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On the requirements of the precursor complex for olefin insertion: reactivity of *cis*- and *trans*-$Pd(C_6F_5)(L)_2^+$ with dienes

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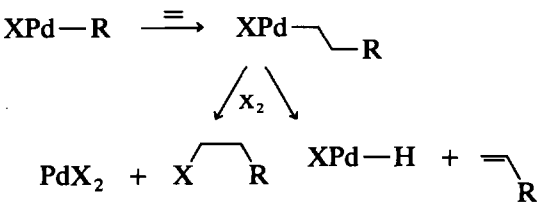
Abstract

The reactivity of synthons of *cis*- and *trans*-$Pd(C_6F_5)(L)_2^+$ towards dienes is studied. *cis*-$Pd(C_6F_5)(bipy)^+$, which has only one coordination site available to the olefin, reacts with dienes under mild conditions to give (C_6F_5-allyl)palladium derivatives, suggesting that the insertion of dienes occurs on an η^2-diene complex and the second double bond is involved in allyl formation in a further step. The lack of reaction of *trans*-$Pd(C_6F_5)(L)_2^+$ under the same conditions supports experimentally earlier theoretical calculations which suggest that insertion is not favoured in a *trans*-M(R)(olefin) arrangement.

1. Introduction

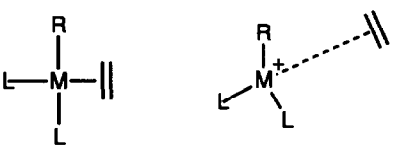
Olefin insertion into Pd–C bonds is a well known reaction which finds wide application in organic synthesis, both stoichiometric and catalytic [1,2] (Scheme 1).



Scheme 1.

The study of the intimate mechanism of such processes has often been hampered by the instability of the intermediates in the reaction. Reports on isolated or detected intermediates such as PdRX(olefin) or PdRX in processes such as the Pd-catalyzed arylation of olefins [Heck reaction (R = aryl)] [2], are scarce [3–5].

Theoretical chemistry has made an important contribution to the understanding of the olefin insertion reaction. In a classic paper, Thorn and Hoffman analysed the energy requirements for insertion of an olefin into M–C or M–H bonds [6]. The precursor species studied contain the moiety MR(olefin), and have different coordination numbers and stereochemistries. According to their calculations, insertions into a *cis* R-olefin, four-coordinate complex (**I**) and into a three-coordinate complex (**II**) are preferred. Later calculations support these results [7].



I II

Pentafluorophenyl is an interesting group in the study of Pd–R addition to olefins. The stability of the Pd–C_6F_5 bond is enough to allow the isolation of synthons of $Pd(C_6F_5)Br$ and [$Pd(C_6F_5)Br$(diene)] (diene = 1,5-cyclooctadiene), yet addition of Pd–C_6F_5 to the olefin is a facile process [4,5]. Our previous work with this system focussed on the reactivity of conjugated and non-conjugated dienes with synthons of $Pd(C_6F_5)Br$ ([$Pd(C_6F_5)Br(CH_3CN)_2$] for example) to give Pd-allyls and/or Pd-σ–π derivatives. Since Pd(C_6F_5)Br synthons offer two easily available coordination sites and a diolefin can be mono- or bi-dentate, the nature of the intermediate Pd–diene complex is not unequivocal. In a previous paper [5a], we suggested

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that coordination of only one double bond followed by insertion and Pd-migration could account for the formation of the observed products, but the structure of the intermediate Pd–diene complex is still an open question.

The availability of Pd–pentafluorophenyl species with a variety of stoichiometries and well-determined stereochemistries let us address this question by using a complex with only one coordination site easily accessible to the unsaturated substrate. This is *cis*-[Pd-(C_6F_5)Br(L–L)], a synthon of the moiety *cis*-Pd(C_6F_5)-$(L–L)^+$. We also examined experimentally other aspects of Pd–R addition to olefins already addressed theoretically. Thus synthons of *trans*-Pd$(C_6F_5)(L)_2^+$ were used to test the geometric requirements for the precursor.

