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## ARTICLE

## Multifaceted role of silver salts as ligand scavengers and different behavior of nickel and palladium complexes: Beyond halide abstraction

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The reaction of  $[\text{NiArBr}(\text{PPh}_3)_2]$  with  $\text{AgBF}_4$  brings about the abstraction of both the halide and phosphine from the nickel center by silver. When the reaction is carried out in  $\text{CH}_2\text{Cl}_2/\text{toluene}$  a mixture of the cationic aquo derivatives  $[\text{NiAr}(\text{H}_2\text{O})(\text{PPh}_3)_2]\text{BF}_4$  (**2**) and  $[\text{NiAr}(\text{H}_2\text{O})_2(\text{PPh}_3)]\text{BF}_4$  (**3**) is formed, along with  $\text{AgBr}$  and  $[\text{Ag}(\text{PPh}_3)_n]\text{BF}_4$ . When the same reaction is carried out in acetone as solvent, it leads to the completely different complex  $[\text{NiAr}(\kappa^2\text{-O, O-MeC(O)CH}_2\text{C(OH)Me}_2)(\text{PPh}_3)]$  (**5**), bearing a chelating ligand formed by the aldol self-condensation of acetone. Phosphine abstraction by silver is less favorable for the analogous palladium(II) complexes and only occurs if a large excess of  $\text{AgBF}_4$  is used. Thus, silver salts can be safely used as halide scavengers for palladium derivatives. However, the generation of cationic Ni complexes from neutral precursors by halide extraction with a silver salt may produce naked species, different than those expected, and highly reactive in certain media.

### Introduction

Organometallic complexes of palladium and nickel are involved in a plethora of catalytic transformations leading to C-C and C-X bond formation.<sup>1,2</sup> In particular, the need to shift from precious metals to earth-abundant metals in catalysis for sustainability reasons has greatly increased the interest in nickel catalysis.<sup>3</sup> The generation of well-established active species *in situ* from a stable precatalyst is crucial to understand the observed catalytic activity and the mechanism of the reaction.<sup>4</sup> The formation of these active species requires, in most cases, the presence of an additive/co-catalyst whose role in the reaction could be less clear than anticipated. One common activation process of a metal precatalyst is the abstraction of a halide ligand to generate a species with an easily available coordination site. In this way the coordination of one of the reaction substrates can occur and the metal species enters the catalytic cycle. Also, if a neutral precatalyst is used, the halide abstraction leads to a cationic, more electrophilic complex, which favors a subsequent reaction of the coordinated reactant, such as migratory insertion or substrate activation towards nucleophilic attack. Silver salts are very common reagents to induce halide abstraction by formation of insoluble silver halides and they are often used as

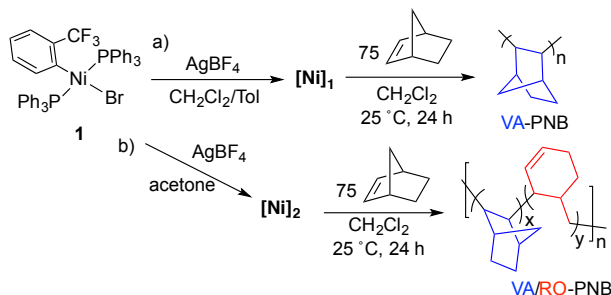
additives for this purpose in many catalytic reactions. They can also play other roles in group 10 metal catalysis,<sup>5</sup> such as terminal oxidant,<sup>6</sup> to promote C-C coupling or C-H activation via generation of intermediate organosilver derivatives,<sup>7</sup> or the formation of bimetallic species.<sup>8</sup> We describe here how silver salts can act as phosphine scavengers, a process concomitant to the halide abstraction when activating a nickel precatalyst bearing these types of ligands.

One of the important processes that use cationic nickel and palladium complexes as catalysts is the addition polymerization of olefins.<sup>9</sup> In these reactions the active catalyst is often formed *in situ* from a neutral precatalyst and a halide scavenger,<sup>10,11</sup> and this species favors the coordination of the olefin and the multiple olefin insertion steps into a M-C bond that lead to polymer growth. In the course of our studies on the vinylic addition polymerization of norbornene using nickel catalysts of the type  $[\text{NiRBr}(\text{PR}_3)_2]$  (R = aryl) we found that we obtained completely different polymers depending on the way the precatalyst was activated by halide abstraction with a silver salt. If the precatalyst was treated with  $\text{AgBF}_4$  in a mixture of  $\text{CH}_2\text{Cl}_2/\text{toluene}$ , the typical vinylic addition polynorbornene was obtained with excellent yields (VA-PNB, Scheme 1, a). However, when acetone was used in the catalyst generation a VA/RO-PNB skeleton was isolated with moderate yields (Scheme 1, b). VA/RO-PNB is a type of polynorbornene that we have disclosed recently and combines the insertion of the norbornene double bond ( $\text{NB}_{\text{VA}}$  units) and the opening of the norbornene ring by a  $\beta$ -carbon elimination ( $\text{NB}_{\text{RO}}$  units) (Scheme 1, b)).<sup>12</sup> Clearly, the reaction conditions during the abstraction of the bromo atom are affecting the structure of

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the cationic organometallic species generated *in situ*, which cannot be the same in both cases. This prompted us to look into it and we found that both the solvent and the silver salt have a deep effect on the resulting nickel species, which can be very different from the anticipated halide-free solvento nickel complex.

