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NMR study on the coordination of dibenzylideneacetone to chiral palladium(0) units. Fluxional behaviour including an intramolecular double bond exchange†

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Received 28th February 2001, Accepted 12th June 2001
First published as an Advance Article on the web 2nd August 2001

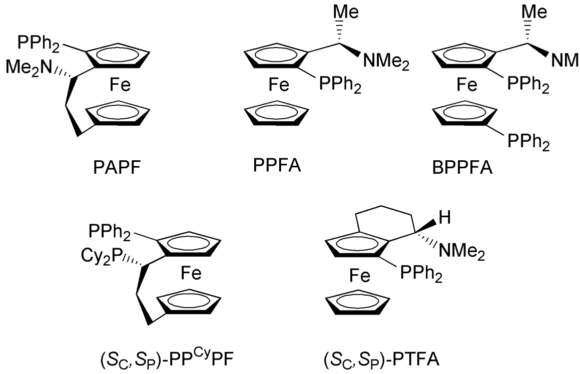
New derivatives with the general formula Pd(L–L)(η^2-dba) (dba = dibenzylideneacetone), L–L = 1-diphenylphosphino-2,1′-(1-dimethylaminopropanediyl)ferrocene, PAPF, **1**; 2-[1-(dimethylamino)ethyl]-1-(diphenylphosphino)ferrocene, PPFA, **2**; *N*,*N*-dimethyl-1-[1′,2-bis(diphenylphosphino)ferrocenyl]ethylamine, BPPFA, **3**; 1-diphenylphosphino-2,1′-(1-dicyclohexylphosphinopropanediyl)ferrocene, PP^{Cy}PF, **4** were synthesized from $Pd_2(dba)_3{\cdot}CHCl_3$ and the appropriate ferrocenyl ligand. When an excess of PPFA was used, the complex $Pd(PPFA)_3$ with P-coordinated PPFA ligands was formed. The dba unit preferentially adopts an *s-cis*,*trans* conformation with the *s-trans* alkene coordinated to the Pd(L–L) fragment. Several intramolecular dynamic processes were identified: at room temperature a fast rotation of dba about the alkene–Pd bond, a Pd–N bond rupture process for complex **2** and, at elevated temperatures, an intramolecular diastereomer interconversion involving an alkene face exchange accompanied by an interchange between the coordinated and non-coordinated dba double bonds. The crystal structure of complex **2** was determined by X-ray diffraction.

Introduction

Palladium complexes of general formula $Pd_x(dba)_y{\cdot}(solv.)_z$[1] (dba = dibenzylideneacetone, solv. = solvent of crystallization) have been extensively used as starting materials in synthesis and catalysis.[2–5] It has been established by means of ^{31}P NMR, UV spectroscopy and electrochemical studies, that dba has a strong influence on both the structure and reactivity of palladium(0) complexes generated *in situ* from $Pd(dba)_2$ and phosphine or P–N ligands.[6,7] However, studies on the coordination mode and the fluxional behaviour of dba at palladium centres[8–10] are very rare and, to the best of our knowledge, coordination of dba to a chiral Pd(0) unit has never been investigated.

The study reported here addresses this problem and is especially relevant considering that alkene coordination is an important topic in asymmetric synthesis and catalysis.[11]

Recently, we synthesized alkene Pd(0) derivatives with chiral ferrocenyl aminophosphine ligands such as [η^5-cyclopentadienyl][η^5-4-(*endo*-dimethylamino)-3-(diphenylphosphino)-4,5,6,7-tetrahydro-1*H*-indenyl]iron(II), PTFA,[12,13] 2-[1-(dimethylamino)ethyl]-1-(diphenylphosphino)ferrocene, PPFA,[13] 1-diphenylphosphino-2,1′-(1-dimethylaminopropanediyl)ferrocene, PAPF,[14] or *N*,*N*-dimethyl-1-[1′,2-bis(diphenylphosphino)ferrocenyl]ethylamine, BPPFA[15] (see Scheme 1).



Scheme 1 Configuration of (S_C,S_P)-PAPF, (R_C,S_P)-PPFA, (R_C,S_P)-BPPFA, (S_C,S_P)-PP^{Cy}PF and (S_C,S_P)-PTFA.

In these examples the electron-accepting olefins maleic anhydride, MA, and dimethyl fumarate, DMFU, of C_{2v} (MA) or C_{2h} (DMFU) symmetry were used. Different isomers were formed depending on the olefin face coordinated to Pd and on the relative orientation of the alkene with respect to the ferrocenyl aminophosphine ligand. Isomerization processes, including alkene rotation, were studied by means of variable temperature NMR.

We report here the preparation of complexes of dba (maximum symmetry C_{2v}) with the asymmetric palladium ferrocenyl–aminophosphine or –diphosphine fragments Pd(PAPF), Pd(PPFA), Pd(BPPFA) and Pd(PP^{Cy}PF); (PP^{Cy}PF = 1-diphenylphosphino-2,1′-(1-dicyclohexylphosphinopropanediyl)ferrocene) (see Scheme 1 for the ligand structures). The syn-

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† This paper is dedicated to Prof. Rafael Usón on the occasion of his 75th birthday.

DOI: 10.1039/b101912k

thesis of Pd(PTFA)(dba) has already been described in one of our previous communications.[12]

NMR studies that mainly focus on the analysis of the coordination selectivity were carried out. In addition, the conformational possibilities of coordinated dba, as well as fluxional processes including Pd–olefin rotation, intra- and inter-molecular exchange phenomena, are described in detail.

Results and discussion

Synthesis of complexes 1–5

Reaction of $Pd_2(dba)_3{\cdot}CHCl_3$ in toluene with the appropriate aminophosphine or diphosphine ligand led, according to the following equation (eqn. (1)), to the new Pd(L–L)(dba) complexes.

$$Pd_2(dba)_3{\bullet}CHCl_3 + 2\ L{-}L \longrightarrow 2\ Pd(L{-}L)(dba) + dba \quad (1)$$

L–L	Complex
PAPF	**1**
PPFA	**2**
BPPFA	**3**
$PP^{Cy}PF$	**4**

The remaining free dba was removed by column chromatography. In order to allow a better proton assignment in the aromatic region of the ^{1}H NMR spectrum of **1** (see below for discussion), the partly deuterated complex Pd(PAPF)(dba-d_{10}), **1-*d***, (where dba-d_{10} = $(C_6D_5CH{=}CH)_2CO$) was synthesized.