2. Results

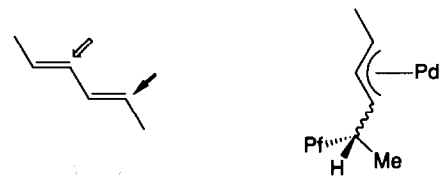
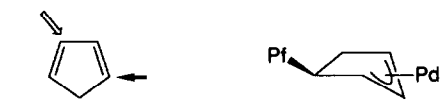
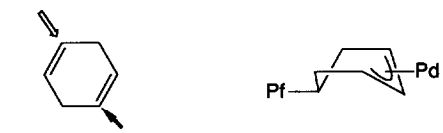
2.1. Reactions with synthons of cis-Pd$(C_6F_5)(L)_2^+$

There is a variety of complexes of the type *cis*-[Pd(C_6F_5)Br(L–L)] where L–L is a bidentate ligand such as bipy (bipy = 2,2′-bipyridine), dppe (dppe = 1,2-diphenylphosphinoethane) or tmen (tmen = tetramethylethylenediamine) [8]. We have studied the behaviour of one of these complexes, [Pd(C_6F_5)Br(bipy)] (**1**), with dienes. Complex **1** does not react with diolefins unless a coordination site is opened by using a silver salt in a non-coordinating solvent such as CH_2Cl_2 (eqn. (1)). The reaction products are Pd-allyls bearing the pentafluorophenyl group in the organic moiety. The dienes and the final products are collected in Table 1.

$$[Pd(C_6F_5)Br(bipy)] + AgClO_4 + \text{diene} \longrightarrow \underset{(1)}{} \underset{(2\text{–}6)}{[Pd(C_6F_5\text{-}\eta^3\text{-allyl})(bipy)]ClO_4} + AgBr \quad (1)$$

Compounds **2–6** give satisfactory C, H, N, microanalyses and conductivity values consistent with 1:1 electrolytes (see Experimental section). Their IR spectra show characteristic absorptions for bipy (1600s cm^{-1}, 1570w cm^{-1} and 770s cm^{-1}) and non-coordinated ClO_4^-(1100vs cm^{-1} and 622s cm^{-1}). The C_6F_5 absorptions which are not obscured by the ClO_4^- bands confirm that the pentafluorophenyl group is no longer attached to Pd but to C [5a]; the most important changes are: (a) the absorption at 1500 cm^{-1} for the moiety Pd–C_6F_5 is replaced in **2–6** by two bands (1515 and 1490 cm^{-1}); (b) the absorption at 780 cm^{-1} in the starting complex disappears in the new compounds. The presence of the C–C_6F_5 moiety in the products is also nicely shown by the ^{19}F NMR spectrum; the range

TABLE 1. Structure of the allyl moiety of complexes **2–6**

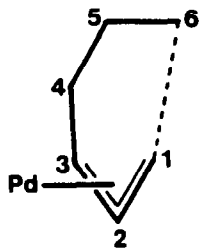
Diolefin	Structure	Complex
		**2a** (1-syn, 3-syn) **2b** (1-syn, 3-anti)
		**3**
		**4**
		**5**
		**6**

→ = position of pentafluorophenyl attack; ⇒ = central carbon of the allyl moiety; Pf = C_6F_5.

of chemical shifts for the three C_6F_5 signals (F_{ortho}, F_{meta} and F_{para}) is 40 ppm for Pd–C_6F_5 versus 15 ppm for C–C_6F_5 systems [5a]. The simplicity of the F_{para} resonance (well resolved triplet) lets us determine the isomeric purity of the products. In all cases except 2,4-hexadiene (see below), only one complex is formed. The structure of the allylic moiety in the Pd-derivatives was ascertained by ^1H NMR spectroscopy. The ^1H NMR spectral patterns shown by complexes **2–6** are analogous to those of the corresponding dimer derivatives synthesized previously, for which the stereochemistry of the Pd–C_6F_5 addition is well established by X-ray crystal analysis [5a]. ^1H NMR data are collected in Table 2.