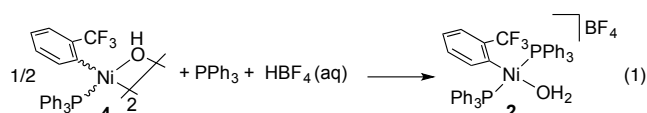


**Scheme 1.** Different behavior of precatalyst **1** upon activation under different conditions in the polymerization of norbornene: a)  $\text{AgBF}_4$  in  $\text{CH}_2\text{Cl}_2/\text{toluene}$ ; b)  $\text{AgBF}_4$  in acetone.

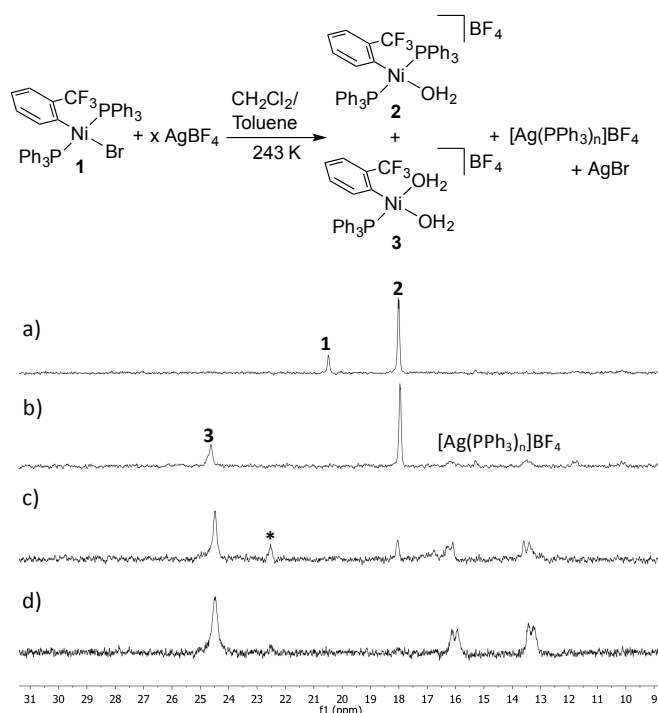
## Results and discussion

The reactions of complex  $[\text{Ni}(o\text{-CF}_3\text{-C}_6\text{H}_4)\text{Br}(\text{PPh}_3)_2]$  (**1**) with  $\text{AgBF}_4$  under different conditions were studied, and the nature of the species formed in solution was ascertained by multinuclear NMR. All the experiments were carried out using dried solvents and Schlenk techniques. However, as can be seen in our results, adventitious water is always present, a fact that is favored by the hygroscopic nature of  $\text{AgBF}_4$ . This is not exclusive of silver tetrafluoroborate, and many other commonly used silver salts are also hygroscopic. First, we tested the abstraction of the bromo atom in complex **1** with  $\text{AgBF}_4$  in a mixture of  $\text{CH}_2\text{Cl}_2/\text{toluene}$  at 243 K. This solvent mixture ensures the complete solubility of both reactants, the silver salt being only slightly soluble in dichloromethane. Figure 1 shows the  $^{31}\text{P}$  NMR spectra for the experiments carried out using different  $\text{AgBF}_4/\mathbf{1}$  mol ratios. A similar comparison of the  $^{19}\text{F}$  NMR spectra can be found in the ESI (Figure S17). The molar percentages of the species detected were calculated by integration of the signals in the  $^{19}\text{F}$  NMR spectra and these are used in the discussion below.

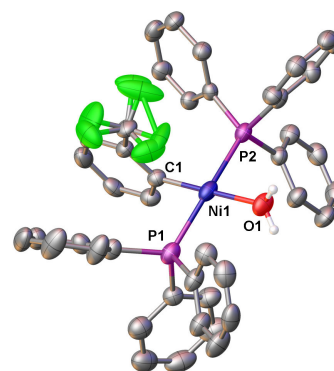
An equimolar amount of  $\text{AgBF}_4$  is not enough to abstract all the bromide from **1** (Figure 1, a). Complex **1** is still visible at 20.5 ppm in the  $^{31}\text{P}$  NMR spectrum (22 mol %). The signal at 18.1 ppm corresponds to  $[\text{Ni}(o\text{-CF}_3\text{-C}_6\text{H}_4)(\text{OH}_2)(\text{PPh}_3)_2](\text{BF}_4)$  (**2**, 78 mol %). Complex **2** was independently prepared following the alternative procedure shown in Eq. 1 (see ESI, section 1.2) and its molecular structure was determined by X-ray crystal diffraction (Figure 2).



The abstraction of the bromo atom is complete using a  $\text{AgBF}_4/\mathbf{1} = 1.25$  mol ratio (Figure 1, b). A mixture of two nickel(II) organometallic species was identified in the  $^{31}\text{P}\{^1\text{H}\}$

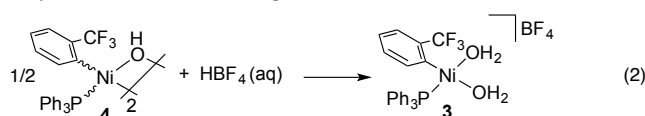


**Figure 1.** Comparative  $^{31}\text{P}\{^1\text{H}\}$  NMR (202.31 MHz, 243 K,  $\text{CD}_2\text{Cl}_2$ ) spectra of the organometallic species generated after reaction of **1** and different amounts of  $\text{AgBF}_4$  in  $\text{CH}_2\text{Cl}_2/\text{toluene}$ : a)  $\text{AgBF}_4/\mathbf{1} = 1$  mol ratio; b)  $\text{AgBF}_4/\mathbf{1} = 1.25$  mol ratio; c)  $\text{AgBF}_4/\mathbf{1} = 1.75$  mol ratio; d)  $\text{AgBF}_4/\mathbf{1} = 2.25$  mol ratio. \*unidentified complex.