In the reaction with PPFA another product, **5**, was formed in addition to **2**. This compound was found not to contain dba and was confirmed as being identical to the major component formed when $Pd_2(dba)_3{\cdot}CHCl_3$ was reacted in an NMR tube with three equivalents of PPFA (in this case a small amount of **2** was formed as a by-product). When four equivalents of PPFA were added, the resonances due to **5** (major) and **2** were observed along with those for free PPFA. Although not obtained in its pure form, we propose the formula $Pd(PPFA)_3$ for product **5**. An analogous complex, $Pd(PhPN)_3$, has been obtained previously[7] when a large excess of ligand was added to $Pd(dba)_2$.

The new complexes are readily soluble in polar solvents but only moderately soluble in toluene or benzene. Although the complexes proved stable enough to run some NMR experiments they do evolve in chlorinated solvents, most probably through oxidative addition processes.

Characterization of the new complexes

The ^{31}P NMR resonances of all complexes are shifted downfield with respect to those in the free ligand, a situation typical for Pd–P coordination.

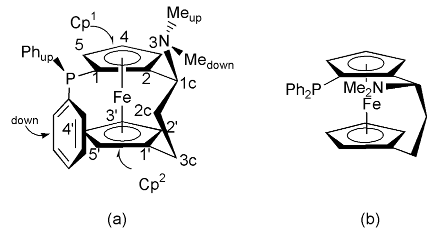
Pd(dba)(PAPF) (1). *(i) General signal assignment and coordination mode of PAPF.* Both the $^{31}P\{^1H\}$ (C_7D_8) and the ^{1}H NMR (C_7D_8, C_6D_6) spectra imply the presence of two isomers (**1M** and **1m**, M = major, m = minor) in an approximate ratio of 80 : 20. (In the $^{13}C\{^1H\}$ NMR spectrum recorded in C_6D_6, only one set of signals was observed; see Table 1 and Experimental section.)

Both species contain dba and a P–N coordinated PAPF ligand, as deduced from the diastereotopic methyl resonances of the aminomethyl groups. It should be mentioned that monodentate coordinated structures have also been described for other P–N ligands.[7] However, in our particular case, the formation of significant amounts of a Pd(dba)(PAPF) complex with mono-coordinated PAPF can be excluded. As we have pointed out previously,[16] only the ligand conformation (a), depicted in Scheme 2, is suitable for chelate coordination. In a similar way to other PAPF–palladium complexes[14] this fact, together with ^{1}H–^{1}H COSY and NOE measurements, allowed us to assign all ligand protons.

Table 1 ^{1}H NMR data of the dba alkene protons of complexes **1**–**4** in C_6D_6 (**1**) or C_7D_8 (**2**–**4**) at room temperature (**1**, **4**), −30 °C (**2**) or −60 °C (**3**). Shifts in ppm, *J* in Hz

	H_a	H_b	H_c	H_d
1M	4.48 (dd) $J_{HP} = 6.6$ $J_{H_aH_b} = 10.6$	4.98 (dd) $J_{HP} = 7.8$	6.74 (d) $J_{H_cH_d} = 15.5$	7.99 (d)
1m	4.80 (m)	5.45 (m)	[a]	[a]
2	4.28 (dd) $J_{HP} = 6.4$ $J_{H_aH_b} = 10.6$	4.95 (dd) $J_{HP} = 8.1$	6.56 (d) $J_{H_cH_d} = 15.4$	7.95 (d)
3	4.74 (m)	5.7 (m)	[a]	[a]
4M	4.33 (m)	5.09 (m)	6.42 (d) $J_{H_cH_d} = 14.9$	7.92 (d)
4m	5.27 (m)	5.27 (m)	7.30 (d) $J_{H_cH_d} = 15.5$	7.74 (d)

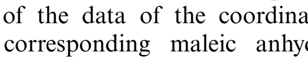
[a] Signals obscured.



(a) (b)

Scheme 2 Preferred (a) and less stable (b) conformation of ligand PAPF. Numbering scheme of PAPF (a).

(ii) Coordination modes and conformers of dba. From the ^{1}H and ^{13}C chemical shifts it follows that dba is coordinated to palladium through only one of its double bonds. For **1M** the resonances of the coordinated alkene are found at 4.98 and 4.48 ppm (J_{HH} = 10.6 Hz) while those of free dba appear at 7.77 and 6.87 ppm (J_{HH} = 16.0 Hz). Two other resonances are observed at lower field (7.99 and 6.74 ppm, J_{HH} = 15.5 Hz), close to the values of free dba, and these correspond to the second, non-coordinated alkene of dba. (For the signals for the corresponding ^{13}C alkene carbons see the Experimental section.) A comparison of the data of the coordinated alkene with those of the corresponding maleic anhydride (MA) or dimethyl fumarate (DMFU) derivatives,[13,14] shows that the shift differences between the olefin protons of coordinated and free dba are correlated to the olefin π-back bonding order: MA >> DMFU > dba. A full assignment of the olefin protons was achieved by NOE, magnetization transfer, INDOR, internuclear double resonances and heteronuclear H–P decoupling experiments. The olefinic protons of the uncoordinated double bond were firstly assigned according to the bibliographic data for free dba. Kawazura and co-workers,[17] concluded from their investigations on differently deuterated free dba that H_d is always the most deshielded proton (see Scheme 3). The assignment of H_a follows from the magnetization transfer (see discussion below) between H_d and the signal at 4.48 ppm, while that between H_c and the resonance at 4.98 ppm defines H_b. For **1m**

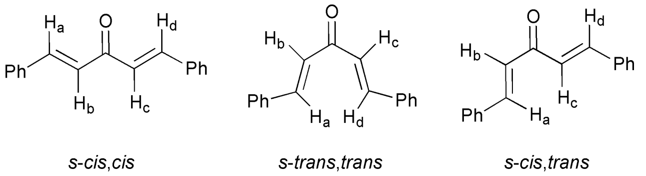


$$PhH_aC\overset{[Pd]}{=}CH_b{-}\overset{O}{\overset{\|}{C}}{-}H_cC{=}CH_dPh$$

Scheme 3

the resonances of the coordinated alkene are seen as broad signals at 5.45 and 4.80 ppm, while those of the free alkene are obscured by other resonances and could not be unambiguously assigned.

Two degrees of rotational freedom are imparted by the two single bonds and this means that coordinated and free dba can exist in the forms of three different and easily interconvertible conformers: *s-cis*,*cis*, *s-trans*,*trans* and *s-cis*,*trans* forms, where *s-cis* or *s-trans* refers to the orientation of the olefin with respect to the keto group (see Scheme 4).



