α-Substituted Benzylic Complexes of Palladium(II) as Precursors of Palladium Hydrides.

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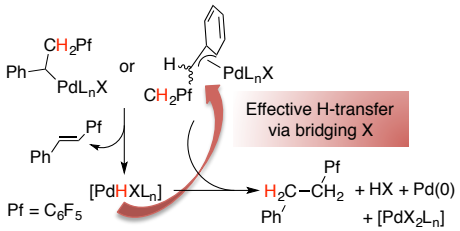
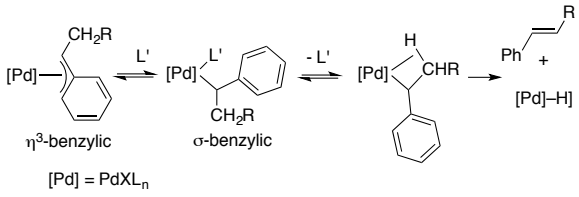
ABSTRACT: The adoption of a pseudoallylic (η^3) form makes palladium benzylic derivatives a class of stabilized palladium alkyls that can undergo β-H elimination reactions in a more controlled way. α-(Pentafluorophenylmethyl)benzyl palladium complexes have been studied and they decompose by β-H elimination to give palladium hydrides that, depending on the auxiliary ligands can: a) transmetalate to another palladium atom and, by reductive elimination, give hydrogenated products; this process is favored for a combination of bridging ligands (i.e halogens) and low coordinating ligands. b) Be used as a hydride source and get trapped by a diene to give palladium allylic derivatives. The presence of carbon monoxide does not induce a β-H elimination reactions and only CO insertion into the Pd-benzyl bond to give acyl derivatives is observed.



INTRODUCTION

The stabilization of palladium alkyls usually requires the absence of hydrogens in the beta position in order to avoid a β-H elimination process that transforms the complex in a palladium hydride and an olefin. Thus, alkyl groups bearing a trisubstituted carbon, methyl, or conformationally rigid cyclic derivatives (often metalacycles) are among the most common organometallic palladium alkyl complexes. These groups are impervious to β-H elimination but they are also reluctant to undergo other types of reactions involved in useful transformations such as reductive elimination with another organic fragment.[1] Benzylic palladium complexes are weakly stabilized alkyls due to the possibility of coordination of the aryl ring in a pseudoallylic (η^3) form (Scheme 1). Even when α-benzylic substitutents (R) provide hydrogens in a beta position, the η^3 bonding mode makes the attainment of a cis Pd–β-H arrangement difficult, preventing elimination, and stabilizing the hydrocarbyl moiety.[2] Yet, this group is reactive enough to participate in other bond-forming processes and benzyl palladium derivatives are involved in many catalytic reactions that use styrene or benzylic halides as substrates.[3,4] β-H elimination is a competing reaction and it would be interesting to find out how efficiently this process can destroy a Pd-benzyl intermediate and, since it requires the return to the σ-benzylic form, how it will be influenced by the ligands present in solution and in the metal coordination sphere (Scheme 1). We have previously prepared a variety of benzylic palladium complexes with different ligands and an α-methylpenta-fluorophenyl substituent (Scheme 2).[5] These derivatives eventually decompose by β-H elimination at very different rates and they are suitable model complexes to analyze this competing reaction.

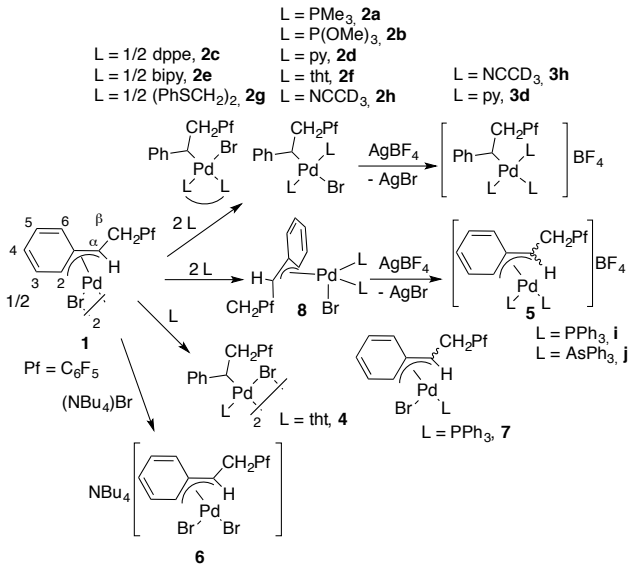
Scheme 1. η^3-benzylic stabilization and β-H elimination in benzylic palladium complexes.