As can be seen from Tables 1 and 2, the reaction with 2,4-hexadiene gives two isomers in the ratio **2a**/**2b** = 3.25:1. No other species are formed, the ^{19}F NMR spectrum showing only two F_{para} signals at −156 (t, ^3J(F–F) = 22 Hz, **2a**) and −156.8 (t, ^3J(F–F) = 21 Hz, **2b**) with the appropriate intensity ratio. The ^1H NMR spectra show that **2a** is the 1-*syn*–3-*syn* isomer whereas **2b** is the 1-*syn*–3-*anti* Pd-allyl derivative. The *syn* ar-

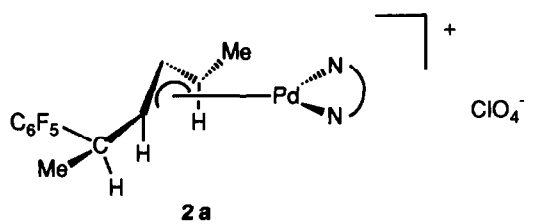
TABLE 2. ^{1}H NMR data for the $|Pd(C_6F_5\text{-}\eta^3\text{-allyl})(bipy)|ClO_4$ derivatives **2–6** [a]



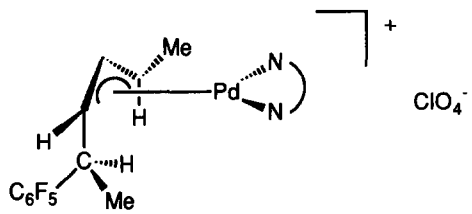
2: $R_1 = H$; $R'_1 = Me$; $R_4 = H$; $R'_4 = Me$
3: $R_1 = R'_1 = R_4 = R'_4 = R_5 = R'_5 = R_6 = R'_6 = H$
4: $R'_1 = H$; $R_4 = H$; $R'_4 = C_6F_5$; $R_5 = R'_5 = H$
5: $R'_1 = H$; $R_4 = H$: $R'_4 = C_6F_5$; $R_5 = R'_5 = R_6 = R'_6 = H$
6: $R'_1 = H$; $R_4 = R'_4 = H$; $R_5 = H$; $R'_5 = C_6F_5$; $R_6 = R'_6 = H$

Compound	R_1 (*anti*)	R'_1 (*syn*)	H_2	H_3	R_4	R'_4	R_5	R'_5	R_6	R'_6	other
2a [b]	4.31m (12;6)	1.68d (6)	5.78dd [c] (12)	4.03m (11.5;3.5)	3.76m (3.5;7)	1.6 [d]					7.6–8.8
2b [b]	4.48m (12;6)	1.73d (6)	5.7m [e]	5.2dd (12;6)	3.2m (12;7)	1.55 [d]					7.6–8.8
3 [b]	3.55d (12.2)	4.2d (6.8)	5.73ddd (12;6.8)	4.1m		1.6–2.0m |4H|			2.9m |2H|		7.6–8.8
4 [f]		5.98 [g]	6.45 [g]	5.62 [g]	3.55m		1.8 [h]	2.56dd (18;4)			7.7–9
5 [f]		5.63m	6.28dd [b]	5.36dd (6.7;3;3)	3.5m (6.7)	(6.7;3)		2–2.7m [f]			7.5–9
6 [f]		5.78dd [c] (6.5)	6.28t (6.5)	5.78dd [c] (6.5)	2.39m [i] (18.1;11.9)	2.65m [i] (18.1;5.8;5.8)	2.99m		2.39m [i]	2.65m [i]	8.7m; 8.4m; 7.88m

[a] δ mult. J values (Hz) are given in parentheses. [b] $CDCl_3$ solution. [c] Pseudotriplet. [d] Resonance obscured by the H_2O signal. [e] Partially hidden into the H_2 signal of **2a**. [f] $(CD_3)_2CO$ solution. [g] Pseudosinglet. [h] Resonance obscured by the solvent signal. [i] AB system.