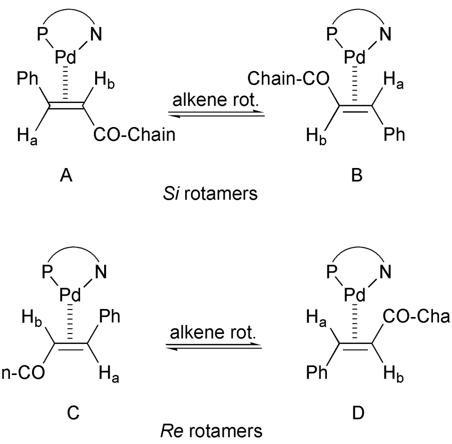
Scheme 4

Free dba in solution adopts predominantly the *s-cis*,*cis* conformation with the *s-cis*,*trans* conformer being the minor component.[17] According to theoretical calculations for free dba, the *s-cis*,*cis* form is the most stable.[17,18] This form has also been found in the solid state[19] for both the free ligand and for some mononuclear palladium derivatives of the type Pd(L–L)(dba) or Pd(L^1)(L^2)(dba) (L–L = N- or P-donor; L^1, L^2 = P-donor ligands).[3–5,20–22] ^{1}H NMR studies of Pd(dba)$_3$ revealed that the coordinated olefin moieties adopt the *s-trans* form, while the uncoordinated ones were fluxional but preferentially existed in the *s-cis* form.[10] In the solid state the three dba units were found to be in the *s-cis*,*trans* form with the *trans* unit coordinated to the metal centre.[23] The *s-trans*,*trans* form is usually considered to be less likely in view of its sterically hindered structure with two olefin protons positioned in close proximity to each other. However, this conformation has been found in CpRh(dba), a complex in which both dba double bonds are coordinated to the metal centre.[24] $Pd_2(dba)_3{\cdot}CH_2Cl_2$ constitutes another example with one dba unit in an *s-trans*,*trans* form.[25] Recently, this structure has been solved more accurately.[26]

Measurements on complex **1M** showed a positive NOE between the dba protons H$_a$ and H$_c$. Hence, in solution the dba unit of **1M** adopts preferentially an *s-cis*,*trans* conformation with the *s-trans* alkene coordinated to the Pd(PAPF) fragment. Unfortunately, low signal intensity prevented proper NOE studies for **1m**.

Kawazura *et al.*[8–10] developed a method to determine the conformation in solution in non-aromatic solvents of dba, not only free but also in complexes, by means of ^{1}H NMR studies. According to their conclusions[8–10,17] the internal shift δ_{AB} (chemical shift difference between the α and β hydrogens of a double bond) is indicative of the conformation of the olefin moiety. For the *s-cis* form a maximum value for δ_{AB} of 0.5 ppm is expected, while for the *s-trans* form a minimum value of 1.0 ppm was predicted. We have tried to evaluate the validity of the Kawazura method for complex **1M** and recorded the ^{1}H NMR resonances of **1M-*d*** in CD$_2$Cl$_2$ and CDCl$_3$. The δ_{AB} values measured in both solvents are 0.30 and 0.46 ppm for the coordinated and 1.00[27] and 1.03 ppm for the non-coordinated alkene, respectively. According to the Kawazura proposal, the coordinated alkene should adopt the *s-cis* form and the non-coordinated the *s-trans* form. This is opposite to the conclusions reached from our NOE data (and from the X-ray structure of the analogous complex **2**, see below). We therefore suggest that the Kawazura method for dba complexes should be used with considerable care (for other examples of non-accordance, see ref. 28).

(iii) Rotamers of dba and Pd–olefin rotation. In solution, conformers of dba are expected to rapidly interconvert on the NMR time scale[9,10,17] resulting in averaged NMR resonances only. Consequently, **1M** and **1m** cannot be considered purely as single conformers but as preferred conformers. Taking into account the fact that different dba conformers cannot be observed on the time scale accessible by our NMR instrument, four isomers (A–D) of complex **1** are feasible and these are depicted in Scheme 5.

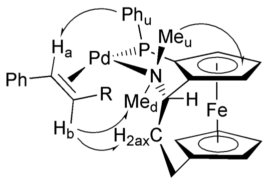


Scheme 5

Isomers A and B, as well as C and D, constitute rotamers that can interconvert by alkene rotation, while A/B and C/D are pairs of diastereomers formed on coordination of the Pd(PAPF) unit to one of the enantiotopic dba alkene faces. At room temperature only two isomers could be observed in solution but the J_{HP} values of the alkene resonances of **1M** (the corresponding signals of **1m** are broad) are intermediate between those expected for pseudo-*cis* or pseudo-*trans* H–P arrangements (see, for example, refs. 13 and 14). This fact is indicative of a fast alkene rotation, a situation confirmed by VT-NMR experiments in C$_7$D$_8$. Upon lowering the temperature to −80 °C no changes were observed in either the ^{31}P NMR or the ^{1}H NMR spectra of the major isomer **1M**. However, clear changes were seen for the minor isomer. At 0 °C the proton signal at 4.9 ppm became resolved into a triplet with a coupling constant of 9.6 Hz. A further decrease in temperature led to splitting of the resonances of both coordinated alkene protons. At −60 °C four signals at 5.88, 5.2 (broad), 4.96 (partially overlapped) and 4.69 ppm were observed, with the latter two signals being similar doublet of doublets ($J_{HH} = 9.6$, $J_{HP} = 18.6$ Hz for the signal at 4.69 ppm). The coupling constant J_{HP} of 18.6 Hz is typical for a pseudo-*trans* H–P arrangement and, therefore, both protons correspond to *trans* protons of two different rotamers. The other two signals corresponding to the pseudo-*cis* protons were found to be broad but their width excludes the possibility of a coupling constant as high as 18 Hz. In CD$_2$Cl$_2$ at −30 °C the resonance due to one proton of a coordinated alkene could be observed (4.8 ppm, doublet of doublets) and had a coupling constant of $J_{HP} = 4.7$ Hz, which is consistent with a pseudo-*cis* arrangement. Furthermore, in C$_7$D$_8$ a splitting of the Me$_{down}$ resonance of **1m** (2.73 and 2.83 ppm at −60 °C) was seen.