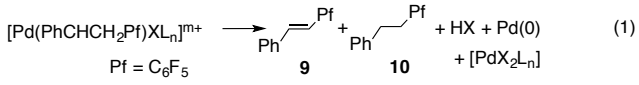
We have also been interested in exploring the ability of benzylic complexes to behave as precursors of Pd-hydrides, the byproducts of the β-H elimination reaction, and their subsequent transformations. The interplay between the stabilizing pseudoallylic (η^3) form and the alkyl σ-benzylic form (that restores the aromaticity of the aryl) slows down the β-H elimination reaction and this could be used as a controlled source of Pd-H fragments; also, the evolution of the generated [$PdHXL_n$] can produce unwanted side reactions. We describe here a study of the decomposition of a number of benzylic palladium complexes by β-H elimination and the fate of the palladium hydrides that are produced.

The benzylic palladium complexes used in this study are shown in Scheme 2. All of them were synthesized from the dimeric complex **1** upon addition of the suitable amount of ligand.[5,6] The rich coordination chemistry of these derivatives allows to form η^3-benzylic and σ-benzylic complexes, as well as tetra- or pentacoordinated compounds. A rich fluxional behavior is also observed in some cases that involves ligand exchange as well as η^3-σ benzylic exchange.[5] As a result of these manifold situations, the stability of the complexes is quite different in solution but all of them decompose

Scheme 2. Benzylic palladium complexes used in this work.



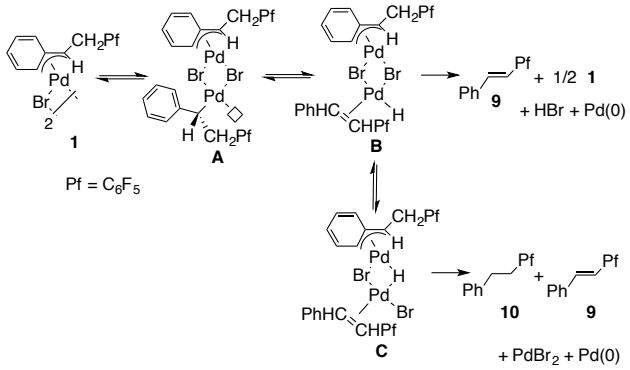
cleanly by β-H elimination to give pentafluorostilbene **9** (the trans isomer is always the major one) and a palladium hydride that has been detected in some cases. This hydride either decomposes or it is transferred to another complex molecule to give, by reductive elimination, the reduction product **10** (Eq. 1).



(1)

We have studied this hydride transfer before using complex **1** and the proposed route is depicted in Scheme 3. A radical reaction or a benzyl protonation were ruled out and an intermolecular hydride transfer between palladium atoms aided by a halogen bridge (hydride transmetalation) is the most plausible pathway (**C**, Scheme 4).[6] In this work we show now how this process is influenced by the presence of additional ligands in the metal coordination sphere.

Scheme 3. Decomposition of 1 by β-H elimination and subsequent hydride transfer.



RESULTS AND DISCUSSION

Decomposition of the benzylic complexes. Table 1 collects the decomposition data for some of the complexes prepared. Half-lives of the complexes in solution and/or the time for complete decomposition are given and they show large differences in stability, clearly related to the availability of an empty coordination site required for β-H elimination, as shown in Scheme 1. It is noteworthy that, as decomposition takes place, free ligand is released in solution and this slows the decomposition down; this is the reason for the long times required for total decomposition when compared to the half-lives of some of the complexes.

