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Synthesis and structure of new palladium complexes with the ligand 2-(diphenylphosphino)-1-methylimidazole: Evidence of hemilability

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This paper is dedicated to Professor Victor Riera on the occasion of his 70th birthday.

Abstract

Several Pd(II) complexes containing the potentially bidentate ligand 2-(diphenylphosphino)-1-methylimidazole, dpim, have been synthesized and characterized: $[PdCl_2(dpim)]_n$ (**1**), $[PdCl_2(H_2O)(dpim\text{-}\kappa P)]$ (**2**), $[PdClMe(\mu\text{-}dpim\text{-}\kappa P,\kappa N)]_2$ (**3**) (previously described), $[PdClMe(dpim\text{-}\kappa P)_2]$ (**4**), $[Pd(C_6F_5)_2(dpim\text{-}\kappa P)_2]$ (**5**) and $[Pd(\eta^3\text{-}2\text{-}Me\text{–}C_3H_4)(\mu\text{-}dpim\text{-}\kappa P,\kappa N)]_2[PF_6]_2$ (**6**). The highly insoluble complex **1** dissolves in wet DMSO-d_6 to give the water adduct **2** in which a hydrogen bond is established between one of the water hydrogens and the imidazolyl nitrogen. Two types of coordination mode have been found for the dpim ligand in these derivatives, with the ligand behaving as *P* monodentate and also as a *P*,*N* bridge. The transformations between **3** and **4** demonstrate the hemilability of the dpim ligand. Complex **6** was obtained as a mixture of two pairs of enantiomers (*R*,*S*)/(*S*,*R*) and (*R*,*R*)/(*S*,*S*). Analysis of the fluxional behaviour of **6**, in which the allyl group acts as a ''reporter ligand'', indicates that Pd–N bond rupture takes place – again providing evidence of the hemilabile character of the dpim ligand.

Keywords: Palladium; Hemilabile ligands; N,P ligands; Allyl ligands; Fluxionality; Coordination modes

1. Introduction

Hemilabile ligands and their coordination chemistry [1] have received increasing attention in recent years. Applications of these compounds as sensors have been described [2] but the main interest lies in their potential as auxiliaries in catalytic processes [3]. Theoretical studies concerned with this application have been performed [4]. In many of the catalytic cycles, steps occur that involve dissociation of monodentate ligands to allow the coordination of substrates. A theoretical alternative to the complete dissociation of a ligand such as a tertiary phosphine is the partial dissociation of a bidentate and hemilabile phosphine, which would probably have a less pronounced effect on the stability of the catalyst. A bidentate PN ligand, when monocoordinated by the phosphorus atom, also offers a free nitrogen that, as a basic centre, could participate in the activation of the substrates. In the presence of OH groups the formation of hydrogen bridges would be feasible and this could favour some sort of activation. Braunstein and Naud [1] differentiated three types of hemilabile behaviour: type I involves the spontaneous formation of a vacant coordination site after partial dissociation of the hemilabile ligand. In type II hemilability, there is intramolecular competition with another donor function while in type III hemilability the coordination of an external ligand takes place. It was also suggested that the reversibility of the process is necessary to assign the hemilabile character to a ligand. These concepts have been applied in palladium

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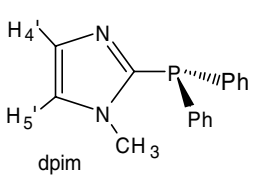
chemistry by Ros et al. [5]. The chemistry and catalytic applications [6]of the ligand 2-(diphenylphosphino)pyridine have been widely explored. In this context, another interesting hemilabile ligand is 2-(diphenylphosphino)-1-methylimidazole, dpim, which was first reported in 1993 [7] (see Scheme 1). A more convenient method of synthesis was published by Nishikawa et al. in 2001. This work also included the formation of dinuclear complexes of Cu(I), Ag(I) and Pd(I) with the dpim ligand acting as a bridge and also of $[PdCl_2(dpim)_2]$ [8]. The dichloro, chloromethyl and methylacetonitrile palladium(II) complexes of the dpim ligand have also been described [9] and a dimeric head-to-tail structure with dpim bridges has been proposed. Complexes of gold(I) and silver(I), some of which are luminescent, have recently been reported with dpim [10,11]. A similar ligand with a *t*-Bu group in the 4-position of the imidazole ring (*t*-Budpim) has been used in the synthesis of the complex $[RuCp(t\text{-}Budpim)_2(H_2O)]Otf$ [12]. It has also been reported the preparation of Pd(0) and Pd(II) complexes with new bulky imidazolylphosphines [13]. In a previous paper we also described the synthesis and characterization of new Ru derivatives that contain the dpim ligand in the three possible coordination modes: monodentate, bidentate chelate and bridging [14]. In the work described here we decided to explore the coordination possibilities of the dpim ligand in palladium complexes in an effort to obtain information about its hemilabile behaviour. We were also interested in analyzing the chelate versus bridging coordination of the ligand when the dpim:Pd ratio is 1:1. Complexes with monodentate or bidentate bridging coordination for the dpim ligand were obtained, including a complex with coordinated water and an allyl derivative whose fluxionality was analysed. The hemilabile behaviour of the ligand was demonstrated.

2. Results and discussion

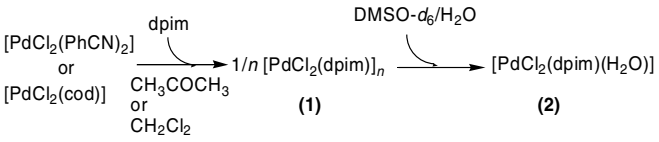
2.1. Preparation and characterization of neutral and cationic complexes

The reaction of $[PdCl_2(PhCN)_2]$ with two equivalents of dpim has already been explored [8] and gives rise to a mixture of *cis*- and *trans*-$[PdCl_2(dpim\text{-}\kappa P)_2]$. The similar derivatives *cis*- and *trans*-$[PdCl_2(PPh_2py)_2]$ have also been described [15]. Given the possibility of synthesizing a derivative containing a chelate phosphine ligand, we carried out the reaction of either $[PdCl_2(PhCN)_2]$ or $[PdCl_2(cod)]$ (cod = 1,5-cyclooctadiene) with only one equivalent of dpim. In both cases an orange solid, **1**, was formed. This product is not soluble in common organic solvents such as acetone, dichloromethane or chloroform. A mass spectrum (MALDI) of the product was obtained and the most intense peak corresponded to a fragment with two palladium atoms. However, a peak clearly due to a fragment with three palladium atoms was also observed. A small peak that could correspond to a fragment with four palladium atoms was detected but, in this case, the low intensity prevented a reliable assignment (see Section 4). Higher mass peaks were not observed. Consequently, the nuclearity of complex **1** can not be unambiguously established. The reaction between $[PdCl_2(cod)]$ and dpim has been previously reported [9]. It is proposed that the obtained complex is a dimmer of formulae $[PdCl_2(dpim)]_2$.



Scheme 1.

Compound **1** was treated with wet DMSO-d_6 and heated at 70 °C, a process that gave rise to a different species, **2**, which was soluble in this solvent (see Eq. (1)).



(1)

The $^{31}P\{^1H\}$ NMR spectrum of the freshly prepared sample in DMSO-d_6 at room temperature (see Table 1 and Fig. 1) showed two singlets at 16.2 and 89.6 ppm. When this solution was heated to 70 °C the first signal almost disappeared while the intensity of the second increased. This observation is consistent with a chemical evolution *in situ*, with the first signal corresponding to the initial sparingly soluble species (or an intermediate evolution product) and the second to derivative **2**, which seems to be the final product. The process was found to be irreversible because when the sample was cooled down to room temperature the spectrum did not change.

The ^1H NMR (DMSO-d_6, 70 °C) spectrum of the sample after the evolution outlined above (see Table 1) exhibited the expected resonances for the ligand. In addition, two other signals were observed at 12.40 (sharp) and 11.2 (broad) ppm, which integrate as one proton each.

NOE experiments were carried out in order to identify these low field signals and clarify the structure of **2** (see Scheme 2). An NOE was found between the methyl group and the signal of $H^{4'}$ or $H^{5'}$ (7.07 ppm, isochronous nuclei by coincidence). Moreover, when the signal at 7.07 ppm was irradiated, a positive effect was observed in the resonance at 12.40 ppm. On the basis of these data, we propose the structure shown in Scheme 2, in which a molecule of water is coordinated to the palladium centre and a hydrogen bond is established between the imidazolyl nitrogen of the ligand and one of the water hydrogens (H_b). In this situation the two water protons become inequivalent.