From these data we conclude that in **1m** at low temperature the rotation about the Pd–alkene bond is slowed down to such an extent that both rotamers are seen separately, while at room temperature a fast rotamer interconversion takes place. In contrast, for **1M** a restricted rotation could not be detected and this fact may be due to a significantly lower rotational barrier or a smaller $\Delta\nu$ value for its corresponding NMR signals. A comparison of the NMR data of **1** with those of the analogous MA and DMFU complexes[13,14] reveals a more facile alkene rotation for the dba complex, a fact in agreement with the lower electron-accepting character of dba. For a dba palladium complex with a chiral P,N ligand four isomers were observed at low temperature and were tentatively assigned to the two rotamers of the *Re* and *Si* diastereomers.[26]

One remaining question concerns which side of the alkene the Pd(PAPF) unit in **1M** and **1m** is coordinated to and this point was elucidated by NOE experiments (for a recent similar study see ref. 29). It should be mentioned that for the synthesis of **1** a racemic mixture of PAPF (*S*,*S* and *R*,*R*) was used and, consequently, the racemate of diastereomers A–D was investigated. In the schemes discussed below only the complexes with (S_C,S_P)-PAPF are represented. For **1M** an NOE was found between H_b and H_{2ax}, a proton of the heteroannular bridge, and also between H_b and one methyl group of the aminomethyl unit (Me_{down}) (see Scheme 6). Such NOEs could only arise from rotamer D, in which proton H_b is oriented in a pseudo-*cis* way with respect to N and also points toward the ferrocenyl core (down). Accepting the rapid rotation around the Pd–alkene bond, the observation of NOE between H_a and the *ortho* protons of one phenyl ring of the PPh_2 group (see Scheme 6) and the absence of NOE between H_a and the Me_{down} and H_{2ax} groups we propose that in the equilibrium depicted in Scheme 5 rotamer D is possibly more populated than rotamer C. This statement is also supported by the different coupling constants of H_a and H_b with ^{31}P.



R = C(O)C(H$_c$)=C(H$_d$)Ph

Scheme 6 NOEs observed for Pd((S_C,S_P)-PAPF)(*Re*-dba), **1M**.

Consequently, when the aminophosphine ligand (PAPF) of **1M** has the (S_C,S_P) configuration, the alkene must be coordinated to Pd with its *Re* face (rotamers C and D), while in **1m** the *Si* face of the olefin coordinates to the Pd(S_C,S_P)-PAPF unit.

(iv) Intramolecular dba double bond exchange and other interconversion processes. As stated above, a magnetization transfer between H_a and H_d, as well as between H_b and H_c, was observed. This process is indicative of an interchange between the non-coordinated and the coordinated dba olefin bonds. In order to determine the activation barrier for this process we studied the evolution of the ^{1}H NMR signals of **1** in C_7D_8 up to 105 °C. On increasing the temperature, all alkene signals broadened until they were indistinguishable from the base line. When this solution of **1** was heated in the presence of free dba (0.5 eq.), the corresponding signals of the free ligand were unaltered over the whole temperature range of 20–105 °C. This fact means that free and coordinated dba do not interchange, but that an intramolecular alkene exchange occurs between the coordinated and the non-coordinated alkene parts of dba. Another phenomenon was observed in the ^{1}H NMR spectra when the temperature was increased. Both aminomethyl signals of **1m** broadened and coalescence was achieved between 80 and 100 °C (due to the presence of other resonances in the same region it was not possible to measure the coalescence temperature more accurately). As we have previously described for other ferrocenylaminophosphine complexes,[13,14] this exchange process is caused by a Pd–N bond rupture. The single signal obtained after the coalescence of the two aminomethyl signals of **1m** broadened again when the temperature was increased further and coalesced with the aminomethyl resonances of **1M** at around 90 °C. Since free dba is not involved, this process is in accordance with an intramolecular **1M** $\rightleftharpoons$ **1m** diastereomer interchange.

Finally, a variable temperature $^{31}P\{^1H\}$ NMR study (C_6D_6) unambiguously demonstrated this diastereomer interchange. The signals of the two isomers broadened as the temperature was increased and coalesced at 75 °C. Therefore, both isomers interchange in an intramolecular process with one another with a calculated free energy of activation of $\Delta G_{348}^{\ddagger} = 66$ kJ mol^{-1}.

Another important question is raised regarding how such an intramolecular interchange could actually occur. Scheme 7 depicts two plausible mechanistic pathways that can both explain the exchange processes observed. However, we do not have experimental evidence to support one pathway over the other.

Sequence 1 proposes a process of double bond interchange *via* intermediate **I** with dba in an *s-trans*,*trans* conformation and coordinated to palladium through both double bonds.[24,25,30] The ease of Pd–N bond rupture, as detected by NMR spectroscopy in solution (see above), might facilitate this process. Such a reaction pathway is associated with an *Re–Si* double bond face exchange, in accordance with the observed diastereomer interconversion.

Alternatively, the dba carbonyl functionality could take part in the exchange process as depicted in sequence 2. In intermediates **II** and **III** the dba would adopt an *s-cis*,*cis* form, while Pd is coordinated to one double bond and to the dba carbonyl group (for an example of such a coordination type see ref. 28). In the crucial step from **II** to **III** the Pd(PAPF) unit slips in an intramolecular fashion from one double bond to the other (without changing the dba side). Such a process would also result in a change of the alkene faces (*Re* → *Si*).

In summary, the experimentally observed intramolecular interchange of diastereomers **1M** $\rightleftharpoons$ **1m** can be rationalized in terms of a series of intramolecular steps involving double bond interchanges and conformational changes of dba.

Pd(dba)(PPFA), 2, and Pd(PPFA)$_3$, 5. The ^{1}H and $^{31}P\{^1H\}$ NMR spectra of complex **2** show only the resonances for one derivative, indicating either a higher dba facial selectivity or a much more facile isomer interconversion (as compared to complex **1**). The signals of the proton spectrum at room temperature were found to be broad but the spectrum recorded at −30 °C (C_7D_8) could be completely assigned (see Table 1 and Experimental section). As far as complex **1M** is concerned, both a double bond interchange (detected by magnetization transfer at −10 °C) and the presence of dba in an *s-cis*,*trans* (*trans* coordinated) conformation were found. Due to the much higher flexibility of the Pd–PPFA chelate ring an attempted assignment of the coordinated olefin face by NOE was considered to be inconclusive. However, in the solid state (see below) dba is coordinated with one alkene *Re*-face to a Pd((R_C,S_P)-PPFA) unit.

In a similar way to **1**, a variable temperature ^{1}H NMR study of complex **2** carried out in C_7D_8 allowed the identification of a number of additional dynamic processes. At temperatures below −10 °C a broadening of some resonances was observed but no signal splitting was reached even at −90 °C. Increasing the temperature from −10 °C, where the alkene signals are narrow, led to progressive broadening of these signals until they totally disappeared. This observation, together with the magnetization transfer results, is again in accordance with an intramolecular double bond interchange.