2a



2b

rangement for the substituents attached to the allylic carbons C-1 (or C-3) and C-2 seems to be less sterically demanding and for this reason Pd-allyl derivatives tend to prefer the *syn* configuration [5,9]. Thus, only the *syn–syn* isomer was isolated in the reaction of $[Pd(C_6F_5)Br(CH_3CN)_2]$ with 2,4-hexadiene to give the dimer $[Pd_2(\mu\text{-}Br)_2\{1,4\text{-}(CH_3)_2\text{-}4\text{-}C_6F_5\text{-}1\text{-}3\text{-}\eta^3\text{-}C_4H_4\}_2]$ [5a]. In the present case, the steric requirement of bipyridine bound to palladium renders the *syn* position more hindered than in the dimeric derivative. This in turn decreases the difference in stabilities between the *syn* and the *anti* positions, leading to a mixture of isomers. This effect has been recently reported for some Pd complexes of 2,9-dimethyl-1,10-phenanthroline (N–N), a more sterically demanding ligand than bipy, that causes the *anti* $[Pd(N\text{–}N)(allyl)]^+$ derivatives to be more stable than the corresponding *syn* isomers [10].

The reaction with 1,4-diphenyl-1-3-butadiene (eqn. (1), diene = 1,4-diphenyl-1-3-butadiene) does not occur, although this diene reacts with $[Pd(C_6F_5)Br(CH_3CN)_2]$ to give the allyl derivative $[Pd_2(\mu\text{-}Br)_2(1,4\text{-}(Ph)_2\text{-}4\text{-}C_6F_5\text{-}1\text{-}3\text{-}\eta^3\text{-}C_4H_4)_2]$ [5a]. The higher steric requirements of bipy or the harder character of the Pd, or both, may prevent the coordination of the olefin.

We have shown that 1,5-hexadiene gives a $\sigma\text{–}\pi$-hexenyl derivative when it reacts with $[Pd(C_6F_5)Br(CH_3CN)_2]$ for 5 min at 0°C [5b]. Isomerization of the $\sigma\text{–}\pi$-hexenyl to the thermodynamically more stable Pd-allyl compound occurs within 3 h at 34°C. In the reaction described here (eqn. (1), diene = 1,5-hexadiene), the slight solubility of $AgClO_4$ in CH_2Cl_2 required the use of longer reaction times and prevented the isolation of any possible intermediate $\sigma\text{–}\pi$ isomer.

2.2. Reactions with synthons of trans-$Pd(C_6F_5)(L)_2^+$

Under similar conditions to those used in the reactions of the unit *cis*-$Pd(C_6F_5)(bipy)^+$, insertion of the diene into the Pd–C bond of *trans*-$[Pd(C_6F_5)Br(L)_2]$ (L = py, **7**; L = PPh_3, **8**) does not occur. The products of the reaction are *trans*-$[Pd(C_6F_5)(OClO_3)(L)_2]$ (eqn. (2)), or alternatively *trans*-$[Pd(C_6F_5)(H_2O)(L)_2]ClO_4$ if the CH_2Cl_2 used is not carefully dried.

$$\textit{trans}\text{-}[Pd(C_6F_5)Br(L)_2] + AgClO_4 + \text{diene} \xrightarrow[(7,8)]{} \textit{trans}\text{-}[Pd(C_6F_5)(OClO_3)(L)_2] + AgBr + \text{diene} \quad (2)$$