The cationic derivatives, with a more electrophilic metal center, are less prone to lose a ligand and create a vacant coordination site, so, in general, they are more stable than their neutral counterparts (cf. decomposition times for entries 2 and 10, 5 and 11, 13 and 17 in Table 1). Besides, an electron poor metal center does not favor the cleavage of the C-H bond, once the agostic interaction has been established (Scheme 1). The complexes bearing chelating ligands, more difficult to dissociate, are more stable that those with monodentate ligands (see entries 3-6 vs. 7-9, Table 1). The dissociation of the bromo ligand is also a possible pathway and, in fact, a distinct

Table 1. Decomposition data for some of the benzylic complexes prepared.[a]

Entry	[Pd]	Ligand	Pd:L	T (K)	$t_{1/2}$[b]	t[c]	*trans*-**9** (%)	*cis*-**9** (%)	**10** (%)	E[d]
1	**1**	----	----	293		7 days	46	----	33	0.72
2[e]	**2h**	CD_3CN	Excess	293		1 day	45.3	12	42.7	0.74
3	**2a**	PMe_3	1:2	283		4 h	49.9	----	38.7	0.78
4	**2b**	$P(OMe)_3$	1:2	293		3 h	69.7	----	30.3	0.44
5	**2d**	py	1:2	293		10 h	50.2	4.1	39.0	0.72
6	**2f**	tht	1:2	293	30 min	17 h	55.4	----	40.8	0.71
7	**2c**	dppe	1:1	293	36 h	10 days	63.3	4.0	20.2	0.3
8	**2e**	bipy	1:1	293	3.5 h	1 day	43.4	31.3	5.4	0.07
9	**2g**	$(PhSCH_2)_2$	1:1	293	48 h	9 days	53.3	----	33.6	0.62
10[e]	**3h**	CD_3CN	Excess	293	72 h	30 days	74.7	18.6	6.7	0.07
11[e]	**3d**	py	1:4	293	40 h	30 days	74.9	7.7	5.2	0.06
12	**4**	tht	1:1	283	1.5 h	15 h	52.1	----	47.9	0.92
13	**5j**	$AsPh_3$	1:2	293	16h	2 days	100	----	---	0
14	**6**	Br	1:5	293		3 h	53.5	----	46.3	0.86
15	**7**	PPh_3	1:1	293		10 min	68	----	31	0.45
16	**8i**	PPh_3	1:2	273		10 min	96	----	4	0.04
17	**8j**	$AsPh_3$	1:2	273		30 min	48.7	----	37.3	0.77

a) $CDCl_3$ as solvent unless otherwise noted. b) Time needed for decomposition of about 50% of the complex. c) Time for complete decomposition. d) E = [**10**]/[**9**]. e) CD_3CN as solvent.

but moderate decrease in the amount of decomposed complex is observed for **2c** (L = dppe) when bromide is added (after 3 days 24% of **2c** remains in solution vs. 38% when one equivalent of bromide per palladium is added).

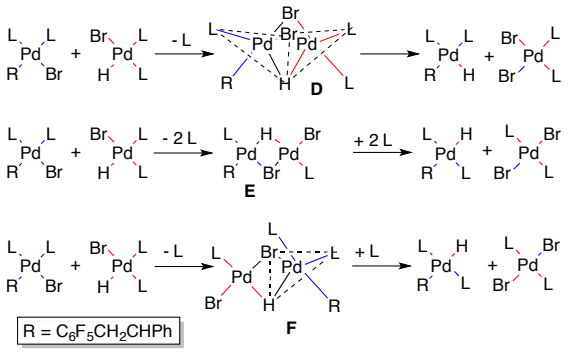
The pentacoordinated complexes **8** decompose fast even at low temperature (entries 16 and 17, Table 1). Both are fluxional and the dynamic behavior of complex **8i** indicates a fast ligand exchange above 253 K.[5] This increases the chances of creating a vacant coordination site for β-H elimination. For complexes **8i** and **8j** both products of β-H elimination, **9** and the corresponding [PdHBrL$_2$], could be detected by ^{1}H NMR: [PdHBr(PPh$_3$)$_2$] (δ = -11.82 t, $^2J_{P\text{-}H}$ = 9.5 Hz); [PdHBr(AsPh$_3$)$_2$] (δ = -14.37, s).[7]