An exchange of both diastereotopic aminomethyl signals was observed with a coalescence temperature of 28 °C. At temperatures above 70 °C the signal narrowed to a singlet at 2.54 ppm. An activation barrier of $\Delta G^{\ddagger}_{301} = 57.1$ kJ mol^{-1} was calculated for this Pd–N bond rupture process. Complex **1** has a significantly higher coalescence temperature than **2** and, although both have similar $\Delta\nu$ values (see above), the activation barrier of the corresponding Pd–N de-coordination in **1** must be of higher energy. This trend is not unexpected in view of our previous investigations. In general, P–N bond breaking processes in PAPF or PTFA complexes were found to be of higher energy than in the analogous PPFA derivatives.[14] Furthermore, the fact that **2** exhibits a lower barrier than the corresponding Pd(PPFA)(MA) and Pd(PPFA)(DMFU) complexes fits in with the picture that the presence of a poor electron-accepting olefin like dba facilitates the Pd–N bond rupture (see ref. 14 for discussion). A solution of **2** was heated in the presence of free dba (1 eq.), which showed narrow signals at 30 °C that became increasingly broad at 50 °C and broader still at 70 °C. This finding is considered to be the result of an intermolecular interchange between free and coordinated dba. A quantitative determination of the exchange barrier was not possible. However, by considering the chemical shift differences and the temperature range of signal broadening, it is possible to propose that such an intermolecular process must be of higher energy than that of the intramolecular double bond interchange. The Pd–N bond rupture observed for complex **2** together with the higher conformational flexibility of PPFA are believed to facilitate this intermolecular dba exchange.

Only one signal was observed in the $^{31}P\{^{1}H\}$ NMR spectrum of complex **5**, a fact that implies the presence of three equivalent P-coordinated PPFA ligands. In the corresponding ^{1}H NMR spectrum the aminomethyl groups gave rise to only one signal, indicating non-coordinated or rapidly interconverting amino groups ($Pd(PPFA)_3$).

Crystals suitable for an X-ray structure determination were obtained for complex **2**. The corresponding ORTEP[31] plot is shown in Fig. 1. The crystallographic data are listed in Table 2 and a selection of bond distances and bond angles is given in Table 3.

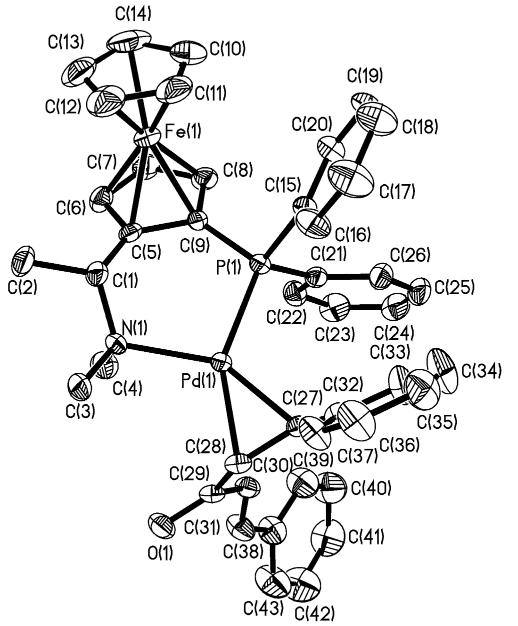


Fig. 1 ORTEP view with atomic numbering of complex **2** showing 30% probability thermal ellipsoids.

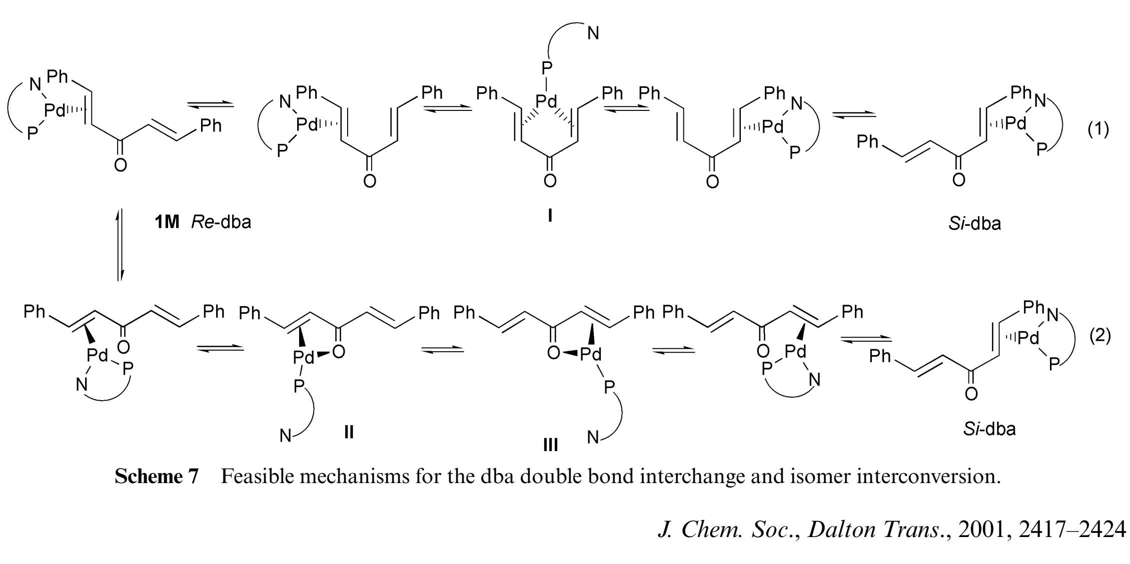
The geometry around the coordinated palladium atom is almost square planar with a slight deviation (−0.29 Å) of P(1) from the N(1)–Pd(1)–C(28)–C(27) plane. The Cp rings of the PAPF ligand are arranged almost parallel to each other with a tilt angle of 3°. The ligand is P,N-coordinated to Pd with a P–Pd–N bond angle of 98°, similar to those found in other related Pd(0) structures. The Pd–P and Pd–N bonding distances are in the range found in other similar ferrocenyl aminophosphine palladium(0) fragments coordinated to alkene ligands.[12,13] Similar Pd–P distances have also been found in dba palladium

