeiser's group described the utilization of both Merrifield and Wang resins as supports of NHC-Pd complexes with pyrimidine moieties instead of imidazoles. They showed high activities in some Heck reactions but no data concerning recovery and reuse were given.[108]

Poly (ethylene glycol) is a water-soluble polymer that can also be found several times in the literature acting as a support of carbenes. The major interest in this type of polymers lies in the possibility of running reactions in water. Nucleophilic substitution of a sulfonate group by an imidazole derivative and at the end of the polymer chain is probably the most direct route to obtain a PEG-supported imidazolium salt susceptible to be transformed in a palladium complex (Figure 3.3, X = RSO_3). Suzuki reactions with this catalyst afforded high yields in short times but the issue of recyclability is not addressed.[109] A similar catalyst was obtained just changing the sulfonate group for iodide before reacting the support with the imidazole leading to the imidazolium salt in Figure 3.3 (X = I). In this case, the catalyst suffered a minimal loss of activity after five runs.[110] Comparable results were obtained when an analogous catalyst was tested in Heck reactions.[111]

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[108] Mayr, M.; Buchmeiser, M. R. *Macromol. Rapid. Commun*. **2004**, *25*, 231-236.

[109] Liu, N.; Liu, C.; Jin, Z. *Green Chem*. **2012**, *14*, 592-597.

[110] Xue, J.; Zhou, Z.; Peng, J.; Du, F.; Xie, L.; Xu, G.; Huang, G.; Xie, Y. *Transition Met. Chem*. **2014**, *39*, 221-224.

[111] Wang, L.; Zhang, Y.; Xie, C.; Wang, Y. *Synlett*, **2005**, 1861-1864.

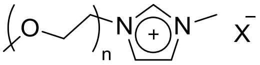

Figure 3.3.

There are some examples where ethylene glycol chains are grafted onto other polymers. In an attempt to run Suzuki reactions in water, Lee's group developed an amphiphilic polymer with PEG as a linker between the Merrifield resin and the heterocyclic carbene. Initially, they formed a PEG-NHC precursor that was then attached to the polystyrene. They observed that the longer the PEG chain the higher the yield in the catalytic reactions but in any case the results were worse than those showed in their previous examples.[112] Steel and Teasdale supported a pincer ligand with two carbenes assembled in a pyridine where an amide group in the para-position of the pyridine was responsible of joining the ligand to the Tentagel resin (Figure 3.4). Heck and Suzuki reactions of aryl iodides gave high yields with long reaction times and remained useful for more than ten cycles under inert atmosphere.[113] PEGA800 is another commercially available polymer which has been used to support palladium catalysts with peptide carbene ligands.[114]

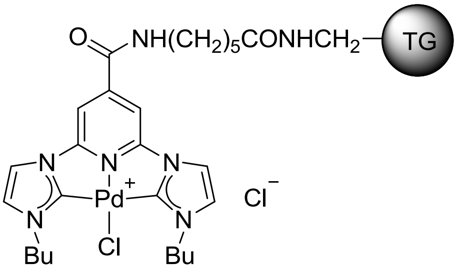

Figure 3.4.

Dendritic polyglycerols[115] or poly (2-oxazoline)s[116] are other water-soluble polymers used to support NHC-Pd catalysts. Both of them show good activity in C-C

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[112] Kim, J. W.; Kim, J. H.; Lee, D. H.; Lee, Y. S. *Tetrahedron Lett*. **2006**, *47*, 4745-4748.

[113] Steel, P. G.; Teasdale, C. W. T. *Tetrahedron Lett*. **2004**, *45*, 8977-8980.

[114] (a) Jensen, J. F.; Worm-Leonhard, K.; Meldal, M. *Eur. J. Org. Chem*. **2008**, 3785-3797. (b) Worm-Leonhard, K.; Meldal, M. *Eur. J. Org. Chem*. **2008**, 5244-5253.

[115] (a) Meise, M.; Haag, R. *ChemSusChem*, **2008**, *1*, 637-642. (b) Lukowiak, M. C.; Meise, M.; Haag, R. *Synlett*, **2014**, *25*, 2161-2165.

coupling reactions (especially high in the case polyglycerols) but neither of them preserves this activity after a few runs.

Polyisobutylene has also been tested as support in Heck and Buchwald-Hartwig reactions. Bergbreiter's work reported that imidazole-based palladium catalysts with a polymeric chain bound to just one nitrogen of the imidazole were useful and recyclable whereas those systems with polyisobutylene on both nitrogens decomposed after the first run (Figure 3.5).[117] A particular characteristic of this system is that the catalyst is soluble in heptane making possible a liquid biphasic separation after the reaction instead of the more common filtration of a solid catalyst.

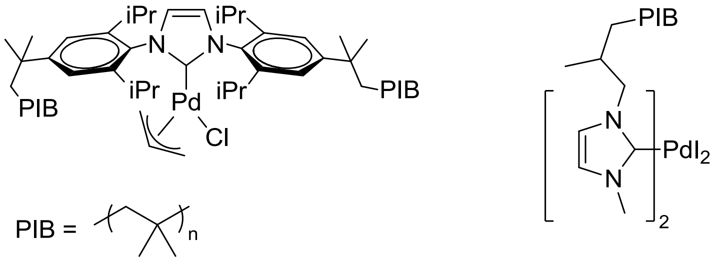

Figure 3.5

Other types of polymers bear the imidazole moieties in the main chain. Within this category there are two groups. On the one hand, those called coordination polymers have the palladium in the backbone bound to two NHCs of different molecules. There are some works by Karimi and Akhavan with linear polymers which show good results especially with an ethylene glycol functionalized, water-soluble polymer (Figure 3.6).[118] Non-linear coordination polymers can also be found in the literature.[119] On the other hand, there are systems forming organic frameworks where the metal is not a link of the chain. Ying and coworkers utilized the same poly-imidazolium salts described in chapter 2 (see Scheme 2.2.b) as well as other analogous structures to synthesize a palladium complex active and

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[116] (a) Schönfelder, D.; Fischer, K.; Schmidt, M.; Nuyken, O.; Weberskirch, R. *Macromolecules*, **2005**, *38*, 254-262. (b) Schönfelder, D.; Nuyken, O.; Weberskirch, R. *J. Organomet. Chem*. **2005**, *690*, 4648-4655.

[117] Bergbreiter, D. E.; Su, H. L.; Koizumi, H.; Tian, J. *J. Organomet. Chem*. **2011**, *696*, 1272-1279.

[118] (a) Karimi, B.; Akhavan, P. F. *Chem. Commun*. **2011**, *47*, 7686-7688. (b) Karimi, B.; Akhavan, P. F. *Inorg. Chem*. **2011**, *50*, 6063-6072.

[119] Xu, S.; Song, K.; Li, T.; Tan, B. *J. Mater. Chem. A*, **2015**, *3*, 1272-1278.

reusable in cross-coupling reactions.[120] Some Suzuki reactions have been catalyzed by a similar porous polymer made by the same methodology (Scheme 3.5).[121]

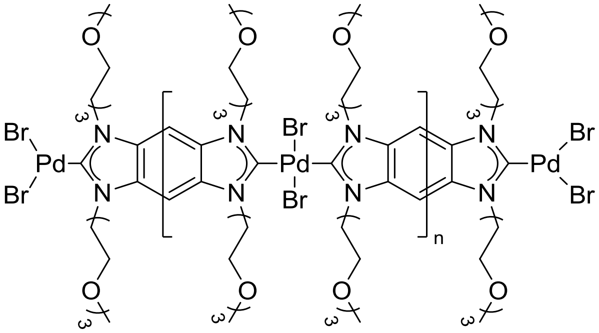
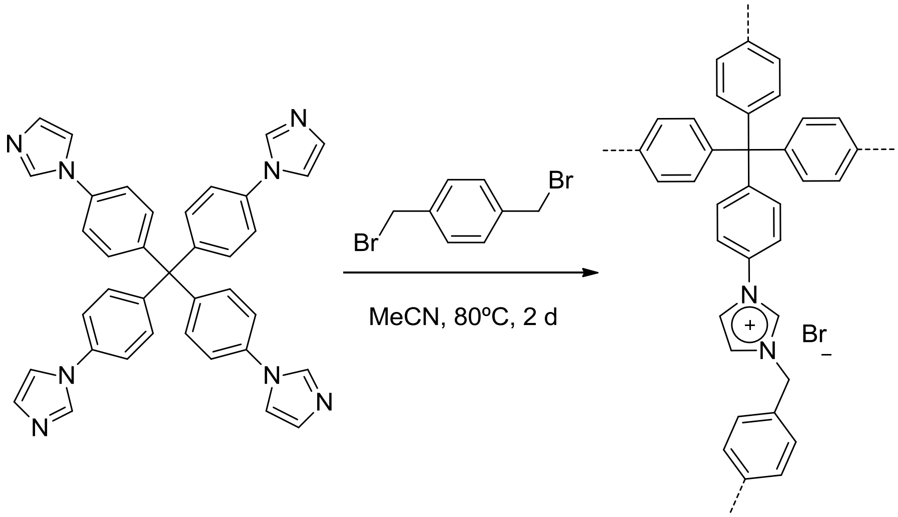


Figure 3.6



Scheme 3.5

There are few examples of Pd-NHCs bound to polynorbornenes and all of them are referred to ROMP-type polymers. Sommer and Weck polymerized several carbene-palladium complexes bound to norbornene by an ester group (Figure 3.7.a). Those polymers catalyzed different cross-coupling reactions with very good performances even in

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[120] Zhang, Y.; Zhao, L.; Patra, P. K.; Hu, D.; Ying, J. Y. *Nano Today*, **2009**, *4*, 13-20.

[121] Lin, M.; Wang, S.; Zhang, J.; Luo, W.; Liu, H.; Wang, W.; Su, C. Y. *J. Mol. Catal. A: Chem*. **2014**, *394*, 33-39.

the case of aryl chlorides but their activity dropped notably after few recycling experiments.[122] Buchmeiser's group has presented two different polynorbornenes with pyrimidine-based carbenes. First, they used a ROMP polymer to support the same catalyst reported with polystyrene resins with worse or similar results in catalysis (Figure 3.7.b).[108] Later, they introduced a palladium complex in the same polymer they had previously employed in organocatalysis[72] (see Figure 2.3) and carried out some Heck reactions but with scarce data about recyclability.

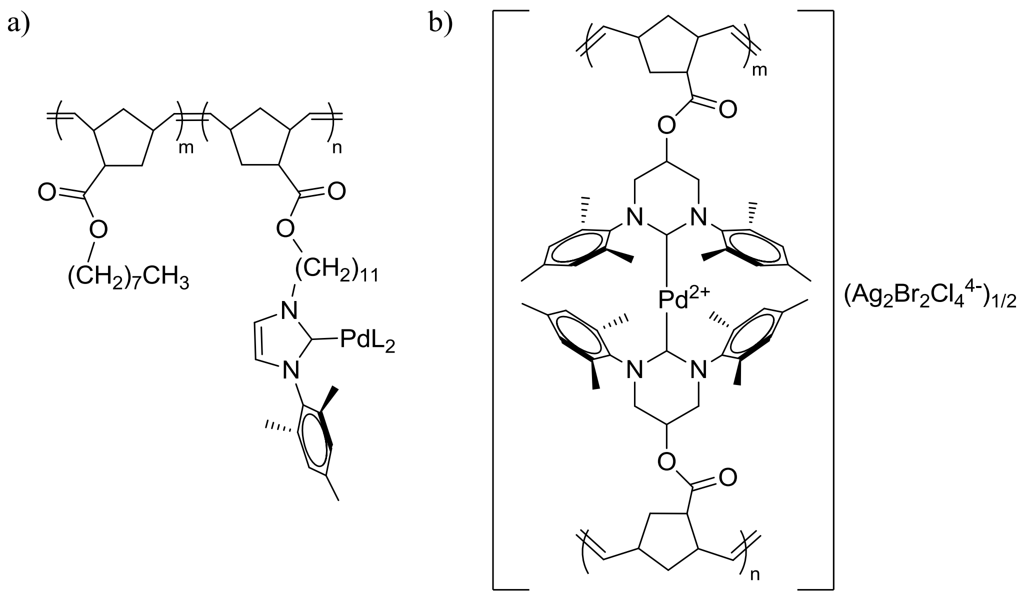

Figure 3.7.

To the best of our knowledge there is no example in the literature where vinylic addition polynorbornenes have been used as support of Pd-NHC complexes. The saturated polymer backbone in VA-PNBs is a clear advantage when compared to ROMP-PNBs to achieve robustness and stability under catalytic conditions. Recently, our group has reported the risks of this type of scaffold in catalysis. We have observed the insertion of the C=C double bond of a ROMP-PNB, in a palladium-aryl complex, leading to the formation of an aryl substituted polymer.[123] Therefore, we decided to utilize polymer **8b**, described in chapter 2, as starting material to synthesize some palladium complexes. In order to check the

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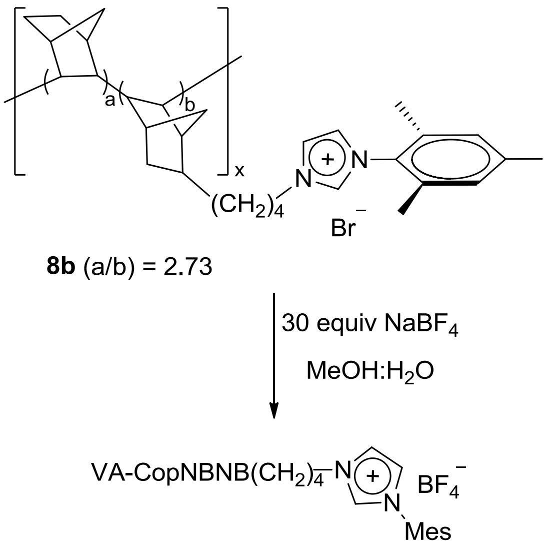
[122] Sommer, W. J.; Weck, M. *Adv. Synth. Catal*. **2006**, *348*, 2101-2113.
[123] García-Loma, R.; Albéniz, A. C. *RSC Adv.* **2015**, *5*, 70244-70254.

activity and recyclability of these new polymers two cross-coupling reactions were tested, namely Suzuki and Negishi couplings.

3.2 RESULTS AND DISCUSSION

3.2.1 Synthesis of VA-PNB supported Pd-NHC complexes

The procedure followed to synthesize the polymer-supported metal-carbene complexes consisted in the addition of a palladium complex to a suspension of the carbene previously formed. The starting polymer was an imidazolium bromide and hence, in order to avoid possible interferences of the bromide with the complex, a change of that anion for a less coordinative one was performed. Namely, polymer **8b** was treated with sodium tetrafluoroborate in a mixture of water and methanol (equation 3.1). The halogen content of polymer **14** was quantitatively analyzed showing no presence of bromide which suggests the complete exchange of anions. Furthermore, the totally absence of halide in this analysis confirmed the complete nucleophilic substitution made to obtain the imidazolium salt described in chapter 2. Infrared spectra showed the appearance of a strong band associated with the ν(B-F) at 1053 cm^{-1}.



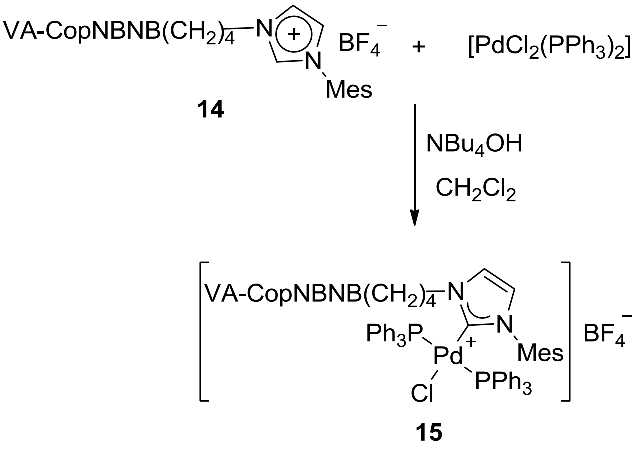
8b (a/b) = 2.73

(3.1)

14

In a similar procedure to that employed in the synthesis of complex **5** (see equation 2.3 in chapter 2), polymer **14** was deprotonated with tetrabutylammonium hydroxide in

CH_2Cl_2. After the formation of the polymeric carbene $[PdCl_2(PPh_3)_2]$ was added and the mixture was stirred for 24 hours (Equation 3.2). Polymer **15** was insoluble in common solvents and was characterized by solid state NMR spectroscopy. A ^{31}P MAS NMR experiment showed a broad signal around 26 ppm corresponding to the phosphines bound to palladium (Figure 3.8). We assumed a cationic complex as it happened in the case of **5**. The palladium content was determined by ICP-MS after digesting the polymer in nitric acid and was found to be 5.75 mg Pd/ g polymer.



(3.2)

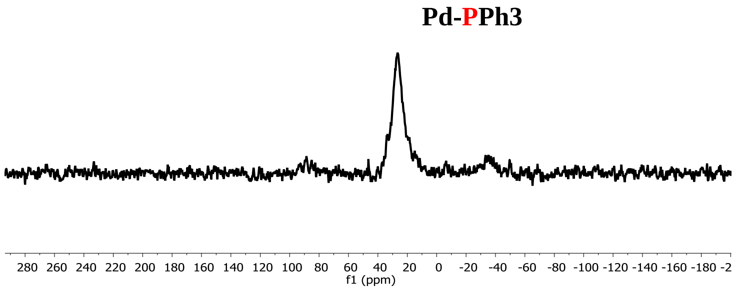
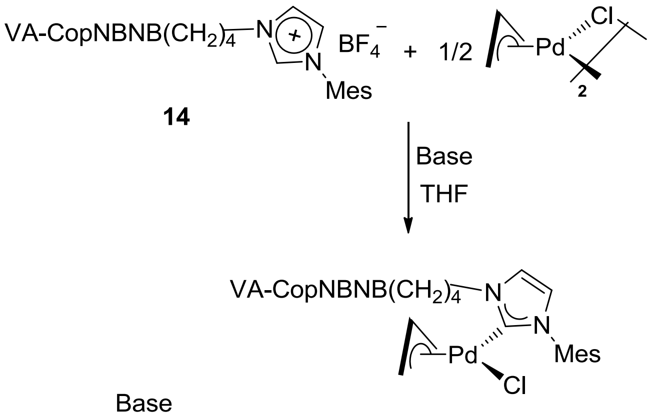


Figure 3.8: ^{31}P MAS NMR of **15**.

A different palladium complex was synthesized using the polymeric imidazolium salt **14** and $[Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}Cl)]_2$ as palladium source giving different results depending on the reaction conditions. When tetrabutylammonium hydroxide was used as base to deprotonate **14**, the contact time between the in situ formed carbene and the organometallic compound was crucial. Even using an equimolar ratio of the base and the imidazolium salt in **14**, incomplete base consumption produces the decomposition of the complex to form allyl alcohol and palladium black. This was confirmed by an independent experiment where $[Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}Cl)]_2$ was mixed with $(NBu_4)OH$ and the resulting dark suspension was analyzed by ^1H NMR where allyl alcohol was clearly detected. Thus, if the polymeric product of the reaction shown in Scheme 3.6 (base = $(NBu_4)OH$) was filtered 24 hours after the addition of $[Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}Cl)]_2$ the resulting solid, **16a**, was black and contains 58.1 mg Pd/ g polymer. When shorter reaction times were allowed, we got a dark red polymer **16b** with 27.9 mg Pd/ g polymer in 2 hours, and a pale brown **16c** with 6.70 mg Pd/ g polymer in 30 minutes (Scheme 3.6). Although the incorporation of palladium increases with time we will see below how the longer the reaction time the worse the catalytic activity of the supported palladium species. When a different base such as DBU was employed in the formation of the carbene, $[Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}Cl)]_2$ did not undergo decomposition even after long reaction times allowing a higher amount of palladium to be attached without decomposition of the starting dimer. In this case polymer **16d** was obtained as a brownish solid with 89.4 mg Pd/ g polymer (Scheme 3.6). ^{13}C CP-MAS NMR of **16d** showed a signal at 180 ppm belonging to the carbene carbon atom bound to palladium, as well as signals for the allyl group at 114 and 70 ppm (Figure 3.9). Those signals are not visible in the ^{13}C CP-MAS NMR spectrum of **16c** probably because the amount of NHC-Pd complex formed is too low.



Base	
NBu_4OH	**16a** (0.546 mmol Pd/g) Black **16b** (0.262 mmol Pd/g) Red **16c** (0.063 mmol Pd/g) Pale Brown
DBU	**16d** (0.840 mmol Pd/g) Pale Brown

Scheme 3.6.

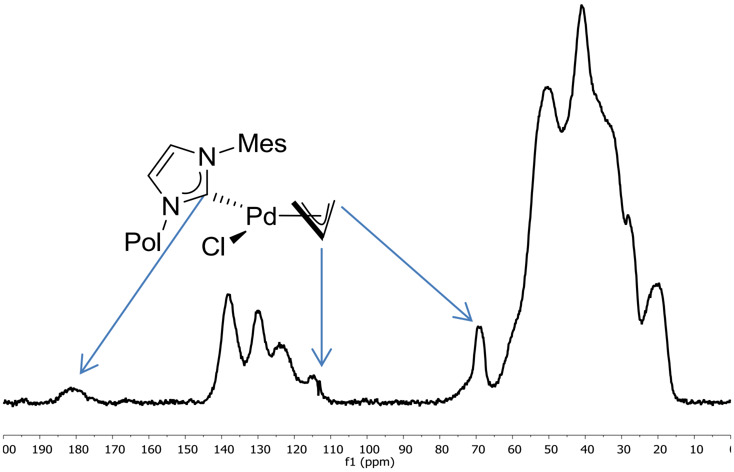
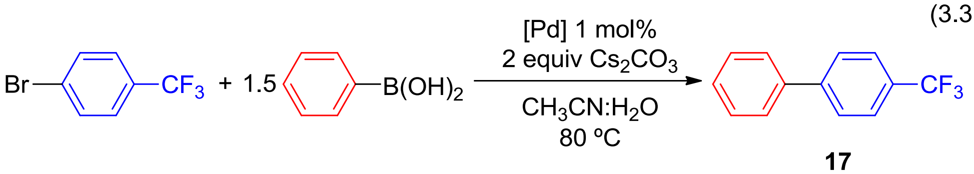


Figure 3.9: ^{13}C CP-MAS NMR of **16d**.

3.2.2 Suzuki reactions catalyzed by VA-PNB supported Pd-NHC complexes

In order to study the catalytic activity of the VA-polynorbornene-supported palladium complexes synthesized, as well as their reusability, some Suzuki reactions were carried out. This is a well-known Pd-catalyzed C-C coupling-reaction[124] and many of the polymers cited in the introduction of the chapter have been tested as catalysts in this reaction. Initially, all our polymers, **16a-d**, were compared in the same reaction conditions to determine which of them afforded the best results. Since the polymers were insoluble in common solvents, a combination of water with an organic solvent was used with the objective of dissolving all the other reactants. In a model reaction the supported palladium precatalyst (1% mol of Pd) was added to a mixture of 4-bromobenzotrifluoride, phenylboronic acid and cesium carbonate in acetonitrile:water (3:1; v/v) (equation 3.3). After heating at 80 ºC for 20 minutes the reaction was cooled down and checked by ^{19}F NMR. Subsequently, the polymer was filtered, washed with the same mixture of solvents, air-dried and reused in the same reaction conditions for 30 minutes this time. The results obtained in both cycles are collected in Table 3.1.

(3.3)



17

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[124] (a) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457-2483. (b) Miyaura, N. In *Metal-Catalyzed Cross-Coupling Reactions*; de Meijere, A.; Diederich, F. Eds.; Wiley-VCH: Weinheim, **2004**, ch. 2. (c) Heravi, M. M.; Hashemi, E. *Tetrahedron*, **2012**, *68*, 9145-9178. (d) Amatore, C.; Le Duc, G.; Jutand, A. *Chem. Eur. J.* **2013**, *19*, 10082-10093.

Table 3.1. Comparative experiments in the Suzuki reaction of several polymer-supported palladium carbene complexes.[a]

Entry	Catalyst	Cycle	**17**, Yield (%)[b]
1	**15**	1	10.4
2	**15**	2	4.1
3	**16a**	1	0
4	**16a**	2	0
5	**16b**	1	95.9
6	**16b**	2	20.9
7	**16c**	1	45.9
8	**16c**	2	63.4
9	**16d**	1	87.2
10	**16d**	2	99.5

a) Reaction conditions shown in equation 3.3. Reaction times of 20 min for first cycles and 30 min for second cycles in every case. b) Crude yields determined by ^{19}F NMR.

Polymer **15** was barely active and after the first run its performance was even worse (Table 3.1, entries 1-2). As mentioned before, the way to attach the palladium seems to be more important than the amount loaded and, in the case of those polymers synthesized with $[Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}Cl)]_2$ as the palladium source, quite different outcomes were found. **16a** showed no activity at all (Table 3.1, entries 3-4). In spite of being one of the polymers with higher loading, the metal seems to be deposited as inactive palladium black. When the catalyst used was **16b** a very high yield was initially achieved but after the first run the yield notably dropped (Table 3.1, entries 5-6). This large difference may indicate that palladium active species were originally present on the surface of the polymer but most of them were removed after the very first use. **16c** and **16d** showed similar trends although the complex prepared with DBU gave better yields in the synthesis of **17** (Table 3.1, entries 7-10). In both cases, the second cycle of the catalyst gave better results due to the increased reaction time (20 and 30 min in the first and second runs respectively).

In view of these results we decided to study the recyclability of polymer **16d**. As mentioned in the introduction of this chapter, to assess the activity and recyclability of a supported catalyst it is advisable to determine the real reaction time for full conversion in each run. In the case of soluble supports the progress of the reaction can be easily followed by NMR spectroscopy, but with heterogeneous systems, like our case, mass transfer effects must be considered and stirring happens to be important. Therefore, we considered to monitor some recycling reactions by using *in situ* infrared spectroscopy, which permits heating and stirring. Although this technique has been known for several decades few examples of its application in palladium catalysis can be found,[125] and to the best of our knowledge, none in the field of supported catalysis. The reaction studied was that depicted in equation 3.3. With a React-IR apparatus the ν(C-Br) IR absorption band at 1012 cm^{-1} belonging to 4-bromobenzotrifluoride could clearly be observed since this signal was not overlapped with the bands of the solvent or any other reagent. This methodology allowed us to track the disappearance of the aforementioned band and thus to follow the progress of the reaction and to know when the conversion was complete (Figure 3.10).

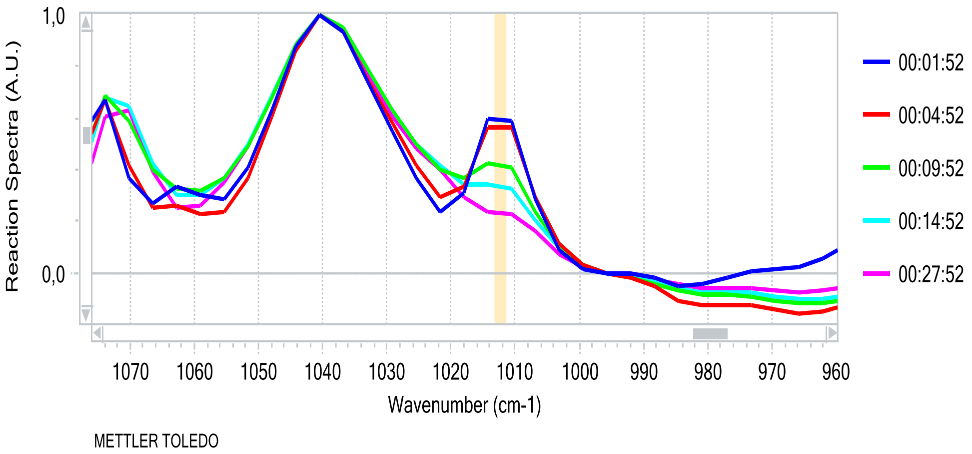

Figure 3.10: *in situ* IR spectra recorded at different times for the first run of the reaction in Table 3.2. The ν(C-Br) absorption of p-$CF_3C_6H_4Br$ is highlighted.

Comparing the heights of the IR band at 1012 cm^{-1} with time we can observe the evolution of the reaction. When no variation of the band was observed for several minutes the heating was stopped and after cooling the yield was evaluated by ^{19}F NMR spectroscopy. This same procedure was applied in the subsequent four recycling

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[125] (a) Zhang, C.; Li, X.; Sun, H. *Inorg. Chim. Acta*, **2011**, *365*, 133-136. (b) Wang, X.; Liu, L. H.; Shi, J. H.; Peng, J.; Tu, H. Y., Zhang, A. D. *Eur. J. Org. Chem*. **2013**, 6870-6877.

experiments after the first run.[126] In all the reactions an induction time could be observed (Figure 3.11). As a general trend this period as well as the overall reaction time increased with every cycle. In the first reaction the induction time was no longer than 5 minutes and the conversion was complete after 26 minutes (Table 3.2, cycle 1), whereas the last run took about 60 minutes with an induction period around 23 minutes (Table 3.2, cycle 5). With the aim of finding out the reasons for this increase of time, palladium leaching was determined by ICP-MS finding a small but constant amount of palladium in the filtrate after every run (Table 3.2).

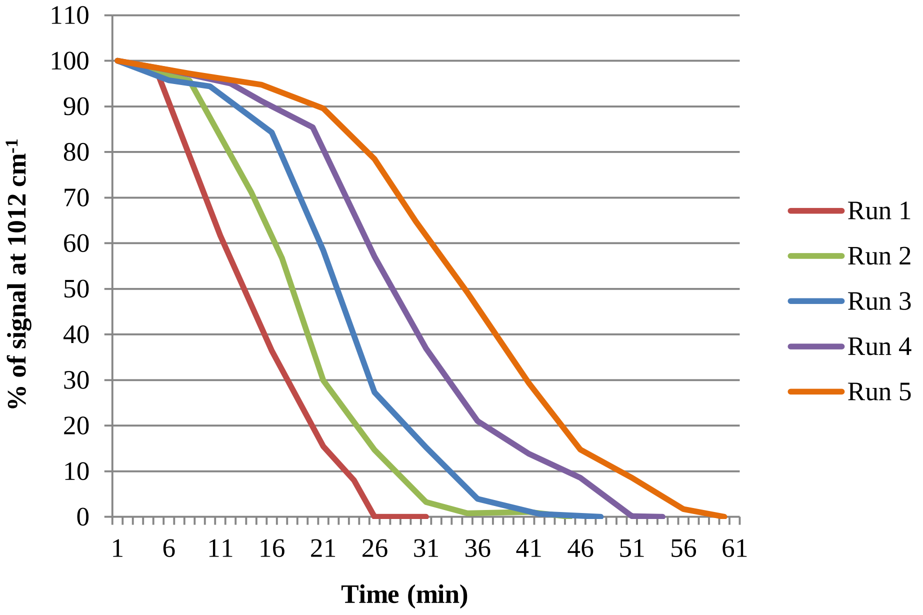

Figure 3.11: Variation of the signal intensity (%) observed at 1012 cm^{-1} with time.

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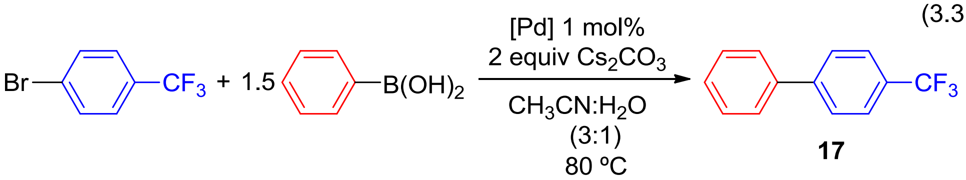
[126] A parallel control experiment was performed by carrying out the reaction in a conventional Schlenk flask and determining the conversion and crude yields by ^{19}F NMR at the same reaction times as those collected in Table 3.2. The results obtained reproduce those in Table 3.2 (see Additional Information in CD support).

Table 3.2. Recycling experiments of **16d** in the Suzuki reaction.[a]

(3.3)



Cycle	Time (min)	Induction time (min)	**17**, Yield (%)[b]	Pd Leaching (%)[c]
1	26	5	98.5	3.2
2	35	10	96.4	0.59
3	41	14	96.1	0.37
4	51	18	96.8	0.35
5	60	23	90.3	1.3

a) Reaction conditions shown in equation 3.3. b) Crude yields determined by ^{19}F NMR. c) Leaching determined by ICP-MS in the crude product of the reaction. Percentage of Pd leached refered to the total amount added.