Besides the different stability discussed above, Table 1 also shows the occurrence of hydride transfer between palladium atoms for each particular complex, using the parameter of efficiency of the transfer E = [**10**]/[**9**] (last column). If all the Pd-H generated is transferred to another palladium atom through an intermediate analogous to **C** in Scheme 3, equimolar amounts of **9** and **10** are formed and E = 1. If no transfer occurs, E = 0. Our previous study on the decomposition of complex **1** ruled out the protonation of a Pd-benzyl as a source of **10**.[6] However, the presence of extra ligands, as in the derivatives shown here, makes the palladium complexes more electron-rich and, therefore more prone to undergo protonation. For this reason we followed up the decomposition of complex **2a**, with the strong donor PMe$_3$ as a ligand, in the presence of D$_2$O. No deuterium incorporation in **10** was observed indicating that protonation of the benzylic-palladium moiety is not responsible of the formation of the saturated compound.

Hydride transfer between palladium atoms is aided by the presence of a bridging ligand that anchor both palladium centers. Bromide is playing that role for the complexes studied and in the absence of Br or other ligand capable of acting as a bridge, the hydride transfer observed is very small or non-existent (entries 10, 11, 13, Table 1). In the case complexes of composition [PdRBrL$_2$] (R = H, benzyl) three possible dimeric intermediates can be proposed for the exchange (**D**-**F**, Scheme 4). The triply bridged intermediate **D** has been proposed in the exchange of aryl groups between palladium atoms where two of the bridging ligands are aryl groups.[8] In our case only the hydride is an electron deficient ligand and, it generally forms a stronger bridge than an aryl ring. For this reason, a triple bridge is probably not necessary for an efficient transfer and presumably the doubly bridging species **E** or **F** are stable enough to support the exchange. In any case, the dissociation of a ligand is required and strongly coordinating species may prevent the transfer. This is observed when comparing complexes **8i** (L = PPh$_3$, E = 0.04) and **8j** (L = AsPh$_3$, E = 0.77) where virtually no transfer occurs for the stronger phosphine ligand but the value of E is high for the less coordinating arsine (entries 16 and 17, Table 1). When the ratio L:Pd decreases, the hydride transfer is more effective (cf. entries 15 and 16, 6 and 12, Table 1). A comparison of the E value for complexes **2c**, **2e** and **2g** with chelating ligands shows that a higher value is observed for the more flexible ditioether followed by dppe, whereas virtually no transfer occurs for the rigid bipy ligand (entries 7-9, Table 1); thus, either partial decoordination of the ligand or a better accommodation to the pentacoordinated structure of the dimeric intermediate in the transfer (as in **F**, for example) must be favorable for **2g**.

As can be seen in Table 1, the hydride transfer mechanism can be quite efficient reaching high values of E (see for example

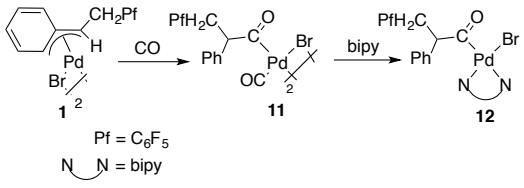
Scheme 4. Plausible dimeric intermediates involved in the hydride transfer between palladium atoms.



entries 12 and 14, Table 1) which implies that almost all the Pd-H produced by β-H elimination is consumed in the reduction of the remaining Pd-R moieties. In a catalytic reaction, this means that if a substituted benzylic halide is used as reactant, a dehalogenation reaction can be a competing process. A Heck-type reaction with styrene can also produce a formal hydrogenation of the product through this mechanism; thus, this pathway could be responsible for the sometimes observed saturated byproducts, or play a role in the mechanism of the reductive Heck-type reactions where palladium hydrides are formed in the presence of suitable hydrogen donors.[9] According to our results, this inter-palladium transfer can be minimized by avoiding the presence of halides in solution (i.e. by using a different benzylic precursor such as a diazonium salts) and using a higher the L:Pd ratio and better coordinating ligands, provided the intended catalytic reaction is not drastically slowed down by such a ligand choice.