Table 2 Crystal data and structure refinement for **2**

Empirical formula	$C_{43}H_{42}FeNOPPd$
Formula weight	782.00
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	*Pna2*(1)
Unit cell dimensions	$a = 21.2180(4)$ Å $b = 10.6229(2)$ Å $c = 16.4624(4)$ Å
Volume	3710.57(13) Å^3
Z	4
Density (calculated)	1.400 Mg m^{-3}
Absorption coefficient	0.952 mm^{-1}
$F(000)$	1608
Crystal size	0.20 × 0.20 × 0.10 mm^3
θ range for data collection	1.92 to 28.30°
Index ranges	$-28 \le h \le 20$, $-12 \le k \le 14$, $-18 \le l \le 21$
Reflections collected	24891
Independent reflections	8374 [R(int) = 0.0627]
Completeness to $\theta = 28.30°$	99.6%
Absorption correction	Empirical
Max. and min. transmission	0.9108 and 0.8324
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	8374/1/433
Goodness-of-fit on F^2	1.015
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0456$, $wR2 = 0.0736$
R indices (all data)	$R1 = 0.0923$, $wR2 = 0.0881$
Absolute structure parameter	0.03(2)
Largest diff. peak and hole	0.411 and −0.493 e Å^{-3}

Table 3 Selected bond distances (Å) and angles (°) of **2**

Pd(1)–C(27)	2.089(5)	N(1)–C(1)	1.505(6)
Pd(1)–C(28)	2.131(4)	C(1)–C(5)	1.521(7)
Pd(1)–N(1)	2.254(4)	C(27)–C(28)	1.427(6)
Pd(1)–P(1)	2.2655(12)	C(30)–C(31)	1.315(7)
P(1)–C(9)	1.814(5)	Averaged C–C Cp	1.412(9)
N(1)–Pd(1)–P(1)	97.96(6)	C(27)–C(28)–C(29)	126.5(4)
C(28)–Pd(1)–N(1)	111.41(15)	C(29)–C(28)–Pd(1)	102.5(3)
C(27)–Pd(1)–P(1)	110.82(3)	C(28)–C(29)–C(30)	119.2(4)
C(28)–C(27)–C(32)	123.1(4)	C(31)–C(30)–C(29)	121.5(5)
C(32)–C(27)–Pd(1)	118.3(3)	C(30)–C(31)–C(38)	129.0(5)



Scheme 7 Feasible mechanisms for the dba double bond interchange and isomer interconversion.

complexes containing chelating diphosphine ligands.[3,4] The conformation of the chelate ring is also comparable to those of known structures with the NMe_2 group and Pd(1) located above Cp[1] (Pd 1.3427 Å and N 1.19 Å above Cp[1]). In the expected way, C(2) is located slightly below (−0.42 Å) while P(1) is forced out of plane by 0.29 Å above Cp[1]. The Pd–C bond distances are similar to those found in other dba Pd(0) complexes containing N or P ligands in *trans* disposition.[3,4,22] The dba ligand adopts an *s-cis,trans* conformation with the *s-trans* double bond coordinated to the palladium centre. In fact, one alkene *Re* face is coordinated to a Pd((R_C,S_P)-PPFA) unit. It is worth mentioning that in both complexes **1** and **2** the ferrocenyl (S_P) configuration relates to the *Re* face of dba. The coordinated alkene and the carbonyl group are almost co-planar, as reflected by the corresponding torsion angles with values all close to zero (maximum deviation of 1.8(4)°). However, C(31) is located at considerable distance out of this plane, as reflected by the torsion angle C(28)–C(29)–C(30)–C(31) of 24.6(5)° and, consequently, in this particular complex dba prefers a skew conformation.

Pd(dba)(BPPFA), 3. Complex **3** is formed in reaction 1 when BPPFA is added to $Pd_2(dba)_3{\cdot}CHCl_3$. At room temperature both the ^1H and ^{31}P NMR resonances are very broad, indicating a high degree of fluxionality. At −60 °C only one proton resonance for the aminomethyl group could be observed, while the phosphorus resonances are shifted to lower field with respect to the free ligand—as one would expect for a *P*,*P*-coordination of the BPPFA ligand.

Pd(dba)(PP^{Cy}PF), 4. At room temperature two isomers (in a 56 : 44 ratio) were identified from the corresponding ^1H and $^{31}P\{^1H\}$ NMR spectra and these, in analogy to **1**, were assigned to facial isomers. The ^{31}P NMR spectrum shows two broad signals (at lower field) and two doublets of comparable intensity. The two doublets correspond to the phosphorus of the diphenylphosphino group, as deduced by decoupling experiments. In addition, four very broad signals and two singlets of low intensity were seen at room temperature. At −80 °C six pairs of doublets of different intensity were obtained. On increasing the temperature above 40 °C all signals broadened but did not coalesce. Unlike in the case of **1**, the number of resonances observed for **4** at low temperature is higher than expected for two pairs of rotamers. Likely causes for the additional isomers include, for example, conformers due to either different arrangements of the cyclohexyl groups or even of the dba ligand. The ^{31}P NMR chemical shifts exclude the presence of complexes with a mono coordinated PP^{Cy}PF unit.

The room temperature ^1H NMR spectrum also showed essentially two isomers to be present. The use of NOE and decoupling experiments allowed all dba olefin signals to be identified. For the major isomer an *s-cis,trans* conformation with the dba *s-trans* double bond coordinated to the palladium centre was deduced. An intramolecular double bond interchange was observed for complex **1**. Unfortunately, the NOE results were not sufficiently conclusive to determine the dba face coordinated to Pd in each particular isomer. As in the ^{31}P NMR spectra, at −80 °C the number of resonances in the region of the coordinated alkene was found to be higher than one would expect for four isomers.

In summary, we have synthesized new dba palladium complexes of chiral ferrocenyl aminophosphine or diphosphine ligands with dba coordinated to palladium by only one olefin bond. In most cases, two isomers with different dba olefin faces coordinated to the metal are formed and all of these compounds exhibit a rich dynamic behaviour. Exchange between dba conformers and internal Pd–alkene rotation were found to be low energy processes. For ferrocenyl aminophosphine ligands, a Pd–N bond rupture process has been observed by ^1H NMR spectroscopy. Intramolecular double bond exchanges accompanied by isomer interconversion processes, as detected by proton NMR spectroscopy, add to the variety of dynamic processes involving coordinated dba.