3. Discussion

The use of dienes as unsaturated substrates in insertion reactions leads to some uncertainty about the nature of the intermediate Pd–diene complex. Conjugated olefins tend to be monodentate, leading to species of the type $[Pd_2(\mu\text{-}Cl)_2Cl_2(\eta^2\text{-diene})_2]$ in solution rather than $[PdCl_2(\eta^4\text{-diene})]$ [11]. Non-conjugated olefins with a suitable arrangement of their double bonds such as 1,5-hexadiene, 1,5-cyclooctadiene or norbornadiene show a marked preference for the $[PdCl_2(\eta^4\text{-diene})]$ and they chelate [12]. Nevertheless there is some evidence supporting the η^4-diene form for conjugated diolefins as the species undergoing *exo* attack by an external nucleophile [13]. In the *cis*-$Pd(C_6F_5)(bipy)^+$ unit there is only one coordination site easily available to the diene and $[Pd(C_6F_5)(bipy)(\eta^2\text{-diene})]^+$ is the reasonable intermediate in the reaction. The regioselectivity observed in C_6F_5 attack on the diolefin in this case and in the reactions with the $Pd(C_6F_5)Br$ moiety, where coordination in the η^4-diene form might be possible, is the same. This supports the idea that when dienes are used as unsaturated substrates, coordination of only one double bond is occurring for insertion into the Pd–C bond and allyl formation. This is the case for conjugated diolefins, where formation of the allyl is immediate, and also for non-conjugated dienes (1,4-cyclohexadiene and 1,5-hexadiene) where insertion creates a vacant coordination site on the palladium thus allowing Pd-migration (via palladium-hydride elimination-readdition) until the uncoordinated double bond eventually coordinates (to give a $\sigma\text{–}\pi$ derivative) or acts as a sink for palladium giving a Pd–allyl.

In contrast with *cis*-$Pd(C_6F_5)(bipy)^+$, *trans*-$Pd(C_6F_5)(L)_2^+$ moieties fail to react with dienes under the same conditions. Thorn and Hoffmann pointed out the unlikeliness of insertion of an unsaturated substrate into M–H or M–C bonds from a *trans* intermediate

[6]. Insertion, however, occurs often in catalytic and stoichiometric processes using *trans* precursors, and the intermediacy of *cis*-M(R)olefin moieties is argued [14]. In our case, the similar coordination environment of Pd in both moieties (specially for L = py and L–L = bipy) suggests that the different behaviour (insertion *versus* no reaction) is to be attributed to the *cis* or *trans* arrangement and to the fact that palladium–pentafluorophenyl complexes are rather inert [8,15], rendering the formation of the *cis* intermediates unlikely under the reaction conditions.

4. Experimental details

^1H and ^{19}F NMR spectra were recorded on a Varian XL-200 or a Bruker AC-80 instrument. ^1H chemical shifts were measured with reference to the residual solvent resonances; ^{19}F chemical shifts were measured with reference to $CFCl_3$. IR spectra were recorded on Perkin-Elmer 599 and 883 spectrometers. Microanalyses were carried out using a Perkin-Elmer 240-B microanalyzer. Λ_M values (Ω^{-1} cm^2 mol^{-1}) were determined with a Crison 522 conductimeter on *ca.* 10^{-3} M solutions of the complexes in nitromethane.

Reagents were purchased from Janssen, Fluka or Aldrich. $[Pd(C_6F_5)Br(bipy)]$ and *trans*-$[Pd(C_6F_5)Br(PPh_3)_2]$ were prepared by published procedures [8]. *trans*-$[Pd(C_6F_5)Br(py)_2]$ was prepared by addition of pyridine to $[Pd(C_6F_5)Br(CH_3CN)_2]$ [5a].