Since the polymer was losing palladium in every reaction, we performed a hot filtration test to know whether the catalysis was occurring onto the polymer or in a homogeneous way with some active palladium species released. In the sixth cycle, after running the reaction at 80 ˚C for 1 hour, the hot mixture was filtered. At that point, the ^{19}F NMR spectrum showed a 31% yield. The filtrate was allowed to react at 80 ˚C for an additional hour affording a yield of 92%. This result clearly evidences that a homogeneous catalysis is operating for our system. In this case the palladium leaching was determined and showed a value of 1.0 % of the original amount added. Comparison of this quantity with those observed in the recycling experiments seems to indicate that the small amount of palladium freed to the solution in every run is enough to catalyze the reaction.

Scanning electron microscopy (SEM) images of the polymer before and after its use exposes a clear change in the distribution of the palladium in the polymer. Before its use **16d** showed a smooth surface (Figure 3.12a), whereas after one run numerous aggregates could be observed on the surface (Figure 3.12b). In order to have a better knowledge of the composition of those particles a microanalysis by Energy Dispersive X-ray Spectroscopy (EDS) was carried out (Figure 3.13). This technique allowed us to see that the concentration of palladium in the aggregates (29% wt) was higher than the average concentration in the polymer matrix (9% wt). These SEM images led us to think about the possibility of being forming nanoparticles responsible of the catalysis. However, in a closer view, these particles could be measured resulting in an average size around 65 nm much larger than common palladium nanoparticles useful in catalysis, rarely larger than 10 nm (Figure 3.12c). This kind of distribution of the palladium aggregates all over the surface was maintained at least for the five runs reported (Figure 3.12d).

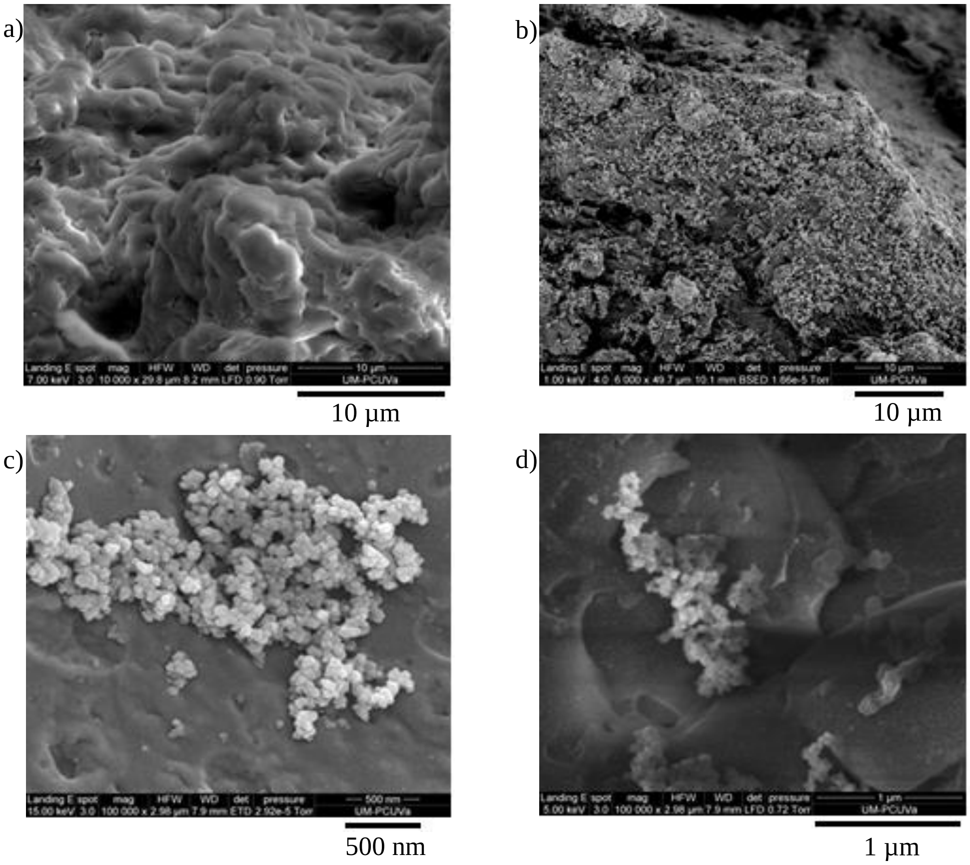


Figure 3.12: SEM images of polymer **16d**: a) before use; b) after 1 use; c) after 1 use augmented; d) after 5 uses.

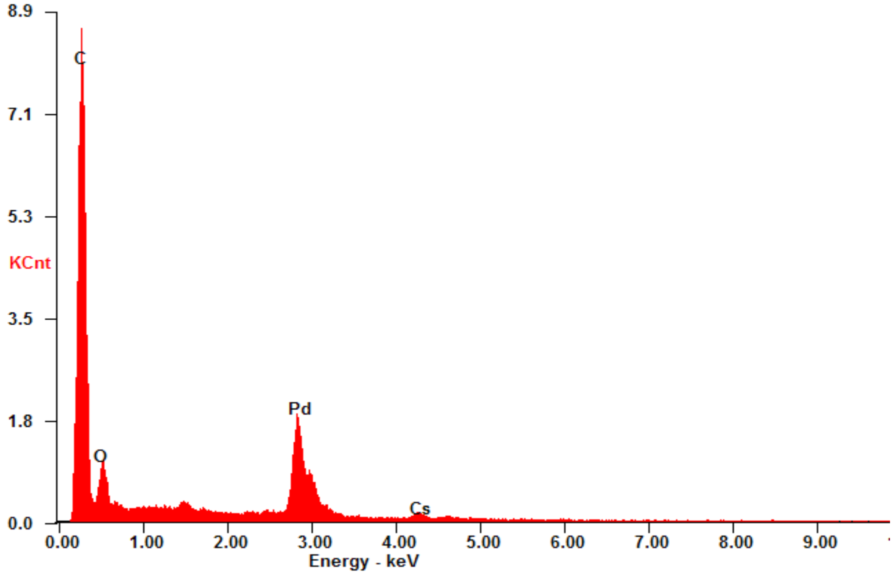
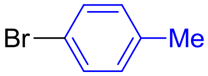
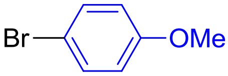
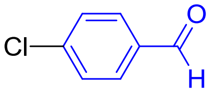
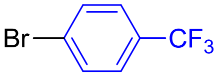


Figure 3.13: SEM-EDS of the aggregates observed in the polymer after one run.

These results show that the complex [Pd(allyl)Cl(NHC-Pol)] does not survive after a first catalytic Suzuki reaction, even if linked to the polymer support through a Pd-NHC bond. Nonetheless the palladium aggregates show a strong interaction with the polymer surface, since they are not washed down easily and they only slowly release the very small amount of Pd (between 1.5%-0.3% of the initial Pd content from the second cycle on) enough for the catalysis in successive reuses. The loss of palladium in the first run was higher (3.2%), probably because in the reaction conditions some starting palladium complex weakly supported was removed. We do not have any experimental data that gives information about the nature of this interaction with the polymer. However, we could hypothesize that the imidazolium centers, formed on the support after the decomposition of the complex, may be playing a leading role, since the interaction with the completely saturated VA-PNB skeleton used as support is expected to be weak.

Other haloarenes were also tested. Those reactions with para-substituted aryl bromides with electron donating groups such as methyl or methoxide required longer times but high yields were achieved (Table 3.3, entries 1-2). Nevertheless when an aryl chloride was used even after 48 hours no activity could be appreciated (Table 3.3, entry 3). The model reaction was also effective when only 0.1 mol% of **16d** was used by increasing the reaction time (Table 3.3, entry 4). Considering all the amount of palladium added, a TOF value of 990 TON/h was achieved, which is a good value in this type of reactions. However, as mentioned above, the actual catalytic species are most probably the homogeneous species released into the reaction medium (around 1%-0.3% of the Pd content, Table 3.2). This means that the TOF number for the actual catalytic species reaches a value of at least 10^5 in each run. The polymeric palladium precatalyst **16d**, being recyclable, can reach a very high cumulative TON.

Table 3.3. Different Suzuki reactions catalyzed by **16d**.[a]

Entry	Haloarene	Time	Product (Yield %)
1		60 min	**18** (90) [b]
2		120 min	**19** (90) [b]
3		48 h	- [b]
4[c]		60 min	**17** (99) [d]

a) Reaction conditions shown in equation 3.3. b) Crude yields determined by ^{1}H NMR. c) Reaction performed with 0.1 mol% of Pd. d) Crude yields determined by ^{19}F NMR.

Additionally, other organic solvents were tested with the model reaction. In the case of a mixture dioxane:water (20:1; v/v) the reaction was clearly slower, a yield of 80% was reached after 2 hours, whereas in the second run the yield dropped and after 2 hours only 50% yield was achieved. When a mixture DMF:water (3:1; v/v) was used some interesting results were found. Polymer **16d** required longer reaction times with DMF than with acetonitrile but quantitative yields were achieved (Table 3.4, entries 1-3). As it happened in the case of acetonitrile, polymer **16c** needed more time to reach high conversions. However, under these conditions the yields obtained with **16c** strongly decreased upon recycling (Table 3.4, entries 4-6). In these conditions, after the third recycling experiment, benzotrifluoride (dehalogenation product of the starting bromide) was found as the major byproduct and its homocoupling dimer was also found in considerable amount. These byproducts were identified by comparison with commercially available samples. The same behavior was observed for **16c** when other arylhalides (p-Me-C_6H_4Br, for example) were used, and the reduction product ArH was again obtained as the major byproduct.

Table 3.4. Recycling experiments of the Suzuki reaction shown in equation 3.3 in DMF:H_2O (3:1).[a]

Entry	Catalyst	Cycle	Time (h)	Conversion (%)[b]	**17**, Yield (%)[b]
1	**16d**	1	0.75	99.2	99.2
2	**16d**	2	1.5	99.4	99.4
3	**16d**	3	3	97.9	97.9
4	**16c**	1	1.5	99.8	98.0
5	**16c**	2	3.5	99.7	89.7
6	**16c**	3	8.5	96.1	34.6

a) Reaction conditions shown in equation 3.3 except DMF was used instead of CH_3CN. b) Conversions and crude yields determined by ^{19}F NMR.

This different behavior of both catalysts upon changing the solvent, led us to think that DMF was interfering, favoring alternative reaction pathways, which are competing when the catalyst is less active for the cross-coupling reaction (i.e. **16c**). These differences can be clearly observed comparing the NMR spectra recorded for the four different combinations of solvent and catalyst (Figure 3.13). No byproducts were observed when acetonitrile was the organic solvent neither when DMF was used with **16d**. In view of these results we decided to study how different solvents favor the formation of dehalogenation (reduction) products in the presence of some palladium complexes. The outcome of this research is collected in chapter 4.

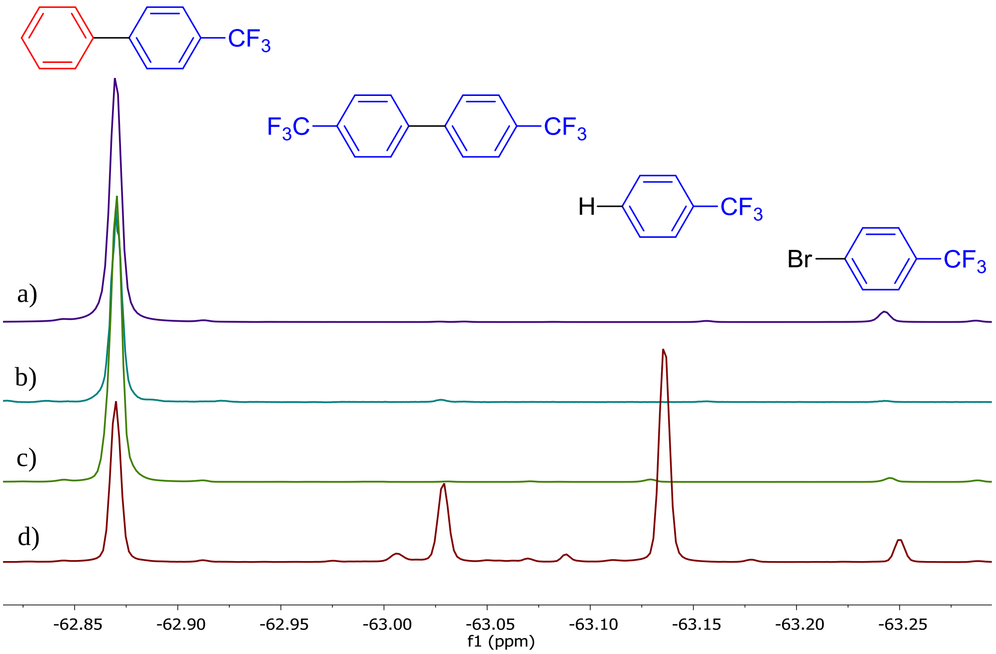


Figure 3.13: ^{19}F NMR spectra recorded after the third reaction cycle of: a) **16d** in CH_3CN:H_2O; a) **16c** in CH_3CN:H_2O; c) **16d** in DMF:H_2O; d) **16c** in DMF:H_2O.

3.2.3 Negishi reactions catalyzed by VA-PNB supported Pd-NHC complexes

After proving the catalytic activity of the VA-polynorbornene-supported palladium complex in some Suzuki reactions, a different coupling such as the Negishi reaction was tested. This is a C-C cross-coupling reaction between an aryl halide and an organometallic reagent containing a metal with intermediate electronegativity, being zinc the most common one. This reaction has been well studied[127] and tolerates many functional groups. Despite the advantages of the reaction, supported palladium catalysts have seldom been assessed using Negishi reactions and only a few reports can be found,[128] none of them involving NHCs,

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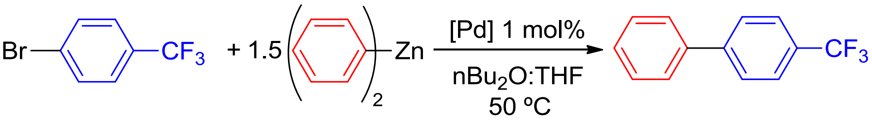
[127] Negishi, E. i.; Zeng, X.; Tan, Z.; Qian, M.; Hu, Q.; Huang, Z. In *Metal-Catalyzed Cross-Coupling Reactions*; de Meijere, A.; Diederich, F. Eds.; Wiley-VCH: Weinheim, **2004**, ch. 15.

[128] (a) Yang, Y. C.; Luh, T. Y. *J. Org. Chem.* **2003**, *68*, 9870-9873. (b) Wu, W. Y.; Lin, T. C.; Takahashi, T.; Tsai, F. Y.; Mou, C. Y. *ChemCatChem*, **2013**, *5*, 1011-1019. (c) Egle, B.; Muñoz, J. d. M.; Alonso, N.; De Borggraeve, W. M.; de la Hoz, A.; Díaz-Ortiz, A.; Alcázar, J. *J. Flow Chem*. **2014**, *4*, 22-25.

despite their many examples in homogenous catalysis. Thus, we decided to explore the behavior of our catalyst in this reaction with a model experiment.

In a standard reaction **16d** as catalyst precursor (1 mol% of palladium) and 4-bromobenzotrifluoride were added to a freshly-prepared solution of diphenylzinc in a 1:1 (v/v) mixture of THF and dibutyl ether (equation 3.4).[129] The reaction was heated at 50 ºC and monitored by *in situ* infrared spectroscopy. The ν(C-Br) IR absorption band was again not overlapped by any other reagent or solvent band and its decrease could be easily followed.



(3.4)

Three recycling experiments were carried out to check the possibility of reuse of **16d**. In this case longer reaction times than in the Suzuki reaction were needed to achieve good results (Table 3.5), but they keep similar values in consecutive uses. Induction times similar to those in the Suzuki reaction were also observed (2, 13 and 15 min in consecutive cycles). Furthermore a small but significant amount of homocoupling product (4,4'-bis(trifluoromethyl)-1,1'-biphenyl) could be observed as byproduct. Leaching measurements showed higher values than those observed in the Suzuki coupling. Assuming that taking the palladium aggregates into solution involves the oxidative addition of the ArX, the presence of residual LiCl in the $ZnPh_2$ solution (see experimental)[129] or even an interaction with the zinc reagent,[130] can increase the rate of that step. This indicates that the supported catalyst could be acting again as a palladium reservoir of homogeneous catalytic active species, in the same fashion as it has been found for the Suzuki reaction. As it happened before, the loss of palladium in the first run was higher (10.7%) than in the subsequent cycles. After the first use the leaching diminished and was between 2.5-5% of the Pd added as **16d** in the reaction mixture, so the catalyst is slowly wasted and useful in several cycles.

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[129] Diphenylzinc was prepared by reaction of a solution of $ZnCl_2$ (1.0 M, THF) and a solution of LiPh (1.9 M Bu_2O). Amatore, C.; Jutand, A.; Suarez, A. *J. Am. Chem. Soc*. **1993**, *115*, 9531-9541.

[130] Böck, K.; Feil, J. E.; Karaghiosoff, K.; Koszinowski, K. *Chem. Eur. J.* **2015**, *21*, 5548-5560.

Table 3.5. Recycling experiments of **16d** in the Negishi reaction.[a]

Cycle	Time (h)	Conversion (%)[b]	**17**, Yield (%)[b]	Pd Leaching (%)[c]
1	4	97.9	88.5	10.7
2	4.5	97.8	88.3	4.4
3	6	90.8	82.9	2.8

a) Reaction conditions shown in equation 3.3. b) Crude yields determined by ^{19}F NMR. c) Leaching determined by ICP-MS in the crude product of the reaction. Percentage of Pd leached from the total amount added.

3.3 CONCLUSIONS

In this chapter we have described the synthesis of Pd-NHC complexes supported on vinylic addition polynorbornenes. Catalyst precursors of the type [Pd(allyl)Cl(NHC-VA-PNB)] (**16**) are the most convenient. For their synthesis, the election of the base in order to generate the carbene from the imidazolium salt is crucial to obtain high loadings and well-defined species.

Polymer **16d** has good activitiy in the Suzuki reaction and can be reused at least five times. It is not acting as a heterogeneous supported catalyst but as a reservoir of palladium active homogeneous species, which are slowly released into the reaction medium. After the first use, palladium aggregates form on the surface of the support, which are most probably the source of the active catalytic species.

In situ infrared spectroscopy in supported palladium catalysis can be used in order to have a better knowledge of the induction and reaction times. Straightforward monitorization of the decrease of the C-Br band of the bromoaryl reagent allows us to follow the reaction course. This is the first time that the C-Br band has been monitored with this technique, and this is a general protocol that can be applied to any bromoaryl reagent, with no need of a specific IR-active substituent on the reagent as has been common practice so far.

We have also reported the first use of a supported Pd-NHC complex as catalyst in the Negishi reaction. **16d** is active even after several cycles

Dehalogenation byproducts (ArH) are competing products of the Suzuki reaction when a moderately active catalyst is used (such as **16c**) and it is strongly solvent dependent, being favored in DMF but not in acetonitrile.

3.4 EXPERIMENTAL PART

3.4.1 General Methods

General methods and techniques employed are the same that those described in chapter 2.

^{31}P MAS NMR spectra were recorded at 161.97 MHz with proton decoupling (tppm), with a 90º pulse length of 5.45 µs. ^{31}P-NMR chemical shifts are in ppm relative to external 85 % H_3PO_4.

The palladium content of the polymers and leaching measurements were determined by ICP–MS, using Agilent 7500i equipment; the samples were dissolved in HNO_3 (65%) using an ETHOS SEL Milestone microwave oven. Microanalysis by Energy Dispersive X-ray Spectroscopy (SEM-EDS) was carried out in the same apparatus described in chapter 2 with an EDAX Génesis accessory.

In situ IR spectra were recorded with a ReactIR 15 equipped with a transmission fiber of 6.3 mm AgBr FiberConduit and a probe DiComp with diamond sensor.

$[PdCl_2(PPh_3)_2]$[131] and $[Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}Cl)]_2$[132] were prepared according to the literature procedures.

3.4.2 Anion exchange in the polymer-supported imidazolium salt

Synthesis of [VA-CopNBNB(CH_2)$_4$IMes]BF_4 (14)

A round-bottom flask was charged with copolymer [VA-CopNBNB(CH_2)$_4$IMes]Br (**8b**) (0.8000 g, 1.190 mmol IMes) and MeOH (100 mL). Then a solution of sodium tetrafluoroborate (3.900 g, 35.52 mmol) in H_2O (30 mL) was added slowly and the mixture was stirred at room temperature for 40 h. After that time H_2O (100 mL) was added and the mixture stirred for 2 h in order to dissolve completely the excess of the salt. The polymer was filtered, washed with a mixture MeOH:H_2O (1:1, v/v, 5 x 20 mL) and air dried. The

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[131] Tayim, H. A.; Bouldoukian, A.; Awad, F. J. *Inorg. Nucl. Chem*. **1970**, *32*, 3799-3803.

[132] Tatsuno, Y.; Yoshida, T.; Seiotsuka, In *Inorganic Syntheses*; Shriver, D. F. Ed.; Wiley-Interscience: New York, **1979**, *Vol 19*, 220-221.

polymer is a white solid (0.7690 g, 95% yield). Halogen analysis: calcd for $[(C_7H_{10})_x\{C_7H_9(CH_2)_4(C_{12}H_{14}N_2)\}_y]BF_4$ (x/y = 2.73) 0.0 mg Br/g (0.0%). Found: Br 0.0 mg Br/g (0.0%). IR (Neat), ν: (C=N) 1548, (B-F) 1052. ^{13}C CP-MAS NMR (100.61 MHz): 150-120 (br, aromatics, N*C*HN, N*C*H=*C*HN), 64-24 (br, polyNB), 24-15 (br, *C*H$_3$).

3.4.3 Synthesis of polymer-supported NHC-Pd complexes

Synthesis of [{VA-CopNBNB(CH$_2$)$_4$IMes}PdCl(PPh$_3$)$_2$]BF$_4$ (15)

NBu_4OH (0.270 g, solution in MeOH, 40% wt, 1.04 mmol) was added to a suspension of **14** (0.604 g, 0.868 mmol) in CH_2Cl_2 (40 mL) under nitrogen. After 30 min $[PdCl_2(PPh_3)_2]$ (0.640 g, 0.911 mmol) was added to the carbene solution and the mixture was stirred at room temperature for 24 h. The polymer was filtered and washed with hot CH_2Cl_2 (5 x 10 mL) until the filtrate showed no yellow color. The product was obtained as a yellow solid (0.605 g, 60% yield). Analysis ICP-MS Pd 5.75 mg Pd/g. ^{13}C CP-MAS NMR (100.61 MHz): 165-159 (br, N*C*N), 144-117 (br, aromatics, N*C*H=*C*HN), 63-23 (br, polyNB), 23-13 (br, *C*H$_3$). ^{31}P MAS NMR (161.97 MHz): 32-20 (br, *P*Ph$_3$).

Synthesis of [{VA-CopNBNB(CH$_2$)$_4$IMes}PdCl(η^3-C$_3$H$_5$)] (16d)

In a Schlenk tube in a nitrogen atmosphere copolymer $[VA\text{-}CopNBNB(CH_2)_4IMes]BF_4$ **14** (0.400 g, 0.589 mmol of IMes), DBU (0.134 g, 0.883 mmol) and THF (10 mL) were stirred at reflux for 8 hours. After cooling to room temperature $[Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}Cl)]_2$ (0.108 g, 0.294 mmol) was added and the mixture was stirred at room temperature for 12 hours. The polymer was then filtered, washed with THF (5 x 10 mL) and air dried. The product was obtained as a pale brown powder (0.415 g, 91% yield). Analysis ICP-MS Pd 89.4 mg Pd/g. IR (neat), cm^{-1}: ν(C=C) 1648, ν(C=N st) 1604. ^{13}C CP-MAS NMR (100.61 MHz): 184-177 (br, N*C*N), 142-117 (br, aromatics, N*C*H=*C*HN), 117-111 (br, allyl C^1), 77-65 (br, allyl C^2, allyl C^3), 64-24 (br, polyNB), 24-15 (br, *C*H$_3$).

16a, **16b**, and **16c** were synthesized in a similar way, but stirring different times (24 h, 2 h and 30 min respectively) with NBu_4OH (solution in MeOH, 40% wt) as base.

3.4.4 General procedure for the Suzuki reactions. Table 3.1, entry 9

Polymer **16d** (0.0024 g, 0.0020 mmol Pd), phenylboronic acid (0.0370 g, 0.300 mmol) and cesium carbonate (0.1410 g, 0.400 mmol) were introduced in Schlenk tube in a nitrogen atmosphere. Then 4-bromobenzotrifluoride (0.0450 g, 0.200 mmol) and a mixture of $CH_3CN{:}H_2O$ (2.0 mL, 3:1; v/v) were added and the mixture was kept in a heat-bath at 80 ºC for 20 min. The reaction mixture was then cooled to room temperature and checked by ^1H NMR and ^{19}F NMR. The polymer was then filtered and washed with a mixture of $CH_3CN{:}H_2O$ (5 x 2.0 mL, 3:1; v/v). The polymer was stored for further use. The acetonitrile was removed under vacuum and the residue was dissolved in CH_2Cl_2 (10.0 mL). The organic phase was washed with water (5 x 5.0 mL) and a saturated aqueous solution of NH_4Cl (2 x 5.0 mL) and dried over $MgSO_4$. After removing the solvent the residue was chromatographed on silica gel (hexane as eluent) to afford the pure product as a colorless solid (**17**, 0.037 g, 83.1% yield).

The other experiments showed in Table 3.1 and Table 3.3 were carried out in the same way. The identity of the products **17**, **18** and **19** was confirmed by comparison of the characterization data with those found in the literature.[133]

3.4.5 General procedure for the Suzuki reactions followed by in situ IR. Table 3.2, entry 1

Polymer **16d** (0.0100 g, 0.00840 mmol Pd), phenylboronic acid (0.154 g, 1.26 mmol) and cesium carbonate (0.547 g, 1.68 mmol) were introduced in a pear-shaped flask with three necks. It was equipped with the IR-probe in the central neck, a gas inlet with stopcock and a septum. Then, in a nitrogen atmosphere, a mixture of $CH_3CN{:}H_2O$ (4.0 mL, 3:1; v/v) was added and the mixture was introduced in a heated bath at 80 ºC. After 5 min 4-bromobenzotrifluoride (0.189 g, 0.840 mmol) was added and the reaction was immediately monitored by IR. When no increase of conversion was observed the reaction was cooled down to room temperature and checked by ^1H NMR and ^{19}F NMR. The polymer was then filtered and washed with a mixture of $CH_3CN{:}H_2O$ (5 x 2.0 mL, 3:1; v/v). The polymer was stored for further use.

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[133] Bandari, R.; Höche, T.; Prager, A.; Dirnberger, K.; Buchmeiser, M. R. *Chem. Eur. J.* **2010**, *16*, 4650-4658.

The other experiments showed in Table 3.2 and Table 3.4 were carried out in a similar way.

3.4.6 General procedure for Negishi reactions followed by in situ IR

Polymer **16d** (0.0200 g, 0.0168 mmol) and THF (4.0 mL) were introduced in a pear-shaped flask with three necks. It was equipped with the IR-probe in the central neck, a gas inlet with stopcock and a septum. The mixture was kept in a heated bath at 50 ºC for 5 min. Then 4-bromobenzotrifluoride (0.378 g, 1.68 mmol) and a solution of $ZnPh_2$ (5.0 mL, 2.5 mmol in THF:*n*Bu_2O 0.5 M) were added and the reaction was immediately monitored by IR. When no increase of the conversion was observed the reaction was cooled down to room temperature and checked by ^1H NMR and ^{19}F NMR. The polymer was then filtered, washed with THF (5 x 5.0 mL) and stored for further use.

Synthesis of $ZnPh_2$

A flamed-dried Schlenk tube was charged with LiPh (10.5 mL, 1.9 M in Bu_2O, ~20.0 mmol) under nitrogen. A solution of $ZnCl_2$ (10.0 mL, 1.0 M in THF, 10.0 mmol) was slowly added at -78 ºC. After stirring for 3 h in the dark, the resulting suspension was allowed to decant and the light yellow solution formed was transferred via cannula to another flamed-dried Schlenk flask and stored in the dark for direct use.

Chapter 4

4. Solvent induced Reduction of Pd-Aryl complexes.

4.1 INTRODUCTION

As it has been previously mentioned in this dissertation, palladium-catalyzed reactions represent an important field in modern chemistry and their development attracts the attention of researchers in both academy and industry. In the last decades many works concerning this subject have reported the development of new processes or catalysts and have identified suitable reaction conditions for many syntheses.[134] Optimization of new methodologies implies the correct selection of reagents as well as solvents. Sometimes, familiar solvents or those which have been useful in similar reactions are directly considered appropriate without regarding their potential risks. In the event of fast reactions, where catalysis proceeds with only a small amount of undesired byproducts, this procedure can be good enough. On the contrary, in those reactions in which longer reaction times are needed, the solvent may play a decisive role interacting with some reagents or the catalyst, and thus producing secondary reactions responsible of the decrease in the selectivity of the processes.

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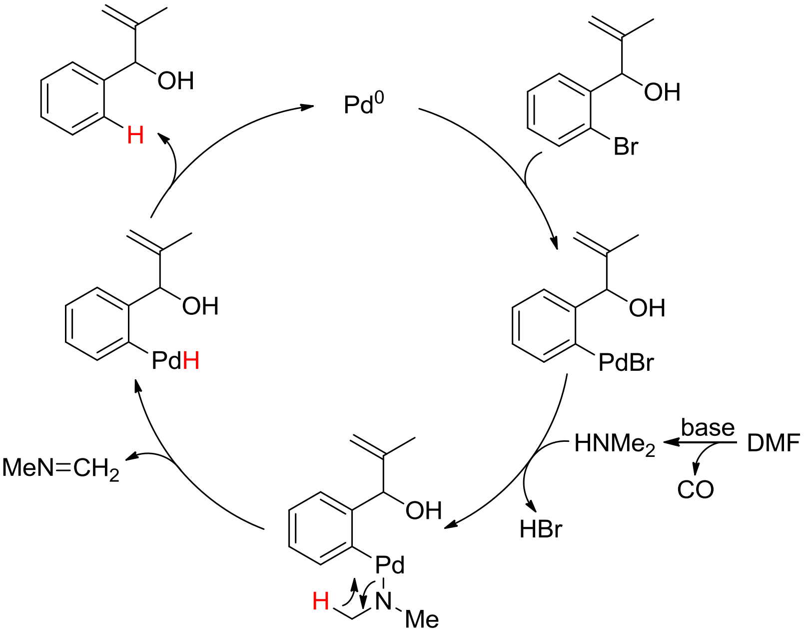
[134] (a) Molnár, A. *Palladium-Catalyzed Coupling Reactions*; Wiley-VCH Verlag GmbH & Co. KGaA.: Weinheim, **2013**. (b) Nicolaou, K. C.; Bulger, P. G.; Sarlah, D. *Angew. Chem. Int. Ed.* **2005**, *44*, 4442-4489.

Crabtree has recently reviewed the many different causes for the deactivation of homogeneous catalysts.[135]

Studies about palladium-catalyzed reactions reporting the formation of byproducts, frequently derived from the reduction of haloarenes or other organic halides, can easily be found in the literature. In some occasions, the solvent has been deemed responsible of these drawbacks and plausible mechanisms for the side reactions have been proposed as, for example, the one shown in Scheme 4.1.[136] Nevertheless, experiments to identify the decomposition products from the solvent have rarely been reported. These experiments could provide some useful data to confirm the proposals made for those side-reaction pathways.



Scheme 4.1: Reaction pathway proposed by Muzart et al. for the hydrogenolysis 1-(*o*-bromophenyl)-2-methylprop-2-en-1-ol in the presence of DMF.[136d]

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[135] Crabtree, R. H. *Chem. Rev.* **2015**, *115*, 127-150.

[136] (a) Legros, J. Y.; Primault, G.; Toffano, M.; Rivière, M. A.; Fiaud, J. C. *Org. Lett.* **2000**, *2*, 433-436. (b) Martins, A.; Candito, D. A.; Lautens, M. *Org. Lett.* **2010**, *12*, 5186-5188. (c) Lau, S. Y. W.; Andersen, N. G.; Keay, B. A.; *Org. Lett.* **2001**, *3*, 181-184. (d) Zawisza, A. M.; Ganchegui, B.; González, I.; Bouquillon, S.; Roglans, A.; Hénin, F.; Muzart, J. *J. Mol. Catal. A: Chem.* **2008**, *283*, 140-145.

It is important to realize that in some coupling reactions there are other processes that could be responsible of the reduction products because they provide an alternative source of hydrogen. For example in a Heck reaction Pd-H species are generated in each catalytic cycle, or in a Stille coupling an undesired transmetallation of a butyl group from a $SnBu_3R$ reagent could generate a Pd-H by β-H elimination.