A FAB^+ experiment confirmed our proposal for **2**. In this regard, DMSO was added to a sample of **1** and the resulting suspension was analysed by FAB^+ mass spectrometry. Two

Table 1
^{1}H and $^{31}P\{^{1}H\}$ NMR data for the dpim ligand and complexes **2**–**6**[a]

Deriv.	^{1}H NMR dpim					^{1}H NMR Other groups	^{31}P NMR
	$H^{4'}$	$H^{5'}$	Me	H_o	H_{m+p}		
dpim[b]	7.25 (dd) $J_{HP} = 2.3$ $J_{HH} = 0.9$	7.03 (d) $J_{HH} = 0.9$	3.79 (s)	7.56–7.44 (m)	7.38–7.28 (m)		−32.20 (s)
2[c]	7.07 (m)	7.07 (m)	3.66 (s)	7.65 (m)	7.2 (m)	12.40 (s) H_b 11.2 (bs) H_a	89.6 (bs)
3M[d]	7.35 (m)	6.70 (m)	3.23 (s)	8.25 (m)	7.35 (m)	0.97 (d), $J_{HP} = 3.2$ Pd–Me	24.09 (s)
4[b]	7.32 (s)	7.08 (s)	3.97 (s)	7.22 (m)	7.46 (m)	−0.01 (t), $J_{HP} = 6.1$ Pd–Me	15.34 (s)
5[d]	7.01 (s)	6.94 (s)	3.55 (s)	7.32 (m)	7.24(t) $J = 6.91$ H_p 7.1 (m) H_m		4.19 (s)
6M[b]	6.67 (s)	7.61 (s)	3.23 (s)	7.42 (m)	7.74–7.64 (m)	4.77 (dd) $J_{HP} = 7.1$, $J_{Hsyn1-Hsyn2} = 3.1$, H_{syn2} 3.92 (d) $J_{HP} = 11.2$, H_{anti2} 3.48 (d) H_{syn1} 3.47 (s) H_{anti1} 2.24 (s) Me-allyl	10.83[e] (s)

[a] Room temperature. *o*, *ortho*; *m*, *meta*; *p*, *para*. *M*, major isomer; *m*, minor isomer. See Section 4 for more data of complex **6M** and those of **6m**.
[b] CD_3COCD_3.
[c] DMSO-d_6.
[d] $CDCl_3$.
[e] The resonance of the PF_6^- group appears at −141.37 ppm (*spt*, $^{1}J_{FP} = 707.4$).

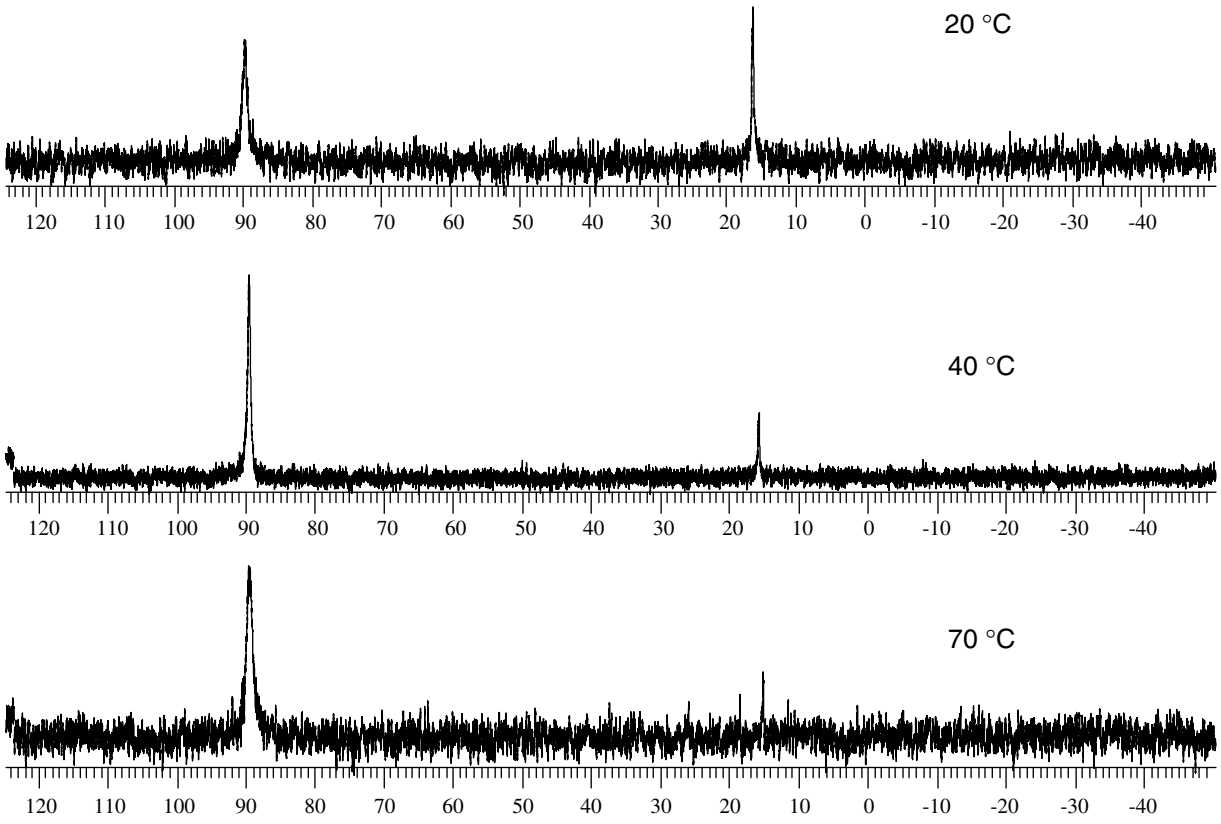
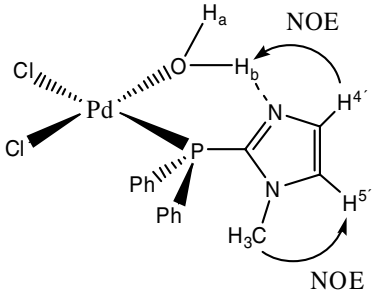


Fig. 1. $^{31}P\{^{1}H\}$ NMR spectra at the temperatures given for the treatment of complex **1** with wet DMSO-d_6 that gives **2**.

spectra were recorded, the first one at room temperature and the second after heating the same sample at 70 °C – at this point the sample readily dissolved. The first spectrum showed peaks corresponding to dimeric fragments $m/z =$ 853 while the second spectrum exhibited a very informative peak at $m/z = 427$, which corresponds to the monocationic fragment $[PdCl(dpim)(H_2O)]^+$. In addition, the base peak appears at $m/z = 389$, a value that is consistent with the



Scheme 2. Proposed structure for **2** and the most important NOEs observed (arrows).

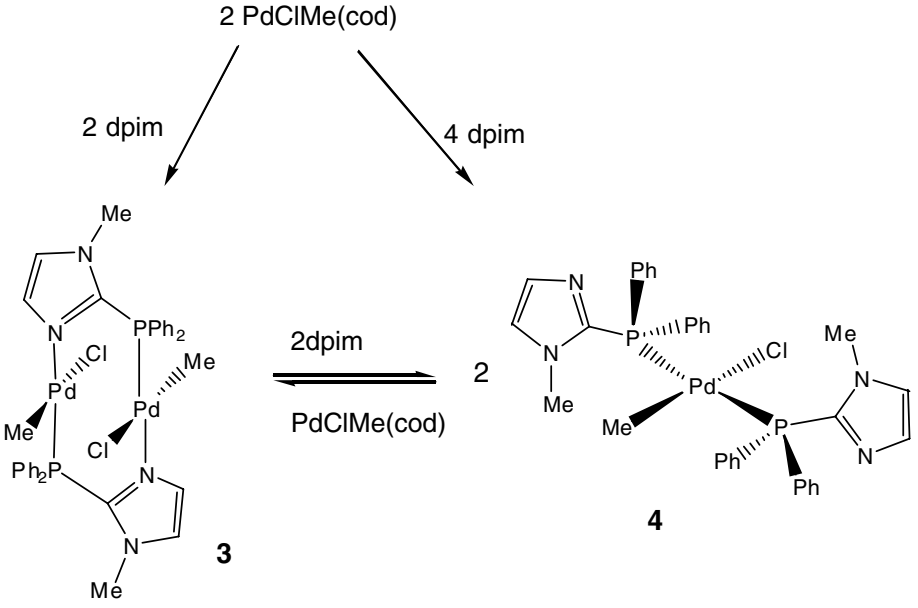
fragment $[Pd(OH)(dpim)]^+$. Furthermore, the intensity of the peak at 853 decreased markedly in the second spectrum. We considered the possibility that complex **2** could contain coordinated DMSO and the water could be hydrogen bonded to both it and the imidazole nitrogen. However, in the mass spectra we did not observe peaks due to species containing DMSO. This complex was isolated and completely characterized by elemental analysis, NMR and IR spectroscopy (see Section 4).

Complex **2** has strong similarities with the previously reported derivative $[RuCp(t\text{-Budpim})_2(H_2O)]OTf$ [12]. In the Ru complex, the two protons of the water molecule are equivalent ($\delta = 9.1$ ppm) because each one participates in the formation of a hydrogen bond with the free nitrogen of one of the two ligands. This complex is very active as a precursor in the catalytic hydration of terminal alkynes to give aldehydes selectively. The process that leads to complex **2** is a sort of water activation and, although at this stage the process is not reversible, it has some similarities with processes described for other complexes containing hemilabile ligands, which behave as humidity sensors [2b]. Hydrogen bonds have also been found between the hydrogens of benzylamine coordinated to a palladium centre and the free nitrogens of two monodentate imidazolylphosphine ligands [13].

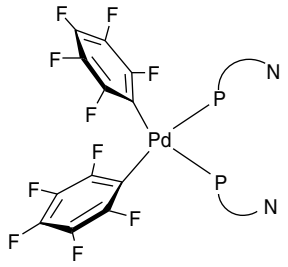
The reaction of [PdClMe(cod)] with the ligand dpim in 1:1 and 1:2 molar ratios, either in acetone or THF, at room temperature gave rise to the products $[PdClMe(\mu\text{-dpim-}\kappa P,\kappa N)]_2$ (**3**) and $[PdClMe(dpim\text{-}\kappa P)_2]$ (**4**), respectively (see Scheme 3). The reaction of the dinuclear complex **3** with two equivalents of the dpim ligand gave the mononuclear derivative **4**. Furthermore, the reaction of **4** with one equivalent of [PdClMe(cod)] gave **3**, among other products. These transformations demonstrate the type III hemilabile behaviour of the dpim ligand in these derivatives [1].