4.1. Synthesis of the bipyridine derivatives: $[Pd(4\text{-}C_6F_5\text{-}1\text{-}3\text{-}\eta^3\text{-}C_6H_8)(bipy)]ClO_4$ (5)

To a suspension of $AgClO_4$ (0.089 g, 0.43 mmol) in CH_2Cl_2 (*ca.* 20 ml) were added $[Pd(C_6F_5)Br(bipy)]$ (0.219 g, 0.43 mmol) and 1,3-cyclohexadiene (0.041 ml, 0.43 mmol). The mixture was protected from light and stirred at 20°C for 24 h. After this time, the suspension was filtered and the precipitate (AgBr) washed with CH_2Cl_2 (5 × 5 ml portions). The pale yellow solution was evaporated to dryness and Et_2O (5 ml) was added to the residue. A white solid was obtained which was filtered, washed with Et_2O and air dried. 73% yield. ^{19}F NMR ($CDCl_3$): δ −162.7 (m, F_{meta}); −157.2 (t, 21, F_{para}); −139.4 (m, F_{ortho}). Anal. Found: C, 43.40; H, 2.80; N, 4.58. $C_{22}H_{16}ClF_6N_2O_4$ Pd calc.: C, 43.33; H, 2.64; N, 4.59%; Λ_M, 93.6.

Compounds **2a,b, 3, 4** and **6** were prepared in a similar way.

2a,b: ^{19}F NMR ($CDCl_3$): δ −162 (m, F_{meta}, **2a**); −161.7 (m, F_{meta}, **2b**); −156 (t, 22, F_{para}, **2a**); −156.8 (t, 21, F_{para}, **2b**); −143.7 (m, F_{ortho}, **2a**); −142.5 (m, F_{ortho}, **2b**). Anal. Found: C, 42.68; H, 3.01; N, 4.78. $C_{22}H_{18}ClF_6N_2O_4Pd$ calc.: C, 43.23; H, 2.97; N, 4.58%. Λ_M, 87.2.

3: ^{19}F NMR ($CDCl_3$): δ −163.9 (m, F_{meta}); −159.3 (t, 21.3, F_{para}); −144.6 (m, F_{ortho}). Anal. Found: C, 42.79; H, 3.23; N, 4.96. $C_{22}H_{18}ClF_6N_2O_4Pd$ calc.: C, 43.23; H, 2.97; N, 4.58%; Λ_M, 89.5.

4: ^{19}F NMR ($CDCl_3$): δ −163 (m, F_{meta}); −157.4 (t, 20.6, F_{para}); −138.1 (m, F_{ortho}). Anal. Found: C, 42.50; H, 2.46; N, 4.98. $C_{21}H_{14}ClF_6N_2O_4Pd$ calc.: C, 42.38; H, 2.37; N, 4.70%; Λ_M, 91.4.

6: ^{19}F NMR ($CDCl_3$): δ −163.1 (m, F_{meta}); −157.6 (t, 20.8, F_{ortho}); −141.4 (m, F_{ortho}). Anal. Found: C, 42.90; H, 2.61; N, 4.71. $C_{22}H_{16}ClF_6N_2O_4Pd$ calc.: C, 43.33; H, 2.64; N, 4.59%; Λ_M, 95.2.

4.2. Reactions of trans-$[Pd(C_6F_5)X(L)_2]$ with dienes: reaction of trans-$[Pd(C_6F_5)Br(PPh_3)_2]$ with 1,4-cyclohexadiene

To a suspension of $AgClO_4$ (0.037 g, 0.18 mmol) in CH_2Cl_2 (10 ml) were added 1,4-cyclohexadiene (17 μl, 0.18 mmol) and *trans*-$[Pd(C_6F_5)Br(PPh_3)_2]$ (0.158 mg, 0.18 mmol). The mixture was stirred for 22 h in the dark. The suspension was filtered, and the filtrate was evaporated to dryness. Et_2O was added to the residue and a white product was obtained and identified as $[Pd(C_6F_5)(OClO_3)(PPh_3)_2]$ [16].

The reaction with $[Pd(C_6F_5)Br(py)_2]$ as substrate was carried out in a similar way.

Safety note. Perchlorate salts have been used and it is well known that they are potentially explosive. Although we had no problem using them, they should be handled with care.

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