Encouraged by the different results observed in the Suzuki couplings described in chapter 3 upon changing the solvents, as well as by the lack of information in this regard, we decided to carry out a study in order to find out which solvents can be considered as safe to perform palladium-catalyzed reactions and which ones may represent a risk. We studied the ability of different common solvents to decompose palladium aryl complexes. Moreover, we analyzed and tried to identify the products derived from the decomposition of the solvent so that we could propose some reaction pathways to explain the interaction between the metal complex and the solvent. Additionally, we tested the influence of some usual additives such as bases or the presence of oxygen. The latter is particularly interesting since an increasing concern in the oxidative versions of the C-C coupling processes can be witnessed.[137] The use of alkanes as substrates rather than organic halides along with the use of oxygen as oxidant is clearly sought as a greener alternative.

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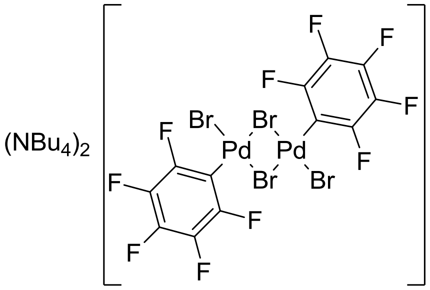
[137] (a) Deng, Y.; Persson, A. K.; Bäckvall, J. E. *Chem. Eur. J.* **2012**, *18*, 11498-11523. (b) Yeung, C. S.; Dong, V. M. *Chem. Rev.* **2011**, *111*, 1215-1292. (c) Bras, J. L.; Muzart, J. *Chem. Rev.* **2011**, *111*, 1170-1214. (d) Liu, C.; Zhang, H.; Shi, W.; Lei, A. *Chem. Rev.* **2011**, *111*, 1780-1824. (e) Chen, X.; Engle, K. M.; Wang, D. H.; Yu, J. Q. *Angew. Chem. Int. Ed.* **2009**, *48*, 5094-5115.

4.2 RESULTS AND DISCUSSION

4.2.1 Election of a model palladium-complex

In order to study the behavior of the solvents with a palladium aryl moiety, the monoaryl-palladium complex **20** was chosen as model (Figure 4.1). This is a robust organometallic compound stable both in the solid state and in solution and can be prepared and stored without difficulty. This complex had formerly been used as catalyst precursor to synthesize alkenes with fluorinated substituents by a Heck reaction.[138] Other similar complexes related to **20** with C_6F_5-Pd moieties are the likely intermediates in the previous reactions as well as some other processes including Stille cross-coupling reactions of halopentafluorobenzenes[56a,c] or oxidative Heck reactions of pentafluorobenzene.[139]



20

Figure 4.1: *Trans* isomer of palladium complex **20**.

Additionally, the pentafluorophenyl group has two main advantages. On the one hand, the fluorinated ligand allowed us to monitor the reactions by ^{19}F NMR and thus, both organometallic species and reduction-derived arenes could be characterized and quantified. In a solution of **20** in a particular solvent, besides the *cis* and *trans* isomers, different complexes can be found due to the coordination of the solvent. The position of the equilibrium between these species is determined by the concentration of the complex, the

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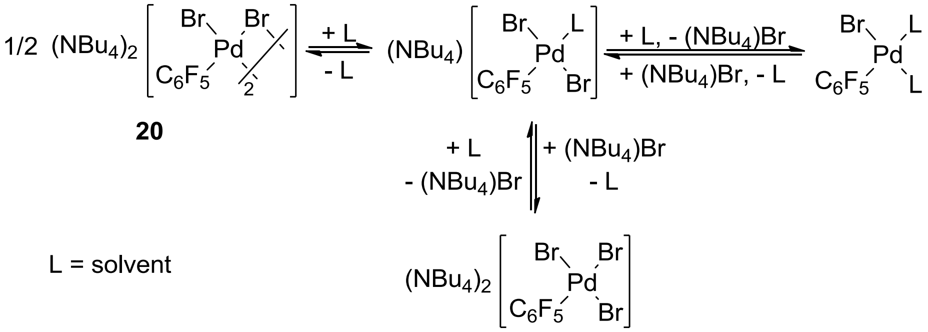
[138] (a) Albéniz, A. C.; Espinet, P.; Martín-Ruiz, B.; Milstein, D. *J. Am. Chem. Soc.* **2001,** *123*, 11504-11505. (b) Albéniz, A. C.; Espinet, P.; Martín-Ruiz, B.; Milstein, D. *Organometallics* **2005**, *24*, 3679-3684.

[139] Zhang, X.; Fan, S.; He, C. Y.; Wan, X.; Min, Q. Q.; Yang, J.; Jiang, Z. X. *J. Am. Chem. Soc.* **2010**, *132*, 4506-4507.

polarity and the coordination ability of the solvent. If the concentration of bromide increases upon decomposition of **20**, even a dianionic complex can be formed (Scheme 4.2). These equilibria have been previously studied by our group and further details are reported elsewhere.[138a] In the present case, characterization of all these compounds was made by looking at the chemical shifts corresponding to the F_{ortho} which were in the range between -112 to -120 ppm for the C_6F_5-Pd moiety in the organometallic complexes whereas the same signal for the pentafluorobenzene, the decomposition product, could be found around -140 ppm in each solvent where it was formed.



Scheme 4.2: Possible equilibria between monoaryl-palladium complexes in solution.

On the other hand, the pentafluorophenyl ligand slows down the usual reactivity of aryl-palladium complexes simulating the situation of a slow catalysis commented above. Previous works have taken advantage of the low reaction rates of this family of fluoroaryl complexes in some common palladium-catalyzed reactions such as 2,1-olefin insertion or 1,1-carbene insertion. Isolation and characterization of intermediates or exhaustive mechanistic studies on isolated steps of the catalytic process have allowed a better knowledge of these reactions.[140]

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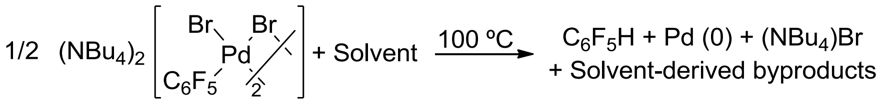
[140] (a) Albéniz, A. C.; Casares, J. A. “Palladium Mediated Organofluorine Chemistry” in *Adv. Organomet. Chem.* Pérez, P. J. Ed. Academic Press, UK; **2014**, Vol. *62*, pp. 1-110. (b) Espinet, P.; Albéniz, A. C.; Casares, J. A.; Martínez-Ilarduya, J. M. *Coord. Chem. Rev.* **2008**, *252*, 2180-2208. (c) Albéniz, A. C.; Espinet, P.; Jeannin, Y.; Philoche-Levisalles, M.; Mann, B. *J. Am. Chem. Soc.* **1990,** *112*, 6594-6600 (Heck-type processes). (d) Casado, A. L.; Espinet, P.; Gallego, A. M.; Martínez-Ilarduya, J. M. *Chem. Commun.* **2001**, 339-340 (Stille reaction). (e) Pérez-Temprano, M. H.; Nova, A.; Casares, J. A.; Espinet, P. *J. Am. Chem. Soc.* **2008,** *130*, 10518-10520 (Sn-Pd transmetalation). (f) Albéniz, A.C.; Espinet, P.; Manrique, R.; Peréz-Mateo, A. *Angew.Chem.Int.Ed.* **2002**, *41*, 2363-2366 (Carbene migratory insertion).

4.2.2 Study of the behavior of $(NBu_4)_2[Pd_2(\mu\text{-}Br)_2Br_2(C_6F_5)_2]$ in several solvents

Complex **20** was heated at 100 °C in eleven different solvents for 2 hours (equation 4.1). Every solvent was tested at least five times in the absence or presence of oxygen and a strong base such as an aqueous NaOH solution with a mol ratio Pd:base = 1:1. **20** is soluble in most solvents, but in some cases such as water, toluene or 1,4-dioxane the palladium complex is scarcely soluble and after the reaction the mixture had to be dissolved or extracted by addition of another solvent (CH_2Cl_2 or acetone). Alcohols were not tested since previous works have shown their excellent activity as reducing agents for palladium complexes and the mechanisms of these reactions are well known.[141] The amount of pentafluorobenzene formed was quantified by ^{19}F NMR. This arene was the only organic product derived from the C_6F_5-Pd moiety.[142] In some solvents, after the heating period, some organometallic compounds appeared, produced by the rearrangement of the pentafluorophenyl ligands in **20** to form other complexes with Pd-$(C_6F_5)_2$ moieties.[143]



(4.1)

20

According to the amount of pentafluorobenzene obtained the solvents can be sorted into two main groups: safe solvents and risky solvents. Table 4.1 collects the results of those solvents that can be considered safe because of the small amount of C_6F_5H observed. THF, water, toluene or nitriles such as acetonitrile or isobutyronitrile showed negligible reduction of **20** to form the fluoroarene. Neither the presence of oxygen nor the base seems to have an important effect in their behavior since in no case the amount of pentafluorobenzene was

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[141] (a) Alonso, F.; Beletskaya, I. P.; Yus, M. *Chem. Rev.* **2002**, *102*, 4009-4091. (b) Chen, J.; Zhang, Y.; Yang, L.; Zhang, X.; Liu, J.; Li, L.; Zhang, H. *Tetrahedron* **2007**, *63*, 4266-4270. (c) Viciu, M. S.; Grasa, G. A.; Nolan, S. P. *Organometallics* **2001**, *20*, 3607-3612. (d) Zask, A.; Helquist, P. *J. Org. Chem.* **1978**, *43*, 1619-1620. (e) Mueller, J. A.; Goller, C. P.; Sigman, M. S. *J. Am. Chem. Soc.* **2004**, *126*, 9724-9734.

[142] In the presence of the base, HC_6F_4OH could be detected in some experiments produced by the nucleophilic aromatic substitution of the *para* fluorine atom by a hydroxyl group: Feldman, D.; Segal-Lew, D.; Rabinovitz, M. *J. Org. Chem.* **1991**, *56*, 7350-7354.

[143] Usón, R.; Forniés, J.; Nalda, J. A.; Lozano, M. J.; Espinet, P.; Albéniz, A. C. *Inorg. Chim. Acta* **1989**, *156*, 251-256.

higher than 3 mol%. Additionally, mixtures of water with acetonitrile or THF in a ratio 1:1 in volume were also tested. In these cases **20** was soluble and the same results were achieved.

Table 4.1. Decomposition data of complex **20** to C_6F_5H (%) in those solvents considered as safe and reaction conditions.[a]

Entry	Solvent	A	B	C	D	E
		N_2	Air	O_2	N_2, NaOH	Air, NaOH
1	THF	0	0	0	0.7	0.6
2	MeCN	0	0	0	2.4	2.4
3	*i*-PrCN	0.2	0.8	0.5	0.6	1.3
4[b]	Toluene	0	0	0	0	0
5[c]	H_2O	0	0	0	0	0

a) All the experiments were carried out at 100 ºC for 2 hours. Mol percentages of C_6F_5H are given. b) **20** is sparingly soluble, CH_2Cl_2 was added after the reaction time to obtain a clear solution to be checked by NMR. c) **20** is insoluble and the mixture was extracted with CH_2Cl_2 after the reaction time and checked by NMR.

By contrast, amides such as dimethylformamide (DMF), dimethylacetamide (DMA) or N-methylpyrrolidone (NMP), cyclohexanone and diethers such as 1,4-dioxane or 1,2-dimethoxyethane (DME) afforded noticeable amounts of C_6F_5H under certain reaction conditions (Table 4.2). Unlike the safe solvents, in these cases the presence of oxygen and NaOH can produce a strong effect in the reduction of **20** to form the fluoroarene. Temperature is a crucial factor since below 50 ºC all these solvents behaved as safe solvents even under oxygen. However, at 80 ºC the decomposition of the complex in DMF is patent (24% of C_6F_5H in 2 hours), though smaller than at 100 ºC (88% in 2 hours, Table 4.2, entry 1C). With the aim of learning about the possible mechanisms of these side reactions, these risky solvents were studied thoroughly and the results are described in different sections attending to their functional groups.

Table 4.2. Decomposition data of complex **20** to C_6F_5H (%) in those solvents considered as risky and reaction conditions.[a]

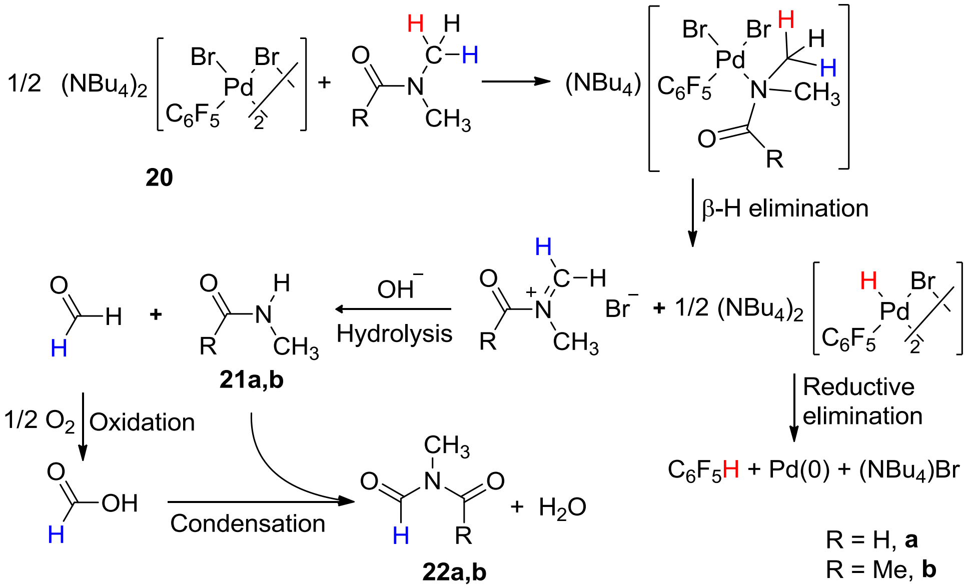
Entry	Solvent	A N_2	B Air	C O_2	D N_2, NaOH	E Air, NaOH	F O_2, NaOH, 72 h
1	DMF	0	22	88	12.4	37.5	97.3
2	DMA	0	0.5	1.1	2.7	4.2	21
3	NMP	1.3	11.5	42.8	5.7	11.8	79
4	Cyclohexanone	3.5	25.5	44.8	62.5	26.2	95
5[b]	1,4-dioxane	0	5.4	23	0.5	0.5	–
6	DME	0.1	0.4	22	0.7	2	–

a) All the experiments were carried out at 100 ºC for 2 hours. Mol percentages of C_6F_5H are given. b) **20** is sparingly soluble, acetone was added after the reaction time to obtain a clear solution to be checked by NMR.

4.2.2.1 Amides

No decomposition of **20** was observed in DMF or DMA when the experiments were carried out without base and under a nitrogen atmosphere (Table 4.2, entries 1A-2A). Similarly, a very little amount of C_6F_5H was founded when NMP was used in the same conditions (Table 4.2, entry 3A). Longer reaction times have an evident but small effect, since heating **20** in deoxygenated DMF for 72 hours produced only a 2% of pentafluorobenzene. The amount of water seems to be irrelevant again because when the reaction was performed under nitrogen with a mixture of NMP:water = 10:1 (v/v) the total of arene formed was only 1.5% (almost identical to that obtained without water, Table 4.2, entry 3A). However, the stability of the complex seems to be clearly affected by the presence of oxygen and to a lesser extent of base. Both factors produce a stronger effect when using DMF than NMP (Table 4.2, entries 1B-E and 3B-E). Although a slight effect is observed with DMA in the same conditions (Table 4.2, entry 2B-E), when **20** was treated in stringent reaction conditions, heated at 100 ºC for 72 hours in DMA in the presence of base and under an oxygen atmosphere, the amount of C_6F_5H raised to a noticeable 21% (Table 4.2, entry 2F).

Identification of the solvent byproducts by ^{1}H-NMR and GC-MS revealed only two products derived from DMF: methylformamide (**21a**) and methylformimide (**22a**). In order to discard alternative origins of these two products, DMF was heated at 100 ºC in the presence of oxygen and base but without complex **20**. After 48 hours none of those byproducts was found. This leads us to propose a possible reaction pathway explaining the formation of pentafluorobenzene, **21a** and **22a** (Scheme 4.3). Given that complex **20** does not react with acids, the formation of C_6F_5H by protonation can be discarded. Moreover, this assumption is reinforced by the fact that when the reactions were performed in the presence of a base, the amount of fluoroarene was similar or even higher. The presence of methylformamide (**21a**) suggests that one of the methyl groups of the amide is involved in a β-H elimination reaction forming an iminium salt and a palladium-hydride complex. Pentafluorobenzene is formed after a reductive elimination step since the formation of R-H from Pd-R involves a Pd-H species.[144] Hydrolysis of the iminium salt gives **21a** and formaldehyde which in the presence of oxygen can be oxidized to formic acid. Methylformimide (**22a**) is formed after reaction of **21a** with this acid. Both, the oxidation of formaldehyde in the presence of oxygen and the formation of **22a** from formic acid have been tested independently.



Scheme 4.3: Decomposition of **20** in DMF and DMA.

The same mechanism is proposed for DMA since analogous byproducts, methylacetamide (**21b**) and imide **22b**, were found when **20** was heated in DMA under harsh conditions (Table 4.2, entry 2F). In the case of the NMP only formimide **23** was

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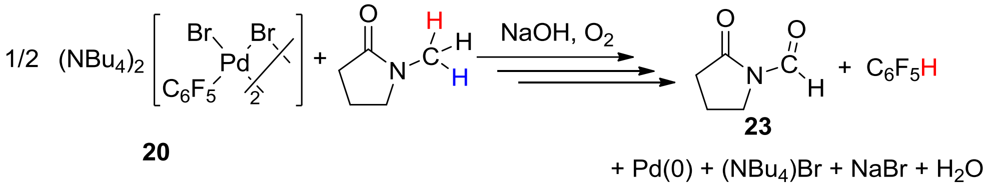
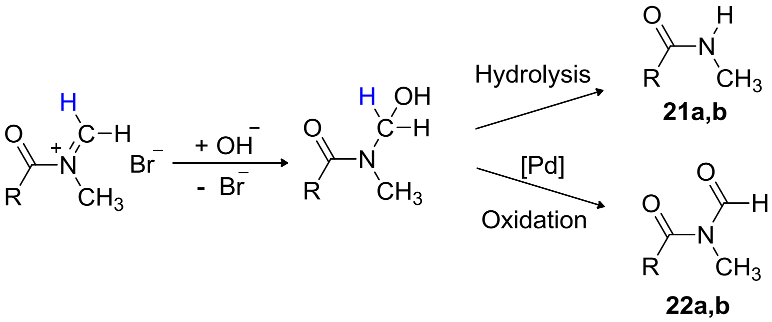
[144] Albéniz, A. C.; Espinet, P.; Lin, Y. S. *Organometallics* **1997**, *16*, 4030-4032.

found. Nevertheless, in spite of not detecting pyrrolidone as by product, we can assume that this is formed and is acting in the same way **21** does with the other solvent amides (Scheme 4.4).



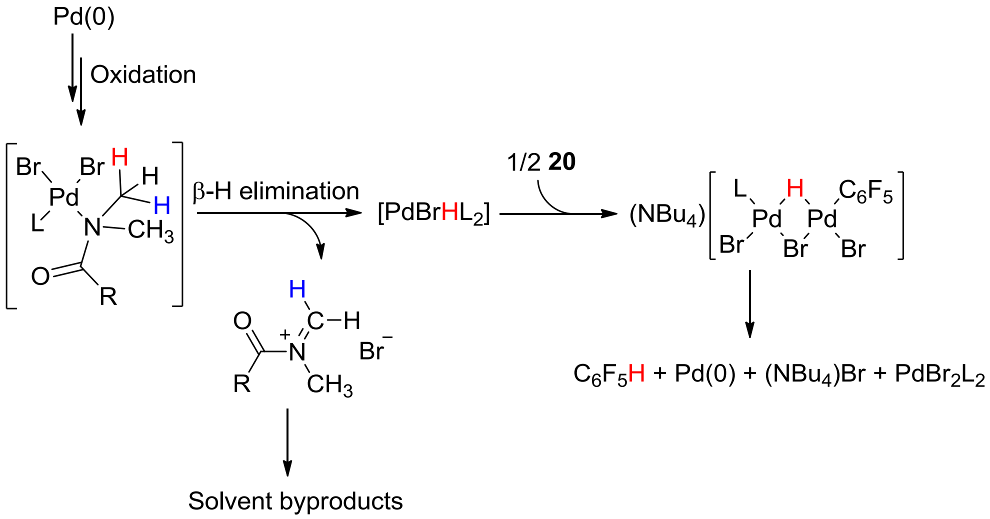
Scheme 4.4: Decomposition of **20** in NMP.

Alternatively, a nucleophilic attack of a hydroxyl group to the iminium salt would produce the hemiaminal R(CO)$NCH_3(CH_2)OH$ which could be oxidized to form **22** or **23** in the presence of palladium. Even though this pathway cannot be ruled out, the coordination of the hemiaminal to palladium, required for a Pd-catalyzed alcohol oxidation, is disfavored in these conditions due to competition with solvent coordination (Scheme 4.5).



Scheme 4.5: Alternative route for the formation of **22**.

Generally, the amount of solvent byproducts **21**, **22** and **23** observed by ^{1}H-NMR is higher than the amount of pentafluorobenzene measured after the complex decomposition. In the presence of oxygen this difference is even higher and the amount of byproducts found indicates that **20**, or palladium species derived from it, are catalyizing the decomposition of the solvent. However, its activity is very low (maximum 10-12 turnovers after 72 hours) and hence, the reaction has no practical application in this matter. Apparently, oxygen is playing two different roles. On the one hand, as has been commented above, it is responsible for the formation of imides **22** and **23**. On the other hand, the catalytic activity of the complex suggests that oxygen is oxidizing Pd(0), formed after reductive elimination of pentafluorobenzene, to Pd(II). New Pd(II) species can coordinate again the amides and perform a new cycle where the β-H elimination step forms new Pd-H complexes. In previous works our group has shown how hydride-transfer between two palladium atoms is possible.[144] Therefore, an additional pathway to form "PdH(C_6F_5)" species can be outlined (Scheme 4.6). This alternative route may explain the higher amount of C_6F_5H observed when the experiments were performed under oxygen. In an independent experiment we observed that **21a** and **22a** were formed by heating $(NBu_4)_2[Pd_2(\mu\text{-}Br)_2Br_4]$ in DMF under oxygen for 2 h (2 turnovers).

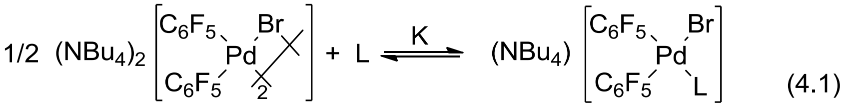


Scheme 4.6: Reaction with the solvent of reoxidized Pd(II) species and hydride transfer.

Even though the possibility of a radical mechanism for these decompositions was also considered, none of these solvents seem to follow this route. When complex **20** was heated in NMP under a nitrogen atmosphere for 2 hours in the dark (1.7% C_6F_5H) or under UV irradiation (λ = 352nm, 2.2% C_6F_5H) no significant difference was observed with the original data (Table 4.2, entry 3A). In these experiments the use of radical traps such as

Galvinoxyl or TEMPO, offers no valuable information since radical traps react with palladium hydride species.[145]

It is obvious that, in almost every reaction condition tested, the decomposition of **20** in these amides follows a trend DMF > NMP > DMA. A plausible explanation for this trend can be obtained by studying the coordination ability of the solvents, since the first step of the mechanism is the coordination of the solvent (see Scheme 4.3). A measure of how good these solvents are as ligands can be obtained by studying the equilibrium for the bridge-splitting reaction (equation 4.2).



24 **25**

24 is a dinuclear complex where all the pentafluorophenyl groups are equivalent. However, after the coordination of the solvent, **25** is a monomeric complex with two nonequivalent pentafluorophenyl moieties. This difference is easily traceable by ^{19}F-NMR (Figure 4.2) and allows a straightforward measure of the equilibrium constant, K = [**25**]/[**24**]$^{1/2}$. The results obtained follow the expected trend, K_{DMF}, 0.097 ± 0.002 > K_{NMP}, 0.0748 ± 0.0018 > K_{DMA}, 0.0443 ± 0.0011.

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[145] Albéniz, A. C.; Espinet, P.; López-Fernández, R.; Sen, A. *J. Am. Chem. Soc.* **2002**, *124*, 11278-11279.

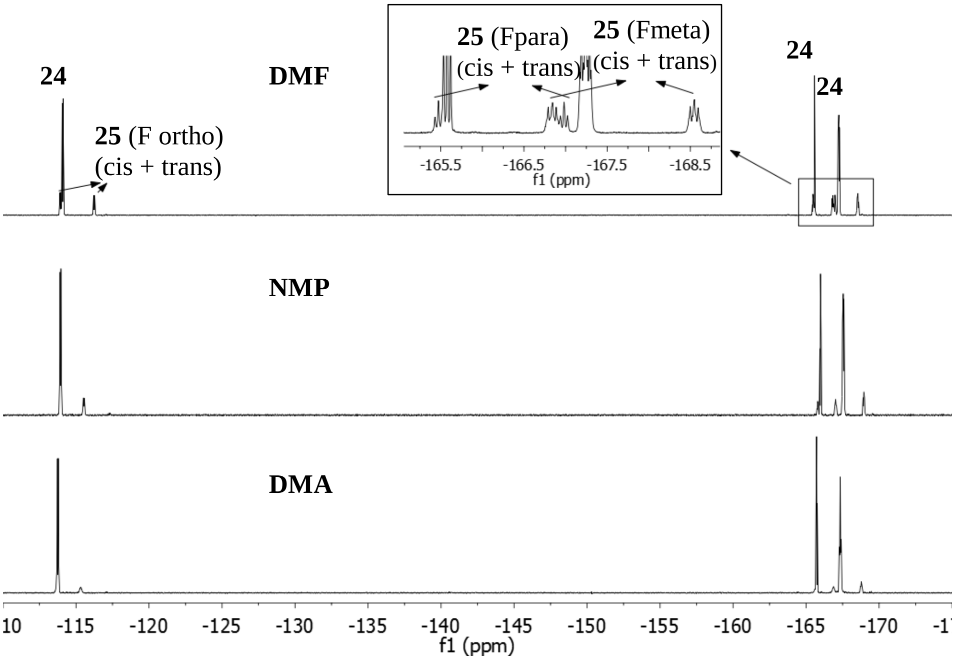

Figure 4.2: Comparison between NMR spectra of **24** and **25** in DMF, NMP and DMA.

The importance of the coordination of the solvents to palladium can also be assessed by looking at to the behavior of [PdBr(C_6F_5)($AsPh_3$)$_2$] in DMF. After being heated at 100 ºC under air for 2 hours no decomposition was observed, whereas complex **20** gave 22% of C_6F_5H in the same conditions (Table 4.2, entry 1B). Despite the fact that $AsPh_3$ is not a strong ligand for Pd(II)[146], it is stronger than DMF and thus, the coordination of the solvent is hampered avoiding the side reactions. Therefore, the risk of undergoing the undesired reactions is higher in those experiments with palladium complexes which have easily available coordination sites. This is the case of the so-called “ligandless catalysis”, where the solvent plays the role of a ligand in an almost inevitable way.

As mentioned above, the presence of oxygen has a stronger effect than the use of base, although the influence of the latter is undeniable especially in the case of DMF. Scheme 4.3 shows how the base plays an important role in some of those equilibria, for instance the hydrolysis of the iminium salt to give **21**. Nevertheless the higher importance of the presence of a base in the decomposition of **20** in the case of DMF seems to indicate that other reaction could be taking place, like a hydrolysis of the amide. The application and

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[146] $AsPh_3$ is at least 50 times less coordinating than PPh_3, although much less oxidizable.

reactivity of DMF as reagent with some transition metal complexes have been reviewed.[147] The role of DMF as a source of CO and hydrogen to give reduction products has previously been reported.[148] In the case of palladium, Zawisza and Muzart suggested that in the presence of a base DMF was hydrolyzed to $NHMe_2$ which, upon coordination to palladium, suffered a β-H elimination affording a Pd-H species (see Scheme 4.1).[149] However, in our experiments with DMF neither dimethylamine nor methylamine (a likely product obtained by hydrolysis of the enamine formed after β-H elimination) was observed in any case. Nonetheless some experiments were performed with the aim of quantifying the amount of pentafluorobenzene which could be attributed to the participation of $NHMe_2$. **20** was heated at 100 ºC for 2 hours in a mixture of *i*-PrCN as solvent, NaOH (aq) and $NHMe_2$ (molar ratio Pd:$NHMe_2$ = 1:2). The amount of C_6F_5H obtained under nitrogen and under oxygen was 9.2% and 13.4% respectively, whereas without base no decomposition was observed. The evident requirement of a base agrees with Hartwig's work that has shown that a palladium amido complex undergoes the β-H elimination.[150] In view of these results we can assume that even if some hydrolysis of the amide is occurring in basic media, the resulting amine is not the main source of hydrogen responsible for the reduction of the complex.

The use of formiates as reducing agents in some metal-catalyzed reactions, including palladium, has been reported,[141a,151] and thus an alternative mechanism where the formyl hydrogen is responsible of the reduction must be considered for DMF. In order to examine the extent of the contribution of the formyl group to the decomposition of **20**, three analogous experiments with DMF, $D(CO)N(CD_3)_2$ (DMF-d7) and $D(CO)N(CH_3)_2$ (DMF-d1) were carried out in the presence of oxygen. When the solvent used was DMF-d7 (99.5% D) a mixture of deuterated and protic pentafluorobenzene was obtained where C_6F_5D was the major product (ratio C_6F_5H:C_6F_5D = 1:4.3, Figure 4.3). The resonance of the F_{ortho} in ^{19}F NMR allows an easy identification of C_6F_5D and C_6F_5H in the reaction mixture. A large isotopic shift is commonly observed in ^{19}F NMR and it is also observed in our case

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[147] (a) Ding, S.; Jiao, N. *Angew. Chem. Int. Ed.* **2012**, *51*, 9226-9237. (b) Muzart, J. *Tetrahedron*, **2009**, *65*, 8313-8323.

[148] (a) Wan, Y.; Alterman, M.; Larhed, M.; Hallberg, A. *J. Org. Chem.* **2002**, *67*, 6232-6235. (b) Serp, P.; Hernández, M.; Richard, B.; Kalck, P. *Eur. J. Inorg. Chem.* **2001**, 2327-2336.

[149] Zawisza, A. M.; Muzart, J. *Tetrahedron Lett.* **2007**, *48*, 6738-6742.

[150] Hartwig, J. F.; Richards, S.; Barañano, D.; Paul, F. *J. Am. Chem. Soc.* **1996**, *118*, 3626-3633.

[151] (a) Logan, M. E.; Oinen, M. E. *Organometallics*, **2006**, *25*, 1052-1054. (b) Rajagopal, S.; Spatola, A. F. *J. Org. Chem.* **1995**, *60*, 1347-1355. (c) Ben-David, Y.; Gozin, M.; Portnoy, M.; Milstein, D. *J. Mol. Catal. A: Chem.* **1992**, *73*, 173-180.

(ca. 0.3 ppm). The multiplicity of the signal for C_6F_5H reflects the value of $^3J_{H\text{-}F}$ = 10 Hz and $^4J_{H\text{-}F}$ = 7 Hz whereas $^3J_{D\text{-}F}$ and $^4J_{D\text{-}F}$ are smaller than the linewidth of the spectrum (expected value for $^3J_{D\text{-}F}$ = 1.5 Hz according to $\gamma_D/\gamma_H = 0.1535$).

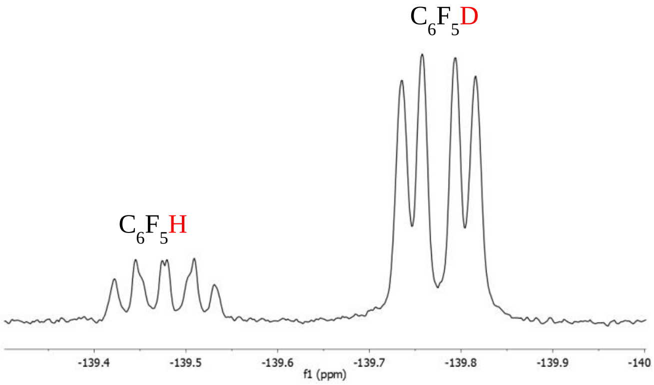


Figure 4.3: ^{19}F NMR of a mixture of C_6F_5D and C_6F_5H (F_{ortho} region).