Reactions with CO. β-H elimination does not take place in the presence of carbon monoxide.[10] The reaction of CO with complex **1** leads to the insertion of carbon monoxide into the Pd-benzyl bond to give complex **11** as a white solid of low solubility, and the formation of stilbene **9** is not observed (Scheme 5). The structure of complex **11** is proposed based on the ^{1}H and ^{19}F NMR spectra as well as the IR spectrum where strong absorptions corresponding to the acyl fragment (1783-1727 cm^{-1}) and the coordinated CO (2112 cm^{-1}) were observed. Complex **11** undergoes a partial loss of CO at room temperature, changing from white to yellow; the process is reversible and the white solid is regenerated in the presence of CO. Pd(II) complexes with coordinated CO are not very common but they are relevant in the Pd-catalyzed copolymerization of olefins and CO as well other carbonylation reactions catalyzed by palladium; some of them have been characterized in the course of those studies.[11] The addition of bipy to **11** led to a more soluble complex **12** that shows a characteristic acyl ^{13}C NMR resonance at 230.5 ppm. The fact that insertion of carbon monoxide into Pd-benzyl bonds is faster than β-H elimination makes carbonylation reactions of substituted benzylic derivatives possible, including copolymerization of

Scheme 5. Carbonylation reaction of complex 1.



styrene and CO.[12] The preferred insertion of CO vs. palladium migration has also been observed before for η^2-σ alkenyl complexes of palladium.[13]

Trap of the Pd-H generated from the benzylic complexes with dienes. In the absence of other reagents in solution the palladium hydride species, formed by β-H elimination from the benzylic complexes in Scheme 2, either decompose or transfer to another palladium benzyl to give the reduction product **10** (Scheme 3 and Table 1). However, these species can be trapped by insertion of an alkene into the Pd-H bond, provided that the reactant alkene coordinates to the metal better than stilbene **9** or other ligands present in solution. This could be a reentrance point of Pd(II) species in a catalytic cycle. Also, the Pd-H species thus generated could be used as reagents and this strategy has been employed by us before to synthesize enantiomerically pure allyls from R(+)-limonene and complex **1** (Scheme 6 and Table 2, entry 1). In this case (2L = Br, n = 0, Scheme 6) the exocyclic, less substituted double bond of limonene inserts into the Pd-H bond and the stereroselective cis-palladium migration occurs with retention of the original stereochemistry of R(+)-limonene to give **13**.[14] We have now used the same diene to analyze how the presence of additional ligands influences the efficiency of the Pd-H trap by a diene.

As can be seen in Table 2 (entry 2), the presence of an equimolar amount of triphenylphosphine is enough to effectively block the coordination and insertion of a double bond of the diene into the Pd-H one. A higher amount of PPh_3 or $AsPh_3$ produces the same result (entries 3,4, Table 2). Complexes **7** and **8** decompose by β-H elimination but the transfer of hydride to the diene is null. Still, the presence of the diene significantly reduces the inter-palladium H-transfer to give **10** and the E factor is reduced to 0.27 and 0.04 for complexes **7** and **8j** (vs. 0.45 and 0.77 without diene, Table 1). This means that the formation of the required dimeric halogen-bridged species is disfavored in the presence of the diene but the insertion may not be observed if the required cis-hydride alkene arrangement is not favored. The same negligible H-transfer to 4-vinylcyclohexene, bearing an exocyclic terminal double bond, was observed when this diene was reacted with complexes **8i**,**j**. The cationic derivatives **5i**, **j** do form a mixture of allylic derivatives from R(+)-limonene (**13** and **14**, Scheme 6) that result from insertion of the exocyclic, less substituted double bond into the Pd-H moiety. The presence of both isomeric complexes **13** and **14** is caused by differences in the Pd-migration process. A straight Pd-migration to reach the endocyclic double bond of limonene leads to **13**; however, in the course of palladium migration a coordinated cyclohexadiene fragment (a terpinene) is formed and if a double bond coordination switch from one to the other occurs, followed by insertion of the initial endocyclic bond into the the Pd-H bond, the Pd-migration changes its course and **14** is formed (Scheme 6). This is not observed for the neutral complex **1** where a fast, direct Pd-migration is observed and **13** is formed selectively. About 60% of the generated Pd-H generated from decomposition of the cationic complexes **5i**,**j** is trapped by R(+)-limonene, a percentage that increases to 73% for the naked palladium hydride derived from **1**.