The synthesis of derivative **3** has been previously reported [9] as a mixture of two isomers. We performed the reaction in order to demonstrate the hemilabile behaviour of the ligand by means of the **3** ↔ **4** transformation. To complement the characterization of this derivative, we also performed a $^{13}C\{^1H\}$ NMR spectrum and a HSQC experiment. We agree with Cavell et al. that the most reasonable structure for this derivative is that with two HT dpim bridges. A *trans* HT disposition of the ligands has also been observed in homodinuclear systems and in the majority of the heterodinuclear derivatives with the PPh_2py ligand [16,17]. They proposed that the difference between the major and minor isomers concerns the relative disposition of the chloride and methyl ligands on the two metal centres (''cisoid'' or ''transoid''). The NMR data do not allow the unequivocal assignment of the major isomer to one of the two structures. However, we tentatively propose the ''transoid'' structure on the basis that this is the type of structure found in similar complexes [18–20].

The $^{31}P\{^1H\}$ NMR (CD_3COCD_3) spectrum of **4** exhibits one singlet (see Table 1), which indicates that the two



Scheme 3.



5

Scheme 4.

phosphorus atoms must be in a *trans* disposition. The chemical shift (15.34 ppm) is lower than that for **2**, although in both cases the ligand is only coordinated by the P atom. This difference may be ascribed to the distinct σ donor character of the groups in the *trans* position. In the ^{1}H NMR (CD_3COCD_3) spectrum (see Table 1), resonances for only one type of dpim ligand were observed. A triplet at −0.01 ppm ($^3J_{PH} = 6.1$ Hz, coupling demonstrated by ^{31}P decoupling experiments) for the corresponding methyl-Pd group is also observed. The low value of the coupling constant confirms the *cis* disposition between the methyl group and the phosphorus atoms. The relative disposition of these groups is in accordance with the high *trans* influence of the methyl group, which prevents the presence of a strong donor ligand such as a phosphine in a *trans* disposition to it [21]. Complexes of the type *trans*-[PdClMe(L)$_2$] have been described in which L = different derivatives of PPh_2py [6e].

The reaction of [Pd(C_6F_5)$_2$(cod)] with dpim, in both 1:1 and 1:2 molar ratios, gave the product [Pd(C_6F_5)$_2$(dpim-κ*P*)$_2$] (**5**). It is noteworthy that the formation of **5** takes place even when one equivalent of ligand per palladium was used. In this case, the excess of the starting palladium compound remains in solution. The IR spectrum in the X–C_6F_5 sensitive region [22] shows two bands at 770 and 780 cm^{-1}, a finding consistent with the presence of two pentafluorophenyl groups in a *cis* disposition (see scheme 4). The ^{31}P{^{1}H} NMR (dichloromethane-d_2) spectrum shows a singlet at 4.19 ppm. This chemical shift is of lower frequency than expected considering the monodentate coordination mode of the phosphines, but this could be interpreted as being the result of the σ-donor character of the pentafluorophenyl ligands *trans* to the phosphorus atoms. This σ-donor character is reflected in the ^{31}P chemical shifts of derivatives of the type [PdR_2(PMe_3)$_2$] (R=C_6BrF_4) which, depending on the starting material used, have been obtained both in the *cis* and *trans* forms. The resonances of the *cis* isomers appear at lower frequencies than those of the *trans* forms [23]. The corresponding ^{1}H NMR (dichloromethane-d_2) spectrum of **5** confirms that both phosphines are equivalent. The ^{19}F NMR spectrum shows the three expected types of F atoms: *ortho*, *meta* and *para* (see Section 4). The expected three-bond couplings were observed in a ^{19}F–^{19}F COSY spectrum. The existence of single resonances for the F_{ortho} and F_{meta} atoms indicates that there is free rotation around the Pd–C bonds and/or that a symmetry plane exists in the complex that makes the two halves of the C_6F_5 groups equivalent.

It is worth noting the different behaviour of the "PdClMe" and "Pd(C_6F_5)$_2$" fragments against the dpim ligand. When two dpim ligands are coordinated, the Cl and Me are situated in a mutually *trans* disposition while the two pentafluorophenyl groups prefer to be in a *cis* orientation. This is again in accordance with the *trans* influence, being bigger for the aryl groups than for the phosphines (some authors have proposed the term "transphobia" to explain this type of behaviour. The transphobia of two aryl groups would be bigger than that of two phosphines) [21a,21b,21c]. Another difference is that in the case of the pentafluorophenyl derivative the adoption of a bidentate coordination through the formation of a dinuclear complex is not favoured. A plausible explanation is that, considering the preference for a mutual *cis* deposition of the two aryl groups, the formation of a dinuclear species would lead to a high steric hindrance.

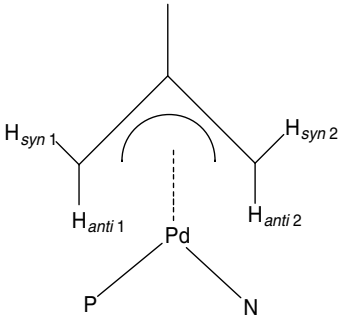
We also performed the reaction of the allyl derivative [Pd(η^3-2-Me–C_3H_4)Cl]$_2$ with the ligand dpim. It was carried out in two steps according to the procedure described by Pregosin and coworkers [24] (see Eq. (2)). Complex **6**, {[Pd$_2$(η^3-2-Me–C_3H_4)$_2$(μ-dpim-κ*N*, κ*P*)$_2$][PF_6]$_2$}, was obtained.

$$\begin{array}{l} [Pd(\eta^3\text{-2-Me–}C_3H_4)Cl]_2 + 2AgPF_6 \xrightarrow{S} 2[Pd(\eta^3\text{-2-Me–}C_3H_4)S_2]PF_6 + 2AgCl \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow 2\text{dpim} \\ S = \text{acetone} \qquad\qquad\qquad\qquad [Pd(\eta^3\text{-2-Me–}C_3H_4)_2(\text{dpim})_2][PF_6]_2\mathbf{6} \end{array} \quad (2)$$

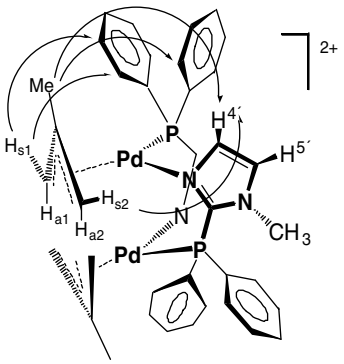
Different peaks observed in the FAB mass spectrum are indicative of a dinuclear structure for **6**. For example, a peak at $m/z = 1001$ Da corresponding to {[Pd$_2$(C_4H_7)$_2$-(dpim)$_2$]PF_6}$^+$ is observed (see Section 4 for more information).

Complex **6** in solution was studied by multinuclear NMR and the results show the presence of two isomers in very different proportions; **6M**:**6m** = 10:1 (**M** = major isomer, **m** = minor isomer). The major isomer gives rise to one singlet in the ^{31}P{^{1}H} NMR spectrum along with the septet due to the PF_6^-, an observation that is consistent

with the presence of two equivalent dpim ligands. The ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **6M** both reflect the existence of a single type of dpim ligand and one type of asymmetric allyl group. The assignment of the allyl ^{1}H NMR (CD_3COCD_3) resonances (see Table 1) was made on the basis of characteristic chemical shifts and coupling constants for allyl derivatives with PN ligands [25] and with the help of some NOESY experiments (both 1- and 2-D). NOEs were found between the methyl resonance and both H_{syn} protons, between H_{syn2} and H_{anti2} (see Scheme 5 for the atom numbering scheme) and also between both H_{anti} protons. The arrangement in which H_{syn2} is *trans* to phosphorus was deduced from the NOE between H_{syn2} and $H^{4'}$, as well as by the NOE between H_{syn1} and some phenyl protons (*ortho* and *meta*) (see Scheme 6). (Intraligand NOEs in the dpim ligand were also observed. Others NOEs detected between allylic protons and the dpim ligand will be considered below). As expected, higher chemical shifts are observed for the terminal protons and the carbon *trans* to phosphorus [25], a situation that is consistent with the higher *trans* influence of this donor atom [26]. The coupling with phosphorus (in the case of the protons, higher for H_{anti}) is only observed for the *trans* nuclei. A small H_{syn1}–H_{syn2} coupling is also detected. A particularly low chemical shift is found for the H_{syn1} proton that is *cis* to phosphorus. This observation can be attributed to the shielding effect of the phenyl rings. The existence of two types of phenyl rings can also be deduced from the $^{13}C\{^{1}H\}$ NMR spectrum.



Scheme 5.



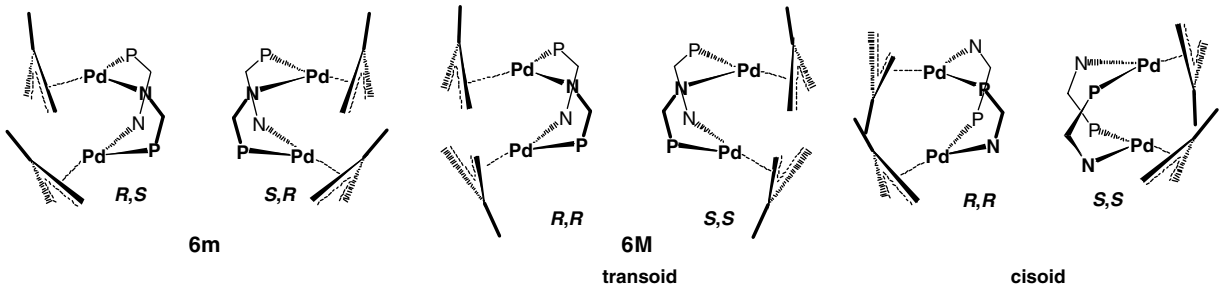
Scheme 6. Some of the NOEs (arrows) found in complex **6M**.