**Figure 2.** Molecular structure of complex **2** (ORTEP 30% probability ellipsoids). Hydrogen atoms and  $\text{BF}_4^-$  are omitted for clarity. The  $\text{CF}_3$  group is affected by disorder and the positions of the F atoms were split. Selected distances (Å): Ni1-C1, 1.885(5); Ni1-P1, 2.3231(19); Ni1-P2, 2.3687(17); Ni1-O1, 1.987(4).

NMR spectrum: **2** (55 mol %) and **3** at 24.5 ppm (45 mol %). **3** is a monophosphine complex whose identity was supported by its independent generation *in situ* from the hydroxo complex **4** and  $\text{HBF}_4(\text{aq})$  (Eq. 2 and Figures S23, S24). The cis arrangement of the phosphine and aryl moieties is expected according to the higher trans influence of these ligands when compared to  $\text{H}_2\text{O}$ , as has been observed for other organometallic Ni complexes with O-donor ligands.<sup>13</sup>

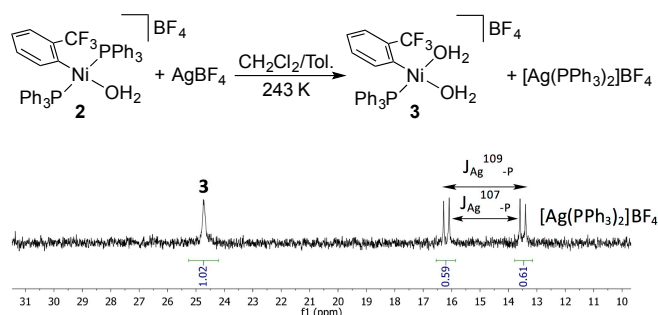


In addition, in the experiment shown in Figure 1, b, several signals at high field were detected in the  $^{31}\text{P}\{^1\text{H}\}$  NMR with no fluorinated aryl ring associated to those species. These signals correspond to the formation of silver-phosphine complexes,  $[\text{Ag}(\text{PPh}_3)_n]\text{BF}_4$  where  $n$  can take the values 2-4, and they can be in equilibrium as reported in the literature.<sup>14</sup> The molar percentage of **3** in solution increased with the amount of  $\text{AgBF}_4$  added. Upon addition of a  $\text{AgBF}_4/\mathbf{1} = 1.75$  mol ratio (Figure 1, c), the molar percentage of **3** raised to 78 %. Another unidentified complex is formed, probably with a structure related to **3**. The complete conversion of **1** to **3** occurs when  $\text{AgBF}_4$  is used in a  $\text{AgBF}_4/\mathbf{1} = 2.25$  mol ratio (Figure 1, d).

Note that we performed all these experiments at low temperature to avoid the decomposition of the cationic complexes generated *in situ*. However, following a similar procedure and a mol ratio  $\text{AgBF}_4/\mathbf{1} = 1.25$ , the same species were detected at room temperature (Figures S18-S19). The molar percentage of the complexes changes at room temperature because **3** decomposes faster than **2**.

Clearly, the role of the silver salt is not only to abstract the bromide from **1**, but some of it is borrowing  $\text{PPh}_3$  from **2**. When isolated complex **2** was mixed with an equimolar amount of  $\text{AgBF}_4$  in a mixture of  $\text{CH}_2\text{Cl}_2$ /toluene the clean formation of complex **3** and  $[\text{Ag}(\text{PPh}_3)_2]\text{BF}_4$  was observed (mol ratio  $\text{Ag-phosphine complex}/\mathbf{3} = 0.5$ , Figure 3). The signal for the silver-phosphine complex appears at 14.75 ppm as a doublet of doublets. The multiplicity is the result of the coupling of  $^{31}\text{P}$  to the two isotopomers present in the silver compound:  $J_{\text{Ag}}^{109-\text{P}} = 584$  Hz and  $J_{\text{Ag}}^{107-\text{P}} = 510$  Hz according to the ratio of  $J_{\text{Ag}}^{109-\text{P}}/J_{\text{Ag}}^{107-\text{P}} = 1.14$ , that is the same ratio of the nuclei gyromagnetic constants. The values of the coupling constants are also consistent with a linear  $[\text{Ag}(\text{PR}_3)_2]^+$  complex vs higher coordination numbers.<sup>14a</sup>

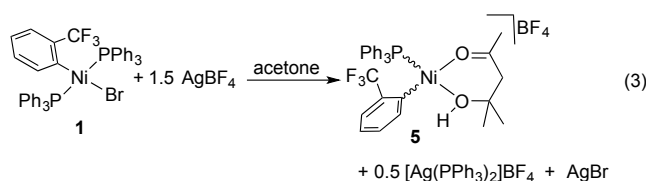
Therefore the silver salt abstracts both halide and phosphine ligands in a sequential but not completely selective way, so a slight excess of halide scavenger, often used to ensure the complete abstraction is not advised with nickel phosphine complexes.