A comparison between the reactions with DMF and DMF-d7 shows clearly that the reaction with the deuterated solvent is slower due to a strong isotopic effect (Figure 4.4). Formation of C_6F_5H in that case can be explained considering the presence of a residual protic solvent (0.5%) and the higher reaction rate for the protic solvent than for the deuterated one.

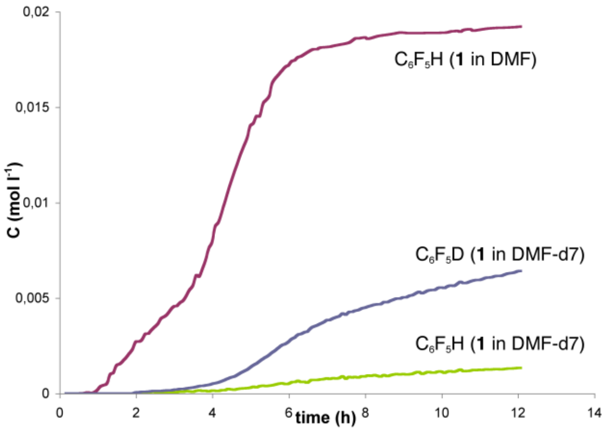
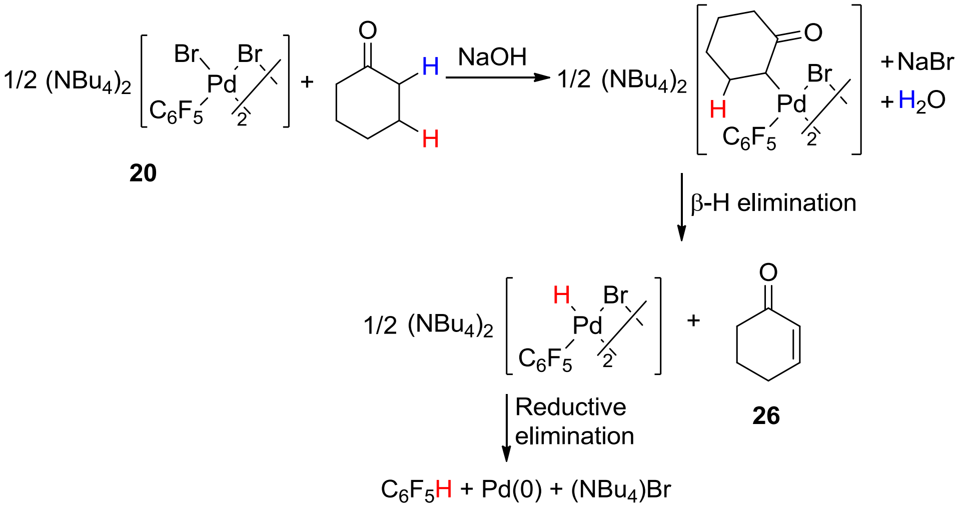


Figure 4.4: Formation of C_6F_5X (X = H, D) when **20** is heating at 100 ºC under an oxygen atmosphere in DMF (red line) and DMF-d7 (blue and green lines).

In the event of using DMF-d1 as solvent, the protic pentafluorobenzene was the major product (ratio C_6F_5H:C_6F_5D = 8:1). Therefore, β-H elimination involving the methyl groups of the amide seems to be the predominant route of decomposition of **20**.

4.2.2.2 Cyclohexanone

Ketones with β-hydrogens are other type of solvent tested in this study. Cyclohexanone was chosen as a model solvent of this family because of its high boiling point and the a priori simpler mixture of byproducts derived from its decomposition. The results observed after heating complex **20** in this solvent suggest that it should be considered as risky (Table 4.2, entry 4). In this case, the use of a base produces a remarkable increase in the amount of pentafluorobenzene formed. When **20** was heated under nitrogen without NaOH only 3.5% of C_6F_5H was observed (Table 4.2, entry 4A), whereas if the base was added up to 62% was formed (Table 4.2, entry 4D). Such a large difference seems to indicate the formation of a palladium enolate. This acts as a precursor of the Pd-H species which is formed after undergoing β-H elimination (Scheme 4.7). Additionally, this step affords cyclohexenone (**26**) as solvent-derived byproduct.



Scheme 4.7: Decomposition of **20** in cyclohexanone.

This dehydrogenation can occur with any ketone with β-hydrogens, a reaction previously reported,[152] and successfully used in the synthesis of α,β-enones from saturated ketones catalyzed by palladium.[153] **26** can be the substrate of a new dehydrogenation to give cyclohexadienone. Tautomerization of the last one produces phenol (**27**) as final product (Scheme 4.8). Stahl and coworkers have optimized the reaction conditions to obtain α,β-enones or phenols as the major product selectively.[153b,154] In our case both **26** and **27** were detected, and their formation is also catalytic (32 turnovers observed for entry 4F, Table 1). When the experiments were performed in the presence of oxygen higher amounts of pentafluorobenzene as well as solvent decomposition byproducts were observed. As it happened in the case of the amides, the effect of the oxygen seems to be related with the oxidation of Pd(0) to Pd(II) enlarging its catalytic activity in the decomposition process.

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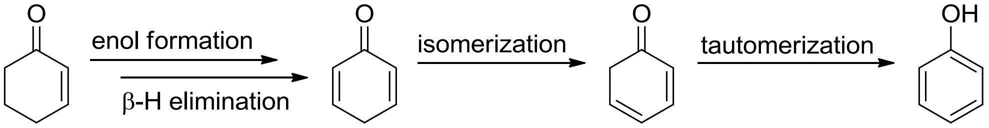
[152] (a) Muzart, J. *Eur. J. Org. Chem.* **2010**, 3779-3790. (b) Muzart, J.; Pète, J. P. *J. Mol. Catal.* **1982**, *15*, 373-376. (c) Theisen, R. J. *J. Org. Chem.* **1971**, *36*, 752-757. (d) Trost, B. M.; Metzner, P. J. *J. Am. Chem. Soc.* **1980**, *102*, 3572-3577. (e) Wenzel, T. T. *J. Chem. Soc., Chem. Commun.* **1989**, 932-933.

[153] (a) Diao, T.; Pun, D.; Stahl, S. S. *J. Am. Chem. Soc.* **2013**, *135*, 8205-8212.(b) Diao, T.; Stahl, S. S. *J. Am. Chem. Soc.* **2011**, *133*, 14566-14569. (c) Tokunaga, M.; Harada, S.; Iwasawa, T.; Obora, Y.; Tsuji, Y. *Tetrahedron Lett*. **2007**, *48*, 6860-6862.

[154] (a) Izawa, Y.; Pun, D.; Stahl, S. S. *Science* **2011**, *333*, 209-213. (b) Pun, D.; Diao, T.; Stahl, S. S. *J. Am. Chem. Soc.* **2013**, *135*, 8213-8221.



26 **27**

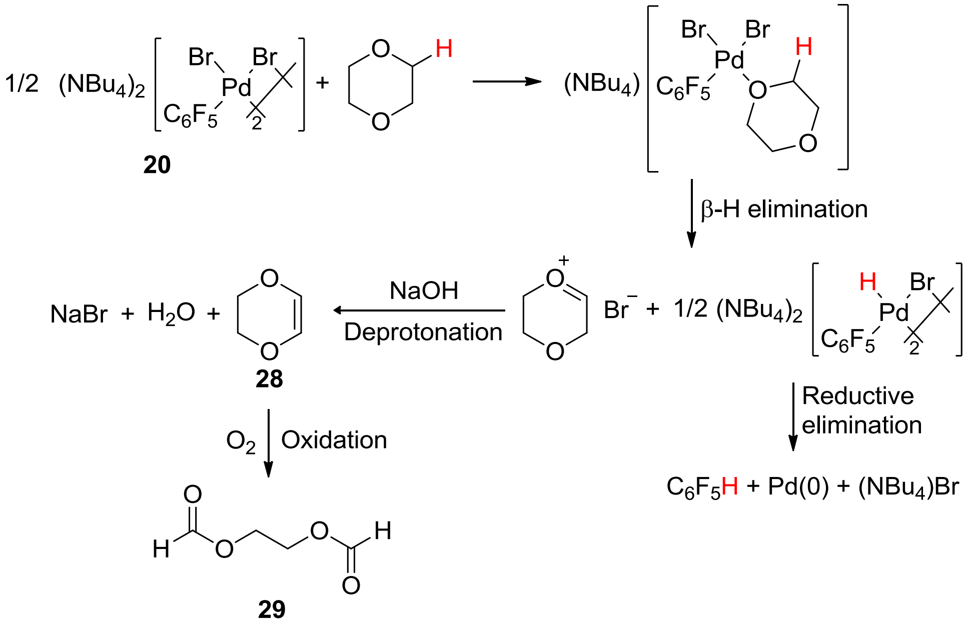
Scheme 4.8: Products derived from **26.**

For comparison, a new series of experiments were performed using acetone as solvent. Although this ketone can form the enolate too, no β-H elimination is possible since it does not have available β-hydrogens. As expected, no pentafluorobenzene was observed in any of the conditions collected in Table 4.2 (columns A-E). This result confirms that reduction of the complex is only likely to occur for ketones with hydrogens in a β position.

It is noteworthy that NMP has a carbonyl moiety with β-hydrogens too, therefore, the generation of a Pd-H species by the enolate mechanism must be considered. In that case, after β-H elimination, the solvent byproduct would be N-methyl pyrroli-2-en-1-one. Since this product was not detected in any of our reactions with NMP, we can assume that the β-H elimination from methyl units bound to nitrogen is dominant in the case of amides.

4.2.2.3 Diethers

The last type of solvents discussed is diethers. Although both solvents tested, 1,4-dioxane and DME, behave as safe solvents in the absence of oxygen, when complex **20** was heated at 100 °C under an oxygen atmosphere the amount of C_6F_5H increased notably (Table 4.2, entries 5-6). Different solvent decomposition byproducts were detected after these reactions. 1,4-dioxene (**28**) and 1,2-diformyloxyethane (**29**) were the products observed when 1,4-dioxane was employed as solvent. Their appearance suggests that β-H elimination on a coordinated dioxane is responsible of the formation of the Pd-H species (Scheme 4.9). Simultaneously, this β-H elimination generates a highly acidic oxonium salt which deprotonates easily and affords **28**. Dehydrogenation of dioxane by this pathway has been proposed to explain the formation of some reduction byproducts detected in a palladium-catalyzed cyclization reaction, but dioxene was not detected in that occasion.[136c]



Scheme 4.9: Decomposition of **20** in 1,4-Dioxane.

The oxidation of dioxene by oxygen via a dioxetane intermediate to give dicarbonyl derivatives analogous to **29** has previously been reported.[155] 1,2-diformyloxyethane (**29**) shows a characteristic *H*C(O)O signal at 8 ppm in ^{1}H NMR and a MS with a characteristic fragmentation pattern which was compared with an authentic sample. The oxidation of **28** to **29** in 1,4-dioxane as solvent was checked in some independent experiments. A small amount of **29** was formed in the absence of a palladium complex, but when the experiment was carried out in the presence of [$PdCl_2(NCMe)_2$] the amount of **29** increased. Thus, it is possible that palladium activates oxygen towards this reaction, possibly through the involvement of a peroxo complex upon reaction of O_2 with Pd(0).[156]

In the event of DME as solvent a similar reaction pattern can be depicted (Scheme 4.10). Although in this case the dienol ether analogous to dioxene was not observed, the subsequent oxidation product **30** was easily detected. The presence of methylformiate (**30**)

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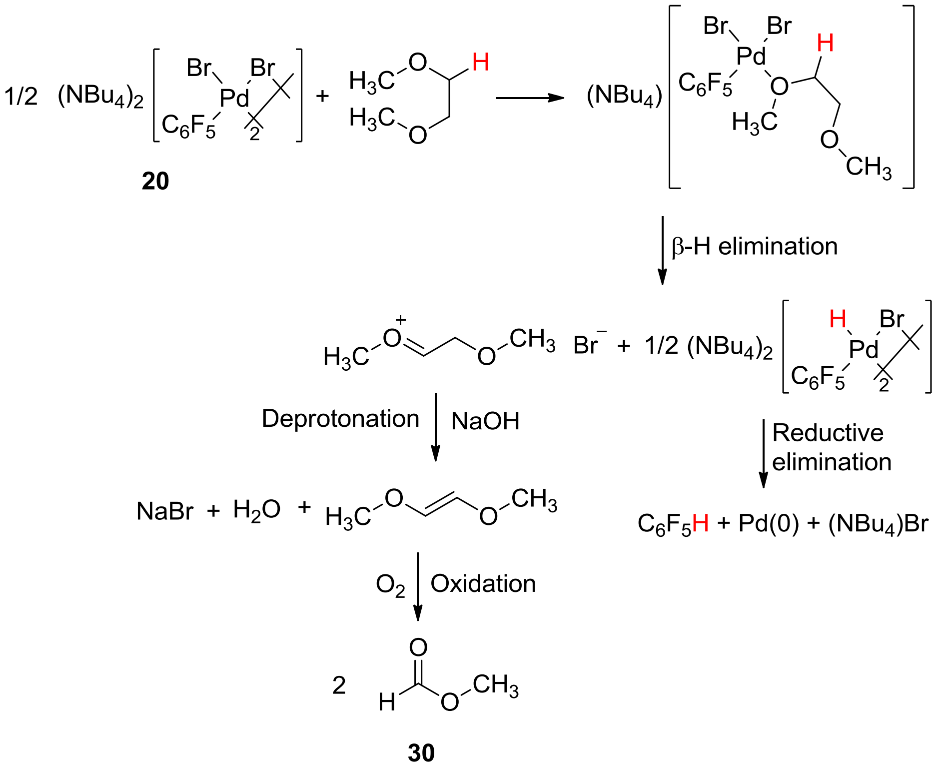
[155] (a) Silverman, S. K.; Foote, C. S. *J. Am. Chem. Soc.* **1991**, *113*, 7672-7675. (b) Cermola, F.; Iesce, M. R. *J. Org. Chem.* **2002**, *67*, 4937-4944.

[156] (a) Stahl, S. S. *Angew. Chem. Int. Ed.* **2004**, *43*, 3400-3420. (b) Gligorich, K. M.; Sigman, M. S. *Angew. Chem. Int. Ed.* **2006**, *45*, 6612-6615. (c) Konnick, M. M.; Guzei, I. A.; Stahl, S. S. *J. Am. Chem. Soc.* **2004**, *126*, 10212-10213. (d) Stahl, S. S.; Thorman, J. L.; Nelson, R. C.; Kozee, M. A. *J. Am. Chem. Soc.* **2001**, *123*, 7188-7189. (d) Mimoun, H.; Charpentier, R.; Mitschler, A.; Fischer, J.; Weiss, R. *J. Am. Chem. Soc.* **1980**, *102*, 1047-1054.

after the reaction indicates that the most likely route implies the formation of an oxonium salt by β-H elimination of a hydrogen atom of a methylene group of the DME. Our results agree with the work of Lautens and coworkers who identified the methylene group as hydrogen source when DME was used as reducing agent.[136b] In spite of being statistically more favorable the β-H elimination in the methyl groups, the higher thermodynamic stability of the oxonium salt involving the methylene groups seems to drive the decomposition reaction.



Scheme 4.10: Decomposition of **20** in DME.

4.3 CONCLUSIONS

In this chapter we have classified several solvents in two groups depending on their ability to reduce a Pd-aryl complex under different reaction conditions. On the one hand THF, nitriles, toluene or water can be considered as safe solvents and used in palladium-catalyzed reactions at high temperatures. However, some solvents can be responsible of the formation of reduction products derived from Pd-aryl complexes. Among these solvents we must consider N-alkyl amides, ketones with hydrogens in a β position or diethers such as 1,4-dioxane or DME. These solvents can be a hydride source leading to the reduction of the palladium hydrocarbyl complexes through a β-H elimination step and affording Ar-H species and Pd(0). In our case a monofluoroaryl complex **20** formed pentafluorobenzene after reduction.

We have studied the solvent byproducts formed after the reactions in order to propose reasonable reaction pathways. In the case of ketones with hydrogens in a β position the β-H elimination occurs in a palladium-enolate formed after the attack of a base. When the solvent is a diether the reduction step takes place after coordination of the solvent generating an oxonium salt. In the event of N-alkyl amides, the β-H elimination seems to occur predominantly in the alkyl group of the amide coordinated to palladium in spite of the previous proposals which considered that the β-H elimination took place in an amine formed after hydrolysis of the amides. The presence of oxygen has a notable effect probably due to the reoxidation of Pd(0) to Pd(II) species able to produce new hydride complexes.

Studies of the equilibria between **24** and **25** in DMF, NMP and DMA show that the coordination ability of the solvent is an important factor since the more coordinating the solvent the larger the reduction of the complex. This factor has a special significance when the so-called “ligandless catalysis” are involved. These systems use simple palladium salts with no more ligands than the solvents, reagents and products formed, and therefore risky solvents with high coordination ability can be troublesome.

4.4 EXPERIMENTAL PART

4.4.1 General Methods

General methods and techniques employed are similar to those previously described in chapter 2.

GC-Mass spectra were recorded on a Thermo Scientific Focus DSQII system. Solvents were purchased from Aldrich, BDH-Prolabo and Panreac (> 99%) and were used without further purification. Palladium complexes $(NBu_4)_2[Pd_2(\mu\text{-}Br)_2Br_2(C_6F_5)_2]$ (**20**),[143] $(NBu_4)_2[Pd_2(\mu\text{-}Br)_2(C_6F_5)_4]$ (**24**),[157] $[PdCl_2(NCMe)_2]$,[158] $[PdBr(C_6F_5)(AsPh_3)_2]$[143] and $(NBu_4)_2[Pd_2(\mu\text{-}Br)_2Br_4]$,[159] were prepared according to procedures reported in the literature. The organic compounds described are known and most of them commercially available; their characterization data in the conditions detected are given below; chemical shifts were compared with authentic commercial samples in the same conditions.

4.4.2 Decomposition experiments of complex 20 in different solvents

Procedure followed for reactions under a N_2 atmosphere without base. Reaction in DMF

A Schlenk tube was charged with **20** (50.0 mg; 0.0370 mmol) and deoxygenated DMF (1.0 mL; 13.0 mmol) under nitrogen. The tube was sealed and the mixture was stirred at 100 ˚C for 2 h. The reaction mixture was allowed to cool down to room temperature. The solution was checked by ^1H NMR, ^{19}F NMR and GC-MS.

Procedure followed for reactions under a N_2 atmosphere with base. Reaction in DMF

A Schlenk tube was charged with **20** (50.0 mg; 0.0370 mmol), NaOH (10 µL; 7.5 M in H_2O, 0.0750 mmol) and deoxygenated DMF (1.0 mL; 13.0 mmol) under nitrogen. The solution

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[157] Usón, R.; Forniés, J.; Martínez, F.; Tomás, M. *J. Chem. Soc., Dalton Trans*. **1980**, 888-894.
[158] Wayland, B. B.; Schramm, R. F. *Inorg. Chem.* **1969**, *8*, 971-976.
[159] Harris, C. M.; Livingstone, S. E.; Stephenson, N. C. *J. Chem. Soc.* **1958**, 3697-3702.

was stirred at 100 ˚C for 2 h. The reaction mixture was allowed to cool down to room temperature. The solution was checked by ^{1}H NMR, ^{19}F NMR and GC-MS.

The same procedures were followed for the reactions carried out under air or under oxygen. All the reactions showed in Table 4.1 and Table 4.2 were carried out in a similar way, just using the appropriate solvent instead of DMF. The decomposition products and the relevant characterization data in the conditions detected for each case are given below.

4.4.3 Experimental data of byproducts detected after decomposition of 20

4.4.3.1 Dimethylformamide

$HC(O)NHCH_3$ (21a): ^{1}H NMR (400 MHz, δ, DMF/acetone-d6 capillary): 7.64 (s, 1H, *H*CO), 2.20 (d, *J* = 4.8 Hz, 3H, CH_3NH). MS (EI, m/z (%)), 59 (100) [M$^+$].

$\{HC(O)\}_2NMe$ (22a): ^{1}H NMR (400 MHz, δ, DMF/acetone-d6 capillary): 8.67 (s, 2H, *H*CO). MS (EI, m/z (%)), 87 (4) [M$^+$], 59 (100) [M$^+$-CO].

C_6F_5H: ^{1}H NMR (400 MHz, δ, DMF-d7/acetone-d6 capillary): 7.32 (m, $^3J_{H\text{-}F}$ = 10 Hz, $^4J_{H\text{-}F}$ = 7 Hz, $^5J_{H\text{-}F}$ = 2 Hz). ^{19}F NMR (376 MHz, δ, DMF/acetone-d6 capillary): -139.5 (m, 2F, F_{ortho}), -155.4 (t, *J* = 20.2 Hz, 1F, F_{para}), -163.2 (m, 2F, F_{meta}). MS (EI, m/z (%)), 168 (100) [M$^+$], 149 (10) [M$^+$-F], 137 (15) [M$^+$-CF], 118 (10) [(M$^+$-CF)-F], 99 (60) [(M$^+$-CF-F)-F].

C_6F_5D: ^{19}F NMR (470 MHz, δ, DMF/acetone-d6 capillary): -139.8 (m, 2F, F_{ortho}), -155.4 (t, *J* = 20.2 Hz, 1F, F_{para}), -163.3 (m, 2F, F_{meta}). MS (EI, m/z (%)), 169 (100) [M$^+$], 150 (10) [M$^+$-F], 138 (15) [M$^+$-CF], 119 (10) [(M$^+$-CF)-F], 100 (60) [(M$^+$-CF-F)-F].

4.4.3.2 Dimethylacetamide

$CH_3C(O)NHCH_3$ (21b): ^{1}H NMR (400 MHz, δ, DMA/acetone-d6 capillary): 7.35 (b, 1H, CH_3N*H*). 2.03 (d, *J* = 4.5 Hz, 3H, CH_3NH). MS (EI, m/z (%)),73 (100) [M$^+$], 58 (40) [M$^+$-Me].

$CH_3C(O)NMeC(O)H$ (22b): ^{1}H NMR (400 MHz, δ, DMA/acetone-d6 capillary): 8.66 (s, 1H, *H*CO), 1.92 (s, 3H, CH_3CO). MS (EI, m/z (%)), 101 (100) [M$^+$], 87 (20) [M$^+$-Me], 72 (85) [M$^+$-HCO], 57 (40) [(M$^+$-HCO)-Me].

C_6F_5H: ^{1}H NMR (400 MHz, δ, DMA /acetone-d6 capillary): 7.27 (m). ^{19}F NMR (376 MHz, δ, DMA/acetone-d6 capillary): -139.4 (m, 2F, F_{ortho}), -155.4 (t, J = 20.2 Hz, 1F, F_{para}), -163.2 (m, 2F, F_{meta}).

4.4.3.3 N-methylpyrrolidone

$\overline{\mathrm{C(O)\text{–}CH_2\text{–}CH_2\text{–}CH_2\text{–}N}}\mathrm{C(O)H}$ (23): ^{1}H NMR (400 MHz, δ, NMP/acetone-d6 capillary): 8.18 (s, 1H, *H*CO). MS (EI, m/z (%)), 113 (8) [M$^+$], 85 (100) [M$^+$-CO], 57 (35) [(M$^+$-CO)-CO].

C_6F_5H: ^{1}H NMR (400 MHz, δ, NMP /acetone-d6 capillary): 7.16 (m). ^{19}F NMR (376 MHz, δ, NMP/acetone-d6 capillary): -139.4 (m, 2F, F_{ortho}), -155.4 (t, J = 20.4 Hz, 1F, F_{para}), -163.2 (m, 2F, F_{meta}).

4.4.3.4 Cyclohexanone

Cyclohexenone (26): ^{1}H NMR (400 MHz, δ, cyclohexanone/acetone-d6 capillary): 6.52 (dt, J = 10.2, 4.1 Hz, 1H, –CH_2C*H*CHCO), 5.36 (dt, J = 10.2, 1.9 Hz, 1H, –CH_2CHC*H*CO). MS (EI, m/z (%)), 96 (30) [M$^+$], 68 (100) [M$^+$-CO].

PhOH (27): ^{1}H NMR (400 MHz, δ, cyclohexanone/acetone-d6 capillary): 6.61 (dd, J = 7.1, 7.8 Hz, H, H_{meta}), 6.34 (d, J = 7.8 Hz, 2H, H_{ortho}), 6.22 (t, J = 7.1 Hz, 1H, H_{para}). MS (EI, m/z (%)), 94 (100) [M$^+$], 66 (30) [M$^+$-CO].

C_6F_5H: ^{1}H NMR (400 MHz, δ, cyclohexanone /acetone-d6 capillary): 6.99 (m). ^{19}F NMR (376 MHz, δ, cyclohexanone /acetone-d6 capillary): -139.9 (m, 2F, F_{ortho}), -154.9 (t, J = 20.2 Hz, 1F, F_{para}), -162.8 (m, 2F, F_{meta}).

4.4.3.5 1,4-Dioxane

1,4-Dioxene (28): ^{1}H NMR (400 MHz, δ, dioxane:acetone = 1:1 /acetone-d6 capillary): 5.65 (s, 2H, -O-C*H*=C*H*-O-), 3.73 (s, 4H, -O-CH_2-CH_2-O-). MS (EI, m/z (%)), 86 (70) [M$^+$], 84 (100) [M$^+$-2H].

$HC(O)OCH_2CH_2OC(O)H$ (29): ^{1}H NMR (400 MHz, δ, dioxane:acetone = 1:1 /acetone-d6 capillary): 7.83 (s, 2H, *H*C(O)OCH_2-), 4.09 (s, 4H, HC(O)OCH_2. MS (EI, m/z (%)), 72 (20) [M$^+$-CO_2H_2], 60 (100) [M$^+$-CO_2CH_2].

C_6F_5H: ^1H NMR (400 MHz, δ, dioxane:acetone = 1:1 /acetone-d6 capillary): 7.13 (m). ^{19}F NMR (376 MHz, δ, dioxane:acetone = 1:1 /acetone-d6 capillary): -139.3 (m, 2F, F_{ortho}), -155.1 (t, J = 20.2 Hz, 1F, F_{para}), -163.0 (m, 2F, F_{meta}).

4.4.3.6 1,2-Dimethoxyethane

$HC(O)OCH_3$ (30): ^1H NMR (400 MHz, δ, DME/acetone-d6 capillary): 7.73 (s, 1H, *H*C(O)OCH$_3$). MS (EI, m/z (%)), 60 (85) [M^+], 31 (100) [M^+-HC(O)].
C_6F_5H: ^1H NMR (400 MHz, δ, DME /acetone-d6 capillary): 7.13 (m). ^{19}F NMR (376 MHz, δ, DME/acetone-d6 capillary): -139.4 (m, 2F, F_{ortho}), -155.7 (t, J = 20.2 Hz, 1F, F_{para}), -163.4 (m, 2F, F_{meta}).

4.4.4 Reaction of formaldehyde under oxygen

A solution of formaldehyde (0.3 mL; 4.03 mmol) in DMF (1.0 mL; 13.0 mmol) under oxygen (1 atm) was heated at 100ºC and stirred for 2h. The reaction mixture was cooled down and checked by ^1H NMR at room temperature.
HCOOH: ^1H NMR (400 MHz, δ, DMF/acetone-d6 capillary): 7.73 (s, 1H, HCOOH).

4.4.5 Reaction of formic acid with secondary amides. Reaction with N-methylformamide

Formic acid (0.32 mL; 8.56 mmol) was added to N-methylformamide (0.5 mL; 8.56 mmol) under oxygen (1 atmosphere) and stirred for 24 h at 100 ˚C. After that time the reaction mixture was allowed to cool to room temperature and checked by ^1H NMR. The corresponding imide was detected.
$\{HC(O)\}_2NMe$ (22a): ^1H NMR (500 MHz, δ, neat mol ratio HCO_2H:HCONHMe = 1:1/acetone-d6 capillary): 8.58 (s, 2H, *H*CO), 2.55 (s, 3H, NC*H*$_3$). MS(EI, m/z (%)), 87 (4) [M^+], 59 (100) [M^+-CO].
The experiments with other secondary amides were carried out in the same way.

$CH_3C(O)NMeC(O)H$ (22b): ^1H NMR (400 MHz, δ, neat mol ratio HCO_2H:MeCONHMe = 1:1/acetone-d6 capillary): 8.73 (s, 1H, *H*CO), 2.52 (s, 3H, NC*H*$_3$), 1.93 (s, 3H, C*H*$_3$CO).

MS(EI, m/z (%)), 101 (100) [M$^+$], 87 (20) [M$^+$-Me], 72 (85) [M$^+$-HCO], 57 (40) [(M$^+$-HCO)-Me].

C(O)–CH$_2$–CH$_2$–CH$_2$–NC(O)H (23): ^{1}H NMR (500 MHz, δ, neat mol ratio HCO$_2$H:pyrrolidone = 1:1/acetone-d6 capillary): 8.24 (s, 1H, *H*CO), 2.92 (t, J = 7.3 Hz, 2H, CH$_2$C*H*$_2$N), 1.85 (t, J = 8.1 Hz, 2H, CH$_2$C*H*$_2$CO), 1.36 (m, 2H, CH$_2$C*H*$_2$CH$_2$). MS(EI, m/z (%)), 113 (10) [M$^+$], 85 (100) [M$^+$-CO], 57 (35) [(M$^+$-CO)-CO].

4.4.6 Reactions with deuterated DMF

Reactions with DMF-d7 (99.5% D) and DMF-d1(98% D) were carried out in a 5 mm NMR tube by placing 0.6 mL of a 0.04 M solution of complex **20** in the corresponding deuterated solvent under an oxygen atmosphere. The sample was introduced in a thermostated NMR probe at 373 K and an acetone-d6 capillary was used as external reference. ^{19}F NMR spectra were recorded every 5 min and the amount of C_6F_5D and C_6F_5H were determined by integration of the corresponding signals against an internal standard (decafluorobiphenyl). The concentration of pentafluorobenzenes was plotted vs. time and the result is shown in Figure 4.4.

4.4.7 Determination of equilibrium constants for the coordination of amides

The equilibrium constants were determined using 0.016 M solutions of **24** in different solvents. The concentrations of **24** and **25** at equilibrium were determined by integration of ^{19}F NMR signals. Errors were calculated by combining the uncertainties in the measured concentration (c_0) and the integral determination.[160]

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[160] Kirkup, L. Experimental Methods: An Introduction to the Analysis and Presentation of Data; Wiley: Milton, **1994**.

Chapter 5

5. Diimine-palladium complexes supported on vinylic addition polynorbornenes.

5.1 INTRODUCTION

In addition to NHCs, we decided to study the ability of vinylic-addition polynorbornenes to support a different type of ligand, namely α-diimines (or 1,4-diazadienes). Although their structure had been known for a long time it was in the 90s when Brookhart and coworkers took advantage of their ability as a bidentate ligand. Different cationic complexes of nickel and palladium with bulky non-coordinating anions proved to be extraordinary catalysts for olefin polymerization.[161] For many years Ziegler-Natta type catalysts had been the system most used in the industrial production of high density polyethylene. The use of late transition metals with diimine ligands (Figure 5.1a) allowed the synthesis of highly branched low density polyethylene or other poly(α-olefins), thus expanding the type of microstructure and properties of polyethylene that can be obtained by metal-catalyzed polymerization.Mechanistic studies to have a better

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[161] (a) Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc*. **1995**, *117*, 6414-6415. (b) Johnson, L. K.; Mecking, S.; Brookhart, M. *J. Am. Chem. Soc*. **1996**, *118*, 267-268.

knowledge of the reaction pathway were carried out and new types of catalysts were tested soon after.[162] Bulky diimine substituents are crucial to ensure polymer formation.

In the event of copolymerization with polar olefins, for instance acrylates or vinyl acetate, traditional metallocene-type catalysts formed with early transition metals (zirconium, titanium or chromium) show a highly oxophilic nature which results in the poisoning of the catalysts with most polar olefins. Although late transition metals are less oxophilic and tolerate a larger variety of functional groups, complete control over the incorporation of both monomers remains a challenge. Brookhart's catalysts that are very active in the polymerization of ethylene usually give copolymers of ethylene and polar olefins with low yields and low incorporation of the polar monomer (around 10%). Nevertheless, the use of cyclophane-based Pd(II) diimine catalysts allowed to increase the amount of polar monomer in the final copolymer, although overall yields remained low (Figure 5.1b).[163]

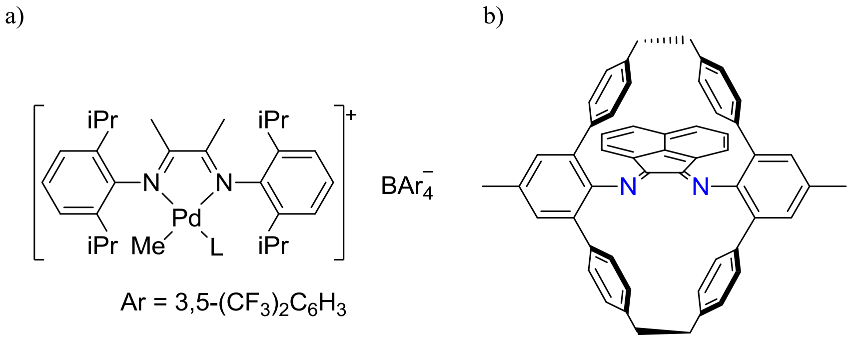

Figure 5.1: a) Brookhart's catalyst. b) Cyclophane-based diimine.