The minor isomer, **6m**, exhibits two singlets in the $^{31}P\{^{1}H\}$ NMR spectrum and resonances corresponding to two different dpim ligands and two asymmetric allyl groups in the ^{1}H NMR spectrum. In fact, in CD_3COCD_3 two different methyl resonances for the dpim ligand and at least 6 allylic protons are detected (some of which have been assigned). In 1,1′,2,2′-tetrachloroethane-d_2 seven allylic protons and the two methyl allylic groups are also clearly seen (see Section 4).

When the different structural possibilities for this dimeric allyl derivative are considered, it is useful to remember that square-planar allyl palladium complexes with PN bidentate ligands show chirality. Both Faller [27] and Hayashi [28] have tried to improve on the previous nomenclature based on the *exo* and *endo* prefixes to establish a more general system that is effective when there is no reference to assign these prefixes. We decided to use the system proposed by Faller because it is similar to that proposed for other η^n donor ligands [29]. This method involves extending the Cahn, Ingold and Prelog (CIP) rules to describe the absolute configuration of both enantiomers. Faller et al. chose to view the Pd system as one would a chiral pyramidal phosphorus atom, considering the allyl as an 18-electron (6×3) pseudoatom [30] located at the centroid of the allyl group (the Pd system is seen from the side of the coordination plane where the methyl group is pointing). In the case of dinuclear allylic complexes there are two different chiral palladium atoms and, therefore, four diastereomers grouped into two pairs of enantiomers: on the one hand (*R*,*S*) and (*S*,*R*) and on the other (*R*,*R*) and (*S*,*S*) (see Scheme 7). In principle, it is also possible to consider another (*R*,*R*) and (*S*,*S*) pair of enantiomers, i.e., those that have the two allyl groups with the methyl fragments oriented towards the inside of the molecule (cisoid orientation of the allyl methyl groups) (see Scheme 7). Strictly speaking, both pairs of (*R*,*R*) and (*S*,*S*) cisoid and transoid enantiomers could interconvert into each other by a boat-to-boat interconversion similar to that found in derivatives containing bis(pyrazol-1-yl)methane ligands [31]. However, this interconversion is much less common in eight-membered cycles and the presence of the phenyl substituents on the phosphorus atom makes this process very unlikely in our system. In any case, this cisoid orientation of the methyl groups would lead to a high level of steric hindrance and this pair of enantiomers is probably not formed in our case and will not be considered in the following discussion.

The pair of enantiomers (*R*,*S*) and (*S*,*R*) contain two different dpim ligands and two inequivalent and asymmetric allyl groups, which fits well with the minor isomer **6m**. On the other hand, the C_2 axis present in the enantiomers (*R*,*R*) and (*S*,*S*) implies that the two dpim and the two allyl groups are equivalent and consequently these correspond to the major isomer **6M**.

Having established the structure for **6M**, it is interesting to consider the NOEs found between the allylic methyl group and different protons of the dpim ligand (see Scheme 6). Indeed, we found NOEs with phenylic *ortho* and *meta*



Scheme 7. Possible structures for complex **6**.

protons and, more interestingly, with the $H^{4'}$ proton of the imidazole ring. This last NOE is strongly consistent with a dimeric structure and it would not be very likely to occur in a monomeric structure with a chelate dpim ligand. In this case, the plane of the imidazolyl ring should be approximately parallel to the coordination plane.

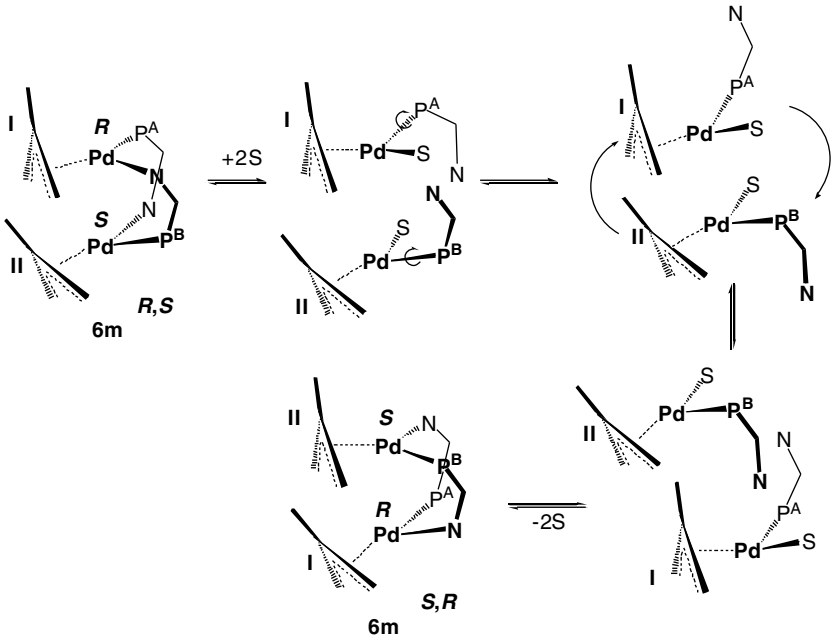
Once studied the NMR characteristics of the new derivatives, we have analysed whether the chemical shift of the imidazolic Me resonance was sensitive to the nitrogen coordination. On comparing our Pd complexes with the previously described compounds of the same metal [8,9], it was observed that when the ligand is monodentate the chemical shift of this group is above 3.5 ppm, while a bidentate coordination gives rise to chemical shifts below this value (2.7–3.5 ppm). The only exception is the dichloride derivative reported by Cavell et al. where a dinuclear structure with dpim bridges is proposed [9].

2.2. Fluxional behaviour of complex *6*

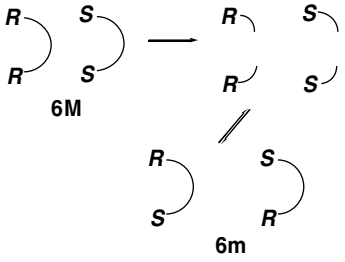
Considering the rich fluxional behaviour usually exhibited by allyl palladium complexes [32], we attempted to study the dynamics of **6**. Processes involving apparent allyl rotation that would interchange the two terminal allylic groups (*syn*-*syn*′ or *anti*-*anti*′ interconversion) have been described [31a,31b,32a,33,34]. Also common are η^3-η^1-η^3 interconversion processes [24b,32,33e,35,36]. Such a process is sometimes selective and in the η^1 intermediate only one of the two terminal carbons remains bonded to the metal [24b,33e,36]. If electronic factors govern the process, the carbon that opens up would be the one situated *trans* to the stronger donor ligand. The η^3-η^1-η^3 process would lead to an H_{syn}–H_{anti} interconversion on the carbon (or carbons) that retains the σ bond to Pd. In the case of complex **6** changes were not observed in the ^{1}H- and ^{31}P NMR spectra at low temperature (−80 °C). When solutions of **6** (CD_3COCD_3) were heated up to 50 °C a slight broadening of the proton signals was observed. It seems that the process or processes that may be in operation are of higher energy than that required for study by the coalescence method. In order to detect possible interchange processes of higher energy we performed a phase-sensitive 2D-NOESY experiment in CD_3COCD_3. Some cross-peaks could not be taken into account because they involve resonances for which there is partial overlap between signals of **6M** and **6m**. However, this experiment does enable three important facts to be deduced: (i) There is chemical interchange between H_{syn2}(**6m**) and H_{syn2}(**6M**); (ii) There is interchange between H_{anti2}(**6m**) and $H_{anti2'}$(**6m**) and (iii) there is no interchange between H_{syn1}(**6M**) and H_{syn2}(**6M**). Point (i) indicates that interconversion between the two isomers is possible and that the observed interchange takes place without changing the nature of the allylic protons (*syn* and *trans* to P) – although in this regard point (ii) is more conclusive. Besides, there is interchange between the two allylic groups of **6m** but without a change in the nature of the allylic protons: i.e., *syn* and *trans* to P. This implies that we are observing neither a process of apparent allyl rotation nor a η^3-η^1-η^3 dynamic process. Even a selective η^3-η^1-η^3 process can be discarded because if it existed – bearing in mind that electronic effects should be operating (high steric effects are not expected) – this would lead to opening of the carbon *trans* to phosphorus due to its higher *trans* influence and, consequently, an H_{syn2}–H_{anti2} interchange should be observed.

When the phase-sensitive 2D-NOESY was recorded in 1,1′,2,2′-tetrachloroethane-d_2 only cross-peaks corresponding to NOEs were detected but there were not observed any interchange. This is consistent with the fact that when the 1,1′,2,2′-tetrachloroethane-d_2 solution was heated up to 130 °C, it was not observed a broadening of the resonances. Consequently, there is a clear effect of the solvent possibly due to its coordinating ability.

The hemilabile character of the dpim ligand provides a possible fluxional process to explain the behaviour observed in solution through the transient formation of the monomeric $[Pd(\eta^3\text{-allyl})(\text{dpim-}\kappa P)(S)]^+$ intermediate, probably stabilized by the coordination of acetone. The observation in the mass spectra of the base peak at 427 Da that correspond to $[Pd(C_4H_7)(\text{dpim})]^+$ is consistent with our proposal. The interconversion between the two different allyl groups in **5m** is represented in Scheme 8. Pd–N bond rupture is followed by rotation about the Pd–P bond and a change in the relative disposition of the two metallic fragments leads to the aforementioned interchange through reformation of the Pd–N bonds. Similarly, the formation of these monomeric metallic fragments and recombination in a different way, as outlined in Scheme 9, can explain the **6M**–**6m** interconversion. If the solvent participates in the formation of the transient intermediate,



Scheme 8. Proposed mechanism for the interchange of the two allyl fragments in **6m**.