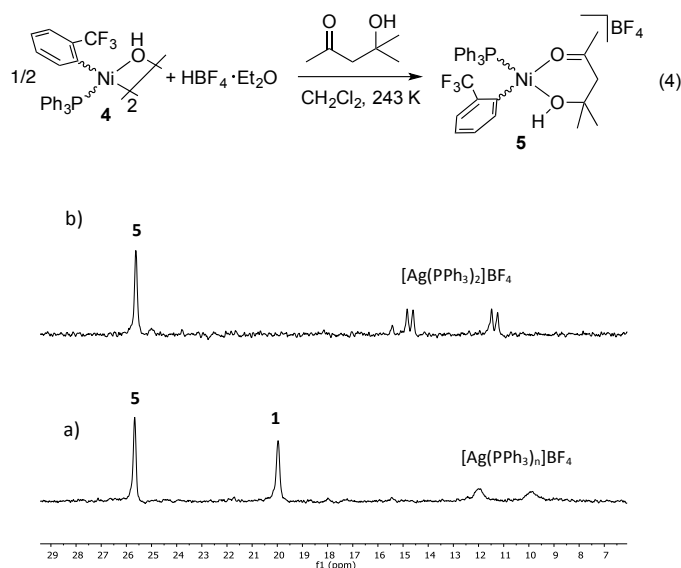
**Figure 3.**  $^{31}\text{P}\{^1\text{H}\}$  NMR (202.31 MHz, 243 K,  $\text{CD}_2\text{Cl}_2$ ) of complex **3** and  $[\text{Ag}(\text{PPh}_3)_2]\text{BF}_4$  generated by mixing **2** and an equimolar amount of  $\text{AgBF}_4$ .

A similar bromide abstraction carried out in acetone produced a completely different outcome. The nickel complex **5** was formed which bears the chelating ligand  $\text{MeCOCH}_2\text{C}(\text{OH})\text{Me}_2$ , the product from the aldol self-condensation of the acetone

(Eq. 3). No free-chelate ligand was detected in the reaction mixture suggesting that the aldol reaction is not catalytic and that it is occurring in the coordination sphere of nickel.



After the generation of the vacant coordination site by the formation of  $\text{AgBr}$ , the acetone coordinates to the nickel cationic intermediate. The acidity of the methyl protons increases, facilitating the deprotonation by a weak base (e.g. water) and the formation of the enolate. Note that to ensure the complete conversion of **1** to **5** it is necessary to use a  $\text{AgBF}_4/\mathbf{1} = 1.5$  mol ratio (Figure 4). The excess of the salt is necessary to remove one phosphine to allow the coordination of a second molecule of acetone, and finally the aldol-condensation. There are very few reports where a nickel or a palladium complex is involved in an aldol reaction.<sup>15</sup> Complex **5** can be generated independently by mixing the hydroxo dimer **4**,  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$  and commercial  $\text{MeCOCH}_2\text{C}(\text{OH})\text{Me}_2$  (Eq. 4). The signals in the  $^{19}\text{F}$  NMR (-58.1 ppm) and  $^{31}\text{P}\{^1\text{H}\}$  NMR (25.4 ppm) spectra match the compound generated from complex **1** and  $\text{AgBF}_4$  in a  $\text{AgBF}_4/\mathbf{1} = 1.5$  mol ratio in acetone.



**Figure 4.**  $^{31}\text{P}\{^1\text{H}\}$  NMR (202.31 MHz, 243 K,  $\text{CDCl}_3$ ) spectra of the complexes generated after reaction of **1** and different amounts of  $\text{AgBF}_4$  in acetone: a)  $\text{AgBF}_4/\mathbf{1} = 1$  mol ratio; b)  $\text{AgBF}_4/\mathbf{1} = 1.5$  mol ratio.

Interestingly **5**, a monophosphine complex with a chelate ligand, is responsible for the formation of the VA/RO-PNB ( $[\text{Ni}]_2$  in Scheme 1). Table 1 collects the polymerization experiments carried out. We reported previously that one necessary condition for the formation of the VA/RO polymer skeleton is that the coordination-insertion of the norbornene is slow, so the competing opening of the norbornene ring is favored.<sup>12</sup> This scenario occurs in the presence of additional

ligands, which compete with norbornene for coordination to Ni, in this case the chelating O-donor ligand. This is formed in acetone but it is not present when the halogen abstraction is carried out in  $\text{CH}_2\text{Cl}_2$ /toluene leading to the conventional VA-PNB (Scheme 1 and entries 1 and 2, Table 1). Because we are also generating a silver complex in solution, we tested the activity of  $[\text{Ag}(\text{PPh}_3)_2]\text{BF}_4$  in the polymerization of norbornene (Table 1, entry 4, and section 1.6, ESI). Neither a polymer nor oligomers were detected. The VA-polymerization of NB is hampered if stronger coordinating ligands are present in the coordination sphere of Ni. A complex analogous to **5** with a more coordinating O, S-donor chelating ligand,  $[\text{Ni}(o\text{-CF}_3\text{-C}_6\text{H}_4)(\text{MeCOCH}_2\text{C}(\text{SMe})\text{Me}_2)(\text{PPh}_3)]\text{BF}_4$  (**6**), was independently synthesized and fully characterized. Its molecular structure shows the trans disposition of the  $\text{PPh}_3$  and the SMe group (Figure S56, ESI). **6** was tested in the VA-polymerization of norbornene but it is inefficient and only the dimerization of norbornene was observed (Table 1, entry 3 and section 1.6, ESI).<sup>12</sup> Thus, the nature of complex **5** is crucial to explain the catalytic results observed, and acetone is not an innocent solvent to generate a cationic nickel solvento complexes.