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[162] (a) Mecking, S.; Johnson, L. K.; Wang, L.; Brookhart, M. *J. Am. Chem. Soc*. **1998**, *120*, 888-899. (b) Gates, D. P.; Svejda, S. A.; Oñate, E.; Killian, C. M.; Johnson, L. K.; White, P. S.; Brookhart, M. *Macromolecules,* **2000**, *33*, 2320-2334. (c) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev*. **2000**, *100*, 1169-1203. (d) Gottfried, A. C.; Brookhart, M. *Macromolecules,* **2003**, *36*, 3085-3100. (e) Popeney, C.; Guan, Z. *Organometallics,* **2005**, *24*, 1145-1155. (f) Nakamura, A.; Ito, S.; Nozaki, K. *Chem. Rev*. **2009**, *109*, 5215-5244. (g) López-Fernández, R.; Carrera, N.; Albéniz, A. C.; Espinet, P. *Organometallics,* **2009**, *28,* 4996-5001. (h) Liu, F. S.; Hu, H. B.; Xu, Y.; Guo, L. H.; Zai, S. B.; Song, K. M.; Gao, H. Y.; Zhang, L.; Zhu, F. M.; Wu, Q. *Macromolecules*, **2009**, *42*, 7789-7796. (i) Chen, C.; Luo, S.; Jordan, R. F. *J. Am. Chem. Soc*. **2010**, *132*, 5273-5284. (j) Guo, L.; Gao, H.; Guan, Q.; Hu, H.; Deng, J.; Liu, J.; Liu, F.; Wu, Q. *Organometallics,* **2012**, *31*, 6054-6062.

[163] (a) Popeney, C. S.; Camacho, D. H.; Guan, Z. *J. Am. Chem. Soc*. **2007**, *129*, 10062-10063. (b) Popeney, C. S.; Guan, Z. *J. Am. Chem. Soc*. **2009**, *131*, 12384-12393.

Despite the fact that nickel and palladium are by far the most common metals used with this type of chelating ligand, the coordinating ability of diimines has also been demonstrated with some other metals such as molybdenum,[164] rhodium,[165] rhenium,[166] platinum,[167] copper or zinc.[168]

Palladium-diimine complexes have also been used in different C-C cross-coupling reactions such as the Heck reaction,[169] Kumada, Negishi or Stille reaction,[170] and the Suzuki reaction.[171] Although much less used for this purpose than in polymerization reactions, the ability of this ligand to support palladium in different oxidation states has been demonstrated as well as its utility in this type of reactions.[172]

As far as supported catalysis is concerned just a few examples can be found in the literature that involve these ligands. Most of these cases showed diimines attached to inorganic solid supports such as SiO_2,[173] $MgCl_2$[174] or clays like montmorillonite.[175] Activated multiwalled carbon nanotubes (MWNTs) have also been used to support covalently diimines forming palladium and nickel complexes tested in olefin

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[164] Fedushkin, I. L.; Skatova, A. A.; Lukoyanov, A. N.; Khvoinova, N. M.; Piskunov, A. V.; Nikipelov, A. S.; Fukin, G. K.; Lysenko, K. A.; Irran, E.; Schumann, H. *Dalton Trans*. **2009**, 4689-4694.

[165] Geier, S. J.; Chapman, E. E.; McIsaac, D. I.; Vogels, C. M.; Decken, A.; Westcott, S. A. *Inorg. Chem. Commun*. **2006**, *9*, 788-791.

[166] Arévalo, R.; Pérez, J.; Riera, L. *Chem. Eur. J.* **2015**, *21*, 3546-3549.

[167] (a) Parmene, J.; Krivokapic, A.; Tilset, M. *Eur. J. Inorg. Chem*. **2010**, 1381-1394. (b) Lohr, T. L.; Piers, W. E.; Parvez, M. *Inorg. Chem*. **2012**, *51*, 4900-4902.

[168] Brodie, A. M.; Otsuka, S. *J. Chem. Soc., Dalton Trans*. **1979**, 1, 199-204.

[169] (a) Grasa, G. A.; Singh, R.; Stevens, E. D.; Nolan, S. P. . *J. Organomet. Chem*. **2003**, *687*, 269-279. (b) Gottumukkala, A. L.; Teichert, J. F.; Heijnen, D.; Eisink, N.; van Dijk, S.; Ferrer, C.; van den Hoogenband, A.; Minnaard A. J. *J. Org. Chem*. **2011**, *76*, 3498-3501.

[170] (a) van Asselt, R.; Elsevier, C. J. *Organometallics*, **1992**, *11*, 1999-2001. (b) van Asselt, R.; Elsevier, C. J. *Organometallics*, **1994**, *13*, 1972-1980. (c) van Asselt, R.; Elsevier, C. J. *Tetrahedron*, **1994**, *50*, 323-334.

[171] (a) Hanhan, M. E. *Appl. Organometal. Chem.* **2008**, *22*, 270-275. (b) Zhou, J.; Guo, X.; Tu, C.; Li, X.; Sun, H. *J. Organomet. Chem*. **2009**, *694*, 697-702. (c) Gholinejad, M.; Karimkhani, V.; Kim, I. *Appl. Organometal. Chem.* **2014**, *28*, 221-224.

[172] Weng, C. M.; Hong, F. E, *Dalton Trans*. **2011**, *40*, 6458-6468.

[173] (a) Preishuber-Pflugl, P.; Brookhart, M. *Macromolecules*, **2002**, *35*, 6074-6076. (b) Zhang, D.; Jin, G. X. *Appl. Catal. A Gen*. **2004**, *262*, 13-18. (c) Lee, J. H.; Liu, S. T. *J. Chin. Chem. Soc*. **2006**, *53*, 1349-1354. (d) Jiang, H.; Wu, Q.; Zhu, F.; Wang, H. *J. Appl. Polym. Sci*. **2007**, *103*, 1483-1489. (e) Li, Y. G.; Pan, L.; Zheng, Z. J.; Li, Y. S. *J. Mol. Catal. A: Chem*. **2008**, *287*, 57-64. (f) Bahuleyan, B. K.; Oh, J. M.; Chandran, D.; Ha, J. Y.; Hur, A Y.; Park, D. W.; Ha, C. S.; Suh, H.; Kim, I. *Top. Catal*. **2010**, *53*, 500-509. (g) Wu, W.; Jiang, Y.; Wu, H.; Lv, C.; Luo, M.; Ning, Y.; Mao, G. *Chin. Sci. Bull*. **2013**, *58*, 1741-1750.

[174] (a) Xu, R.; Liu, D.; Wang, S.; Mao, B. *Macromol. Chem. Phys*. **2006**, *207*, 779-786. (b) Jiang, H.; He, F.; Wang, H. *J. Polym. Res*. **2009**, *16*, 183-189.

[175] Scott, S. L.; Peoples, B. C.; Yung, C.; Rojas, R. S.; Khanna, V.; Sano, H.; Suzuki, T.; Shimizu, F. *Chem. Commun*. **2008**, 4186-4188.

polymerization.[176] In the case of polymer-supported diimines scarce examples can be found and most of them involve Merrifield type resins (Figure 5.2).[173b,e,177] A different approach was proposed by Jin and Zhang who described single nickel-diimine catalysts with allyl groups capable to be self-supported in the presence of ethylene. That system produces micron-granula polyolefins (Scheme 5.1).[178]

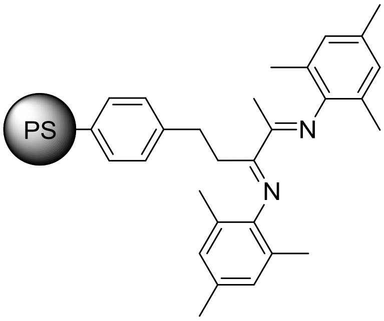
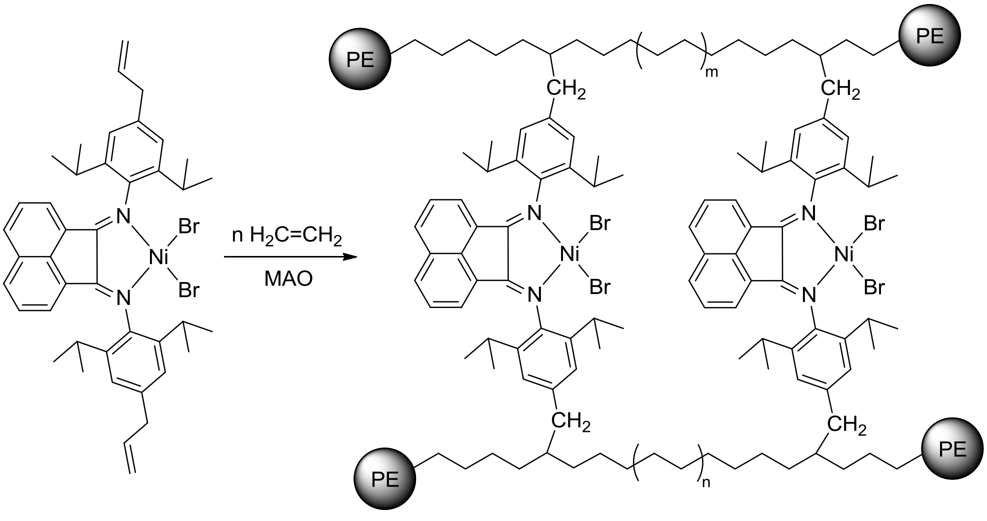


Figure 5.2: Polystyrene-supported diimine.



Scheme 5.1: Self-supported Ni-diimine catalyst.

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[176] Huo, P.; Liu, W.; He, X.; Chen, Y. *J. Polym. Sci. A: Polym. Chem.* **2014**, *52*, 3213-3220.

[177] (a) Boussie, T. R.; Coutard, C.; Turner, H.; Murphy, V.; Powers, T. S. *Angew. Chem. Int. Ed.* **1998**, *37*, 3272-3275.

[178] Jin, G.; Zhang, D. *J. Polym. Sci. A: Polym. Chem.* **2004**, *42*, 1018-1024.

In view of the great applicability of this type of ligand we decided to incorporate them into VA-polynorbornene due to the suitable structure of norbornene to bear α-diimine moieties (Figure 5.3a). Although comparable [2.2.1] bicyclic molecules such as norbornane[179] or camphor[168],[180] (Figure 5.3b) have already been used as backbone substituents of diimines, to the best of our knowledge, no examples of ROMP-PNBs or VA-PNBs have been found in the literature as support of diimines.

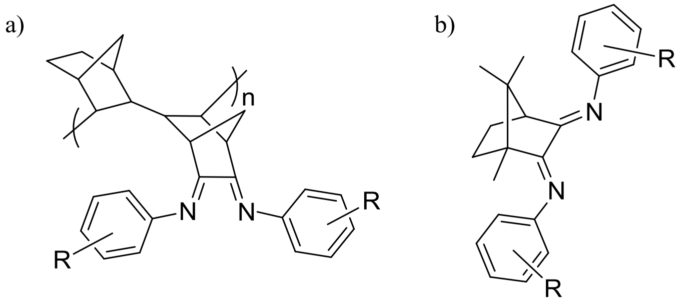

Figure 5.3: a) VA-PNB supported α-diimine. b) General structure of a camphor-based 1,4-diazadiene ligand.

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[179] Al-Omari, M.; Banert, K.; Hagedorn, M. *Angew. Chem. Int. Ed.* **2006**, *45*, 309-311.

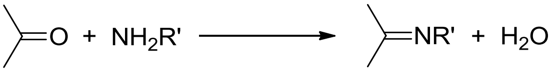
[180] (a) M. Dvolaitzky, *Compt. Rend.* **1969**, *C268,* 1811-1812. (b) van Asselt, R.; Elsevier, C. J.; Smeets, W. J. J.; Spek, A. L.; Benedix, R. *Recl. Trav. Chim. Pays-Bas*, **1994**, *113*, 88-98. (c) Schleis, T.; Heinemann, J.; Spaniol, T. P.; Mülhaupt, R.; Okuda, J. *Inorg. Chem. Commun.* **1998**, *1*, 431-434.

5.2 RESULTS AND DISCUSSION

5.2.1 Synthesis of VA-polynorbornene-supported diimines

The most common procedure to synthesize imines is by condensation of a primary amine with a ketone (Scheme 5.2). Since we wanted to obtain a α-diimine a molecule with two contiguous carbonyl moieties able to perform the condensation was required.

In order to obtain VA-PNBs with diimines in their structure we have synthesized a series of functionalized norbornene monomers which are precursors of the diimine and, then, we have tried their polymerization.



Scheme 5.2: Synthesis of imines by condensation.

5.2.1.1 Synthetic route to obtain a diimine-functionalized norbornene

Although we have not found in the literature examples of norbornene bearing diimines, there are some reports describing the synthesis of a norbornenyl diketone which can be used as precursor of the desired molecule.[181] We decided to use a method reported by Kobayashi with three different steps.

The first step was a Diels-Alder reaction with cyclopentadiene and vinylene carbonate in toluene (equation 5.1).[182] A small amount of hydroquinone was also added to prevent undesired radical reactions. After heating the mixture at 180 ºC for 20 hours, the norbornene derivative (NBCO$_3$, **31**) was obtained as a mixture of isomers endo:exo (97:3) with a yield higher than 90 %. Furthermore, this reaction is carried out with an excess of dienophile which can be easily recovered during the purification of **31** by distillation.

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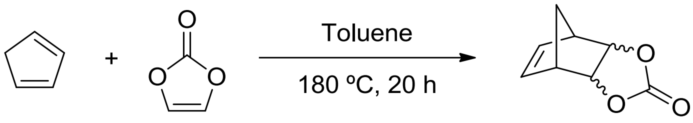
[181] (a) Scharf, H. D.; Küsters, W. *Chem. Ber.* **1972**, *105*, 564-574. (b) Kobayashi, T.; Kobayashi, S. *Molecules*, **2000**, *5*, 1062-1067.

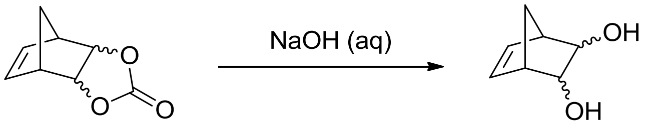
[182] Newman, M. S.; Addor, R. W. *J. Am. Chem. Soc.* **1955**, *77*, 3789-3793.



(5.1)

31
endo:exo = 97:3

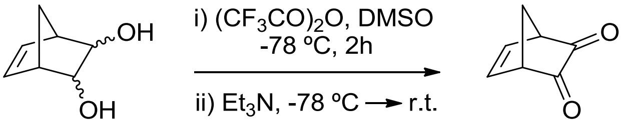
NBCO$_3$ was then hydrolyzed in a second step by treatment with a base (equation 5.2). When **31** was added to an aqueous solution of NaOH and stirred for 3 hours the corresponding diol (NB(OH)$_2$, **32**) was formed, but many liquid-liquid extractions were required to reach good yields (~80 %). As expected, the ratio endo:exo remained unaltered.



(5.2)

31 **32**

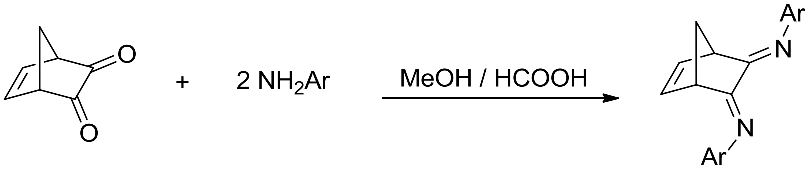
The final step needed in the synthesis of the diketone was a Swern oxidation of diol **32**. Usually this kind of oxidation is performed with oxalyl chloride, nevertheless Kobayashi and coworkers got better yields with trifluoroacetic anhydride (equation 5.3). In our hands this reaction yielded poorer than expected (45 %) and some minor impurities could not be removed from the diketone (NB(C=O)$_2$, **33**) neither by distillation nor chromatography.



(5.3)

32 **33**

Among the different methodologies commonly used to form diimines from diketones our group had previously used the one described by Brookhart and coworkers with good results.[162g] Thereby we decided to use the same procedure (equation 5.4). Diketone **33** was stirred with the selected aniline in a mixture of methanol and formic acid affording the desired diimine (NB(C=N-Ar)$_2$, **34**). The final product was isolated by crystallization in MeOH but with very low yield (11 %) due to the high solubility of the diimine in every solvent tested.



(5.4)

33 Ar =2,6-diisopropylphenyl **34**

Diimime **34** has a structure with a high steric hindrance, as it is important for some catalytic applications, which avoids rotation in the C-N single bond. This effect can be easily observed by ^{1}H-NMR. There is a plane of symmetry that bisects the molecule through C^7 and between C^2-C^3 and C^5=C^6 bonds (Figure 5.4). If the N-C^8 or N-$C^{8'}$ bonds were able to rotate, there would be a unique signal corresponding to the hydrogen atoms located on the tertiary carbons of the isopropyl groups. However, in the ^{1}H-NMR spectrum, two different septets can be assigned for these hydrogens with a difference in their chemical shifts close to 0.3 ppm. Furthermore, the lack of rotation of those heteronuclear bonds provokes the appearance of four doublets corresponding to the methyl groups instead of two doublets typical of diasterotopic isopropyl moieties.

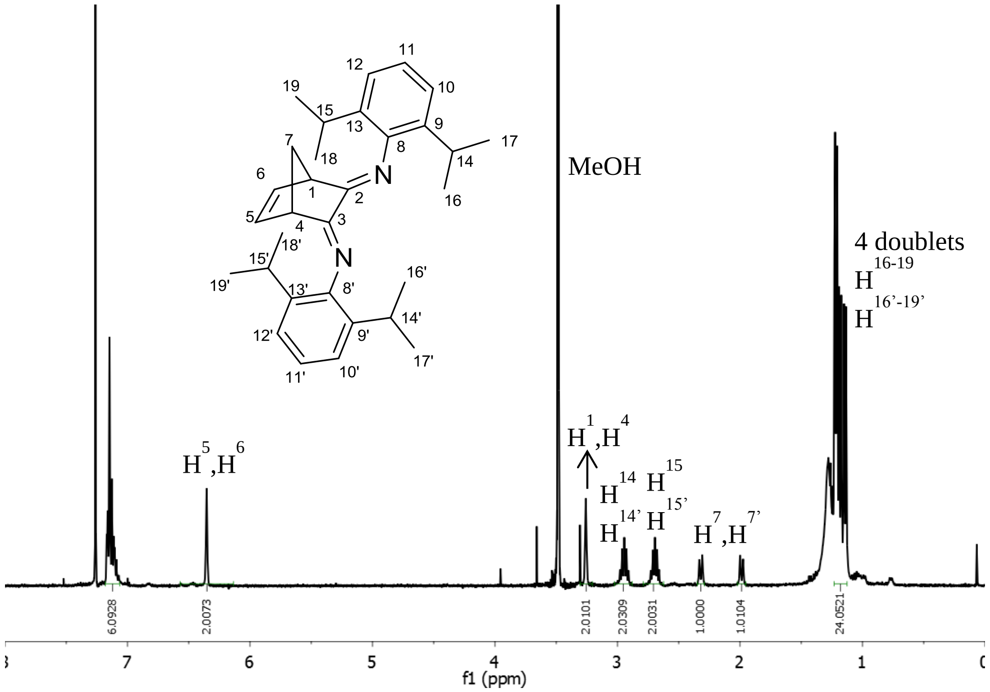


Figure 5.4: ^{1}H-NMR spectrum of **34**

5.2.1.2 Copolymerization experiments with the diimine precursors

Once the diimine and its precursors were synthesized we studied which one showed the best results in the copolymerization with norbornene. We used again the nickel catalyst $[Ni(C_6F_5)_2(SbPh_3)_2]$ (**3**) in these experiments. Diimine **34** was not tested because it is a good ligand and could coordinate **3** inhibiting the catalysis. Furthermore, the overall yield achieved in its synthesis was very low and this ia a drawback.

In the literature there are some works describing polymerization reactions of monomers **31** and **32** via ROMP,[183] but no examples concerning vinyl addition polymerization have been found.

Copolymerization experiments of norbornene with carbonate **31**, was then tried in the same conditions discussed previously in this dissertation (Scheme 5.3). Both comonomers were initially introduced in a 1:1 ratio in CH_2Cl_2 and then 2% mol of catalyst

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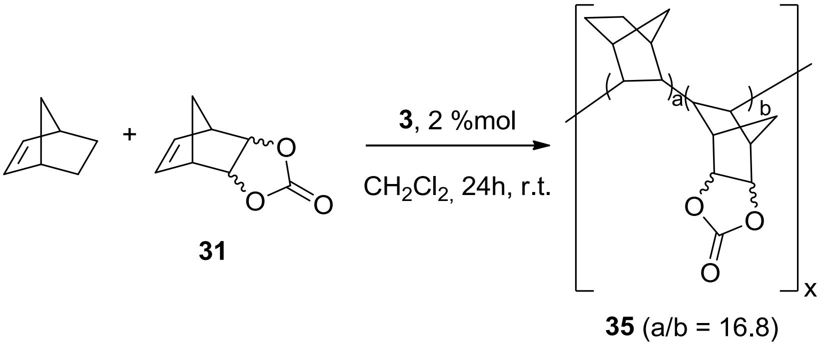
[183] (a) Hino, T.; Inoue, N.; Endo, T. *J. Polym. Sci. A: Polym. Chem.* **2006**, *44*, 395-405. (b) Czelusniak, I.; Heywood, J. D.; Kenwright, A. M.; Khosravi, E. *J. Mol. Catal. A: Chem.* **2008**, *280*, 29-34.

was added. 0.8% mol of $SbPh_3$ was also added to avoid fast decomposition of the catalyst. The initial concentration of **3** was 0.0056 M. The mixture was stirred 24 hours at room temperature and copolymer **35** (VA-CopNBNBCO$_3$) was obtained as a white powder after washing with MeOH and filtering. Copolymerization reactions with diol **32** and diketone **33** were carried out identically to form copolymers **36a** and **37a** respectively (Table 5.1).



Scheme 5.3: Copolymerization reaction of **31** and norbornene.

Table 5.1. Copolymerization experiments of norbornene with O-functionalized norbornenes (NBO) precursors of diimine.[a]

Entry	Monomer (NBO)	NB:NBO:**3**	Yield (%)[b]	Copolymer a/b (a/b = NB/NBO)[c]
1	**31**	50:50:1	**35** (54)	16.8
2	**32**	50:50:1	**36a** (8)	-
3	**33**	50:50:1	**37a** (17)	-

a) Reaction conditions shown in Scheme 5.3. Experiments performed under nitrogen atmosphere. b) Yields are referred to the total monomer mass. c) Ratio of monomers in the copolymer determined by ^{1}H-NMR.

Only **31** afforded a moderate yield in the copolymerization reaction (Table 5.1, entry 1). The polymer obtained **35**, was soluble and a composition that shows a ratio norbornene:**31** = 16.8:1 could be determined by ^{1}H NMR by comparison of integrals of the protons bound to C^2 and C^3 of the carbonate and the broad signal associated to the rest of the aliphatic protons. The infrared spectrum of the polymer showed a strong signal corresponding to the ν(C=O st) IR absorption band at 1809 cm^{-1} typical of carbonates. The copolymerization of monomers **32** and **33** yielded poorly (Table 5.1, entries 2-3). Both polymers were insoluble and their composition could not be determined. Infrared spectra showed a broad band at 3400 cm^{-1} characteristic of ν(O-H st) in **36a** and a weak band at 1746 cm^{-1} ν(C=O st) in **37a** typical of carbonyl moieties. In view of these results we chose to copolymerize **31** because **35** was the only polymer obtained with moderate yields and it was soluble so we were able to determine the degree of functionalization. Thus, the synthesis of the diimine polymer will have to be carried out by postpolymerization functionalization of **35**.

In order to reach better yields and higher incorporations of the functionalized monomer, different polymerization reactions were performed. Initially, we studied the homopolymerization of the carbonate. In a NMR tube monomer **31** and catalyst **3** were dissolved in $CDCl_3$, and $C_6H_3Br_3$ was added as standard. ^{1}H-NMR spectra were recorded regularly for 72 hours showing no polymerization at all. This is not unexpected because this catalyst proved to be useless before in the polymerization of O-functionalized norbornene like 5-norbornene-2-carboxaldehyde.[55a] Unlike our case, the coordinating ability of the oxygen in that monomer is strong enough even to avoid copolymerization with norbornene.

Different copolymerization experiments were carried out varying catalyst loading, initial monomer feed ratio and procedure conditions. Table 5.2 summarizes the results of those reactions.

Table 5.2. Copolymerization experiments of norbornene with **31**.[a]

Entry	NB:**31**:**3**	**35**, Yield (%)[b]	Copolymer a/b (a/b = NB/**31**)[c]
1[d]	50:50:1	54	16.8
2[d]	100:100:1	30	25.2
3[d]	1000:1000:1	1.5	58.2
4[e]	50:50:1	44	4.8
5[e]	100:50:1	73	5.7
6[e]	150:50:1	67	10
7[f]	150:50:1	38	6.4

a) Reactions performed under nitrogen atmosphere, in CH_2Cl_2 at r.t. b) Yields are referred to the total monomer mass. c) Ratio of monomers in the copolymer determined by ^{1}H-NMR. d) **3** is added to a solution of both monomers in CH_2Cl_2. e) Norbornene (5.9 M in CH_2Cl_2) was added dropwise for 1 hour. f) Norborne (2.7 M in CH_2Cl_2) was added dropwise for 3 hours.

These data show that the catalyst loading affects not only the yields but also the incorporation of the carbonate monomer. The lower the amount of catalyst, the lower the presence of **31** in the copolymer (Table 5.2, entries 1-3). Since no homopolymerization of $NBCO_3$ was observed we decided to test a different procedure in order to increase its incorporation in the polymer **35**. Instead of adding both monomers at the beginning, before the addition of the catalyst, a solution of norbornene was slowly added (over a period of 1 hour) to a solution of **31** and **3** in CH_2Cl_2. The addition was controlled by a syringe pump. Comparing both procedures we can see that this protocol leads to a higher amount of carbonate in the copolymer, though a small reduction of yield is also observed (Table 5.2, entries 1 and 4). We studied the influence of the monomer feed ratio when using this methodology (Table 5.2, entries 4-6). In this case the best result was obtained when the monomer ratio was 2:1 ($NB:NBCO_3$). This mixture allowed us to obtain a polymer with moderate incorporation of the carbonate monomer and good yield (Table 5.2, entry 5). Finally, we performed the same reaction but stretching on the time of the addition of norbornene (3 hours). Although higher incorporation of **31** was achieved, the decrease of the yield was too high, probably because of a partial deactivation of the catalyst (Table 5.2, entry 7).

While studying the ^1H-NMR spectra of **35** we observed a signal at 5.7 ppm. This signal appeared most clearly in those polymers synthesized with slow addition of norbornene but was visible in both cases (*, Figure 5.5). That signal can hardly be observed in other copolymers of norbornene, so the presence of the carbonate moiety seems to favor its formation. However, no direct association between this signal and monomer **31** can be established because the relative integration of this signal with the signal corresponding to H^2 and H^3 changes depending on the composition of the copolymer observed. The largest signal is observed for **35** (a/b = 5.7) and its integration is thrice smaller than the signal associated to H^2 and H^3. Usually, that chemical shift correspond to olefinic protons. Furthermore, hydrogenation of the polymer with p-toluenesulfonylhydrazide led to the total dissapearance of that signal without modification of the carbonate moiety. Therefore, we can assume that some side reaction responsible of the formation of a double bond is taking place in the polymerization process.

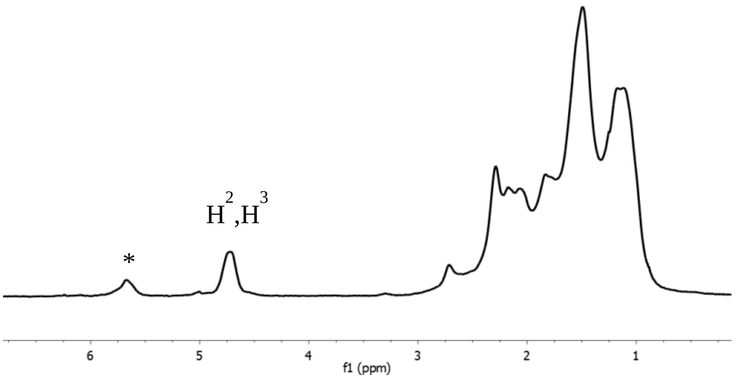
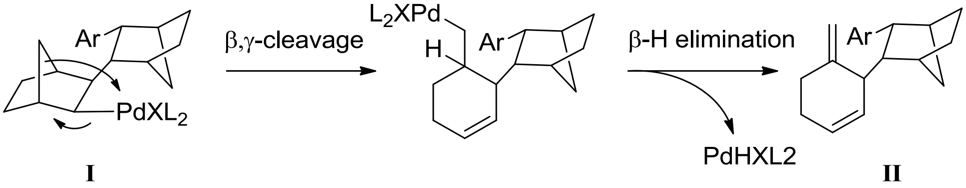


Figure 5.5: 1H-NMR spectra of polymer **35** (a/b = 5.7)

At first, we consider the possibility of some undesired metathesis reaction, but we discarded it because generally, in ROMP-PNBs the olefinic signals appear around 5.3-5.2 ppm. Another possibility can be taken from Catellani and Chiusoli's study about the palladium mediated β,γ-cleavage of a C-C bond.[184] In that work they suggested a decomposition step in the reaction of an aryl-palladium complex with two molecules of norbornene (Scheme 5.4). In their proposal, after the insertion of the second norbornene (**I**), the palladium catalyst is unable to perform a β-H elimination and promotes a β,γ-cleavage of the C-C bond between C^1 and C^7. In this new compound there are hydrogen atoms susceptible to undergo β-H elimination to give **II**.



Scheme 5.4.

In their case the final product **II** has a six-membered ring with an internal double bond as well as an exocyclic methylene group. The ^{1}H-NMR spectra of this kind of terminal

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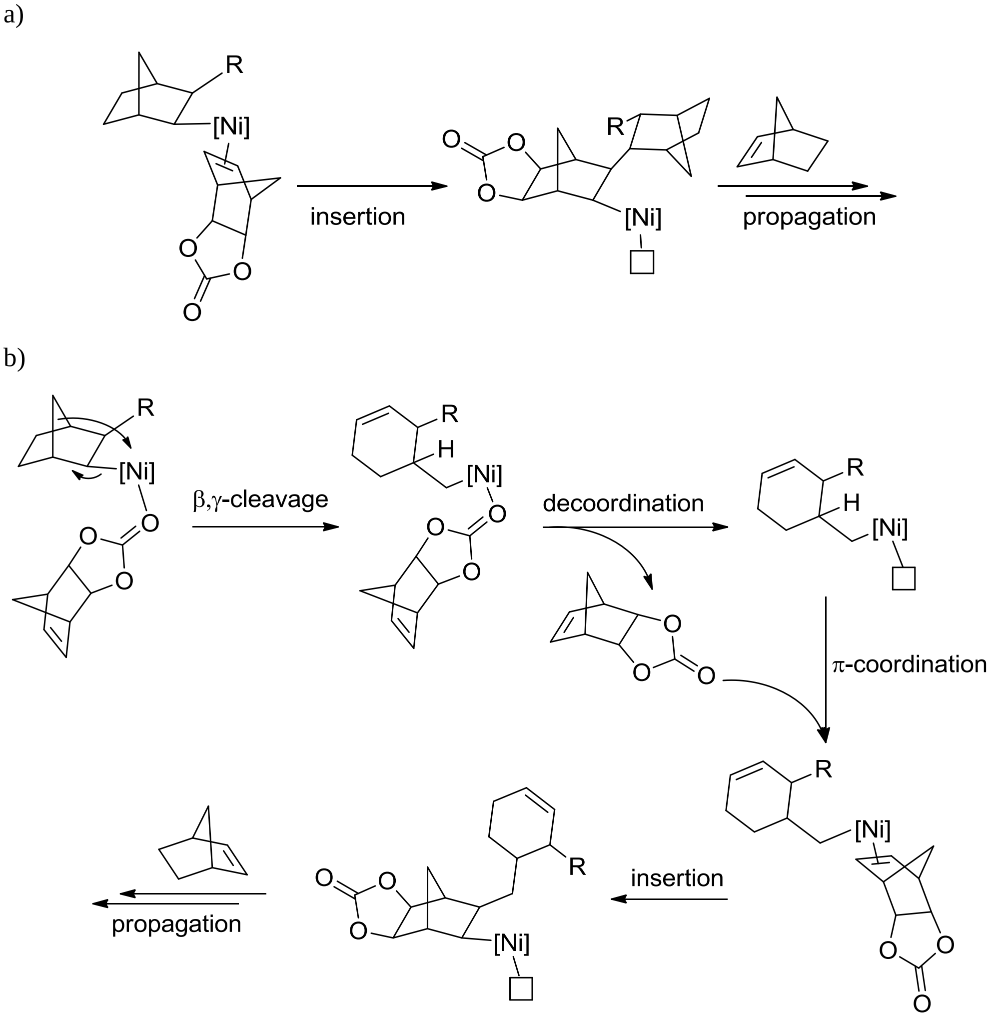
[184] Catellani, M.; Chiusoli, G. P. *J. Organomet. Chem*. **1983**, *247*, C59-C62.

double bonds usually shows a signal at 5 ppm or lower, whereas the chemical shift of the hydrogen atoms of the endocyclic double bond in cyclohexene rings is close to 5.6 ppm. Since our spectra reveals a signal at 5.7 ppm, we can assume that our system experiences some process where a cyclohexene ring is formed in similar way to that described by Catellani and Chiusoli but without the subsequent β-H elimination. Considering that we use nickel instead of palladium we can expect some differences in the reaction pathway that explain our results. Although we have no definitive evidence of the undergoing mechanism we have hypothesized a possible explanation depicted in Scheme 5.5.