Scheme 9. **6M/6m** interconversion.

the hemilabile behaviour in this case, as in the chloromethyl derivatives **3** and **4**, is also of type III. The equilibrium between the dimeric μ-PN and the κ^1 species seems to be fast even at −80 °C because, at this temperature, splitting of the ^{1}H NMR signals is not observed. Faller et al. recently pointed out that the effects of κ^2–κ^1 interconversions, although they can be hidden or subtle, may be important in certain fluxional processes observed in allyl complexes containing hemilabile ligands [27]. Processes involving Pd–N bond rupture have been widely described [24b,27b,33b,33c,33j,36c,37,38]. A case with a certain similarity to our example was reported by Espinet et al., [39] who described a cisoid/transoid interconversion through cleavage of both bridges and statistical rearrangement in dimeric allyl-palladium derivatives with two aryl bridges. It is worth noting that in our proposed process for the observed interchanges, the absolute configuration of each metallic fragment does not change throughout the dynamic process. We must emphasize that although we did not observe the apparent allyl rotation or the η^3-η^1-η^3 processes in our study, they could be present as higher energy processes.

According to the mechanism proposed for this derivative, it is the allyl group that offers information about the hemilabile behaviour of the dpim ligand. The allyl moiety behaves as a kind of "reporter ligand". This concept has been used in allyl-derivatives to refer to an accompanying ligand that, usually by means of NOE studies, can give information about the stereochemistry and selective distortions of the allylic moiety [32b,34a]. Interestingly, in our case, the concept of the reporter ligand can be used in the other sense and the NMR data for the allyl group allow the detection of the dynamic behaviour of the other ligand at the coordination centre.

2.3. X-ray diffraction study for *6*

Crystals of complex **6** were obtained from a mixture of acetone and hexane by slow diffusion and its structure was determined by X-ray diffraction analysis. The monocrystal corresponded to the isomer **6m**. Despite having obtained crystals on three separate occasions, we always found the same complex **6m**. Consequently, although **6M** is thermodynamically more stable in solution, it is **6m** that always crystallizes better. A selection of bond distances and angles are gathered in Table 2 and the crystallographic data are given in Table 3. The asymmetric unit of this crystal shows two slightly different (*S*,*R*) stereoisomers for the cationic dinuclear complex of **6m**, $(S,R)_\alpha$ and $(S,R)_\beta$, which differ from each other in some structural features. The corresponding enantiomers $(R,S)_\alpha$ and $(R,S)_\beta$, were generated through the inversion center that has the space group $P\bar{1}$. In consequence the unit cell consist of two pairs of enantiomers (*R*,*S*) and (*S*,*R*). From this point on, and to make clear which enantiomer is designated by using the descriptors *R* and *S* we have adopted the following criterion. The

Table 2
Selected bond distances (Å) and angles (°) for **6m**

Bond lengths			
$(S,R)_\alpha$			
Pd(1)–C(21)	2.085(8)	Pd(2)–C(19)	2.081(8)
Pd(1)–C(22)	2.216(9)	Pd(2)–C(18)	2.191(9)
Pd(1)–C(23)	2.185(8)	Pd(2)–C(17)	2.175(9)
Pd(1)–N(3)	2.140(6)	Pd(2)–N(1)	2.116(6)
Pd(1)–P(1)	2.318(2)	Pd(2)–P(2)	2.288(2)
$(S,R)_\beta$			
Pd(3)–C(57)	2.079(8)	Pd(4)–C(63)	2.094(8)
Pd(3)–C(58)	2.179(9)	Pd(4)–C(62)	2.214(8)
Pd(3)–C(59)	2.190(8)	Pd(4)–C(61)	2.185(8)
Pd(3)–N(7)	2.132(6)	Pd(4)–N(5)	2.133(6)
Pd(3)–P(1)	2.2900(19)	Pd(4)–P(4)	2.314(2)
Bond angles			
$(S,R)_\alpha$			
C(21)–Pd(1)–C(23)	67.2(4)	C(19)–Pd(2)–C(17)	66.0(3)°
N(3)–Pd(1)–P(1)	97.32(16)	N(1)–Pd(2)–P(2)	96.21(17)°
C(21)–C(22)–C(23)	115.8(9)	C(17)–C(18)–C(19)	113.8(10)
$(S,R)_\beta$			
C(57)–Pd(3)–C(59)	66.6(4)	C(63)–Pd(4)–C(61)	67.0(4)
N(7)–Pd(3)–P(3)	97.08(17)	N(5)–Pd(4)–P(4)	96.22(17)
C(59)–C(58)–C(57)	114.1(10)	C(61)–C(62)–C(63)	116.2(9)

Table 3
Crystal data and structure refinement for **6m**

Empirical formula	$C_{40}H_{44}F_{12}N_4P_4Pd_2$
Formula weight	1145.47
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	13.6354(14)
b (Å)	17.1523(18)
c (Å)	19.653(2)
α (°)	86.086(2)
β (°)	82.525(2)
γ (°)	88.826(2)
Volume (Å^3)	4546.3(8)
Z	4
D_{calc} (Mg/m^3)	1.674
Absorption coefficient (mm^{-1})	1.016
$F(000)$	2288
Crystal size (mm)	$0.15 \times 0.15 \times 0.10$
θ Range for data collection (°)	1.05–26.00
Index ranges	$-16 \leqslant h \leqslant 16$, $-21 \leqslant k \leqslant 21$, $-24 \leqslant l \leqslant 24$
Reflections collected	48,328
Independent reflections [R_{int}]	17,752 [0.0754]
Completeness to $\theta = 26.00°$ (%)	99.3
Absorption correction	Semi-empirical from equivalents
Maximum and minimum transmission	0.903 and 0.792
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	17,752/0/1125
Goodness-of-fit on F^2	$S = 0.995$
R indices [for 10,871 reflections with $I > 2\sigma(I)$]	$R_1 = 0.0672$, $wR_2 = 0.1676$
R indices (for all 17752 data)	$R_1 = 0.1157$, $wR_2 = 0.2006$
Weighting scheme	$w^{-1} = \sigma^2(F_o^2) + (aP)^2 + (bP)$, where $P = [\max(F_o^2, 0) + 2F_c^2]/3$ $a = 0.101400$, $b = 0.0000$
Largest difference in peak and hole (e Å^{-3})	1.105 and −0.914

first absolute descriptor in between the brackets refers to the Pd atom whose allylic methyl group points outwards the eight-membered metallacycle, meanwhile the second refers to the Pd atom with its methyl group pointing inwards the same dipalladium cycle. Moreover, we have added α and β subscripts to the absolute configuration to distinguish between the structural isomers. The corresponding ORTEP diagrams for the two (S,R) stereoisomers are shown in Fig. 2.

The molecular structure of each (S,R) enantiomer can be described as a dimeric molecule with square planar environments for both Pd atoms although distortions from the ideal geometry are significant due to the small bite angle of the allyl group (C–Pd–C). The N–Pd–P angle in each coordination plane is slightly bigger than the ideal value of 90°. The dpim ligands coordinate to the metal atoms in a bridged bidentate "head-to-tail" arrangement, forming an eight-membered metallacycle with a "boat" conformation. The allyl groups are planar and form angles of more than 90° with the metallic coordination planes, although both angles are slightly different in the same

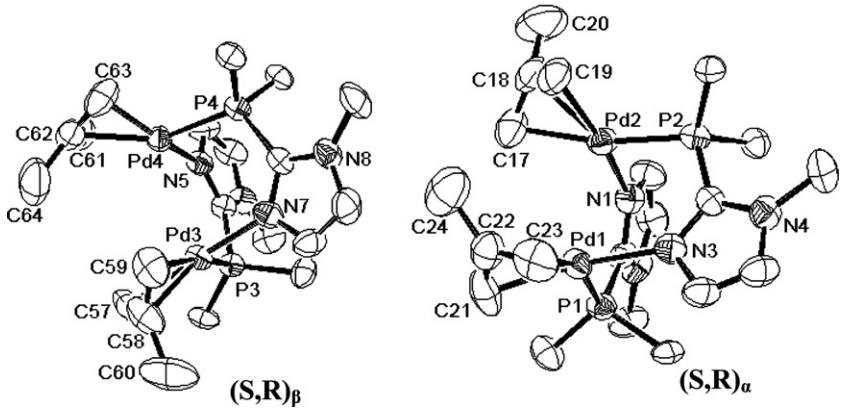


Fig. 2. ORTEP diagram for both (S,R) enantiomers of **6m** found in the same unit cell. Counteranions, as well as phenyl groups and hydrogen atoms have been omitted for clarity.

(*S*,*R*) isomer, with average values for the two stereoisomers being 105.67° and 139.11°. The two allylic methyl groups have the same relative orientation. It is worth noting that, in contrast to the situation found in **6m**, in all X-ray structures of dinuclear palladium η^3-allyl derivatives with eight-membered metallacycles described to date, both allyl groups have the central carbon pointing outward from the molecule. In other words, both methyl groups have opposite orientations [40]. We found only one exception to this trend – an example in which the allyl group possesses a large steroid substituent that makes the usual disposition impossible [41]. The two coordination planes in each enantiomer are not completely parallel, with a dihedral angle of 17.49° (average for the two enantiomers).

As expected, the Pd–C bonds *trans* to the N atoms are, in all cases, shorter than the Pd–C bonds *trans* to the P atoms and this is due to the higher *trans* influence of the P-donor atom. The Pd–N and Pd–P bond distances are in the expected range. The Pd–Pd distances are Pd(1)–Pd(2) = 3.1896(8) and Pd(3)–Pd(4) = 3.2046(8). Finally, four octahedral PF_6^- counterions were found between each pair of cationic enantiomers. We verified that the distances between protons that showed an NOE in the NMR studies are in the range 3.346–3.732 Å.