Scheme 6. Reactions with R(+)-limonene.

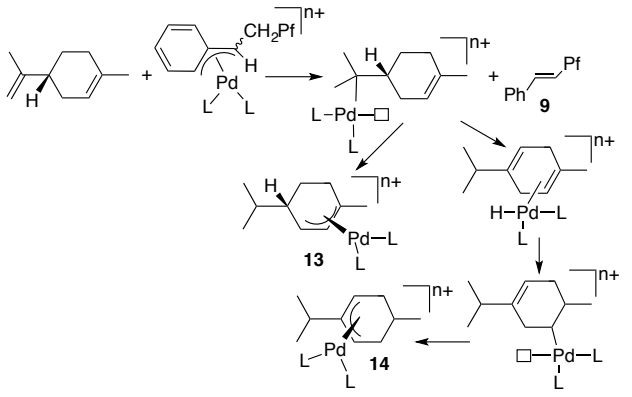


Table 2. Data for the reactions depicted in Scheme 8.

Entry	Complex	L, n	Ratio **13**:**14**	H-transfer to diene (%)[a]
1	**1**	Br, 0	1:0[b]	73
2	**7**	Br, PPh_3, 0	–	0
3	**8i**	Br, 2 PPh_3, 0	–	0
4	**8j**	Br, 2 $AsPh_3$, 0	–	0
5	**5i**	2 PPh_3, 1	1:3.8	58
6	**5j**	2 $AsPh_3$, 1	1.6:1	61

a) Calculated by integration in the crude ^{1}H NMR spectra: %H-transfer to diene = (**13**+**14**)/**9** x100. b) A small amount of an allyl complex resulting from insertion of the endocyclic double bond is observed (2% of the allyl mixture, see ref. 14).

CONCLUSIONS

Benzylic palladium complexes with an α-substituent on the benzyl can be prepared and used as precursors of palladium hydrides since they decompose cleanly by β-H elimination. In the absence of any competing substrate and provided a bridging ligand such as a halide is available, hydride transfer occurs in a dimer that leads, by reductive elimination, to the saturated compound **10**. The use of different combination of ligands leads to complexes with quite different stability towards β-H elimination and to the occurrence of the subsequent hydride transfer. Maximum H-transfer is observed for either η^3- or σ-benzylic complexes with a bromide and ligands of low or moderate coordination ability completing the metal coordination sphere. The absence of a bromide, as in the cationic η^3-benzylic derivatives, completely halts the H-transfer. This reduction pathway may play a role in the origin of saturated byproducts in Pd-catalyzed transformations of benzyl precursors, either benzylhalides or styrene derivatives.

EXPERIMENTAL SECTION

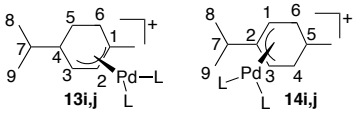
General Methods. ^{1}H, ^{19}F, ^{13}C and ^{31}P NMR spectra were recorded on Bruker AC-300, ARX-300 and AV-400 as well as Agilent MR-500 instruments. Chemical shifts (in δ units, ppm) were referenced to Me_4Si (^{1}H and ^{13}C), $CFCl_3$ (^{19}F) and H_3PO_4 (85%, ^{31}P). Signal assignments were made with the aid of heteronuclear ^{1}H-^{13}C HMQC and homonuclear ^{1}H COSY experiments. C, H and N elemental analyses were performed on a Perkin-Elmer 2400 CHN microanalyzer. Solvents were dried using a solvent purification system SPS PS-MD-5 or distilled from appropriate drying agents under nitrogen, prior to use. The benzylic complexes **1**,[6] and **2**-**8** were prepared as previously reported.[5]