Scheme 5.5.

Nickel catalyst **3** does not homopolymerize **31** but polymerizes norbornene easily. However, in the case of the slow norbornene addition experiments, the initial concentration of norbornene is very low compared to that of **31**. Initially, most of the catalyst will be coordinated to the O-functionalized norbornene either by the double bond or, probably through the oxygen atom (vide infra). Whenever a molecule of norbornene coordinates to the metal, the polymerization starts since its insertion into a Ni-C bond is very fast. As far as norbornene is the monomer coordinated to the catalyst the propagation step occurs. But there are two different possibilities in the case of **31**. When this monomer is coordinated through the double bond to **3**, an insertion is expected, so the propagation step can go on (Scheme 5.5a). But, if the catalyst is coordinated to the oxygen atom no insertion is possible and the propagation step stops. The coordination equilibrium seems to be displaced to the O-coordinated species, supported by the fact that homopolymerization of **31** does not occur. In that case nickel may be responsible of a β,γ-cleavage similar to that observed with palladium (Scheme 5.5b).[185] However, in the case of nickel β-H elimination is less favorable and slower.[186] The Ni-σ-C may be stable enough to allow the substitution of the coordinated monomer and insertion of the new one resuming the propagation of the chain. It must be consider the possibility that the C-C cleavage can occur in the functionalized norbornene after insertion of **31**, but in that case the signals corresponding to H^2 and H^3 would have a noticeable different chemical shift, because one of them would be in an allylic position and such difference has not been appreciated on the spectra.

An additional NMR experiment was carried out to support this proposal. **3** was dissolved in a solution with a tenfold molar amount of ethylene carbonate in $CDCl_3$. Two minutes later a twofold molar amount of norbornene was added. After 15 minutes a ^{1}H-NMR spectrum was recorded revealing the presence of unreacted norbornene, some norbornene oligomers and a small but clear signal at 5.6 ppm. That signal grows for 3 hours until norbornene is completely consumed. Ethylene carbonate is capable of slowing down the polymerization of norbornene by **3**, usually very fast, but without poisoning the catalyst so the polymerization is still working. This must occur by O-coordination to the metal so, in the presence of this competing ligand, the coordination of norbonene is disfavored. We can assume that $NBCO_3$ (**31**) is acting in a similar way, slowing the polymerization down and allowing time for the side reaction to occur.

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[185] Yoshikawa, S.; Aoki, K.; Kiji, J.; Furukawa, J. *Tetrahedron*, **1974**, *30*, 405-407.

[186] Koga, N.; Obara, S.; Kitaura, K.; Morokuma, K. *J. Am. Chem. Soc.* **1985**, *107*, 7109-7116.

5.2.1.3 Functionalization of VA-CopNBNBCO$_3$ to synthesize a VA-PNB supported diimine

In view of the results achieved in the copolymerization reactions we chose as starting point for the synthesis of the diimine, a polymer obtained by controlled addition of norbornene over a solution of **31**, namely **35** (a/b = 5.7, M_w = 3.19 x 10^4, M_w/M_n = 1.75, Table 5.2, entry 5). The synthetic route followed was analogous to that used with the monomers: hydrolysis of the carbonate to obtain a diol, oxidation to form a diketone and condensation with an aniline derivative to produce the diimine. As has been mentioned previously, treatment of polymer **35** with p-toluenesulfonylhydrazide in chlorobenzene provokes the disappearance of the olefin signals without affecting the carbonate moiety in the hydrogenated polymer (**35H**).[187] ν(C=O st) IR absorption band at 1809 cm^{-1} remains unaltered as well as characteristic signals in solid state ^{13}C CP-MAS NMR at 161 and 85 ppm corresponding to C^8 (carbonate) and C^2 and C^3 respectively. The polynorbornene copolymer **35H** has a complex structure that contains bicyclic norbornene units and some cyclohexanyl-methyl units derived from the process discussed in the previous section. Regardless the backbone "mistakes" in this VA-PNB, it meets the two important requirements for our purposes: i) It has an all-aliphatic, robust backbone and ii) the carbonate group is on the bicylic norbonene units, as discussed above.

Hydrolysis of **31** was carried out in an aqueous solution of sodium hydroxide, but in the case of **35H** the polymer was insoluble and no effective contact between polymer and water was achieved, some parts of the polymer did not get wet even after stirring. Therefore, we used a solution of NaOH in mixture H_2O:MeOH to facilitate the contact between the polymer and the base (equation 5.5). Although the polymer remained undissolved in that mixture it got completely soaked.

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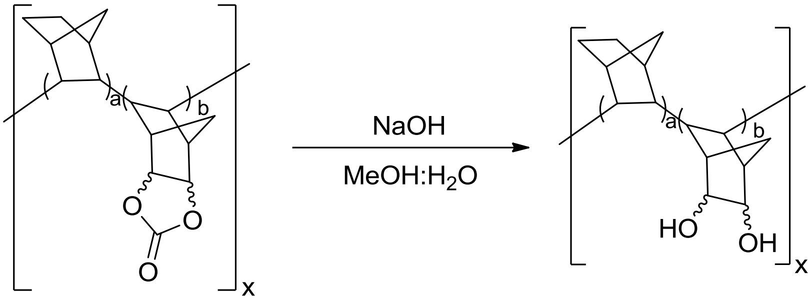
[187] To facilitate the understanding of the figures, polymer **35H** and subsequent derivatives are represented as a chain of byciclic norbornenes without considering those units that could have undergone a ring opening.

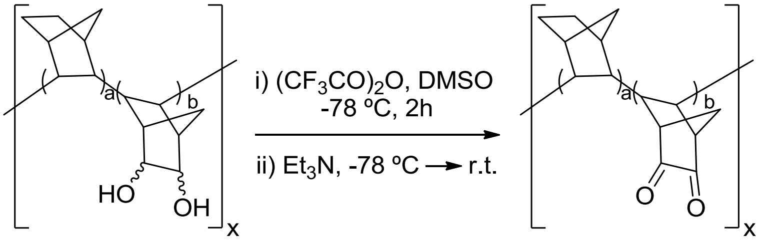


35H (a/b = 5.7) **36b**

(5.5)

The resulting polymer **36b** (VA-CopNBNB(OH)$_2$) is insoluble but can be characterized by IR spectroscopy and solid state NMR. The ν(C=O st) band at 1809 cm^{-1} typical of carbonates, visible in **35H**, disappears completely and a new broad signal ν(O-H st) at 3405 cm^{-1} appears. ^{13}C CP-MAS NMR of **36b** shows a signal at 76 ppm associated with the carbon atoms bound to the hydroxyl groups (C^2 and C^3) but there are no traces of those signals observed in **35** and **35H** at 161 and 85 ppm, characteristic of the carbonate group.

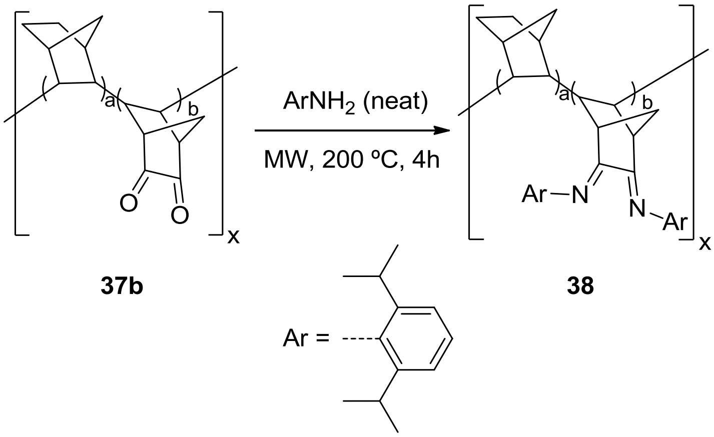
Swern oxidation of **36b** was performed in the same conditions used for diol **32** (equation 5.6). In this case **37b** (VA-CopNBNB(C=O)$_2$) was purified by washing the polymer first with a mixture H$_2$O:MeOH and then with MeOH. This purification is considerably easier than that needed in the synthesis of **33**. In this case the solid state ^{13}C CP-MAS NMR spectrum shows no signal around 200 ppm common of ketones, but the signal at 76 ppm has disappeared. Additionally, infrared spectrum of **37b** shows a strong signal at 1755 cm-1 corresponding to the ketone moiety ν(C=O st).



36b **37b**

(5.6)

The final step in the synthesis of VA-PNB supported diimine is the condensation of **37b** with 2,6-diisopropylaniline. Unlike hydrolysis or Swern oxidation of the polymers, when this reaction was attempted in similar conditions to those described in the synthesis of **34**, only a small amount of imine was formed. We tried different solvents such as MeOH or toluene, at different temperatures and in different conditions (presence or absence of formic acid, use of a Dean-Stark apparatus to remove the water formed) but the total amount of diimine formed was very low. We decided to change the method and carried out several experiments with microwave heating. The best results were obtained when polymer **37b** was heated in neat aniline at 200 ºC for 4 hours (equation 5.7).



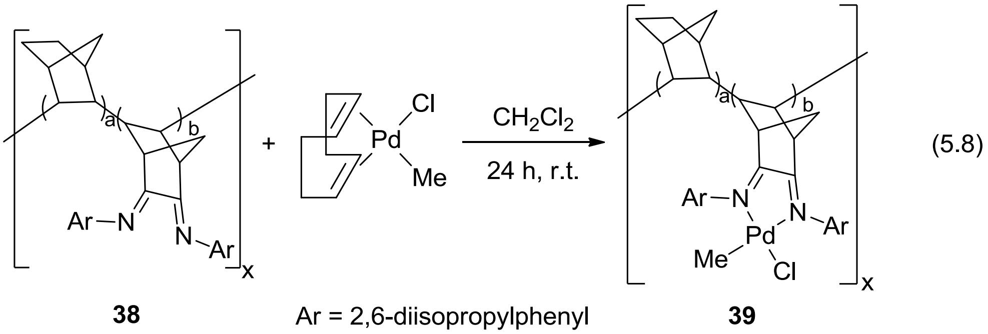
37b **38**

(5.7)

Resulting polymer **38** (VA-CopNBNB(C=N-Ar)$_2$) was soluble in chlorinated solvents and the amount of diimine formed could be determined by ^{1}H NMR. In this case the integral of the aromatic protons can be compared with the broad signal that comprehends all the other protons. About 46% of aniline was incorporated into the polymer, giving a diimine content of 0.570 mmol pergram of polymer. In the IR spectrum of **38** we can still see a signal at 1755 cm^{-1} ν(C=O st) with lower intensity than in **37b**, and a new signal appears at 1677 cm^{-1} corresponding to the ν(C=N st). ^{13}C CP-MAS NMR spectrum shows a signal at 175 ppm corresponding to the carbon atom of the imine. There are some other signals between 157-124 ppm associated with the aromatic carbons and a new signal at 30 ppm typical of the methyl groups of the aryl substituents.

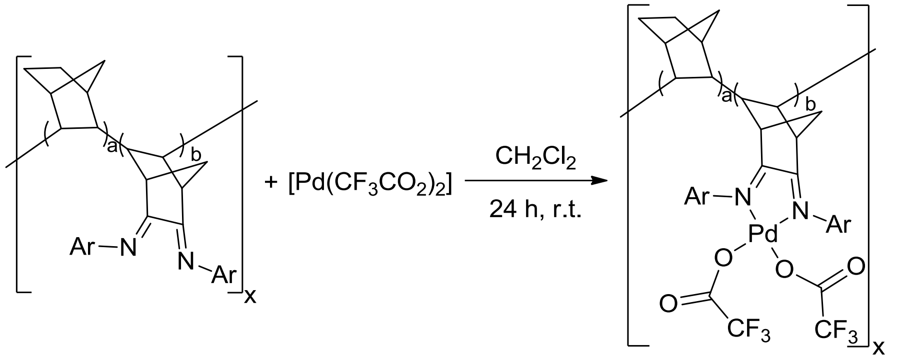
5.2.2 Synthesis of polymer-diimine palladium complexes

In order to test the ability of polymer **38** as supported ligand we decided to synthesize two different palladium complexes. In the first case, we used PdMeCl(COD) as palladium source to obtain a precursor of a cationic methylpalladium complex similar to those used by Brookhart et al. in olefin polymerization (equation 5.8). The starting palladium complex and polymer **38** were dissolved in CH_2Cl_2, mixed and stirred for 24 hours at room temperature. The resultant polymer (**39**, [{VA-CopNBNB(C=N-Ar)$_2$}PdClMe]) showed a palladium incorporation of 8.1 mg Pd/ g polymer, 15% of the maximum content. Due to the small amount of palladium incorporated in **39**, clear differences can be seen neither in the IR spectrum nor in the NMR spectra when comparing **39** with **38**.



(5.8)

Palladium (II) trifluoroacetate was used as metal source in the synthesis of a new polymer-supported complex (**40**, [{VA-CopNBNB(C=N-Ar)$_2$}Pd(CF$_3$CO$_2$)$_2$]). We decided to use this fluorinated complex instead of more common palladium(II) acetate because the characteristic signals of the CF_3 moieties in infrared spectroscopy and ^{19}F NMR would allow us to characterized the polymer easier (equation 5.9). In this case the incorporation of palladium raised to 29.6 mg Pd/ g polymer, 58% yield considering the maximum possible content.



(5.9)

38 Ar = 2,6-diisopropylphenyl **40**

In this case the resulting polymer is insoluble in common solvents. IR spectrum shows two bands at 1182 and 1146 cm^{-1} characteristic of the trifluoromethyl group. Furthermore, the band at 1677 cm^{-1}, corresponding to the ν(C=N st) in **38** is partially overlapped by another band at 1686 cm^{-1}, associated with the ν(CO_2 asym) band of the acetate in the same region. The ν(CO_2 asym) resonance has a high value, higher than the parent palladium trifluoroacetate, which is consistent with a monodentate fashion.[188] ^{19}F MAS NMR shows a signal at -73 ppm slightly displaced from the signal of the starting complex $Pd(CF_3CO_2)_2$ (-76 ppm). Such difference can be a sign of the new coordination mode for the trifluoroactate. In the ^{13}C CP MAS NMR spectra there are a new signal at 167 ppm corresponding to the carbon in the carboxylate group. Moreover there is a quartet of signals corresponding to the *C*F_3 with an average chemical shift of 120 ppm with a coupling constant $^1J_{C\text{-}F} = 280$ Hz.

5.2.3 Application of the polymer-supported diimine palladium complexes in catalysis

5.2.3.1 Use of [{VA-CopNBNB(C=N-Ar)$_2$}PdClMe] in olefin polymerization

Polymer **39** was used as a precatalyst in the polymerization of some olefins in a similar way to that described by Brookhart et al.[161a] In our case we generated the cationic

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[188] (a) Stephenson, T. A.; Wilkinson, G. *J. Inorg. Nucl. Chem*. **1967**, *29*, 2122-2123. (b) Efimenko, I. A.; Podobedov, R. E.; Churakov, A. V.; Kuz'mina, L. G.; Garbuzova, I. A.; Lokshin, B. V.; Maksimov, A. L.; Flid, V. R. *Russ. J. Coord. Chem*. **2011**, *37*, 625-634.

complex *in situ* by treatment of the palladium complex with the sodium salt of a bulky-non coordinating anion such as $[B[3,5-(CF_3)_2C_6H_3]_4]^-$ (BARF).

In a first experiment **39** and the BARF salt were introduced in a Fischer-Porter flask under an ethylene atmosphere. The mixture was cooled at -78 ºC and CH_2Cl_2 was added so the concentration of the catalyst was 1.1 x 10^{-3} M. Then the ethylene pressure was set at 2.5 atm and the reaction was stirred for 24 hours while it was allowed to warm up to room temperature. In order to separate our starting polymer from the polyethylene formed we removed completely the solvent and washed the resulting solid with pentane. In this solvent **39** is insoluble and can be easily separated by filtration whereas polyethylene is soluble and can be collected after removing the filtrate.

With our system we obtained 54 mg of polyethylene (10.9 g/ mmol Pd) with high molecular weight (M_w = 2.97 x 10^4) and a polydispersity of 2.4. Following the method described by Brookhart to calculate the number and type of branches,[162d] we observed by analysis of the ^{1}H-NMR spectrum that it is a highly branched polyethylene with 91 branches per 1000 carbon atoms (Figure 5.8). Although in a lower yield, the polyethylene synthesized with our VA-PNB supported catalyst is similar to that obtained with analogous molecular catalysts (about 450 g/mmol Pd).[161a]

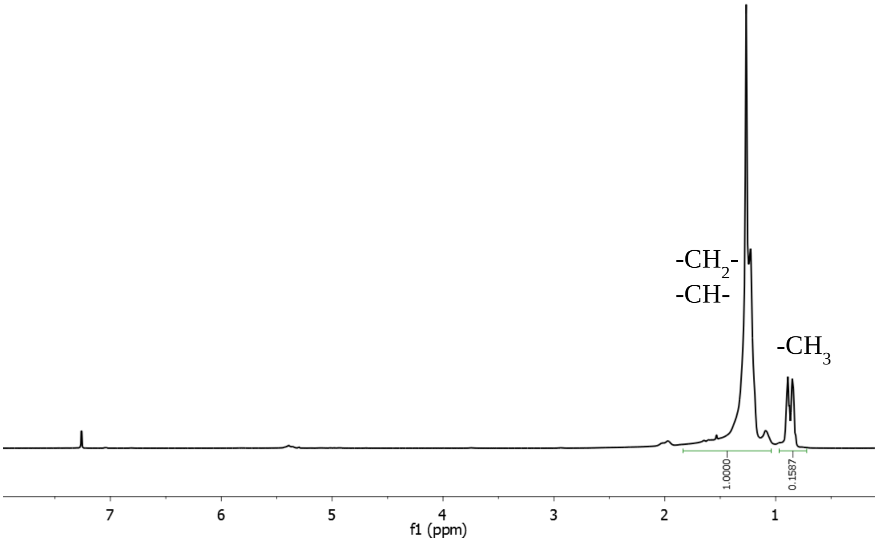


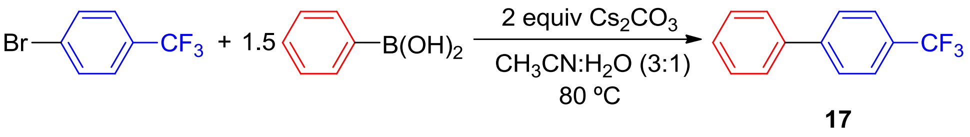
Figure **5.8**: ^{1}H NMR of polyethylene obtained with **39**.

Then we decided to study the recyclability of **39** in this reaction. To the best of our knowledge, in the literature there are no examples in the literature of diimine-supported catalysts being reused in olefin polymerization. When we carried out an experiment in the same reaction conditions than the previous one, we got only 16 mg of polyethylene (3.5 g/ mmol Pd) with similar structure than the former one.

Considering that in our case we have a palladium catalyst supported on a polymer we contemplated the possibility that the VA-PNB backbone could act as a bulky ligand and therefore, play a role similar to that seen with cyclophane-based diimines (see section 5.1). Thereby, we also tested the ability of our catalyst in the copolymerization of ethylene with a polar olefin such methyl acrylate (MA). In this case we used an ethylene pressure of 6 atm and molar ratio MA:Pd = 5800:1. We found out that two different polymerizations were having place. We managed to obtain polyethylene with no content of MA and a copolymer of poly(methyl acrylate) with low content of polyethylene, but the yield of both processes was very low. The amount of polyethylene was 8 mg (1.75 g/ mmol Pd) and the amount of the copolymer 6 mg (75 %mol MA, 1.31 g/ mmol Pd). (75% mol MA, 1.31 g/ mmol Pd). The high amount of MA in this polymer suggests a radical polymerization mechanism, which can be initiated by palladium complexes.[189] Thus, either monomer polymerizes by its preferred mechanism and no control of the copolymerization process can be achieved.

5.2.3.2 Use of [{VA-CopNBNB(C=N-Ar)$_2$}Pd(CF$_3$CO$_2$)$_2$] in the Suzuki reaction

We tested the catalytic activity of polymer **40** in some Suzuki reactions. We chose as model reaction the same described in chapter 3 with 4-bromobenzotrifluoride and phenylboronic acid as reagents (equation 5.10).



17

(5.10)

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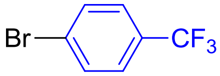
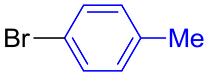
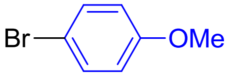
[189] (a) Albéniz, A. C.; Espinet, P.; López-Fernández, R. *Organometallics*, **2003**, *22*, 4206-4212. (b) Albéniz, A. C.; Espinet, P.; López-Fernández, R. *J. Polym. Sci. A: Polym. Chem*. **2006**, *44*, 5682-5691.

In this case the *in situ* infrared spectroscopy showed that the reaction was finished in 15 minutes (Table 5.3, entry 1). Subsequent recycling experiments revealed that the reaction time increases for the following runs but only slightly (Table 5.3, entries 2-5). After five cycles 30 minutes were enough to reach very high conversions.

Table 5.3. Suzuki reactions catalyzed by **40**.[a]

Entry	ArX	Cycle	Time (min)	Yield (%)
1		1	15	**17** (97)[b]
2		2	20	**17** (98)[b]
3		3	25	**17** (96)[b]
4		4	30	**17** (98)[b]
5		5	30	**17** (99)[b]
6		1	60	**18** (95)[c]
7		1	120	**19** (91)[c]

a) Reaction conditions shown in equation 5.10. b) Crude yields determined by ^{19}F NMR. c) Crude yields determined by ^{1}H NMR.

Polymer **40** was also used with other para-substituted aryl bromides such as 4-bromotoluene or 4-bromoanisole. As it happened with the polymer-supported NHC-Pd **16d**, these haloarenes required longer times but high yields were obtained (Table 5.3, entries 6-7). Leaching measurements showed similar results to those observed with the NHC complex. In the first run 4.3 % of the initial amount of palladium was leached, but in the next runs the leaching was around 0.4-0.2%.

Finally we studied if the catalyst was acting homogenous or heterogeneously. We performed a hot filtration test in the sixth cycle of the catalyst in the reaction with 4-bromobenzotrifluoride. After running the reaction at 80 ºC for 20 minutes, the hot mixture was filtered. ^{19}F NMR spectrum at that point showed an 80% yield. When the filtrate was allowed to react other 30 minutes at 80 ˚C the yield increased until 99%. As it happened with **16d** this behavior proves that the catalysis is being performed in a homogeneous way. The leaching result of this experiment is 0.26 %, analogue to the values of the previous cycles.

5.3 CONCLUSIONS

We have synthesized a norbornene-based diimine for the first time, in a four step route. We have studied which precursor of the diimine was the most convenient in the vinylic-addition copolymerization with norbornene, catalyzed by the nickel complex **3**. Copolymerization of the norbornene carbonate, **31**, by slow addition of norbornene showed the best results. The norbornene-diol or norbornene-diketone derivatives did not undergo polymerization.

The copolymerization of **31** and norbornene gives a polymer that contains an olefinic moiety. We have given a plausible explanation for this side reaction which involves a β,γ-cleavage of the C-C bond between C^1 and C^7 and leads to a cyclohexenyl group. The olefinic moiety formed can be reduced without altering the carbonate group, thus affording an all-aliphatic polymer, **35H**, to be used as a support.

Hydrolysis and subsequent Swern oxidation of polymer **35H** has allowed us to obtain a vinylic-addition copolymer with a norbornene-based diimine (**38**). This polymer has been used as a ligand to form two different supported palladium complexes (**39** and **40**).

Polymer **39** has been used as a precatalyst in the polymerization of ethylene showing moderate results. The palladium-supported complex can be recycled but with a decrease of its activity. Copolymerization experiments with ethylene and methyl acrylate provided very low amount of polyethylene and a copolymer with high content of methyl acrylate.

Polymer **40** has shown good activity in the Suzuki reaction and it is recyclable. As it happened with **16d**, **40** is acting as a reservoir of palladium active homogeneous species, but in this case the increment of the reaction time needed in each cycle is small.

5.4 EXPERIMENTAL PART

5.4.1 General Methods

General methods and techniques employed are the same that those described in previous chapters.

^{19}F MAS NMR spectra were recorded at 376.5 MHz with a 90° pulse length of 5.5 µs. ^{19}F-NMR chemical shifts are in ppm relative to $CFCl_3$.

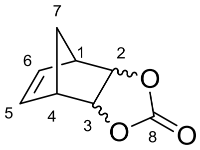
Controlled addition of norbornene in the copolymerization reaction was done with a Thermo Scientific Orion M365 Sage Syringe Pump.

[PdMeCl(COD)],[190] [Pd(CF_3CO_2)$_2$][191] and NB(C=O)$_2$ (**33**)[181b] were prepared according to the literature procedures.

5.4.2 Synthesis of norbornene-diimine precursors.

Synthesis of NBCO3 (31)

A Schlenk flask with J Young Teflon tap was charged with vinylene carbonate (25.00 g, 290.5 mmol), dicyclopentadiene (6.401 g, 48.42 mmol), hydroquinone (0.0100 g, 0.0908 mmol) and toluene (8.0 mL). The reaction was heated at 180 ºC for 20 hours. After removing the volatiles under vacuum at 65 ºC a pale brown solid was obtained. The solid was dissolved in CH_2Cl_2 (15 mL) and crystallized in cold hexane (60 mL). Then it was filtered and washed with cold hexane (3 x 10 mL). The product was obtained as a pale yellow solid (13.43 g, 91% yield). The product is a mixture of isomers endo:exo = 97.6:2.4.



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[190] Ladipo, F. T.; Anderson, G. K. *Organometallics,* **1994**, *13*, 303-306.

[191] Stephenson, T. A.; Morehouse, S. M.; Powell, A. R.; Heffer, J. P.; Wilkinson, G. *J. Chem. Soc.* **1965**, 3632.

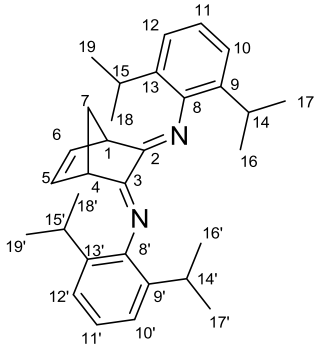
31 endo: ^{1}H NMR (300.13 MHz, δ, $CDCl_3$): 6.21 (m, 2H, H^5, H^6), 4.98 (m, 2H, H^2, H^3), 3.27 (m, 2H, H^1, H^4), 1.75 (d, $J_{7\text{-}7'}$ = 10.4 Hz, 1H, H^7), 1.26 (d, $J_{7'\text{-}7}$ = 10.4 Hz, 1H, $H^{7'}$). ^{13}C{^{1}H} NMR (75.4 MHz, δ, $CDCl_3$): 155.59 (s, C^8), 134.35 (s, C^5, C^6), 78.96 (s, C^2, C^3), 45.57 (s, C^1, C^4), 42.55 (s, C^7).
31 exo: ^{1}H NMR (300.13 MHz, δ, $CDCl_3$): 6.10 (m, 2H, H^5, H^6), 4.55 (m, 2H, H^2, H^3), 3.13 (m, 2H, H^1, H^4), 1.84 (m, 1H, H^7), 1.70 (m, 1H, $H^{7'}$). ^{13}C{^{1}H} NMR (75.4 MHz, δ, $CDCl_3$): 155.59 (s, C^8), 135.95 (s, C^5, C^6), 78.81 (s, C^2, C^3), 45.57 (s, C^1, C^4), 40.94 (s, C^7).

Synthesis of NB(OH)$_2$ (32)

31 (3.650 g, 24.00 mmol) was dissolved in a solution of NaOH (1.0 M solution in H_2O, 50.00 mL, 50.00 mmol). The mixture was stirred at room temperature for 5 hours and the product was extracted with Et_2O (5 x 15 mL). The organic phase was washed with saturated $NaHCO_3$ aqueous solution (20 mL), water (20 mL) and dried over $MgSO_4$. The solvent was removed and the product was obtained as a white solid. (2.658 g, 88% yield). **32** was obtained as a mixture of isomers in a ratio endo:exo = 97.6:2.4 that parallel the starting material (**31**).
32 endo: ^{1}H NMR (400.13 MHz, δ, $CDCl_3$): 6.26 (m, 2H, H^5, H^6), 4.18 (m, 2H, H^2, H^3), 3.02 (m, 2H, H^1, H^4), 2.25 (br, 2H, -O*H*), 1.51 (d, $J_{7\text{-}7'}$ = 9.7 Hz, 1H, H^7), 1.22 (d, $J_{7'\text{-}7}$ = 9.7 Hz, 1H, $H^{7'}$). ^{13}C{^{1}H} NMR (100.6 MHz, δ, $CDCl_3$): 135.04 (s, C^5, C^6), 70.92 (s, C^2, C^3), 47.59 (s, C^1, C^4), 41.81 (s, C^7).
32 exo: ^{1}H NMR (400.13 MHz, δ, $CDCl_3$): 6.04 (m, 2H, H^5, H^6), 3.71 (m, 2H, H^2, H^3), 2.70 (m, 2H, H^1, H^4), 2.25 (br, 2H, -O*H*), 1.89 (d, $J_{7\text{-}7'}$ = 9.2 Hz, 1H, H^7), 1.62 (d, $J_{7'\text{-}7}$ = 9.2 Hz, 1H, $H^{7'}$). ^{13}C{^{1}H} NMR (100.6 MHz, δ, $CDCl_3$): 136.29 (s, C^5, C^6), 68.80 (s, C^2, C^3), 47.85 (s, C^1, C^4), 42.11 (s, C^7).

Synthesis of NB(C=N-Ar)$_2$, Ar = 2,6-diisopropylphenyl (34)

Diketone **33** (0.2853 g, 2.336 mmol) and 2,6-diisopropylaniline (0.8283 g, 4.672 mmol) were dissolved in a mixture of MeOH (2.5 mL) and formic acid (0.25 mL). The mixture was stirred at room temperature for 24 hours. Volatiles were removed and MeOH (1.0 mL) was added and cooled to -78 ºC. The solid formed was filtered and air dried. (0.1164 g, 11% yield).