3. Conclusions

We have synthesised several palladium complexes containing the hemilabile ligand 2-(diphenylphosphino)-1-methylimidazole (dpim) and different modes of coordination have been found (*P* monodentate and *P*,*N* bridge). It has been found that small changes in the other ligands present in the complexes influence the type of coordination of the dpim ligand. An unexpected coordination of water to the palladium centre has been achieved in one complex. For the chloromethyl derivatives, the transformations between mononuclear and dinuclear species demonstrate the existence of type III hemilability. The allyl derivative that is present as a mixture of two pairs of enantiomers exhibits double HT dpim bridges with a relative *cis* disposition. In the minor isomer whose structure has been determined by X-ray diffraction the two allylic methyl groups have the same relative orientation, a very unusual fact for dinuclear palladium η^3-allyl derivatives with eight-membered metallacycles. A solvent dependent fluxional process that involves Pd–N bond rupture has been found for this derivative. The dynamic process implies that the allyl group acts as a reporter ligand and shows the hemilabile behaviour of the dpim ligand.

4. Experimental

4.1. General remarks

All manipulations were carried out under Ar using standard Schlenk techniques. Solvents (Merk) were dried and distilled under N_2 prior to use. NMR spectra were recorded at room temperature (≈22 °C), unless otherwise stated, on a VARIAN UNITY INOVA-500, on a VARIAN UNITY-300 or on a VARIAN INOVA-400 spectrometers. Chemical shifts (ppm) are relative to TMS (^{1}H, ^{13}C NMR), H_3PO_4 (85%) (^{31}P NMR) and $CFCl_3$ (^{19}F NMR). ^{1}H–^{1}H COSY spectra: standard pulse sequence with an acquisition time of 0.214 s, pulse width 10 ms, relaxation delay 1 s, number of scans 16, number of increments 512. 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. NOESY spectra for **6** (VARIAN INOVA-500) standard parameters: relax delay 1.000 s, mixing 1.00 s, acquisition time 0.128 s, width 7996.0 Hz, 2D width 7996.0 Hz, 16 repetitions, 2 × 256 increments, DATA PROCESING Gauss apodization 0.059 s, F1 DATA PROCESING Gauss apodization 0.030 s. ^{19}F–^{19}F-COSY spectra: standard pulse gCOSY sequence, standard parameters: VARIAN INOVA-400, relax delay 1.000 s, acquisition time 0.181 s, width 22624.4 Hz, 2D width 22624.4 Hz, single scan, 128 increments, Sq sine bell 0.091 s. HSQC, VARIAN INOVA-400 Temp = 40 °C, Relax. delay 1.000 s, Acq. time 0.211 s,Width 4861.4 Hz, 2D Width 20110.6 Hz, 128 repetitions, 2 × 256 increments. For variable temperature spectra, the probe temperature (±1 K) was controlled by a standard unit calibrated with a methanol reference. IR spectra were recorded on a Nicolet Impact 410 spectrophotometer as KBr pills, or on a Jasco FT/IR – 6300 type A (630–150 cm^{-1} range) in Nujol mulls, or on a Perkin–Elmer 883 (4000–200 cm^{-1} range) in Nujol mulls. Elemental analyses were performed in a LECO CHNS932 microanalyser. FAB^+ mass spectra were recorded in a VG AutoSpec using a ionization Liquid Secondary Ion Mass Spectrometry (LSMIS+) and Cs and NBA ions as the matrix and in a 4700 Proteomics Analyzer (MALDI-TOFTOF) of Applied Biosystems (dry sample preparation with dithranol). The ligand dpim [8] and the complexes $[PdCl_2(cod)]$ [42], $[PdCl_2(PhCN)_2]$ [43], [PdClMe(cod)] [44], $[Pd(\eta^3\text{-2-Me–}C_3H_4)Cl]_2$ [45] and $[Pd(C_6F_5)_2(cod)]$ [46] were prepared as previously described. *o* = *ortho*, *m* = *meta*, *p* = *para*, *d* = doublet, *m* = multiplet, *s* = singlet, *b* = broad.

4.2. Synthesis of $[PdCl_2(dpim)]_n \cdot n/2CH_2Cl_2$ (1)

The ligand dpim (74.56 mg, 0.28 mmol) was added to a solution of $[PdCl_2(cod)]$ (80 mg, 0.28 mmol) in CH_2Cl_2 (20 mL). The mixture was stirred at room temperature. After 15 min an orange precipitate was formed and one hour later this orange solid (**1**) was filtered, washed with diethylether (2 × 10 mL) and dried under vacuum. Yield: 102.4 mg (0.22 mmol, 79%). *Note.* Alternatively the reaction can be carried out using $[PdCl_2(PhCN)_2]$ as the starting material in acetone or THF. $PdCl_2(dpim) \cdot 1/2CH_2Cl_2$, $C_{16.5}H_{16}Cl_3N_2PPd$ (486.06): calcd. C, 40.77; H, 3.32; N, 5.76. Found: C, 40.61; H, 3.57; N, 5.81%. MALDI mass spectra: *m*/*z* = 598 Da, $[PdCl(dpim)_2–C_6H_5]^+$; 675 Da, $[PdCl(dpim)_2]^+$; 781 Da $[Pd_2Cl(dpim)_2]^+$; 816 Da, $[Pd_2Cl_2$-

$(dpim)_2]^+$; 853 Da (base peak), $[Pd_2Cl_3(dpim)_2]^+$; 895 Da, $[Pd_2Cl_5(dpim\text{-}Me)_2]^+$; 1034 $[Pd_3Cl_6(dpim\text{-}Me)_2]^+$; 1214 Da, tentatively assigned to: $[Pd_4Cl_8(dpim\text{-}CH_2)_2]^+$.

4.3. Synthesis of [$PdCl_2(H_2O)(dpim\text{-}\kappa P)$] (2)

Complex **1** was solved at 70 °C in wet DMSO-d_6 to give a yellow solution of complex **2** which was characterized by NMR. The solid was isolated as follows: the solvent was removed by heating the solution under vacuum. The oily residue was then solved in THF and precipitated with diethylether. The resulting yellowish-white solid was dried under vacuum and completely characterized. $C_{16}H_{17}Cl_2N_2OPPd$ (461.62): calcd. C, 41.63; H, 3.71; N, 6.07. Found: C, 41.20; H, 3.78; N, 6.16%. IR (KBr pellet, cm^{-1}), ν(O–H, H_2O and C–H, aromatic) = 3201 (b), 3163, 3134, 3113, 3056, 3028; far-IR (nujol mull, cm^{-1}), ν(Pd–O) = 490; ν(cis-$PdCl_2$) = 293, 306. See Table 1 for the ^1H and ^{31}P NMR data.$^{13}C\{^1H\}$ NMR (DMSO-d_6, 75.432 MHz, 298 K): δ = 139.6 (d, $^1J_{PC}$ = 41.3, 1C, $C^{2'}$–Im), 130.8 (m, 6C, $C_{o,p}$-Ph), 127.8 (d, $^3J_{PC}$ = 11.1, 4C, C_m-Ph), 122.0 (s, 1C, CH–Im), 119.5 (s, 1C, CH–Im), 36.5 (s, 1C, Me–Im) ppm. It was confirmed that the ^1H NMR spectra of the solid obtained is the same than that observed after solving 1 in DMSO-d_6. FAB^+ mass spectra: m/z = 427 Da, $[PdCl(H_2O)(dpim)]^+$; m/z = 389 Da, $[Pd(OH)(dpim)]^+$.

4.4. Synthesis of [$PdClMe(\mu\text{-}dpim\text{-}\kappa N,\kappa P)]_2$ (3)

The ligand dpim (57 mg, 0.21 mmol) was added to a solution of [PdClMe(cod)] (55 mg, 0.21 mmol) in THF (15 mL). The mixture was stirred for 30 min at room temperature. A pale yellow precipitated was formed that was filtered, washed with diethylether (2 × 10 mL) and dried under vacuum. Yield: 81.68 mg (0.19 mmol, 93%). $C_{17}H_{18}ClN_2PPd$ (423.18): calcd. C, 48.25; H, 4.29; N, 6.62. Found: C, 47.93; H, 4.32; N, 6.72%. IR (nujol mull, cm^{-1}), ν(Pd–Cl) = 311. See Table 1 for the ^1H and ^{31}P NMR data. FAB^+ mass spectrum: m/z = 811 Da $[Pd_2Cl\text{-}Me_2(dpim)_2]^+$ (base peak). $^{13}C\{^1H\}$ NMR (100.577 MHz, DMSO-d_6, 298 K): δ = 139.4 (d, $^1J_{PC}$ = 74.2, 2C, C_{ipso}–Ph); 136.3 (d, $^1J_{PC}$ = 74.22, 2C, C_{ipso}–Ph); 134–125 (m, Ph+Im); 36.9 (d, J_{PC} = 29.4, 2C, *Me*–Im); 11.2 (d, $^2J_{PC}$ = 72.9, 2C, *Me*–Pd).