Table 1. Activity of Ni and Ag complexes in the polymerization of norbornene (NB)<sup>a</sup>

Entry	Complex	VA-PNB (% yield) <sup>b</sup>	VA/RO-PNB (% yield) <sup>b</sup>
1	<b>2/3</b> <sup>c</sup>	91	–
2	<b>5</b> <sup>d</sup>	–	57
3	<b>6</b> <sup>e</sup>	–	–
4	$\text{AgBF}_4/\text{PPh}_3$ <sup>f</sup>	–	–

a) Reactions carried out at 25 °C for 24 h using a ratio NB:catalyst = 75:1 in  $\text{CH}_2\text{Cl}_2$ . b) Polymer structure shown in Scheme 1. c) Generated in situ by reaction of **1** and  $\text{AgBF}_4$  in  $\text{CH}_2\text{Cl}_2$ /toluene ( $\text{AgBF}_4/\mathbf{1} = 1.25$  mol ratio), filtration and evaporation of the solvent. d) Generated in situ by reaction of **1** and  $\text{AgBF}_4$  in acetone ( $\text{AgBF}_4/\mathbf{1} = 1.6$  mol ratio), filtration and evaporation of the solvent. e) Only the dimerization of norbornene was observed. f) Ratio NB: $\text{AgBF}_4$ : $\text{PPh}_3 = 75:1:2$ .

Since the use of silver salts is also widespread in palladium chemistry, it is worth testing the ability of silver as phosphine scavenger when using Pd(II) complexes and to compare this behavior to the analogous Ni(II) species. The parent palladium complex  $[\text{Pd}(o\text{-CF}_3\text{-C}_6\text{H}_4)\text{Br}(\text{PPh}_3)_2]$  (**7**) shows some differences in its reactivity with the silver salt in  $\text{CH}_2\text{Cl}_2$ /toluene when compared to Ni(II). In the same way observed for complex **1** (Figure 1, a) equimolar amounts of  $\text{AgBF}_4$  are not enough to completely eliminate the bromide from the coordination sphere of Pd and the initial complex **7** is still visible in the mixture in a 21 mol % (Figure 5, a) (for  $^{19}\text{F}$  NMR spectra see Figure S31). The other species present in the mixture is the aquo complex **8**. This complex was isolated and fully characterized (see ESI). In contrast to Ni, an excess of  $\text{AgBF}_4$  (up to 2 equiv.) can be used to abstract the bromide from **7** without significant elimination of the phosphine (Figure 5). When the amount of  $\text{AgBF}_4$  increases to a  $\text{AgBF}_4/\mathbf{7} = 2.5$  mol ratio the di-aquo complex **9** starts to be visible (Figure 5, c) in 11.5 mol % by integration in the  $^{19}\text{F}$  NMR spectrum (see Figure S37, ESI).

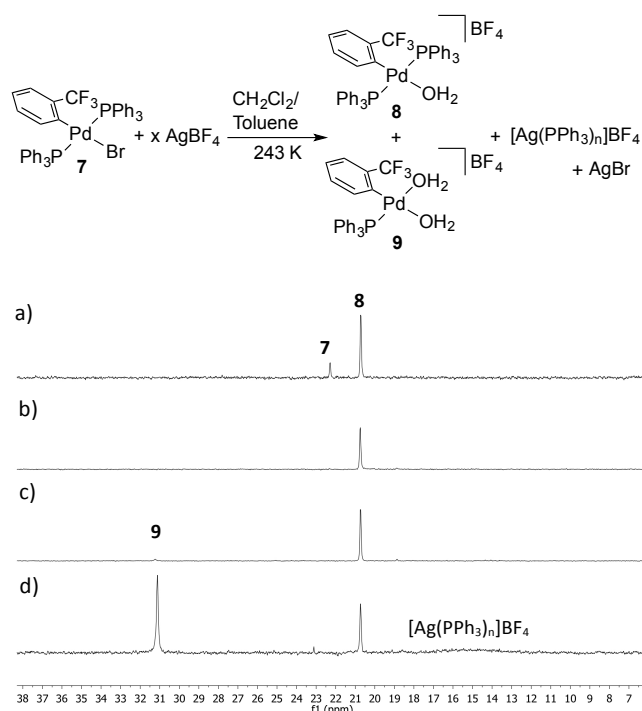
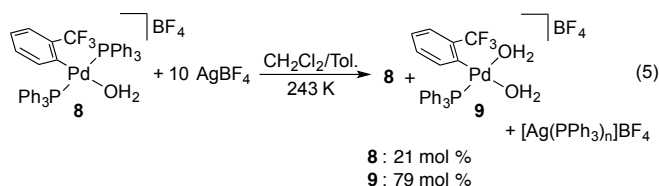


Figure 5. Comparative  $^{31}\text{P}\{^1\text{H}\}$  NMR (202.457 MHz, 243 K,  $\text{CD}_2\text{Cl}_2$ ) spectra of the organometallic species generated from complex **7** and different amounts of  $\text{AgBF}_4$  in  $\text{CH}_2\text{Cl}_2$ /toluene: a)  $\text{AgBF}_4/\mathbf{7} = 1$  mol ratio; b)  $\text{AgBF}_4/\mathbf{7} = 1.25$  mol ratio; c)  $\text{AgBF}_4/\mathbf{7} = 2.5$  mol ratio; d)  $\text{AgBF}_4/\mathbf{7} = 10$  mol ratio.

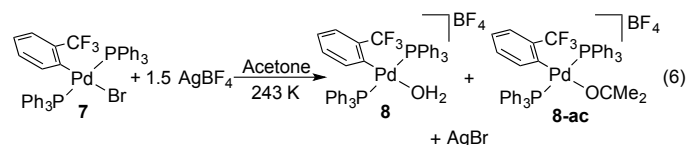
Only considerably increasing the amount of  $\text{AgBF}_4$  to a  $\text{AgBF}_4/\mathbf{7} = 10$  mol ratio, **9** is detected as the major species in the mixture (83 mol %, see Figure 5, d) along with complex **8** (17 mol %). The di-aquo complex **9** was also synthesized and characterized independently adding  $\text{HBF}_4$  (aq) to the hydroxo dimer  $[\text{Pd}(o\text{-CF}_3\text{-C}_6\text{H}_4)(\mu\text{-OH})(\text{PPh}_3)_2]$  (**10**), an analogous reaction to that shown in Eq. 2 (see ESI, section 1.5.3). Furthermore, when isolated complex **8** was mixed with  $\text{AgBF}_4$  in a  $\text{AgBF}_4/\mathbf{8} = 10$  mol ratio (Eq. 5), the mixture detected matches with the one generated in Figure 5 (d). If the same reaction is carried out at room temperature, a similar mixture is detected with a little increase of the mol % of **9** (94 % at 298 K vs 83 % at 243 K, Figures S43–S45, ESI).