Experimental

General comments

All manipulations were carried out under an atmosphere of dry oxygen-free nitrogen using standard Schlenk techniques. Solvents were distilled from the appropriate drying agents and degassed before use. Elemental analyses were performed with a Perkin-Elmer 2400 microanalyzer. ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian Unity 300 spectrometer. Chemical shifts (ppm) are relative to TMS (^1H, ^{13}C NMR) or 85% H_3PO_4 (^{31}P NMR) (the abbreviations pt and pq refer to pseudo triplet and pseudo quartet). The NOE difference spectra were recorded with 5000 Hz, acquisition time 3.27 s, pulse width 90°, relaxation delay 4 s, irradiation power 5–10 dB. For variable temperature spectra, the probe temperature (±1 K) was controlled by a standard unit calibrated with a methanol reference. Free energies of activation were calculated[32] from the coalescence temperature (T_c) and the frequency difference between the coalescing signals (extrapolated at the coalescence temperature) with the formula $\Delta G_c^{\ddagger} = aT[9.972 + \log(T/\delta\nu)]$, $a = 1.914 \times 10^{-2}$. The estimated error in the calculated free energies of activation is ±1.0–1.1 kJ mol^{-1}. $Pd_2(dba)_3{\cdot}CHCl_3$,[33] PPFA,[34] BPPFA,[34] PAPF[35] and PPCyPF[36] were prepared according to literature methods.

Crystallography

Data were collected using a Bruker SMART CCD based diffractometer operating at room temperature. A total of 1271 frames of data were collected using the Φ–ω scan method with a scan width of 0.3° per frame for 20 s. Additional parameters are available in the CIF file. The first 50 frames were recollected at the end of data collection to monitor for decay. Cell parameters were retrieved using SMART software (V. 4.210, Bruker Analytical X-Ray Systems, Madison, WI, 1995) and refined using SAINT (V. 4.050, Bruker Analytical X-Ray Systems, Madison, WI, 1995) on all observed reflections. Data reduction was performed using the SAINT software. Absorption corrections were applied using SADABS.[37] The structures were solved by the direct method using the SHELXS-97 program (G. M. Sheldrick, University of Göttingen, Germany, 1997) and refined by the least-squares method on F^2 using SHELXL-97, which is incorporated in SHELXTL-PC V 5.1 (PC version, Bruker Analytical X-Ray Systems, Madison, WI, 1995). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions and refined as a riding model. The crystal used for the diffraction study showed no decomposition during data collection. Crystal data and details on the data collection and refinement are summarized in Table 2.

CCDC reference number 160867.

See http://www.rsc.org/suppdata/dt/b1/b101912k/ for crystallographic data in CIF or other electronic format.

Syntheses

Preparation of Pd(PAPF)(dba) (1). PAPF (60.0 mg, 0.13 mmol) and $Pd_2(dba)_3{\cdot}CHCl_3$ (62.3 mg, 0.060 mmol) were dissolved in *ca.* 10 mL of toluene. After 1.5 h of stirring the colour of the solution changed from deep red to orange. The solvent was partially removed and free dba and complex **1** were separated by chromatography on a silica gel 60 column. At first, free dba was eluted with toluene and finally complex **1** with THF. The THF solution was evaporated to dryness and the addition of hexane and filtration resulted in the obtention of 63.8 mg of complex **1** as an orange solid. Yield:

67%. ^{1}H NMR (C_6D_6, 300 MHz, M, m = major and minor isomer, respectively) δ 8.20–6.60 (m, P$Ph_{2\text{-M-m}}$), 4.01 (m, 1H, $Cp_{\text{up-M}}$), 3.93 (m, 1H, $Cp_{\text{up-M}}$), 3.63 (m, 2H, H_3, $Cp_{\text{up-down-M}}$), 3.54 (m, 1H, $Cp_{\text{down-M}}$), 3.39 (m, 1H, $Cp_{\text{down-M}}$), 2.95 (s, 3H, N(CH_3)$_{\text{down-M}}$), 2.80 (s, 3H, N(CH_3)$_{\text{down-m}}$), 2.50 (m, 1H, $H_{5'}$-$Cp_{\text{down-M}}$), 2.38 (pq, 1H, $H_{\text{2ax-chain-M}}$), 2.20 (s, 3H, N(CH_3)$_{\text{up-m}}$), 2.12 (s, 3H, N(CH_3)$_{\text{up-M}}$), 1.92 (d, 1H, $H_{\text{3eq-chain-M}}$), 1.82 (d, 1H, $H_{\text{1ax-chain-M}}$), 1.22 (pt, 1H, $H_{\text{3ax-chain-M}}$). ^{13}C{^{1}H} NMR (C_6D_6, 75.4 MHz, major isomer) δ 184.11 (s, *C*O), 147.18 and 143.13 (s, non-coordinated C=C), 137.70–124.86 (PPh_2), 90.28 (s, Cp), 89.23 (s, Cp), 76.49 (d, Cp, J_{CP} = 2.3 Hz), 73.20 (d, Cp, J_{CP} = 8.9 Hz), 72.28 (s, Cp), 72.11 (s, Cp), 71.90 (s, Cp), 71.55 (s, Cp), 71.37 (d, Cp, J_{CP} = 14.5 Hz), 70.44 (d, Cp, J_{CP} = 2.9 Hz), 68.73 (s, C_{1C}), 50.31 and 50.19 (s, NMe_2), 44.56 (bs, coord. C=C) 42.43 (d, J_{CP} = 5.9 Hz, C_{2C}), 38.20 (d, J_{CP} = 18 Hz, coord. C=C), 25.05 (s, C_{3C}). ^{31}P{^{1}H} NMR (CD_2Cl_2, 121.4 MHz) δ 14.25 (s, *P*$Ph_{2\text{-m}}$), 11.79 (s, *P*$Ph_{2\text{-M}}$). Anal. Calcd. for $C_{45}H_{44}NFeOPPd$: C, 66.56; H, 5.33; N, 1.76. Found: C, 66.01; H, 5.68; N, 1.64%.

Preparation of Pd(PAPF)(dba-*d*^{10}) (1-*d*). The procedure is similar to that of complex **1** using Pd_2(dba-d_{10})$_3$·$CHCl_3$ as starting material. The partly deuterated dba-d_{10} was prepared from benzaldehyde-d_5 and $(CH_3)_2CO$.

Preparation of Pd(PPFA)(dba) (2). The procedure is similar to that of complex **1** except that the reaction mixture was stirred for 7 hours. Amounts are as follows: 60.0 mg (0.14 mmol) of PPFA and 72.4 mg (0.070 mmol) of $Pd_2(dba)_3$·$CHCl_3$. A dark red solid was obtained which corresponds to a mixture of **2** and **5**. Complex **2** is obtained as a pure product (60.2 mg) after recrystallization from toluene–ether. Yield: 55%. Suitable crystals for X-ray diffraction were obtained from toluene–ether. ^{1}H NMR (C_7D_8, 300 MHz, −30 °C) δ 7.79–6.69 (m, 10H, PPh_2), 4.02 (q, 1H, C*H*CH$_3$, J_{HH} = 6.3 Hz), 3.85 (m, 1H, Cp_{up}), 3.80 (m, 1H, Cp_{up}), 3.76 (m, 1H, H_3-Cp_{up}), 3.14 (s, 5H, Cp_{down}), 3.03 (s, 3H, N(CH_3)$_{\text{down}}$), 1.82 (s, 3H, N(CH_3)$_{\text{up}}$), 0.79 (d, 3H, CHCH_3). ^{13}C{^{1}H} NMR: signals too broad to be assigned. ^{31}P{^{1}H} NMR (C_7D_8, 121.4 MHz) δ 13.57 (s). Anal. Calcd. for $C_{43}H_{42}NFeOPPd$: C, 66.04; H, 5.41; N, 1.79. Found: C, 66.05; H, 5.44; N, 1.80%.