34 ^1H NMR (400.13 MHz, δ, $CDCl_3$): 7.19-7.07 (m, 6H, H^{10}, $H^{10'}$, H^{11}, $H^{11'}$, H^{12}, $H^{12'}$), 6.36 (m, 2H, H^5, H^6), 3.27 (m, 2H, H^1, H^4), 2.95(qq, $J_{14-16, 14-17, 14'-16', 14'-17'}$, = 6.8 Hz, 2H, H^{14}, $H^{14'}$), 2.70 (sp, $J_{15-18, 15-19, 15'-18', 15'-19'}$, = 6.8 Hz, 2H, H^{15}, $H^{15'}$), 2.32 (d, $J_{7-7'}$ = 9.6 Hz, 1H, H^7), 1.97 (d, $J_{7'-7}$ = 9.6 Hz, 1H, $H^{7'}$), 1.23, 1.22, 1.19, 1.15 (4 d, $J_{16-14, 16'-14', 17-14, 17'-14', 18-15, 18'-15', 19-15, 19'-15'}$ = 6.8 Hz, 24H, H^{16}, $H^{16'}$, H^{17}, $H^{17'}$, H^{18}, $H^{18'}$, H^{19}, $H^{19'}$). $^{13}C\{^1H\}$ NMR (100.6 MHz, δ, $CDCl_3$): 168.27 (s, C^2, C^3), 146.13 (s, C^8, $C^{8'}$), 137.44 (s, C^5, C^6), 136.70, 136.53 (2 s, C^9, $C^{9'}$, C^{13}, $C^{13'}$), 124.04, 122.82, 122.76 (3 s, C^{10}, $C^{10'}$, C^{11}, $C^{11'}$, C^{12}, $C^{12'}$), 48.90 (s, C^7), 46.08 (s, C^1, C^4), 28.31, 27.91 (2 s, C^{14}, $C^{14'}$, C^{15}, $C^{15'}$), 23.78, 23.70, 23.46, 23.15 (4 s, C^{16}, $C^{16'}$, C^{17}, $C^{17'}$, C^{18}, $C^{18'}$, C^{19}, $C^{19'}$).

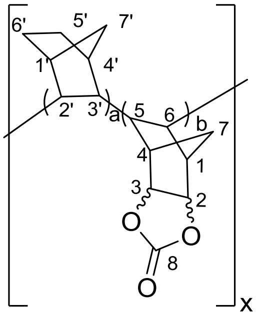
5.4.3 Copolymerization of O-functionalized norbornenes precursors of the diimine

Synthesis of copolymer VA-CopNBNBCO$_3$ (35)

Method a (Table 5.1, entry 1): In a Schlenk flask under a nitrogen atmophere **31** (0.4900 g, 3.22 mmol) and norbornene (0.85 mL, 3.80 M in CH_2Cl_2, 3.22 mmol) were dissolved in CH_2Cl_2 (5.0 mL). To this mixture was slowly added a solution of **3** (0.0708 g, 0.0644 mmol) and triphenylstibine (0.0091 g, 0.0258 mmol) in CH_2Cl_2 (5.0 mL). After stirring 24 h at room temperature the viscous solution was poured into MeOH (30 mL). The resulting polymer was filtered, washed with MeOH (5 x 5 mL) and air dried. The product was obtained as a white solid (0.4278 g, 54% yield). NB:NBCO$_3$ = 16.8:1.

Method b (Table 5.2, entry 5): To a solution of **31** (4.000 g, 26.29 mmol) in CH_2Cl_2 (20 mL) a mixture of **3** (0.5778 g, 0.5258 mmol) and triphenylstibine (0.0740 g, 0.2103 mmol) in

CH_2Cl_2 (15 mL) was added. Then norbornene (5.890 M in CH_2Cl_2, 8.900 mL, 52.58 mmol) was added in a controlled flow of 0.15 mL / min for 1 h. The reaction was stirred at room temperature for 24 hours. After this time it was poured into MeOH (250 mL) where a solid appeared, which was filtered, washed with MeOH (5 x 20 mL) and air dried. The copolymer is a white powder. (6.491 g, 73% yield). NB:NBCO$_3$ = 5.66:1.



35: NB:NBCO$_3$ = 5.66:1. M_w (Daltons) = 3.19 x 10^4. M_w /M_n = 1.7. IR (neat), cm^{-1}: 1812 ν(C=O st), 1129 ν(O-C-O st as), 1086 ν(C-O-C st as). ^{1}H NMR (500.15 MHz, δ, $CDCl_3$): 5.83-5.53 (br, 2H, olefin), 5.1-4.3 (br, 2H, H^2, H^3), 3.0-0.3 (br, 16H). ^{13}C NMR (125.72 MHz, δ, $CDCl_3$): 155 (br, C^8), 136 (br, olefin), 128 (br, olefin), 79 (br, C^2, C^3), 54-50 and 48-45 (br, C^5, C^6, $C^{2'}$, $C^{3'}$), 44-38 (br, C^1, $C^{1'}$, C^4, $C^{4'}$), 37-34 (br, C^7, $C^{7'}$), 33-28 (br, $C^{5'}$, $C^{6'}$).

Copolymers **36a** and **37a** were synthesized following method a. They are insoluble in common organic solvents.

36a (0.0410 g, 8.0% yield). IR (neat), cm^{-1}: 3408 ν(O-H st), 1079 ν(C-O st).

37a (0.1033 g, 17.0% yield). IR (neat), cm^{-1}: 1746 ν(C=O st).

5.4.4 Functionalization of VA-CopNBNBCO$_3$

Hydrogenation of 35

Copolymer **35** (6.300 g, 3.305 mmol of CH=CH) was dissolved in deoxygenated chlorobenzene (150 mL). p-Toluenesulfonhydrazide (24.60 g, 132.2 mmol) was added and the reaction was vigorously stirred at reflux for 4 hours. The formation of the foams was observed. After cooling to room temperature the mixture was poured into MeOH (400 mL) and stirred for 3 hours. The polymer was filtered and washed with a mixture of MeOH:H_2O (1:1, v/v, 5 x 20 mL) and air dried. The solid was then dissolved in CH_2Cl_2 (100 mL) and poured again into MeOH (400 mL). After stirring for 3 hours the polymer was filtered, washed with MeOH (3 x 20 mL), hexane (2 x 20 mL) and Et_2O (2 x 20 mL) and finally dried in a vacuum oven at 35 ºC for 24 hours.. The product was obtained as a white powder (5.840 g, 93% yield). IR (neat), cm^{-1}: 1809 ν(C=O st), 1127 ν(C-O st as), 1085 ν(C-O-C st as). ^1H NMR (500.15 MHz, δ, $CDCl_3$): 5.1-4.3 (br, 2H, H^2, H^3), 3.0-0.3 (br, 16H). ^{13}C NMR (125.72 MHz, δ, $CDCl_3$): 155 (br, C^8), 79 (br, C^2, C^3), 54-50 and 48-45 (br, C^5, C^6, $C^{2'}$, $C^{3'}$), 44-38 (br, C^1, $C^{1'}$, C^4, $C^{4'}$), 37-34 (br, C^7, $C^{7'}$), 33-28 (br, $C^{5'}$, $C^{6'}$).

Synthesis of VA-CopNBNB(OH)$_2$ (36b)

Copolymer **35H** (5.600 g, 8.174 mmol of carbonate) was dissolved in THF (120 mL). Tetrabutylammonium hydroxide (1.000 M in MeOH, 81.74 mL, 81.74 mmol) was added and the reaction was stirred for 9 hours at reflux. After cooling to room temperature the mixture was poured into a mixture of MeOH:H_2O (1:1, v/v, 300 mL) and stirred overnight. The solid was filtered, washed with MeOH (5 x 20 mL) and dried in a vacuum oven at 35 ºC for 24 hours. The polymer is a white powder barely soluble in common solvents (5.255 g, 98% yield). IR (neat), cm^{-1}: 3240 ν(O-H st), 1110 and 1076 ν(C-O st). ^{13}C CP-MAS NMR (100.61 MHz): 74-65 (br, C^2, C^3), 63-18 (br, polyNB).

Synthesis of VA-CopNBNB(C=O)$_2$ (37b)

A two-necked round-bottom flask under a nitrogen atmosphere was charged with copolymer **36b** (5.000 g, 7.586 mmol diol) and CH_2Cl_2 (200 mL) and cooled to -78 ºC. In another

Schlenk with a mixture of dimethyl sulfoxide (7.112 g, 91.03 mmol) and CH_2Cl_2 (50 mL) stirring at -78 ºC, trifluoroacetic anhydride (15.93 g, 75.86 mmol) was added dropwise. Ten minutes later this solution was added slowly via cannula to the polymer suspension at -78 ºC. After 4 hours triethylamine (15.35 g, 151.7 mmol) was added. The reaction was stirred for 3 hours and allowed to warm up to room temperature. Half the CH_2Cl_2 was removed and the mixture was poured into a mixture of MeOH:H_2O (3:1, v/v, 400 mL) and stirred overnight. The polymer was filtered, washed with a mixture of MeOH:H_2O (1:1, v/v, 5 x 20 mL) and MeOH (5 x 20 mL) and dried in a vacuum oven at 35 ºC for 24 hours. The polymer was obtained as a yellowish powder (4.440 g, 89% yield). IR (neat), cm^{-1}: 1755 ν(C=O st). ^{13}C CP-MAS NMR (100.61 MHz): 63-18 (br, polyNB).

Synthesis of VA-CopNBNB(C=N-Ar)$_2$, Ar = 2,6-diisopropylphenyl (38)

Copolymer **37b** (1.000 g, 1.527 mmol diketone) and 2,6-diisopropylaniline (11.28 g, 63.62 mmol) were placed in a 30 mL microwave reaction vessel. The mixture was heated to 200 ºC and stirred for 4 hours in the microwave oven. The reaction was then poured into MeOH (100 mL) and stirred for 3 hours at room temperature. The solid was filtered, washed with MeOH (3 x 20 mL) and CH_3CN (3 x 20 mL) and dried in a vacuum oven at 35 ºC for 24 hours. The polymer is a pale orange powder (1.1400 g, 77 %, 45% incorporation of aniline; 0.570 mmol of diimine/g polymer) IR (neat), cm^{-1}: 1755 ν(C=O st), 1677 ν(C=N st). ^1H NMR (500.15 MHz, δ, $CDCl_3$): 7.3-6.7 (br, 6H, H^{10}, H^{11}, H^{12}), 3.2-0.3 (br, $CH(CH_3)_2$, $CH(CH_3)_2$ polyNB). ^{13}C NMR (125.72 MHz, δ, $CDCl_3$): 146 (br, C^8), 135-133 (br, C^9, C^{13}), 125-121 (br, C^{10}, C^{11}, C^{12}) 54-50 and 48-45 (br, C^5, C^6, $C^{2'}$, $C^{3'}$), 44-38 (br, C^1, $C^{1'}$, C^4, $C^{4'}$), 37-34 (br, C^7, $C^{7'}$), 33-28 (br, $C^{5'}$, $C^{6'}$), 28 (br, $CH(CH_3)_2$), 24-21 (br, $CH(CH_3)_2$).

5.4.5 Synthesis of polymer-supported diimine-palladium complexes

Synthesis of [{VA-CopNBNB(C=N-Ar)$_2$}PdClMe] (39)

Chloro(1,5-cyclooctadiene)methyl palladium(II) (0.0344 g, 0.1296 mmol) was added to a solution of copolymer **38** (0.2500 g, 0.1426 mmol diimine) in CH_2Cl_2 (20 mL). The reaction was stirred for 24 hours at room temperature. After that time the mixture was poured into acetone (100 mL). The solid was filtered, washed with acetone (4 x 20 mL) and air dried.

The polymer was obtained as a pale brown solid (0.1892 g, 70% yield). Analysis ICP-MS Pd 8.080 mg Pd/g. The NMR spectra of **39** are indistinghisable from those of **38**. No characteristic signals of the complex could be observed.

Synthesis of [{VA-CopNBNB(C=N-Ar)$_2$}Pd(CF$_3$CO$_2$)$_2$] (40)

Palladium(II) trifluoroacetate (0.0431 g, 0.1296 mmol) was added to a solution of copolymer **38** (0.2500 g, 0.1426 mmol diimine) in CH_2Cl_2 (20 mL). The reaction was stirred for 24 hours at room temperature and poured into acetone (100 mL). The solid was filtered, washed with acetone (4 x 20 mL) and air dried. The polymer was obtained as a brown solid insoluble in common solvents (0.2776 g, 95% yield). Analysis ICP-MS Pd 29.58 mg Pd/g. IR (neat), cm^{-1}: 1755 ν(C=O st, polymer ketone), 1686 ν(COO st as), 1677 ν(C=N st), 1182 and 1146 ν(CF$_3$ st). ^{13}C CP-MAS NMR (100.61 MHz): 175 (br, C^2, C^3), 168 (br, CF$_3$*C*O$_2$), 155-126 (br, aromatic), 120 (q, *C*F$_3$CO$_2$, $^1J_{C\text{-}F}$ = 280 Hz), 63-18 (br, *C*H(CH$_3$)$_2$, CH(*C*H$_3$)$_2$, polyNB). ^{19}F MAS NMR (376.50 MHz): -72.9 (br, CF3).

5.4.6 Polymerization reactions with 39

Polymerization of ethylene

A Fischer-Porter flask with **39** (0.0600 g, 4.56 x 10^{-3} mmol Pd) and NaB[3,5-(CF$_3$)$_2$C$_6$H$_3$]$_4$ (0.0041 g, 4.56 x 10^{-3} mmol), was cooled at -78 ºC. Upon cooling the system was evacuated and it was purged with ethylene, and CH_2Cl_2 (4.0 mL) was added. The pressure was then raised to 2.5 atm and the mixture was stirred for 24 h while the temperature raised to room temperature. After that time the pressure was released and the volatiles were removed. The solid obtained was extracted with pentane (5 x 5 mL). The undissolved solid was separated by filtration and the solution was evaporated to dryness. Polyethylene was obtained as a white solid (54 mg, 10.9 g/ mmol Pd). M_w (Daltons) = 3.19 x 10^4. M_w/ M_n = 2.4.). ^{1}H NMR (500.15 MHz, δ, CDCl$_3$): 1.53-1.03 (br, C*H*$_2$), 0.93-0.80 (br, C*H*$_3$). 91 branches/ 1000 carbon atoms.[192]

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[192] Calculated following the formula: branches/1000 C = (CH$_3$ integral x 2 x 1000)/(total integral x 3). See reference 161d.

Copolymerization of ethylene with methyl acrylate

A Fischer-Porter flask was protected from light and charged with **39** (0.0600 g, 4.56 x 10^{-3} mmol Pd) and $NaB[3,5-(CF_3)_2C_6H_3]_4$ (0.0041 g, 4.56 x 10^{-3} mmol). The system was cooled to -78 ºC and, after being evacuated, refilled with ethylene. Methyl acrylate (2.242 g, 26.4 mmol) and CH_2Cl_2 (2.1 mL) were added and the pressure of ethylene was elevated to 6.0 atm. After 20 h the pressure was released and the mixture was evaporated to remove the solvent and the unreacted methyl acrylate. The residue was extracted with pentane (5 x 5 mL) to separate the polyethylene formed (8.0 mg, 1.75 g/ mmol Pd). The remaining solid insoluble in pentane was extracted with acetone (5 x 5mL) to separate the copolymer of ethylene and methyl acrylate, which was obtained as a colorless gum-like solid (6.0 mg, 1.31 g/ mmol Pd, 75 %mol content of MA). In addition to the typical methyl, methylene and methyne signals of polyethylene new signals can be observed. ^1H NMR (400.15 MHz, δ, $CDCl_3$): 3.66 (s, 6H, OCH_3), 2.3 (br, 2H, $CH(CO_2CH_3)^s$, $CH(CO_2CH_3)^i$),* 1.9 (a, 1H, CHH^i),* 1.69 (a, 2H, $CH_2{}^s$), 1.5 (a, 1H, CHH^i).* $^{13}C\{^1H\}$ NMR (100.6 MHz, δ, $CDCl_3$): 174.9 (s, CO_2CH_3), 51.7 (s, OCH_3), 41.3 (m, $CH(CO_2CH_3)$).
* i = isotactic, s = syndiotactic.

5.4.7 General procedure for the Suzuki reactions followed by in situ IR. Table 5.3

For all the Suzuki reactions described in Table 5.3 the experimental procedure followed was the same described in the experimental part of chapter 3 when using the *in situ* IR. The only difference was the use of **40** (0.0300 g, 0.0084 mmol) as catalyst instead of **16d**.

Polinorbornenos de adición vinílica como soporte de catalizadores: Aplicaciones en organocatálisis y en reacciones de acoplamiento C-C catalizadas por paladio

Resumen

PRESENTACIÓN

La catálisis soportada es un importante recurso en la química moderna porque engloba propiedades interesantes y beneficiosas tanto los catalizadores heterogéneos (reutilización, facilidad de separación…) como de los homogéneos (selectividad, capacidad para modificar las características estéreas y electrónicas…). Desde el punto de vista de la sostenibilidad es una buena solución para reducir gastos y residuos de algunos procesos aún por mejorar. Entre los muchos y diferentes soportes sólidos empleados, los polímeros generan un creciente interés debido a la mejora en su síntesis. La introducción de nuevas funcionalidades y poseer un mejor control sobre la incorporación de éstas, hace a los polímeros una buena elección en este campo.

Nuestro grupo de investigación ha desarrollado anteriormente una serie de nuevos polinorbornenos de adición vinílica con diferentes grupos funcionales como cadenas alquílicas con halógenos en la posición terminal o derivados de estaño que han demostrado ser útiles como reactivos soportados en la reacción de Stille. Por lo tanto, consideramos que este tipo de polímeros podría también ser eficaz como soporte de catalizadores, dadas algunas de sus provechosas características: alta estabilidad térmica y robustez (su estructura posee exclusivamente enlaces sencillos C-C o C-H, no hay heteroátomos, ni enlaces múltiples o anillos aromáticos ni posiciones bencílicas susceptibles de sufrir reacciones secundarias indeseadas que pueden degradar el esqueleto polimérico).

El trabajo presentado en esta tesis se centra en la síntesis de diferentes catalizadores soportados en polinorbornenos de adición vinílica y su aplicación en varias reacciones comunes. Está dividido en cinco capítulos. El Capítulo 1 es una introducción general sobre la catálisis soportada y los diferentes tipos de polinorborneno. Los cuatro capítulos restantes describen los resultados obtenidos en la investigación llevada a cabo.

El Capítulo 2 y el Capítulo 3 engloban los resultados obtenidos al soportar Carbenos N-Heterocíclicos en el polímero. El primero de ellos contiene las diferentes rutas intentadas para sintetizar sales de imidazolio soportadas y la aplicación de sus correspondientes carbenos libres como organocatalizadores en algunas transformaciones orgánicas. El segundo de ellos describe el resultado de nuestro trabajo en la síntesis de complejos Pd-NHC soportados y su uso en reacciones comunes como Suzuki o Negishi.

El capítulo 5 contiene el trabajo referido al uso de polinorbornenos de adición vinílica como soporte de complejos de paladio con ligandos diimina. En él se comentan los diferentes enfoques empleados para sus síntesis y los resultados obtenidos cuando estos complejos se emplearon como catalizadores.

En el capítulo 4 se incluye un estudio realizado sobre el comportamiento de varios disolventes en presencia de algunos complejos de paladio y los posibles riesgos existentes. Aunque este apartado no está completamente relacionado con el objetivo principal de esta tesis, algunos resultados observados durante el desarrollo de la investigación central nos hicieron considerar el interés que conllevaría tener un mejor conocimiento de dichos riesgos.

Esta tesis es presentada para la obtención del Doctorado Internacional. Como parte de la formación del doctorado se ha decidido escribirla en inglés. De acuerdo a la regulación vigente en la UVa, se incorpora un breve resumen de los resultados en español con su propia bibliografía así como un índice y unas conclusiones generales.

CAPÍTULO 1

Introducción general.

Una gran mayoría de las reacciones catalizadas tanto por complejos de metales de transición como por organocatalizadores se desarrollan en fase homogénea y presentan algunos inconvenientes que las hacen poco atractivas para su aplicación a escala industrial. La dificultad e incluso imposibilidad de reutilización y los problemas generados en la separación del catalizador de los productos finales hacen que la catálisis homogénea tenga que mejorarse en estos aspectos para hacerla económica y medioambientalmente más benigna. Los esfuerzos en este sentido se enmarcan dentro de los objetivos de la denominada química verde.[i]

Una de las soluciones propuestas a estos inconvenientes se basa en la inmovilización de estos organocatalizadores o catalizadores organometálicos en soportes sólidos de forma que las reacciones se lleven a cabo de manera heterogénea. De esta forma se intenta mantener las características de los catalizadores homogéneos y la selectividad que presentan añadiendo la facilidad de separación y manejo de los catalizadores heterogéneos. A tal efecto se han descrito numerosos catalizadores soportados sobre óxidos de metales, especialmente SiO_2 (amorfa o mesoporosa), nanopartículas magnéticas, arcillas o polímeros. En particular, el trabajo aquí presentado se centra en el uso de polímeros como soporte sólido.

Nuestro grupo tiene experiencia en la síntesis y aplicación de polinorbornenos funcionalizados. Se puede obtener polinorbornenos mediante métodos de polimerización diferentes (ROMP, radicalaria o catiónica y vinílica) que llevan a polímeros con estructuras y propiedades distintas (Esquema I).

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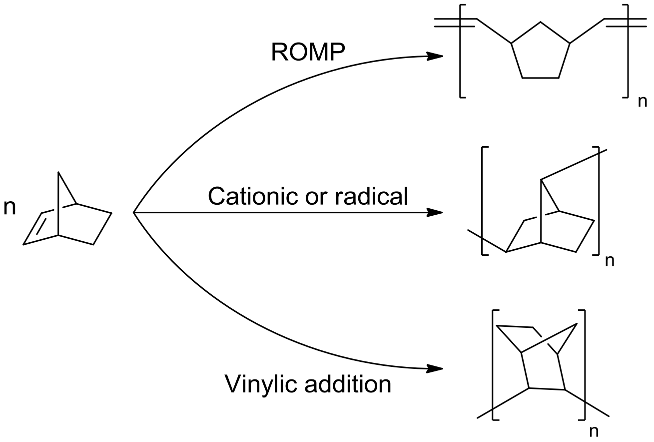
[i] (a) Anastas, P. T.; Warner, J. C. *Green Chemistry: Theory and Practice*; Oxford University Press*:* New York, **1998**. (b) Winterton, N. *Green Chem.* **2001**, *3*, G73-G75. (c) Horvath, I. T.; Anastas, P. T. *Chem. Rev*. **2007**, *107*, 2169-2173.



Esquema I: Mecanismos de polimerización de norborneno.

De entre esos métodos sintéticos el que nos interesa especialmente es la polimerización vinílica ya que permite obtener polímeros con largas cadenas alifáticas y alto peso molecular. Esto hace de este tipo de polinorborneno una macromolécula notablemente inerte de manera que los grupos funcionales que se introducen a través de copolimerizaciones o derivatizaciones sean los únicos centros reactivos. En concreto nuestro grupo de investigación ha obtenido interesantes resultados en la síntesis de polinorbornenos de adición vinílica halogenados útiles para la introducción de otros grupos funcionales por sustitución nucleofílica,[ii] así como en el uso de polinorbornenos estannilados como reactivos reciclables en la reacción de Stille.[iii] Teniendo en cuenta las características de estos polímeros, decidimos estudiar sus propiedades y aplicaciones como soporte de diferentes catalizadores.

[ii] Martínez-Arranz, S.; Albéniz, A. C.; Espinet, P. *Macromolecules*, **2010**, 43, 7482-7487.

[iii] (a) Carrera, N.; Gutiérrez, E.; Benavente, R.; Villavieja, M. M.; Albéniz, A. C.; Espinet, P. *Chem. Eur. J.* **2008**, *14,* 10141-10148; (b) Meana, I.; Albéniz, A. C.; Espinet, P. *Adv. Synth. Catal.*, **2010**, *352*, 2887-2891; c) Martínez-Arranz, S.; Carrera, N.; Albéniz, A. C.; Espinet, P.; Vidal-Moya, A. *Adv. Synth. Catal.* **2012**, *354*, 3551-3560. d) Albéniz, A. C.; Martínez-Arranz, S; Espinet, P.; WO2012/160228 A1, **2012**.

CAPÍTULO 2

Carbenos N-Heterocíclicos soportados en polinorbornenos de adición vinílica. Usos en organocatálisis.

Desde principios de los 90, tras el exitoso avance de Arduengo en su aislamiento,[iv] son numerosos los trabajos publicados sobre la síntesis y la aplicación de NHCs. Aunque la mayoría de ellos se refieren a su uso como ligandos en complejos de metales de transición, en la última década los carbenos han demostrado ser interesantes agentes organocatalizadores en diferentes reacciones como condensaciones, esterificaciones o polimerizaciones por apertura de anillo.[v] En numerosas ocasiones estos NHCs se encuentra en moléculas de síntesis compleja y alto coste. Dado que muchas de estas catálisis se desarrollan en fase homogénea, la pérdida del catalizador tras cada uso es un coste añadido susceptible de ser evitado si se trabajara con un sistema soportado. La investigación desarrollada para este trabajo se ha centrado en concreto en los carbenos de tipo imidazol-2-ilidenos (Figura I).

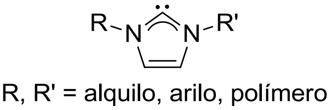


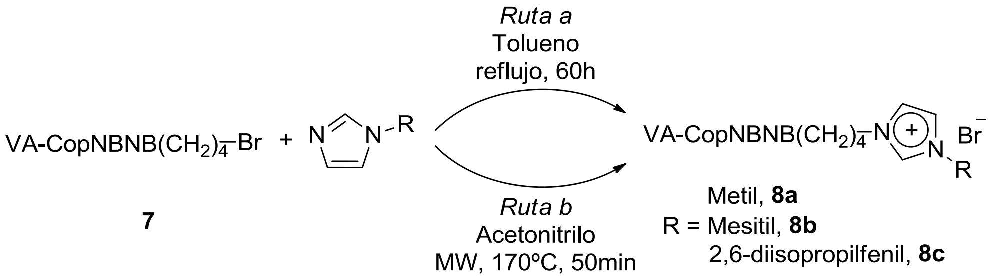
Figura I.

Para lograr obtener NHCs soportados en polinorbornenos de adición vinílica hicimos una primera aproximación en la que buscábamos la polimerización de sales de imidazolio ancladas en una molécula de norborneno. Para esto se sintetizaron diferentes sales de amonio e incluso un complejo de paladio (II) con un ligando NHC. Desafortunadamente, ninguno de estos intentos dio un resultado satisfactorio y se decidió afrontar la cuestión desde un nuevo enfoque.

[iv] (a) Arduengo III, A. J.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361-363. (b) Arduengo III, A. J.; Rasika Dias, H. V.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1992**, *114*, 5530-5534.

[v] (a) Nair, V.; Bindu, S.; Sreekumar, V. *Angew. Chem. Int. Ed.* **2004**, *43*, 5130-5135; *Angew. Chem.* **2004**, *116*, 5240-5245. (b) Enders, D.; Niemeier, O.; Henseler, A. *Chem. Rev.* **2007**, *107*, 5606-5655. (c) Díez-González, S.; Nolan, S. P.; Marion, N. *Angew. Chem. Int. Ed.* **2007**, *46*, 2988-3000; *Angew. Chem.* **2007**, *119*, 3046-3058.

Como se ha mencionado en la introducción general nuestro grupo de investigación ha desarrollado una serie de copolímeros de norborneno con cadenas alifáticas halogenadas susceptibles de participar en diferentes reacciones de sustitución nucleofílica. En vista a los buenos resultados de estas reacciones se decidió usar estos polímeros como soporte para los NHCs. Cuando **7** (VA-CopNBNB(CH_2)$_4$Br) se hizo reaccionar con 1-metilimidazol a reflujo de tolueno durante 60 horas se obtuvo la sal de imidazolio soportada deseada (**8a**, esquema II, *ruta a*). Sin embargo, estas condiciones no sirven para introducir otros imidazoles con sustituyentes aromáticos como 1-mesitilo o 1-(2,6-diisopropil)fenilo. Durante la búsqueda de otras condiciones de reacción se comprobó que cuando la reacción se llevaba a cabo en acetonitrilo bajo radiación microondas a 170 ºC durante 50 minutos se obtenían los productos deseados (**8b** y **8c**, esquema II, *ruta b*). El exceso de imidazol empleado se puede recuperar tras la filtración del polímero por simple evaporación del disolvente. Esto es interesante porque la mayoría de derivados de imidazol comerciales son bastante caros y otros muchos derivados interesantes hay que sintetizarlos mediante una ruta de varias etapas.



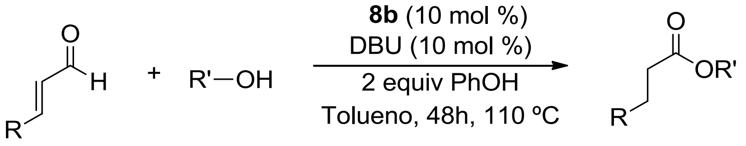
Esquema II.

Entre las sales de imidazolio poliméricas obtenidas sólo **8a** era soluble y pudo ser caracterizada por resonancia magnética nuclear (NMR) en disolución. En cualquier caso todas ellas pudieron ser caracterizadas por NMR en estado sólido y por espectroscopía de infrarrojo. Mientras que la banda de absorción ν(C-Br, st) presente en **7** desaparece completamente, aparecen nuevas bandas correspondientes al enlace C=N. Para conocer el rendimiento de la reacción se hicieron análisis elemental (C,H,N) y se determinó la cantidad de bromo por valoración mercurimétrica del residuo de la combustión de los polímeros en medio básico.

Una vez obtenidas las sales de imidazolio soportadas se decidió comprobar su utilidad como precursoras de carbenos. El método habitual para obtener el carbeno a partir de la sal de imidazolio es mediante el tratamiento de ésta con una base. Dado que la mayoría de los NHCs son inestables al aire y a la humedad, éstos no se han aislado sino que se ha formado el carbeno in situ y se ha hecho reaccionar bien como ligando con un complejo de paladio (ver capítulo 3) o bien como organocatalizador en diferentes transformaciones orgánicas.

La reacción de **8b** con DBU a temperatura ambiente en THF durante 30 minutos generaba el carbeno deseado. Éste fue utilizado como organocatalizador en dos reacciones diferentes.

La primera reacción fue la conversión de aldehídos α,β-insaturados en ésteres saturados (ecuación I).[vi] El polímero **8b** demostró ser muy eficaz en dicha transformación con diferentes sustratos y además se comprobó que podía reciclarse de manera efectiva por al menos 5 ciclos de reacción (Tabla I). Además el tratamiento del carbeno con un ácido permite regenerar la sal de imidazolio de manera que puede almacenarse al aire y reutilizarse posteriormente con buenos resultados.



(I)

R = Ph, nPr
R' = $PhCH_2$, Ph

[vi] Chan, A.; Scheidt, K. A. *Org. Lett.* **2005**, *7*, 905-908.

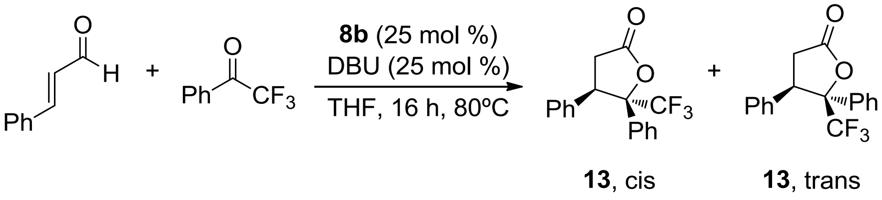
Tabla I. Resultados de la conversión de aldehídos α,β-insaturados en ésteres saturados catalizada por **8b**.[a]

Entrada	Aldehído	Alcohol	Ciclo	Rdto (%)[b]
1	PhCH=CH-C(O)H	$PhCH_2OH$	1	99
2	PhCH=CH-C(O)H	$PhCH_2OH$	2	97
3	PhCH=CH-C(O)H	$PhCH_2OH$	3	94
4	PhCH=CH-C(O)H	$PhCH_2OH$	4	99
5	PhCH=CH-C(O)H	$PhCH_2OH$	5	99
6[c]	PhCH=CH-C(O)H	$PhCH_2OH$	6	99
7	C_3H_7-CH=CH-C(O)H	$PhCH_2OH$	1	80
8	C_3H_7-CH=CH-C(O)H	$PhCH_2OH$	2	82
9	C_3H_7-CH=CH-C(O)H	$PhCH_2OH$	3	92
10	C_3H_7-CH=CH-C(O)H	$PhCH_2OH$	4	87
11	C_3H_7-CH=CH-C(O)H	$PhCH_2OH$	5	85
12	PhCH=CH-C(O)H	PhOH	1	53

a) Condiciones de reacción mostradas en ecuación I. Las reacciones se llevaron a cabo con 5 equiv de alcohol (R'OH). b) Rendimientos determinados por ^{1}H NMR. c) El catalizador se recupera por protonación tras el ciclo 5, se almacena varios días al aire y se reutiliza.