The distinct behavior of both metals against the silver salt can be explained in terms of hard and soft bases and acids. The coordination equilibrium of the soft  $\text{PPh}_3$  base is shifted to Ag(I) rather than to the small harder nickel center in cationic complex **2** (Figure 3). In contrast, the Pd(II) center in complex **8** is softer than its 3d metal counterpart and probably a stronger Lewis acid than Ag(I) making the coordination of the phosphine to palladium favorable. The trap of the phosphine by the silver salt is detected for Ni even when  $\text{AgBF}_4$  is added in a  $\text{AgBF}_4/\text{Ni} = 1.25$  mol ratio (Figure 1, b), whereas a larger

excess of silver is necessary to shift the equilibrium and detect monophosphine species for Pd (Figure 5, d).

No self-condensation of acetone was observed for palladium. When the bromide abstraction in **7** was carried out with AgBF<sub>4</sub> in acetone, only the solvento complexes **8** and **8-ac**, with coordinated water and acetone respectively, were detected (Eq. 6, Figures S49-S51, ESI). The same mixture of complexes was detected when complex **8** was dissolved in acetone (Figures S52-S53, ESI).



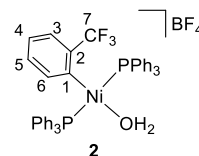
## Conclusions

A seemingly simple abstraction of a halide from the coordination sphere of a Ni phosphino complex with a Ag(I) salt occurs with concomitant phosphine abstraction by silver. Starting from the common [NiXAr(PPh<sub>3</sub>)<sub>2</sub>] complexes, cationic monophosphino aquo complexes are readily formed in non-coordinating solvents. Acetone is a risky solvent in this reaction since, in addition to phosphine abstraction, the Ni-mediated aldol self-condensation of the solvent leads to a κ<sup>2</sup>-O,O chelating ligand bound to Ni(II) and therefore a completely different species from the expected solvento complex. Phosphine abstraction is less important for palladium phosphino complexes and silver salts can be safely used as halide scavengers in this case, even in moderate excess. This reflects the softer nature of Pd(II) when compared to Ni(II). For the latter, the coordination of PPh<sub>3</sub> to the soft Ag(I) is favored.

## Experimental

**Synthesis of [Ni(o-CF<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>)(OH<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>](BF<sub>4</sub>) (**2**).** In a Schlenk tube the dimeric complex **4** (75 mg, 0.0776 mmol) and PPh<sub>3</sub> (41 mg, 0.156 mmol) were placed under N<sub>2</sub>. The mixture was dissolved in 5 mL of dry CH<sub>2</sub>Cl<sub>2</sub> and the orange solution was cooled to 243 K in an acetone bath for 10 min until constant temperature. Subsequently, a solution of HBF<sub>4(aq)</sub> (25 μL, 0.194 mmol; 48 % wt) was added. Immediately, the solution turned yellow and it was stirred for 20 min at 243 K. After this time, the yellow solution was evaporated to dryness. The residue was redissolved in 4 mL of CH<sub>2</sub>Cl<sub>2</sub> and 12 mL of dry hexane were added inducing the formation of a yellow solid. The solid was decanted and the supernatant solution was transferred via cannula. The same process was repeated twice. The yellow solid was dried in vacuo (0.1 g, 77% yield). <sup>1</sup>H NMR (499.73 MHz, δ, 243 K, CD<sub>2</sub>Cl<sub>2</sub>): 7.52 (m, 6H, H<sub>para</sub>, Ph PPh<sub>3</sub>), 7.39 (m, 12H, H<sub>meta</sub> Ph PPh<sub>3</sub>), 7.29 (m, 12H, H<sub>ortho</sub>, Ph PPh<sub>3</sub>), 7.21 (d, 1H, J = 7.6, 1H, H<sup>6</sup>), 6.70 (vt, J = 7.6, 1H, H<sup>4</sup>), 6.61 (d, J = 7.6, 1H, H<sup>3</sup>), 6.58 (vt, J = 7.6, 1H, H<sup>5</sup>), 2.76 (s, 2H, OH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (125.67 MHz, δ, 243 K, CD<sub>2</sub>Cl<sub>2</sub>): 139.4 (t, J<sub>C-P</sub> = 35 Hz, C<sup>1</sup>), 136.3 (C<sup>6</sup>), 134.6 (q, <sup>2</sup>J<sub>C-F</sub> = 29 Hz, C<sup>2</sup>), 134 (C<sub>ortho</sub>, Ph PPh<sub>3</sub>), 129.1 (C<sub>meta</sub>, Ph

PPh<sub>3</sub>), 131.3 (C<sub>para</sub> Ph PPh<sub>3</sub>), 126.4 (vt, J<sub>C-P</sub> = 22 Hz, C<sup>ipso</sup> PPh<sub>3</sub>), 128.7 (C<sup>5</sup>), 128.5 (q, <sup>1</sup>J<sub>C-F</sub> = 276 Hz, C<sup>7</sup>), 128.2 (C<sup>3</sup>), 123.10 (C<sup>4</sup>). <sup>19</sup>F NMR (470.17 MHz, δ, 243 K, CD<sub>2</sub>Cl<sub>2</sub>): -59.7 (t, J<sub>P-F</sub> = 6 Hz, CF<sub>3</sub>), -150.7 (BF<sub>4</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (202.31 MHz, δ, 243 K, CD<sub>2</sub>Cl<sub>2</sub>): 18 (q, J<sub>P-F</sub> = 6 Hz, 2P). Analysis calc. for C<sub>43</sub>H<sub>36</sub>BF<sub>7</sub>OP<sub>2</sub>Ni: C, 61.98; H, 4.35; found: C, 61.81; H, 4.42.