4.5. Synthesis of [$PdClMe(dpim\text{-}\kappa P)_2$] (4)

The ligand dpim (114 mg, 0.42 mmol) was added to a solution of [PdClMe(cod)] (55 mg, 0.21 mmol) in THF (15 mL). The mixture was stirred for 30 min at room temperature and afterwards the solvent was removed under vacuum. The resulting pale yellow solid was washed with diethylether (2 × 10 mL) and dried under vacuum. Yield: 137.4 mg (0.2 mmol, 96%). $C_{33}H_{33}ClN_4P_2Pd$ (689.46): calcd. C, 57.49; H, 4.82; N, 8.13. Found: C, 57.21; H, 4.79; N, 8.41%. IR (nujol mull, cm^{-1}), ν(Pd–Cl) = 304. See Table 1 for the ^1H and ^{31}P NMR data. $^{13}C\{^1H\}$ NMR (75.432 MHz, CD_3COCD_3, 298 K): δ = 135.3 (d, $^2J_{PC}$ = 10.3, 8C, C_o–Ph), 131.4 (d, $^1J_{PC}$ = 46.3, 4C, C_{ipso}–Ph), 130.7 (d, $^4J_{PC}$ = 2.6, 4C, C_p–Ph), 129.3 (d, $^1J_{PC}$ = 41.2, 2C, $C^{2'}$–Im), 129.8 (s, 2C, *C*H–Im), 128.3 (d, $^3J_{PC}$ = 10.3, 8C, C_m–Ph), 125.7 (s, 2C, *C*H–Im), 35.39 (s, 2C, *Me*–Im), 1.5 (s, 1C, *Me*–Pd) ppm.

4.6. Synthesis of [$Pd(C_6F_5)_2(dpim\text{-}\kappa P)_2$] (5)

The ligand dpim (83.5 mg, 0.32 mmol) was added to a solution of $[Pd(C_6F_5)_2(cod)]$ (86 mg, 0.16 mmol) in dichloromethane (30 mL). The mixture was stirred at room temperature for 30 min and then the solvent was removed under vacuum. The residue was washed with pentane (2 × 10 mL) and dried under vacuum. A pale yellow solid of complex **5** was obtained. Yield: 126.63 mg (0.13 mmol, 83%). $C_{44}H_{30}F_{10}N_4P_2Pd$ (973,09): calcd. C, 54.31; H, 3.11; N, 5.76. Found: C, 54.25; H, 3.01; N, 5.96%. IR (KBr, cm^{-1}), 1500, 1057, 958, 780 and 770 (C_6F_5). See Table 1 for the ^1H and ^{31}P NMR data. $^{13}C\{^1H\}$ NMR (100.577 MHz, $CDCl_3$, 298 K): δ = 133.1, 130.4, 130.3, 128.2 and 125.5 (Ph+Im), 36.04 (s, 1C, *Me*–Im) ppm. ^{19}F NMR (376.308 MHz, $CDCl_3$, 298 K): δ = −114.92 (d, $^3J_{FF}$ = 21.56, 4F, F_{ortho}, C_6F_5), −161.91 (t, $^3J_{FF}$ = 21.56, 2F, F_{para}, C_6F_5), −162.95 (m, 4F, F_{meta}, C_6F_5) ppm. FAB^+ mass spectrum: m/z = 372 Da $[Pd(dpim)]^+$, 433 Da $[(dpim)(C_6F_5)]^{+\cdot}$ (base peak), 539 Da $[Pd(C_6F_5)(dpim)]^+$, 639 Da $[Pd(dpim)_2{+}H]^+$, 746 Da $[Pd_2(dpim)_2]^+$, 805 Da $[Pd(C_6F_5)(dpim)_2]^+$, 913 Da $[Pd_2(C_6F_5)(dpim)_2]^+$.

4.7. Synthesis of [$Pd(\eta^3\text{-}2\text{-}Me\text{–}C_3H_4)(dpim\text{-}\kappa N,\kappa P)]_2[PF_6]_2$ (6)

$AgPF_6$ (160.5 mg, 0.5 mmol) was added to a solution of $[Pd(C_4H_7)Cl_2]_2$ (100 mg, 0.25 mmol) in acetone (100 mL). The mixture was stirred for 3 h in the absence of light and the resulting yellow solution was filtered and the solid residue, AgCl, washed with acetone (2 × 5 mL) to extract some additional palladium complex. The washing liquor was added to the yellow solution and both together treated with dpim, (135.2 mg, 0.5 mmol). This mixture was stirred 1.5 h and then the solvent was removed under vacuum. The resulting oil became a white solid after treatment with pentane (20 mL) and drying under vacuum. Yield: 106.1 mg (0.19 mmol, 73%). $C_{20}H_{22}N_2P_2PdF_6$ (572.75): calcd. C, 41.94; H, 3.87; N, 4.89. Found: C, 41.84; H, 3.92; N, 5.11%. IR (KBr, cm^{-1}): ν(P–F) = 835, δ(FPF) = 557, 547 (PF_6). ^1H NMR (500 MHz, CD_3COCD_3, 293 K): **6m**: the following signals have been identified: 7.20 (s, 1H, $H^{5'}$–Im), 6.75 (s, 1H, $H^{4'}$–Im), 5.03 (m, 1H, H_{syn2}), 4.74 (m, 1H, $H_{syn2'}$), 4.37 (d, J_{PH} = 8.8, 1H, H_{anti2}), 3.82 (d, J_{PH} = 10.7, 1H, $H_{anti2'}$), 3.74 (m, 1H, H_{allyl}), 3.37 (bd, 1H, H_{syn1}), 3.23 (s, 3H, *Me*–Im), 3.19 (s, 3H, *Me*–Im) ppm. ^1H NMR (500 MHz, 1,1′,2,2′-tetrachloroethane-d_2, 293 K): **6M**: 7.6 (m, 12H, H_{meta} and H_{para}), 7.3 (m, 4H, H_{ortho}), 7.12 (s, 2H, $H^{5'}$–Im), 7.0 (m, 4H, H_{ortho}, protons situated near to Me–Im), 6.12 (s, 2H, $H^{4'}$–Im), 4.40 (dd,

2H, $J_{Hsyn2–Hsyn1} = 2.9$, $J_{HP} = 6.8$, H_{syn2}), 3,45 (d, 2H, $J_{HP} = 11.2$, H_{anti2}), 3.26 (d, 2H, H_{syn1}), 3.06 (s, 6H, *Me*–Im), 2.96 (s, 2H, H_{anti1}), 2.04 (s, 6H, *Me*-allyl). **6m**: the following signals have been identified: 6.72 (s, 1H, C*H*–Im), 6.23 (s, 1H, C*H*–Im), 4.56 (m, 1H, H_{syn2}), 4.36 (m, 1H, $H_{syn2'}$), 3.90 (d, 1H, $J_{HP} = 8.8$, H_{anti2}), 3.30 (d, 1H, $J_{HP} = 10.7$, $H_{anti2'}$), 3.19 (bs, 1H, H_{allyl}), 3.14 (bs, 1H, H_{allyl}), 3.04 (s, 3H, *Me*–Im), 2.99 (s, 3H, *Me*–Im), 2.92 (s, 1H, H_{allyl}), 1.98 (s, 3H, Me–allyl), 1.93 (s, 3H, Me-allyl). $^{13}C\{^1H\}$–NMR (75.432 MHz, CD_3COCD_3, 298 K, **6M**): $\delta = 139.8$ (d, $^3J_{PC} = 5.0$, 2C, $C^{4'}$–Im), 138.7 (d, $^1J_{PC} = 61.8$, 2C, $C^{2'}$–Im), 133.0 (d, $^3J_{PC} = 14.6$, 2C, $C^{5'}$–Im), 132.0 (d, $^2J_{PC} = 9.5$ Hz, 4C, C_o-Ph), 131.9 (s, 2C, C_p–Ph), 131.6 (d, 4C, $^2J_{PC} = 12.9$ Hz, C_o–Ph), 130.5 (d, $^3J_{PC} = 10.3$ Hz, 4C, C_m–Ph), 130.3 (s, 2C, C_p–Ph), 130.2 (d, $^3J_{PC} = 9.3$ Hz, 4C, C_m–Ph), 128.2 (d, $^1J_{PC} = 44.0$, 2C, C_{ipso}–Ph), 125.0 (d, $^1J_{PC} = 45.0$, 2C, C_{ipso}–Ph), 78.4 (d, $J_{PC} = 31.2$, 2C, C^2-allyl), 64.4 (s, 2C, C^1-allyl), 36.8 (s, 2C, *Me*–Im), 23.2 (s, 2C, *Me*-allyl) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, CD_3COCD_3, 293 K, **6m**): $\delta = 10.43$ (s, 1P), 9.93 (s, 1P) ppm. FAB^+ mass spectrum: $m/z = 1001$ Da $\{[Pd_2(C_4H_7)_2(dpim)_2]PF_6\}^+$, $m/z = 801$ Da $[Pd_2(C_4H_7)\text{-}(dpim)_2]^+$, $m/z = 746$ Da $[Pd_2(dpim)_2]^+$, $m/z = 427$ Da $[Pd(C_4H_7)\text{-}(dpim)]^+$ (base peak), $m/z = 372$ Da $[Pd\text{-}(dpim)]^+$, $m/z = 265$ Da $[(dpim\text{-}H)]^+$.

4.8. NMR experiment

The ligand dpim (2.7 mg, 0.01 mmol) was added to a suspension of $[PdClMe(\mu\text{-}P,N\text{-}dpim)]_2$ (4.3 mg, 0.005 mmol) in $CDCl_3$ (0.5 mL) in an NMR tube. After shaking the initial suspension, a yellow solution was formed. ^{31}P and ^1H NMR spectra confirmed the formation of **4** as the only product. Then [PdClMe(cod)] (2.69 mg, 0.01 mmol) was added to the previous solution and the mixture was monitored by ^{31}P NMR during the next 24 h. Solid formation was observed, and the presence of **3** detected along with other minor products.

4.9. X-ray crystallographic study of 6

A single crystal of **6** was mounted on a glass fiber. X-ray measurements were made using a Bruker SMART CCD area-detector diffractometer with Mo Kα radiation ($\lambda = 0.71073$ Å) [47]. Intensities were integrated [48] from several series of exposures, each exposure covering 0.3° in ω, and the total data set being a sphere. Absorption corrections were applied, based on multiple and symmetry-equivalent measurements [49]. The structure was solved by direct methods and refined by least squares on weighted F^2 values for all reflections (see Table 3) [50]. All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints. All hydrogen atoms were constrained to ideal geometries and refined with fixed isotropic displacement parameters. Refinement proceeded smoothly to give the residuals shown in Table 3. Complex neutral-atom scattering factors were used [51].