Preparation of Pd(BPPFA)(dba) (3). The procedure is similar to that of complex **1** except that the reaction mixture was stirred for 5 hours. Amounts are as follows: 60.0 mg (0.096 mmol) of BPPFA, 49.6 mg (0.048 mmol) of $Pd_2(dba)_3$·$CHCl_3$. Complex **3** was obtained after recrystallization from toluene–ether as an orange solid (yield 30.6 mg, 33%). ^{1}H NMR (C_7D_8, 300 MHz, −60 °C) δ 8.11–6.58 (m, 10H, PPh_2), 5.04 (q, 3H, C*H*CH$_3$, J_{HH} = 7.1 Hz), 4.65 (s, 1H, Cp), 3.92 (s, 1H, Cp), 3.86 (s, 1H, Cp), 3.79 (s, 1H, Cp), 3.71 (s, 2H, Cp), 3.47 (s, 1H, Cp), 1.94 (s, 6H, N(CH_3)$_2$), 0.45 (d, 3H, CHCH_3). ^{13}C{^{1}H} NMR: signals too broad to be assigned. ^{31}P{^{1}H} NMR (C_7D_8, 121.4 MHz, −60 °C) δ 23.05 (s), 20.87 (s). Anal. Calcd. for $C_{55}H_{51}NFeOP_2Pd$: C, 68.37; H, 5.32; N, 1.45. Found: C, 68.05; H, 5.44; N, 1.39%.

Preparation of Pd(PP$^{\text{Cy}}$PF)(dba) (4). The procedure is similar to that of complex **1** except that the reaction mixture was stirred for 7 hours. Amounts are as follows: 60.0 mg (0.099 mmol) of PP$^{\text{Cy}}$PF and 51.2 mg (0.049 mmol) of $Pd_2(dba)_3$·$CHCl_3$. Complex **4** was obtained after recrystallization from toluene–ether as a brown-orange solid (32.8 mg, 35%). ^{1}H NMR (C_7D_8, 300 MHz) δ 8.04–6.54 (m, PPh_2); the *ortho* protons have been assigned: 8.03 (pt, *o*-$PPh_{2\text{-down-m}}$, J = 8.7 Hz), 7.33 (pt, *o*-$PPh_{2\text{-M}}$, J = 7.9 Hz), 7.14 (pt, *o*-$PPh_{2\text{-M}}$, J = 9.0 Hz), 6.57 (pt, *o*-$PPh_{2\text{-up-m}}$, J = 8.8 Hz), 4.19 (s, Cp_m), 4.16 (s, Cp_m), 4.01 (s, Cp_M), 3.83 (s, Cp), 3.69 (s, Cp), 3.67 (s, Cp), 3.64 (s, Cp), 2.50–0.80 (m, PCy_2). ^{13}C{^{1}H} NMR: signals too broad to be assigned. ^{31}P{^{1}H} NMR (C_7D_8, 121.4 MHz, rt) δ 73.30 (s), 44.47 (bs, *P*$Cy_{2\text{-M}}$), 38.32 (bs, *P*$Cy_{2\text{-m}}$), 16.03 (s), 11.71 (d, J_{PP} = 14.0 Hz, *P*$Ph_{2\text{-m}}$), 8.01 (d, J_{PP} = 14.0 Hz, *P*$Ph_{2\text{-M}}$). ^{31}P{^{1}H} NMR (C_7D_8, 121.4 MHz, −80 °C), corresponding signals δ 51.20, 10.98 (J = 33.3 Hz); 49.06, 13.03 (J = 16.2 Hz); 47.58, 15.7 (J = 13.4 Hz); 46.04, 40.30 (J = 24.4 Hz); 45.28, 14.92 (J = 23.5 Hz); 40.30, 15.52 (J = 33.3 Hz). Anal. Calcd. for $C_{54}H_{58}FeOP_2Pd$: C, 68.47; H, 6.17. Found: C, 68.35; H, 6.23%.

Preparation of Pd(PPFA)$_3$ (5). When the reaction between $Pd_2(dba)_3$·$CHCl_3$ and PPFA was carried out in an NMR tube with a Pd : L ratio of 1 : 3 (5.0 mg, 0.005 mmol of $Pd_2(dba)_3$·$CHCl_3$ and 12.8 mg, 0.029 mmol of PPFA in 0.5 mL of C_6D_6) complex **5** was obtained as the major component. With a Pd : L ratio of 1 : 4 (5.0 mg, 0.005 mmol of $Pd_2(dba)_3$·$CHCl_3$ and 17.1 mg, 0.039 mmol of PPFA in 0.5 mL of C_6D_6), again **5** was the major component of the mixture but in addition free PPFA was observed. ^{1}H NMR (C_6D_6, 300 MHz, 70 °C) δ 7.96–6.82 (m, PPh_2), one *ortho* proton has been assigned: 7.92 (m, 2H, *o*-PPh_2), 4.65 (q, 1H, C*H*CH$_3$, J_{HH} = 6.9 Hz), 4.17 (m, 1H, Cp_{up}), 4.12 (s, 5H, Cp_{down}), 3.98 (m, 1H, Cp_{up}), 3.86 (m, 1H, Cp_{up}), 1.74 (s, 6H, N(CH_3)$_2$), 1.06 (d, 3H, CHCH_3). ^{31}P{^{1}H} NMR (C_7D_8, 300 MHz) δ 27.13 (s).

Acknowledgements

We gratefully acknowledge the Subdirección General de Cooperación Internacional for an "Acción Integrada" project (HU-1999-0017) as well as Österreichischer Akademischer Austauschdienst ("Acción Integrada", project 18/2000). This work was kindly supported by the Dirección General de Enseñanza Superior e Investigaciones Científicas, Spain (Grant N. PB98-0315) and the Österreichische Nationalbank, Austria (project 7516).

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