### Generation of [Ni(o-CF<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>)(OH<sub>2</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>](BF<sub>4</sub>) (**3**).

**Method A.** AgBF<sub>4</sub> (5.7 mg, 0.0293 mmol) was placed in a vial under N<sub>2</sub>. The solid was dissolved in 2 mL of toluene and the solution was cooled in an acetone bath at 243 K for 10 min to ensure a constant temperature. In another vial complex **2** (24.4 mg, 0.0293 mmol) was dissolved in 2 mL of CH<sub>2</sub>Cl<sub>2</sub> and cooled at 243 K for 10 min. The yellow solution of **2** was added to the solution of AgBF<sub>4</sub> and it was stirred for 10 min. After this time, the solution was evaporated to dryness. The residue was redissolved in cold CD<sub>2</sub>Cl<sub>2</sub>. The mixture was checked by NMR spectroscopy. It contains **3** and [Ag(PPh<sub>3</sub>)<sub>2</sub>]BF<sub>4</sub>. (Figures S20-S22, ESI).

**Method B.** In a Schlenk tube complex **4** (20 mg, 0.0207 mmol) was dissolved in 2 mL of CH<sub>2</sub>Cl<sub>2</sub>. The solution was cooled in an acetone bath at 243 K for 10 min. HBF<sub>4</sub> (aq) (8 μL, 0.0633 mmol; 48 wt. %) was added to the mixture and the orange solution was stirred for 10 min at 243 K. After this time, the orange solution was evaporated to dryness and the residue was redissolved in 0.6 mL of dry and cooled CD<sub>2</sub>Cl<sub>2</sub>. The solution of **3** was analyzed by NMR spectroscopy (Figures S23, S24, ESI).

**3:** <sup>1</sup>H NMR (499.73 MHz, δ, CD<sub>2</sub>Cl<sub>2</sub>, 243 K): 7.53–6.8 (H<sup>arom</sup>), 3.3 (br, H<sub>2</sub>O). <sup>19</sup>F NMR (470.17 MHz, δ, CD<sub>2</sub>Cl<sub>2</sub>, 243 K): -58.8 (br, CF<sub>3</sub>), -150.7 (BF<sub>4</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (202.31 MHz, δ, CD<sub>2</sub>Cl<sub>2</sub>, 243 K): 25.2 (bs).

[Ag(PPh<sub>3</sub>)<sub>2</sub>](BF<sub>4</sub>): <sup>31</sup>P{<sup>1</sup>H} NMR (202.31 MHz, δ, CDCl<sub>3</sub>, 243 K): 13 (dd, J<sub>Ag<sup>109</sup>-P</sub> = 584 Hz; J<sub>Ag<sup>107</sup>-P</sub> = 510 Hz).

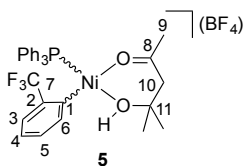
### Generation of [Ni(o-CF<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>)(κ<sup>2</sup>-O, O-MeC(O)CH<sub>2</sub>C(OH)Me<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>](BF<sub>4</sub>) (**5**).

**Method A.** In an oven-dried vial AgBF<sub>4</sub> (8 mg, 0.0408 mmol) was dissolved in 3 mL of dry acetone under N<sub>2</sub>. The solution was cooled to 243 K for 10 min until constant temperature. Complex **1** (20 mg, 0.0247 mmol) was added to the mixture and instantly a white solid (AgBr) appeared. The suspension was stirred for 15 min at 243 K. The white solid was removed employing a 0.2 μm PTFE filter and the orange solution was transferred to an oven dried and cooled Schlenk tube. The solution was evaporated to dryness. The residue was redissolved in 0.6 mL of CDCl<sub>3</sub> and the solution was checked by NMR spectroscopy. The mixture contained **5** as well as [Ag(PPh<sub>3</sub>)<sub>2</sub>](BF<sub>4</sub>) in a molar ratio 1:0.5 (Figures S69-S72, ESI).

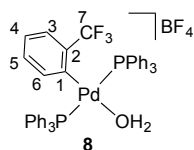
**Method B.** In a Schlenk tube, complex **4** (20 mg, 0.0213 mmol) was dissolved in 3 mL of dry CH<sub>2</sub>Cl<sub>2</sub> under N<sub>2</sub>. The solution was cooled in an acetone bath at 243 K for 10 min until constant

temperature. The ligand MeCOCH<sub>2</sub>C(OH)Me<sub>2</sub> (27 μL, 0.216 mmol) and HBF<sub>4</sub>·Et<sub>2</sub>O (9 μL, 0.066 mmol) were added. The orange solution was stirred at 243 K for 10 min. After this time, the solution was evaporated to dryness and the orange residue was redissolved in 0.6 mL of dry CDCl<sub>3</sub> at 243 K. The solution was checked by NMR spectroscopy showing the formation of **5** as major species and free ligand (Figures S27–S29, ESI).