En vista a los buenos resultados obtenidos, se decidió probar la utilidad del polímero como organocatalizador en una reacción diferente como es la síntesis de γ-butirolactonas (ecuación II).[vii] En este caso, los rendimientos que se alcanzaron son comparables a los registrados por Kaskel y colaboradores en la bibliografía con otro organocatalizador soportado, con una relación de diastereoisómeros similar y buenos datos de reciclaje (Tabla II). Después de cinco ciclos de reciclaje, el polímero se dejó sumergido en THF en atmósfera de N_2 durante dos meses. Cuando se repitió la reacción tras ese tiempo se obtuvieron de nuevo los mismos resultados comprobando así la estabilidad del polímero con el tiempo.

[vii] Rose, M.; Notzon, A.; Heitbaum, M.; Nickerl, G.; Paasch, S.; Brunner, E.; Glorius, F.; Kaskel, S. *Chem. Commun*. **2011**, *47*, 4814-4816.



(II)

Tabla II. Resultados en la síntesis de butirolactonas catalizada por **8b**.[a]

Ciclo	**13**, Rdto (%)[b]	dr (*cis*/*trans*)[b]
1	58	2.22
2	56	2.22
3	59	2.17
4	60	2.26
5	61	2.14
6[c]	60	2.15

a) Condiciones de reacción mostradas en ecuación II. Las reacciones se llevaron a cabo con 3 equiv de cetona. b) Rendimientos brutos y relación de diastereoisómeros determinados por ^{19}F NMR. c) El catalizador se conserva en THF bajo una atmósfera de nitrógeno tras el ciclo 5 durante 3 meses y se reutiliza.

En ambas reacciones se llevaron a cabo experimentos de control sin adición de base o del polímero para comprobar que la especie activa en la catálisis es verdaderamente el carbeno generado.

CAPÍTULO 3

Complejos Pd-NHC soportados en polinorbornenos de adición vinílica. Usos en reacciones de acoplamiento C-C.

Existen numerosos ejemplos de complejos de metales de transición que poseen al menos un ligando de tipo NHC y muchos de ellos han sido utilizados como catalizadores en reacciones diversas como pueden ser acoplamientos C-C o C-N, cicloisomerizaciones, metátesis de olefinas, u oxidaciones. Estos carbenos son ligandos σ-dadores estabilizados por dos heteroátomos π-dadores que forman fuertes enlaces con el metal correspondiente. En nuestro caso nos centraremos en los complejos de paladio.[viii]

Existen multitud de trabajos sobre la obtención de ligandos y complejos de este tipo soportados en diferentes polímeros,[ix] pero no se han encontrado en la bibliografía referencias a NHCs soportados en polinorbornenos de adición vinílica. Tan sólo existen unos pocos ejemplos de carbenos soportados en polinorbornenos sintetizados por ROMP, los cuales tienen dobles enlaces en su estructura y, por ello, su estabilidad en condiciones de catálisis es mucho menor.

En primer lugar, para evitar posibles interferencias del bromuro presente en la sal de imidazolio (**8b**) con el complejo de paladio a formar, se decidió llevar a cabo un cambio de anión por otro menos coordinante como es el tetrafluoroborato. El tratamiento de la sal de imidazolio soportada con $NaBF_4$ en una mezcla $MeOH/H_2O$ durante un día condujo a un nuevo polímero con completa sustitución del anión.

Cuando dicho polímero se hacía reaccionar con NBu_4OH se formaba un carbeno que se ha empleado en la síntesis de dos complejos de paladio soportados usando $[PdCl_2(PPh_3)_2]$ y $[Pd(\mu\text{-}Cl)(\eta^3\text{-}C_3H_5)]_2$ como fuente de paladio. El uso de DBU como base resultó ser mucho más efectiva en el segundo caso pues se evitaba la descomposición del

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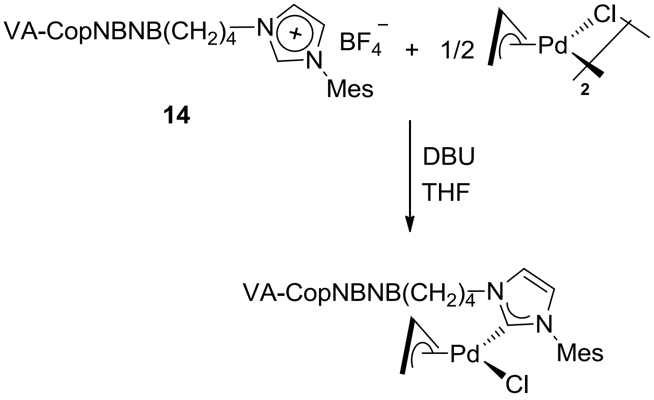
[viii] (a) Kantchev, E. A. B.; O'Brien, C. J.; Organ, M. G. *Angew. Chem. Int. Ed*. **2007**, *46*, 2768-2813. (b) Marion, N.; Nolan, S. P. *Acc. Chem. Res*. **2008**, 41, 1440-1449. (c) Fortman, G. C.; Nolan, S. P. *Chem. Soc. Rev*. **2011**, 40, 5151-5169. (d) Normand, A. T.; Cavell, K. J. En *N-Heterocyclic Carbenes*; Díez-González, S. Ed.; RSC Publishing: Cambridge, **2011**, cap. 9. (e) Valente, C.; Çalimsiz, S.; Hoi, K. H.; Mallik, B.; Sayah, M.; Organ, M. G. *Angew. Chem. Int. Ed*. **2012**, *51*, 3314-3332.

[ix] (a) Uozumi, Y. *Top. Curr. Chem*. **2004**, *242*, 77-112. (b) Albéniz, A. C.; Carrera, N. *Eur. J. Inorg. Chem*. **2011**, 2347-2360. (c) Karimi, B.; Abedi, S.; Zamani, A. En *Palladium-Catalyzed Coupling Reactions;* Molnár, A. Ed.; Wiley-VCH Verlag GmbH & Co. KGaA.: Weinheim, **2013**, cap. 5.

complejo de partida, permitiendo alargar el tiempo de reacción y obtener una mayor incorporación del metal en el polímero (**16d**, ecuación III). Los complejos poliméricos resultantes son insolubles pero pueden ser caracterizados por NMR en estado sólido.



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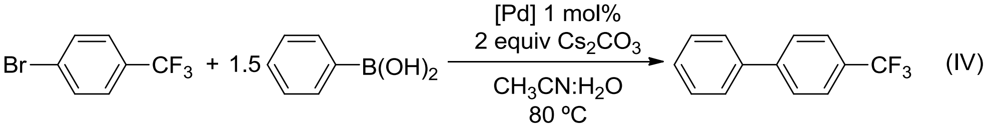
(III)

16d (0.840 mmol Pd/g)

Una vez obtenidos estos complejos de paladio soportados se procedió a estudiar su utilidad como catalizador en la reacción de Suzuki. Para esto se eligió una reacción modelo y se comprobó que los mejores resultados durante dos ciclos de reciclaje los ofrecía el polímero **16d** usando una mezcla acetonitrilo:agua como disolvente (ecuación IV). Durante este estudio se observó que dependiendo del catalizador y el disolvente empleados la cantidad de subproductos de reacción aumentaba notablemente. Esto nos motivó a estudiar el comportamiento de algunos complejos paladio-arilo en presencia de diferentes disolventes (ver capítulo 4). A continuación se estudió la actuación del catalizador **16d** durante cinco ciclos de reciclaje usando espectroscopía de infrarrojo *in situ* para conocer el avance de la reacción a tiempo real. En concreto, se observó la disminución de la intensidad de la banda ν(C-Br, st) a 1012 cm^{-1} del haloareno de partida con el tiempo hasta su desaparición. Esta técnica nos permite detener la reacción cuando no se observa aumento de la conversión y tener una mejor idea del comportamiento del catalizador en los experimentos de reciclaje (Tabla III).



(IV)

Tabla III. Experimentos de reciclaje de **16d** en la reacción de Suzuki[a]

Ciclo	Tiempo (min)	Tiempo de inducción (min)	Rdto. (%)[b]	Pérdida Pd (%)[c]
1	26	5	98.5	3.2
2	35	10	96.4	0.59
3	41	14	96.1	0.37
4	51	18	96.8	0.35
5	60	23	90.3	1.3

a) Condiciones de reacción mostradas en ecuación III. b) Rendimientos brutos determinados por ^{19}F NMR.c) Pérdida de Pd determinada por ICP-MS en el crudo de producto de reacción. Expresado como porcentaje de Pd perdido respecto a la cantidad original añadida.

El catalizador se mantiene activo aunque se observa un aumento de los tiempos de inducción y reacción con cada ciclo. El análisis de pérdida de paladio reveló que un pequeño porcentaje del paladio añadido se libera del polímero en cada ciclo. Para conocer si el proceso tenía lugar de una manera homogénea o heterogénea se llevó a cabo un experimento de filtración en caliente. Este estudió demostró que la reacción continuaba avanzando aun cuando el polímero era retirado del medio y que por lo tanto la catálisis se producía de una manera homogénea. El mismo catalizador se utilizó para otras reacciones de Suzuki con diferentes haloarenos con buenos resultados.

Imágenes de microscopía electrónica de barrido y un microanálisis por espectroscopía de rayos X de dispersión de energías demostraron que tras la primera reacción el complejo de partida desaparece y se forman unos agregados de paladio en la superficie. Aparentemente no se trata de nanopartículas activas en catálisis pues éstas suelen tener un tamaño cercano a los 10 nm y las encontradas en nuestro polímero tienen un tamaño medio de 60 nm. Considerando estos datos junto con los obtenidos en los experimentos de catálisis podemos asumir que el polímero está actuando como un reservorio de especies de paladio homogéneas activas en catálisis. Éstas se liberan lentamente y permiten reutilizar el catalizador durante al menos seis ciclos de reciclaje.

El catalizador **16d** también se usó en la reacción de Negishi con $ZnPh_2$ y 4-bromotrifluorometilbenzeno (ecuación V). Aunque la pérdida de paladio es mayor que en el caso de Suzuki, el polímero mostró ser reciclable al menos durante 3 ciclos.

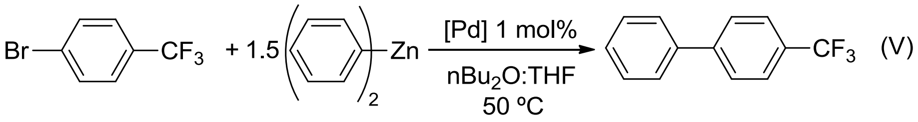


Tabla IV. Experimentos de reciclaje de **16d** en la reacción de Negishi.[a]

Ciclo	Tiempo (h)	Conv. (%)[b]	Rdto. (%)[b]	Pérdida Pd (%)[c]
1	4	97.9	88.5	10.7
2	4.5	97.8	88.3	4.4
3	6	90.8	82.9	2.8

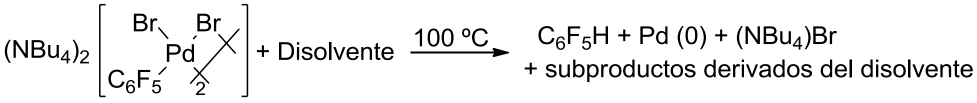
a) Condiciones de reacción mostradas en ecuación V. b) Rendimientos brutos determinados por ^{19}F NMR.c) Pérdida de Pd determinada por ICP-MS en el crudo de productos de reacción. Expresado como porcentaje de Pd perdido respecto a la cantidad original añadida.

CAPÍTULO 4

Reducción de complejos paladio-arilo inducida por el disolvente.

Las reacciones catalizadas por paladio utilizan todo tipo de disolventes. Ciertos disolventes pueden no ser inocentes en la catálisis y llegar a provocar reacciones secundarias que conduzcan a una disminución del rendimiento de la reacción principal. Entre los subproductos es frecuente observar arenos derivados de la reducción de haloarenos y esto es especialmente importante si el catalizador no es muy activo. Aunque en muchos trabajos se comenta la aparición de estos subproductos y se atribuye su formación a la intervención del disolvente, hay muy pocos trabajos que profundicen en estas reacciones y sus causas.

En esta parte del trabajo se presenta un estudio de la reducción de arilos de paladio provocada por diferentes disolventes comunes en catálisis (Esquema III). Concretamente se ha utilizado el complejo **20** como modelo. Se han probado las reacciones en diferentes condiciones como la presencia de oxígeno, ligandos habituales como $AsPh_3$ o aditivos comunes como son las bases.



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Esquema III.

Entre los disolventes analizados destacan el THF, nitrilos, tolueno o agua como aptos para ser usados sin riesgo. Por el contrario las amidas N-alquílicas (DMF, DMA y NMP), cetonas con β-hidrógenos o diéteres como dioxano o DME resultan disolventes peligrosos, capaces de ser fuente de hidruro y responsables de la reducción de los arilos. En general se observa que en presencia de oxígeno y de base el complejo se descompone en mayor medida. También tiene importancia la capacidad coordinante del disolvente (a mayor coordinación, mayor descomposición) así como la presencia de otros ligandos que puedan inhibir la coordinación del disolvente. Este hecho tiene especial relevancia en la denominada "catálisis sin ligandos" donde es presumible que el disolvente entre en la esfera de coordinación del metal.

Se han llevado a cabo experimentos de resonancia magnética con marcaje isotópico y se han identificado los productos derivados de los disolventes por NMR y por GC-MS. Teniendo en cuenta los datos obtenidos de estos análisis se han descrito las posibles rutas de descomposición. En todos los casos donde se observa reducción del complejo, una β-eliminación de hidrógeno del disolvente coordinado es responsable de la formación de una especie Pd-H que tras una eliminación reductora genera el areno final y Pd(0). En presencia de oxígeno parte de ese paladio puede reoxidarse y continuar participando en la formación de subproductos del disolvente.

CAPÍTULO 5

Complejos Pd-diimina soportados en polinorbornenos de adición vinílica.

Los ligandos diimina son conocidos desde hace tiempo, pero fue el descubrimiento de Brookhart y colaboradores acerca de la utilidad de los complejos catiónicos de paladio y níquel con ligandos de tipo α-diimina, como catalizadores en reacciones de polimerización de olefinas no polares de lo que supuso un gran avance en este campo y la revitalización del uso de estos ligandos (Figura II).[x] Los complejos de Brookhart permiten la obtención de polímeros con elevado peso molecular y numerosas ramificaciones, diferentes de los obtenidos con complejos de metales de la izquierda de las series de transición comúnmente usados en los catalizadores de tipo Ziegler-Natta.

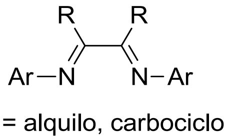

Figura II.

La copolimerización de etileno con olefinas polares (acrilatos, acetatos vinílicos, etc.) es muy interesante y todavía se está trabajando en la búsqueda de un sistema catalítico eficaz que permita controlar la composición de los copolímeros a voluntad manteniendo altos rendimientos. En los últimos años se ha comprobado la importancia que posee el esqueleto de los ligandos α-diimina en estas reacciones. La estabilidad de los complejos metálicos viene muy determinada por la estructura, y la accesibilidad al centro metálico de los monómeros determina su relación de incorporación en el polímero final obtenido, de modo que diiminas muy voluminosas, como son aquellas integradas en la estructura del ciclofano, han llevado a obtener copolímeros con mayor incorporación del monómero

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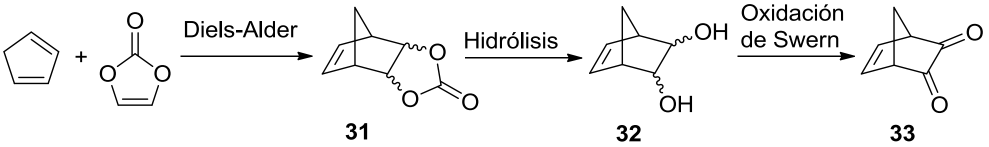
[x] (a) Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc*. **1995**, *117*, 6414-6415. (b) Johnson, L. K.; Mecking, S.; Brookhart, M. *J. Am. Chem. Soc*. **1996**, *118*, 267-268.

polar.[xi] También hay descritos complejos de paladio con ligandos tipo diimina usados en reacciones de acoplamiento cruzado.[xii]

En vista a la utilidad de este tipo de complejos, nuestro trabajo propone la síntesis polímeros en los que se aproveche la estructura del norborneno para incorporar la α-diimina en el esqueleto. No se trata de un ligando en un grupo colgante del polímero, sino incorporado en su propia estructura, aprovechando así las propiedades que este tipo de estructuras proporcionan, entre ellas el mayor volumen que proporciona tener un esqueleto polimérico como sustituyente de la diimina.

Un método habitual para la síntesis de diiminas es la condensación de dicetonas con la anilina deseada. Para obtener un polímero con la dicetona deseada se optó por sintetizar una serie de monómeros precursores en última instancia de la diimina y se comprobó cual ofrecía mejores resultados en su copolimerización con norborneno por vía vinílica. El primero de los monómeros (**31**) se obtiene por una reacción de Diels-Alder entre ciclopentadieno y carbonato de vinileno con un rendimiento del 90%. La hidrólisis del nuevo carbonato en medio básico permitió obtener un diol (**32**) con un buen rendimiento (85%). Por el contrario la oxidación de Swern del diol y su dificultosa purificación resultaron en la obtención de la dicetona (**33**) con un rendimiento del 45% (Esquema IV).



Esquema III.

A continuación se intentó la copolimerización con norborneno (NB) de los tres monómeros siendo **31** el único que daba un copolímero (**35**) con un rendimiento notable. Además era el único copolímero soluble de manera que se podía conocer la incorporación relativa del monómero de interés. Se llevaron a cabo diferentes experimentos para intentar optimizar dicha copolimerización y se comprobó que la adición controlada de norborneno

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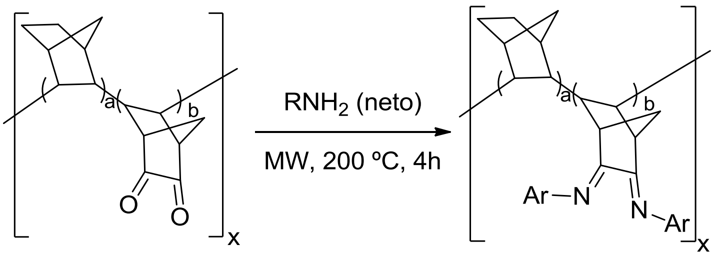
sobre una disolución de **31** y el catalizador de níquel empleado (**3**) permitía obtener buenos rendimientos con una mayor incorporación del carbonato. También se observó que esta polimerización generaba la aparición de dobles enlaces, posiblemente debido a reacciones de β,γ-ruptura de enlace C-C.

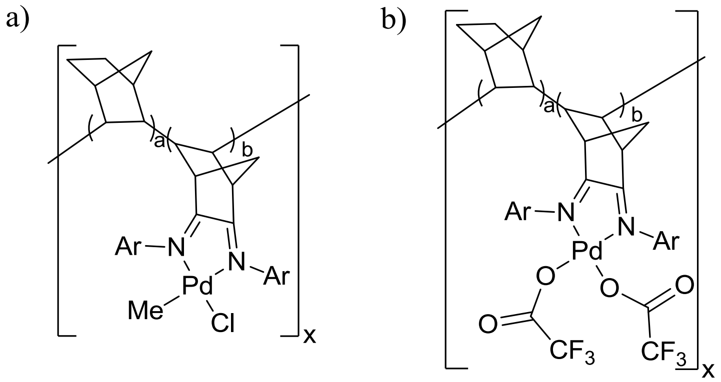
La hidrólisis de **35** y la oxidación de Swern del diol soportado correspondiente (**36b**) condujeron a **37b** con una completa conversión del monómero funcionalizado obteniendo así la dicetona polimérica precursora de la diimina deseada. Para obtener dicha diimina se probaron muchas y diferentes condiciones de reacción, siendo la más efectiva el uso de radiación microondas, obteniendo un polímero (**38**) con una conversión del 45% de la dicetona (ecuación VI).



(VI)

37b Ar = 2,6-diisopropilfenil **38**

El polímero **38** se ha usado como ligando para la síntesis de dos complejos de paladio diferentes. Por un lado se obtuvo un polímero (**39**) con un complejo metilo cloro similar a los descritos por Brookhart (Figura IIIa) y se empleó en la polimerización de etileno y su copolimerización con acrilato de metilo. En el primer caso se obtiene un polietileno con rendimiento bajo (10.9 g/ mmol Pd) pero altamente ramificado (91 cadenas por 1000 carbonos) similar a los obtenidos con catalizadores homogéneos. En el caso de la copolimerización se obtiene una mezcla de polietileno y un copolímero de ambos monómeros muy rico en acrilato de metilo (75%) y con rendimiento muy bajo.



39 **40**

Figure III.

El segundo complejo formado (**40**) se obtiene por reacción de la diimina polimérica con trifluoroacetato de paladio (Figura IIIb). Este complejo soportado se ha usado en la reacción de Suzuki dando buenos resultados de reciclabilidad, algo mejores que los obtenidos con **16d** peo con un comportamiento similar como reservorio de especies homogéneas activas en la catálisis.

CONCLUSIONES GENERALES

Se han sintetizado por primera vez una serie de sales de imidazolio, precursoras de NHCs, soportadas en cadenas de polinorborneno de adición vinílica. Dichas sales se obtienen por sustitución nucleofílica directa entre un polímero halogenado y la molécula de imidazol deseada, sin necesidad de llevar a cabo una polimerización cada vez que se desee modificar las propiedades electrónicas o estéreas del imidazol. Las condiciones necesarias varían en función del sustituyente presente en el imidazol, pero en general el uso de radiación microondas es muy efectivo.

El tratamiento de dichas sales con una base como DBU permite generar los NHCs correspondientes. Estos carbenos han demostrado su utilidad como organocatalizadores en la obtención de ésteres saturados a partir de aldehídos insaturados y en la síntesis de butirolactonas. La actividad catalítica se mantiene durante varios ciclos de reciclaje tras los cuales el catalizador se puede recuperar como sal de imidazolio y almacenar para un uso posterior.

Cuando al carbeno generado por tratamiento de la sal de imidazolio con DBU se le hace reaccionar con un complejo de paladio (II), se obtiene un complejo de tipo Pd-NHC soportado. El complejo tipo [Pd(allyl)Cl(NHC-VA-PNB)] (**16d**) ha probado ser útil en las reacciones de acoplamiento cruzado de Suzuki y Negishi. El estudio de estas catálisis por espectroscopia de infrarrojo *in situ* permite tener un mejor conocimiento de los tiempos de inducción y reacción. Estudios de microscopía de los polímeros y análisis sobre la homogeneidad del sistema nos conducen a decir que tenemos un polímero que actúa como reservorio de especies de paladio homogéneas activas en la catálisis que se liberan lentamente ciclo tras ciclo al medio de reacción. En los casos donde la actividad del catalizador es moderada es posible observar la formación de productos de reducción de haloarenos dependiendo del disolvente empleado (DMF o acetonitrilo).

Se ha estudiado la conveniencia de diferentes disolventes cuando se manejan sistemas con entornos Pd-Ar. Se ha observado que disolventes como el agua, THF, nitrilos o tolueno se pueden usar sin problema. Sin embargo, el uso de amidas como DMF, NMP o DMA, cetonas con hidrógenos en posición β o diéteres como dioxano o DME, puede resultar problemático puesto que el disolvente puede interaccionar con el complejo de paladio. Hemos estudiado los subproductos derivados del disolvente y propuesto diferentes mecanismos para explicar su aparición. En general, tras la coordinación del disolvente con el paladio, una β eliminación de hidrógeno produce la aparición de especies Pd-H que pueden derivar en la eliminación reductora del areno correspondiente. Se ha observado que la presencia de oxígeno o base en el medio puede aumentar la reducción de los complejos y la aparición de subproductos del disolvente. La presencia de algún ligando en el medio disminuye el riesgo de sufrir estas reacciones secundarias debido a la competencia con el disolvente para coordinarse al paladio.

Se ha sintetizado por primera vez un polinorborneno de adición vinílica que contiene grupos α-diimina incorporados en su estructura (**38**). Para esto se ha seguido una ruta de cuatro etapas: i) copolimerización de norborneno con un derivado suyo con grupos carbonato para obtener un polímero de composición conocida (**35**); ii) hidrólisis del carbonato para obtener un diol (**36**); iii) oxidación de Swern para generar la dicetona correspondiente (**37**); iv) condensación de la dicetona con anilina por calentamiento en microondas. El polímero con grupos diimina se ha usado como ligando soportado para sintetizar dos complejos de paladio diferentes. **39** ha resultado ser moderadamente activo en la polimerización de olefinas y con **40** se han obtenidos buenos rendimientos y reciclajes en la reacción de Suzuki, comportándose de manera similar a **16d**.

Appendix

ABBREVIATIONS AND ACRONYMS

General

Ad	Adamantyl
Ar	Aryl
BARF	Anion $[B[3,5\text{-}(CF_3)_2C_6H_3]_4]^-$
Bipy	2,2’-bipyridine
Bu	n-Butyl
COD	1,5-cyclooctadiene
COF	Covalent Organic Framework
Cop	Copolymer
CTA	Chain Transfer Agent
Cy	Cyclohexyl
dr	diastereomeric ratio
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DMA	Dimethylacetamide
DME	Dimethoxyethane
DMF	Dimethylformamide
DMSO	Dimethyl sulfoxide
DVB	Divinylbenzene
E	Electrophile
EDS	Energy Dispersive X-ray Spectroscopy
EOF	Elemental Organic Framework
Et	Ethyl
GC	Gas Cromatography
ICP	Inductively Coupled Plasma
iPr	iso-Propyl
IR	Infrared
L	Monodentate neutral ligand
MA	Methyl acrylate
MAO	Methylaluminoxane

Me	Methyl
M_n	Number average molar weight
MOF	Metal Organic Framework
MS	Mass Spectroscopy
M_w	Weight average molar weight
MW	Microwave
MWNT	Multiwalled Carbon Nanotube
NB	Norbornene
NBO	O-functionalized norbornene
NHC	Nitrogen Heterocyclic Carbene
NMP	N-Methylpyrrolidone
nPr	n-Propyl
Nu	Nucleophile
PCP	Porous Coordination Polymer
PE	Polyethylene
PEG	Poly (ethylene glycol)
Ph	Phenyl
PIB	Polyisobutylene
PNB	Polynorbornene
Pol	Polymer
PS	Polystyrene
ROMP	Ring Opening Metathesis Polymerization
SEM	Scanning Electron Microscopy
tBu	tert-Butyl
TEMPO	2,2,6,6-Tetramethylpiperidine-1-oxyl
THF	Tetrahydrofuran
TOF	Turn Over Frequency
TON	Turn Over Number
UV	Ultraviolet
VA	Vinylic Addition
X	Halogen

Abbreviations used in NMR

br	broad
CP	Cross Polarization
δ	chemical shift
d	doublet
dd	doublet of doublets
ddd	doublet of doublet of doublets
dt	doublet of triplets
J	spin-spin coupling constant
m	multiplet
MAS	Magic Angle Spinning
NMR	Nuclear Magnetic Resonance
ppm	parts per million
s	singlet
sp	septet
t	triplet

Abbreviations used in GC-MS

EI	Electronic Impact
M^+	Molecular ion peak

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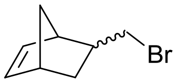
191. Stephenson, T. A.; Morehouse, S. M.; Powell, A. R.; Heffer, J. P.; Wilkinson, G. *J. Chem. Soc*. **1965**, 3632.
192. Branches/1000 C = (CH_3 integral x 2 x 1000)/(total integral x 3). See 161d.

COMPOUNDS INDEX

Chapter 2



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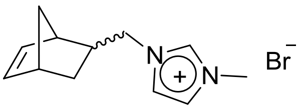
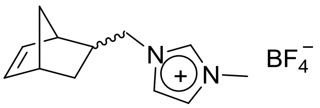


2

$[Ni(C_6F_5)_2(SbPh_3)_2]$

3



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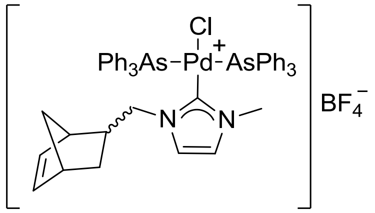

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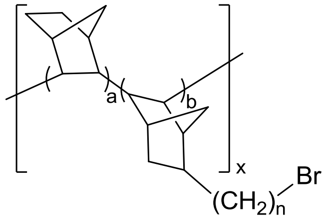
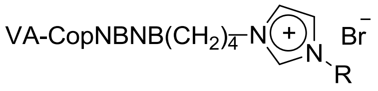
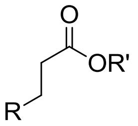


n = 1, **6** = VA-CopNBNB(CH_2)–Br

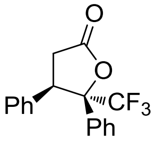
n = 4, **7** = VA-CopNBNB($(CH_2)_4$)–Br



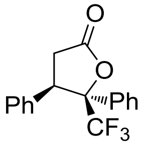
8a: R = Methyl
8b: R = Mesityl
8c: R = 2,6-diisopropylphenyl



9: R = Ph, R' = $PhCH_2$
10: R = Ph, R' = Ph
11: R = nPr, R' = $PhCH_2$
12: R = nPr, R' = Ph

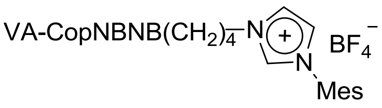


13, cis



13, trans

Chapter 3



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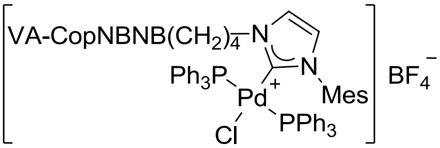

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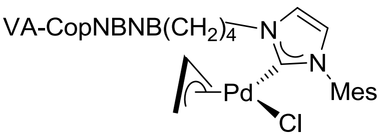
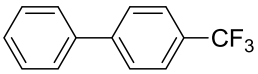


16a (0.546 mmol Pd/g) Black
16b (0.262 mmol Pd/g) Red
16c (0.063 mmol Pd/g) Pale Brown
16d (0.840 mmol Pd/g) Pale Brown



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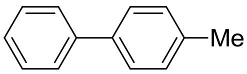

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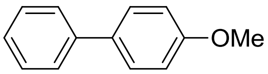

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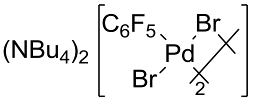
Chapter 4



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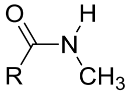
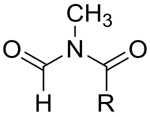
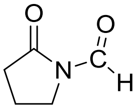


21a: R = H
21b: R = Me



22a: R = H
22b: R = Me



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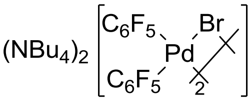

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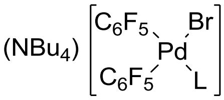

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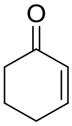

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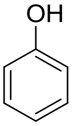

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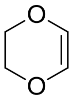

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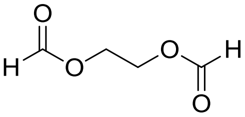

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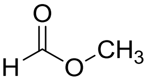

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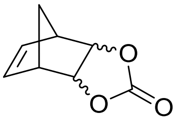
Chapter 5



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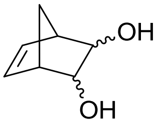

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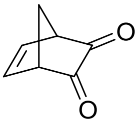

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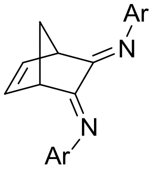
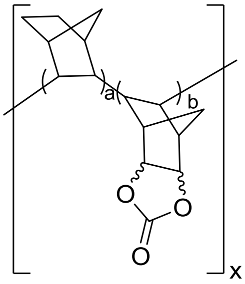


34: Ar =2,6-diisopropylphenyl



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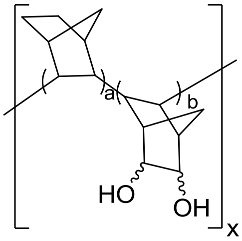

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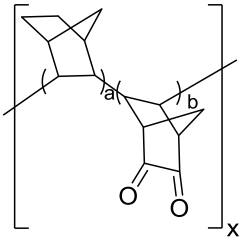

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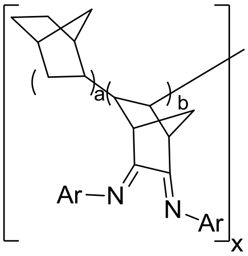

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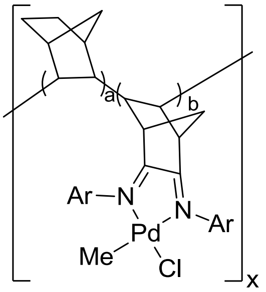

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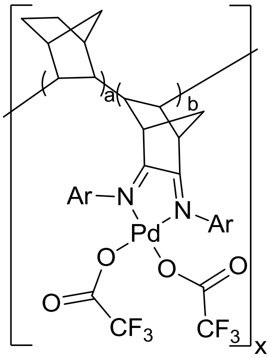

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