Decomposition reactions. Solutions of 0.02 mmol of the corresponding complex were prepared in the corresponding deuterated solvent ($CDCl_3$ or CD_3CN, 0.6 mL). For the less stable derivatives, the complex was prepared in situ by addition of the appropriate ligand to a suspension of **1** at 223 K and characterization of the mixture before the decomposition follow up. The evolution of the complexes was monitored by ^{19}F, ^{31}P and ^{1}H NMR until complete decomposition has occurred. The information is collected in Table 1.

Reactions with CO. Syntheis of 11. CO was bubbled through a suspension of **1** (0.1 g, 0.109 mmol) in CH_2Cl_2 (5 mL) for 5 min. The initial yellow solid dissolved and then a greyish solid precipitated. This suspension was cooled down to 273 K and the solid was filtered, washed with cold CH_2Cl_2 (5 mL) and diethyl ether (5 mL) and air dried (89.7 mg, 80% yield). Analysis calc. for $C_{32}H_{16}Br_2F_{10}O_4Pd_2$: C, 37.42; H, 1.57; found: C, 37.02; H, 1.58. IR (Nujol mull): ν = (cm^{-1}) 2112 (CO), 1783, 1750, 1727, 1661 (CO acyl). ^{19}F NMR (282 MHz, δ, $CDCl_3$): -162.56 (m, F_{meta}), -155.98 (t, F_{para}), -142.53 (m, F_{ortho}). ^1H NMR (300 MHz, δ, $CDCl_3$): 7.3-7.5 (m, 5H, Ph), 4.75 (m, X, ABX system, J_{AX} = 7.2 Hz, J_{BX} = 7.8 Hz, 1H, H^{α}), 3.45, 3.17 (m, AB, ABX system, J_{AB} = 13.6 Hz, 2H, H^{β}, $H^{\beta'}$).

Synthesis of 12. To a suspension of **11** (0.0372 g, 0.036 mmol) in CH_2Cl_2 was added 2,2'-bipy (0.0113 g, 0.072 mmol). The resulting yellow solution was filtered through activated charcoal and Kieselgur. The solvent was partially evaporated until crystals appeared. After a day at –20 ˚C the yellow crystals were filtered and air dried (0.0266 g, 57% yield). Analysis calc. for $C_{25}H_{16}BrF_5N_2OPd$: C, 46.79; H, 2.82; N, 4.36; found: C, 46.95; H, 2.75; N, 4.22. ^{19}F NMR (282 MHz, δ, $CDCl_3$): -163.74 (m, F_{meta}), -158.13 (t, F_{para}), -141.87 (m, F_{ortho}). ^1H NMR (300 MHz, δ, CDCl3): 9.0-6.9 (m, 13H, Ph, bipy), 5.31 (m, X, ABX system, J_{AX} = 6.3 Hz, J_{BX} = 9.8 Hz, 1H, H^{α}), 3.59, 3.28 (m, AB, ABX system, J_{AB} = 14 Hz, 2H, H^{β}, $H^{\beta'}$). $^{13}C\{^1H\}$ NMR (74.5 MHz, δ, CDCl3): 230.51 (s, CO); 154.13, 152.25, 135.57 (s, bipy, Ph); 151,05, 150.08, 139.13, 138.56, 129.21, 128.44, 127.26, 126.09, 125.89, 122.17, 121.55 (s, bipy, Ph), 66.95 (s, 1CH, C^{α}), 24.77 (s, $1CH_2$, C^{β}).