**5**: <sup>1</sup>H NMR (499.73 MHz, δ, CDCl<sub>3</sub>, 243 K): 7.88 (d, 1H, <sup>1</sup>J<sub>H-H</sub> = 6.9 Hz, H<sup>6</sup>), 7.5–7.12 (m, PPh<sub>3</sub>), 6.9–6.7 (m, 3H, H<sup>5</sup>, H<sup>4</sup>, H<sup>3</sup>), 5.05 (bs, 1H, OH), 3.22 (d, 1H, <sup>1</sup>J<sub>H-H</sub> = 19.7 Hz, H<sup>10</sup>), 2.73 (d, 1H, <sup>1</sup>J<sub>H-H</sub> = 19.7 Hz, H<sup>10</sup>), 1.75 (s, 3H, H<sup>9</sup>), 1.65 (s, 3H, CH<sub>3</sub>), 1.29 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (125.758 MHz, δ, CDCl<sub>3</sub>, 233 K): 222.2 (C<sup>8</sup>), 137.07 (C<sup>6</sup>), 133.9, 129.7, 127.7 (PPh<sub>3</sub>), 128.5, 126.7, 124.1 (C<sup>5</sup>, C<sup>4</sup>, C<sup>3</sup>), 71.6 (C<sup>11</sup>), 51.35 (C<sup>10</sup>), 32.13 (C<sup>9</sup>), 27.8 (CH<sub>3</sub>), 27.17 (CH<sub>3</sub>). <sup>19</sup>F NMR (470.17 MHz, δ, CDCl<sub>3</sub>, 243 K): -58.1 (d, J<sub>P-F</sub> = 6 Hz, CF<sub>3</sub>), -150.2 (BF<sub>4</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (202.31 MHz, δ, CDCl<sub>3</sub>, 243 K): 25.4 (bs).



**Synthesis of [Pd(*o*-CF<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>)(OH<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>](BF<sub>4</sub>) (**8**).** In an oven-dried vial AgBF<sub>4</sub> (51 mg, 0.262 mmol) was placed under N<sub>2</sub>. The solid was dissolved in 5 mL of dry toluene. In a Schlenk tube complex **7** (180 mg, 0.21 mmol) was dissolved in 3 mL of CH<sub>2</sub>Cl<sub>2</sub>. The vial and the Schlenk tube were cooled to 243 K during 10 min to ensure a constant temperature. The solution of AgBF<sub>4</sub> was transferred to the yellow solution of complex **6**. Immediately, a white solid (AgBr) appeared and the suspension was stirred for 15 min at 243 K. After this time, the solvent was evaporated to dryness. The residue was suspended in 2 mL of dry CH<sub>2</sub>Cl<sub>2</sub> and the solution was transferred via cannula. *n*-Hexane (10 mL) was added to the clear yellow solution inducing the formation of a white solid. The solid was decanted and the supernatant solution was transferred via cannula. The same process was repeated twice. The white solid was dried in vacuo (0.155 g, 84.2% yield). <sup>1</sup>H NMR (499.73 MHz, δ, 243 K, CD<sub>2</sub>Cl<sub>2</sub>): 7.5 (m, 6H, H<sub>para</sub>, Ph PPh<sub>3</sub>), 7.38 (m, 12H, H<sub>meta</sub>/H<sub>ortho</sub> Ph PPh<sub>3</sub>), 7.25 (m, 12H, H<sub>meta</sub>/H<sub>ortho</sub> Ph PPh<sub>3</sub>), 7.18 (d, J = 7.6, 1H, H<sup>6</sup>), 6.83 (vd, J = 7.6, 1H, H<sup>3</sup>), 6.8 (vt, J = 7.6, 1H, H<sup>4</sup>), 6.65 (t, J = 7.6, 1H, H<sup>5</sup>), 3.33 (s, 2H, OH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (125.67 MHz, δ, 243 K, CD<sub>2</sub>Cl<sub>2</sub>): 142.8 (C<sup>1</sup>), 136.1 (C<sup>6</sup>), 134.2 (q, <sup>2</sup>J<sub>C-F</sub> = 29 Hz, C<sup>2</sup>), 133.8, 129 (C<sub>meta</sub>, C<sub>ortho</sub> Ph PPh<sub>3</sub>), 131.3 (C<sub>para</sub> Ph PPh<sub>3</sub>), 127.5 (vt, J<sub>C-P</sub> = 23 Hz, C<sup>ipso</sup> PPh<sub>3</sub>), 130.3 (C<sup>5</sup>), 126.3 (q, <sup>1</sup>J<sub>C-F</sub> = 273 Hz, C<sup>7</sup>), 128.8 (C<sup>3</sup>), 123.7 (C<sup>4</sup>). <sup>19</sup>F NMR (470.17 MHz, δ, 243 K, CD<sub>2</sub>Cl<sub>2</sub>): -58.9 (t, J<sub>P-F</sub> = 6 Hz, CF<sub>3</sub>), -150.8 (BF<sub>4</sub><sup>-</sup>). <sup>31</sup>P{<sup>1</sup>H} NMR (202.31 MHz, δ, 243 K, CD<sub>2</sub>Cl<sub>2</sub>): 21.2 (q, J<sub>P-F</sub> = 6 Hz). Analysis calc. for C<sub>43</sub>H<sub>36</sub>BF<sub>4</sub>OP<sub>2</sub>Pd: C, 58.63; H, 4.12; found: C, 58.90; H, 4.25.



## Data availability

Data supporting this article have been uploaded as ESI.

## Author Contributions

I.P.O. conducted the investigation under A. C. A. supervision. All authors contributed to the conceptualization of the project and the writing, review and editing of the manuscript.

## Conflicts of interest

There are no conflicts to declare.

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