Reactions with dienes. Reaction of complex 5j with R(+)-limonene. Complex **5j** (15 mg, 0.0139 mmol) was placed in an NMR tube and dissolved in dry $CDCl_3$ (0.7 mL) at 233 K. R-(+)-Limonene (4.5 μL, 0.0278 mmol) was added and the reaction was followed by ^{19}F and ^1H NMR at room temperature. After 24 h, the ^{19}F NMR clearly shows the complete decomposition of the benzylic complex and the formation of stilbene **9**. The ^1H NMR of the crude mixture shows the formation of complexes **13j** (62%) and **14j** (38%). The ratio **13j**+**14j**/**9** indicates a hydride transfer efficiency of 61%. The dark mixture was treated with activated carbon and it was filtered through Kieselgur. The orange solution was evaporated to dryness and the orange residue was washed with 2 x 2ml of hexane. The solid was dried and characterized by NMR.



13j: ^1H NMR (400.13 MHz, δ, $CDCl_3$): 6.05 (d, J = 6.6 Hz, 1H, H^2), 4.94 (d, J = 6.6 Hz, 1H, H^3), 1.80 (m, 1H, H^6), 1.66 (m, 1H, $H^{6'}$), 1.64 (m, 1H, H^5), 1.39 (s, 3H, Me^1), 1.28 (m, 1H, H^4), 1.02 (m, 1H, H^7), 1.09 (m, 1H, $H^{5'}$), 0.57 (d, J = 5.8 Hz, 3H, H^8), 0.55 (d, J = 5.8 Hz, 3H, H^9).

14j: ^1H NMR (400.13 MHz, δ, $CDCl_3$): 5.03 (bm, 2H, H^1, H^3), 2.29 (m, 1H, H^7), 2.25 (m, 1H, H^5), 1.66 (m, 2H, H^4, H^6), 1.25 (m, 2H, $H^{4'}$, $H^{6'}$), 1.03 (d, J = 6.8 Hz, 6H, H^8, H^9), 0.75 (d, J = 6.3 Hz, 3H, Me^5).

The reaction of **5i** with R-(+)-limonene was carried out in the same way. The ratio of complexes in the crude mixture was **13i** (21%) and **14i** (79%).

13i: ^1H NMR (500.13 MHz, δ, $CDCl_3$): 6.01 (t, J = 7 Hz, 1H, H^2), 4.50 (t, J = 7 Hz, 1H, H^3), 1.73 (m, 1H, H^6), 1.51 (m, 1H, $H^{6'}$), 1.49 (s, 3H, Me^1), 1.19 (m, 1H, H^5), 1.03 (m, 1H, H^4), 0.95 (m, 1H, H^7), 0.99 (m, 1H, $H^{5'}$), 0.54 (d, J = 5.3 Hz, 3H, H^8), 0.52 (d, J = 5.3 Hz, 3H, H^9). $^{31}P\{^1H\}$ NMR (161.976 MHz, δ, $CDCl_3$): 26.29 (d, P_A, J = 40.5), 21.91 (d, P_B, J = 40.5).

14i: ^1H NMR (400.13 MHz, δ, $CDCl_3$): 4.6 (m, 2H, H^1, H^3), 2.33 (m, 1H, H^7), 2.05 (m, 1H, H^5), 1.2 (m, 2H, H^4, H^6), 1.07 (d, J = 6.8 Hz, 6H, H^8, H^9), 1.05 (m, 2H, $H^{4'}$, $H^{6'}$), 0.65 (d, J = 6.3 Hz, 3H, Me^5). $^{31}P\{^1H\}$ NMR (161.976 MHz, δ, $CDCl_3$): 22.54 (s).

Reaction of complex 8j with R(+)-limonene. Complex **1** (15 mg, 0.0163 mmol) and $AsPh_3$ (20 mg, 0.0652 mmol) were placed in an NMR tube. The solids were dissolved in 0.7 ml of dry $CDCl_3$ at 213 K. R-(+)-Limonene (10.5 μl, 0.0652 mmol) was added to the orange solution. The reaction was followed by ^1H and ^{19}F NMR at room temperature. After 24 hours the complete decomposition of **8j** to stilbene **9** was observed and no formation of any palladium-allyl complex.

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