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Appendix A. Supplementary material

CCDC 607744 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.11.045.

References

[1] P. Braunstein, F. Naud, Angew. Chem. Int. Ed. 40 (2001) 680.
[2] (a) C.W. Rogers, M.O. Wolf, Chem. Commun. (1999) 2297;
(b) C.W. Rogers, Y. Zhang, W.E. Jones Jr., M.O. Wolf, Inorg. Chem. 41 (2002) 1162.
[3] (a) I.D. Kostas, J. Organomet. Chem. 634 (2001) 90;
(b) I.D. Kostas, J. Organomet. Chem. 626 (2001) 221;
(c) I.D. Kostas, B.R. Steele, A. Terzis, S.V. Amosova, Tetrahedron 59 (2003) 3467;
(d) M. Kuriyama, K. Nagai, K. Yamada, Y. Miwa, T. Taga, K. Tomioka, J. Am. Chem. Soc. 124 (2002) 8932;
(e) C. Roch-Neirey, N. Le Bris, P. Laurent, J.C. Clement, H. des Abbayes, Tetrahedron Lett. 42 (2001) 643;
(f) J.L. Ruiz, T. Flor, J.C. Bayón, Inorg. Chem. Commun. 2 (1999) 484.
[4] (a) T.J.M. de Bruin, L. Magna, P. Raybaud, H. Toulhoat, Organometallics 22 (2003) 3404;
(b) S. Tobisch, T. Ziegler, Organometallics 22 (2003) 5392;
(c) A. Ramírez, E. Lobkovsky, D.B. Collum, J. Am. Chem. Soc. 125 (2003) 15376.
[5] J. García-Antón, J. Pons, X. Solans, M. Font-Bardia, J. Ros, Eur. J. Inorg. Chem. (2003) 3952.
[6] (a) G.R. Newkone, Chem. Rev. 93 (1993) 2067;
(b) P. Espinet, K. Soulantica, Coord. Chem. Rev. 195 (1999) 499;
(c) S. Doherty, J.G. Knight, M. Betham, Chem. Commun. (2006) 88;
(d) T. Oshiki, H. Yamashita, K. Sawada, M. Utsunomiya, K. Takahashi, K. Takai, Organometallics 24 (2005) 6287;
(e) J.M. de Pater, C.E.P. Maljaars, E. de Wolf, M. Lutz, A.L. Spek, B.-J. Deelman, C.J. Elsevier, G. van Koten, Organometallics 24 (2005) 5299;
(f) A. Scrivanti, V. Beghetto, E. Campagna, M. Zanato, U. Matteoli, Organometallics 17 (1998) 630.
[7] A.A. Tolmachev, A.A. Yurchenko, M.G. Semenova, N.G. Feshchenko, Russ. J. Chem. 63 (1993) 504.
[8] M.A. Jalil, T. Yamada, S. Fujinami, T. Honjo, H. Nishikawa, Polyhedron 20 (2001) 627.
[9] M.C. Done, T. Rüther, K.J. Cavell, M. Kilner, E.J. Peacock, N. Braussaud, B.W. Skelton, A. White, J. Organomet. Chem. 607 (2000) 78.
[10] V.J. Catalano, S.J. Horner, Inorg. Chem. 42 (2003) 8430.
[11] F. Bachechi, A. Burini, R. Galassi, B.R. Pietroni, M. Ricciutelli, Inorg. Chim. Acta 357 (2004) 4349.

[12] (a) D.B. Grotjahn, C.D. Incarvito, A.L. Rheingold, Angew. Chem., Int. Ed. Engl. 40 (2001) 3884;
(b) D.B. Grotjahn, D.A. Lev, J. Am. Chem. Soc. 126 (2004) 12233.
[13] D.G. Grotjahn, Y. Gong, L. Zakharov, J.A. Golen, A.L. Rheingold, J. Am. Chem. Soc. 128 (2006) 438.
[14] G. Espino, F.A. Jalón, M. Maestro, B.R. Manzano, M. Pérez-Manrique, A.C. Bacigalupe, Eur. J. Inorg. Chem. (2004) 2542.
[15] (a) H.G. Ang, W.E. Kow, K.F. Mok, Inorg. Nucl. Chem. Lett. 8 (1972) 829;
(b) T. Suzuki, M. Kita, K. Kashiwabara, J. Fujita, Bull. Chem. Soc. Jpn. 63 (1990) 3434;
(c) W. Zhao, X. Guan, S. Zhang, Y. Fang, H. Wang, R. Wang, Huaxue Xuebao 50 (1992) 300;
(d) X. Guan, W. Zhao, S. Zhang, Y. Fang, X. Yun, D. Kou, Y. Li, Fenzi Cuihua 6 (1992) 303.
[16] (a) T. Suzuki, J. Fujita, Bull. Chem. Soc. Jpn. 65 (1992) 1016;
(b) T. Suzuki, N. IItaka, S. Kurachi, M. Kita, K. Kashiwavara, S. Ohba, J. Fujita, Bull. Chem. Soc. Jpn. 65 (1992) 1817;
(c) A. Maisonnat, J.P. Farr, A.L. Balch, Inorg. Chim. Acta 53 (1981) L217;
(d) Y. Xie, C. Lee, Y. Yang, S.J. Rettig, B.R. James, Can. J. Chem. 70 (1992) 751;
(e) A. Dervisi, P.G. Edwards, P.D. Newman, R.P. Tooze, S.J. Coles, M.B. Hursthouse, J. Chem. Soc., Dalton Trans. (1998) 3771.
[17] J.P. Farr, M.M. Olmstead, N.M. Rutherford, F.E. Wood, A.L. Balch, Organometallics 2 (1983) 1758.
[18] (a) S.J. Young, B. Kellenberger, J.H. Reibenspies, S.E. Himmel, M. Manning, O.P. Anderson, J.K. Stille, J. Am. Chem. Soc. 110 (1988) 5744;
(b) J.A. Davis, S. Dutremez, A.A. Pinkerton, M. Vilmer, Organometallics 10 (1991) 2956;
(c) A. Mentes, R.D.W. Kemmitt, J. Fawcett, D.R. Russeli, Polyhedron 18 (1999) 1141;
(d) M.K. Richmond, S.L. Scott, G.P.A. Yap, H. Alper, Organometallics 21 (2002) 3395.
[19] A.D. Burrows, M.F. Mahon, S.P. Nolan, M. Varrone, Inorg. Chem. 42 (2003) 7227.
[20] L. Manojlovic-Muir, S.S.M. Ling, R.J. Puddephat, J. Chem. Soc., Dalton Trans. (1986) 151.
[21] (a) Other ways to explain the same phenomena are in terms of the typical transphobia of ligands (alkyl, phosphine) with such donor atoms: J. Vicente, A. Arcas, D. Bautista, M.C. Ramírez de Arellano, J. Organomet. Chem. 663 (2002) 164;
(b) J. Vicente, A. Arcas, D. Bautista, P.G. Jones, Organometallics 16 (1997) 2127;
(c) J. Vicente, A. Arcas, D. Bautista, A. Tiripicchio, M. Tiripicchio-Camellini, New J. Chem. 20 (1996) 345;
(d) Or the antisymbiotic effect between carbon and phosphorus donors. P. Braunstein, F. Naud, A. Dedieu, M.-M. Rohmer, A. De Cian, S.J. Rettig, Organometallics 20 (2001) 2966 (theoretical calculations) and references therein.
[22] (a) E. Masslowsky Jr., Vibrational Spectra of Organometallic Compounds, Wiley, New York, 1977, p. 437 and references therein;
(b) R. Usón, J. Forniés, Adv. Organomet. Chem. 28 (1988) 219, and references therein.
[23] A.C. Albéniz, A.L. Casado, P. Espinet, Organometallics 16 (1997) 5416.
[24] (a) C. Breutel, P.S. Pregosin, R. Salzmann, A. Togni, J. Am. Chem. Soc. 116 (1994) 4067;
(b) P.S. Pregosin, R. Salzmann, A. Togni, Organometallics 14 (1995) 842.
[25] (a) See for example: G. Wilkinson, F.G.A. Stone, E.W. Abel, Comprehensive Organometallic Chemistry, vol. 1, Pergamon Press, Oxford, UK, 1982, p. 409;
(b) F. Gómez-de la Torre, F.A. Jalón, A. López-Agenjo, B.R. Manzano, A. Rodríguez, T. Sturm, W. Weissensteiner, M. Martínez-Ripoll, Organometallics 17 (1998) 4634;
(c) R. Férnandez-Galán, B.R. Manzano, A. Otero, J. Organomet. Chem. 577 (1999) 271;
(d) P. Dotta, P.G.A. Kumar, P.S. Pregosin, Magn. Reson. Chem. 40 (2002) 653;
(e) B. Åkermark, B. Krakenberger, S. Hansson, A. Vitagliano, Organometallics 6 (1987) 620;
(f) M. Kollmar, B. Goldfuss, M. Reggelin, F. Rominger, G. Helmchen, Chem. Eur. J. 7 (2001) 4913;
(g) J. Park, Z. Quan, S. Lee, H. Ahn, C.-W. Cho, J. Organomet. Chem. 584 (1999) 140.
[26] T.G. Appleton, H.C. Clark, L.E. Manze, Coord. Chem. Rev. 10 (1973) 335.
[27] (a) J.W. Faller, H.L. Stokes-Huby, M.A. Albrizzio, Helv. Chim. Acta 84 (2001) 3031;
(b) J.W. Faller, N. Sarantopoulos, Organometallics 23 (2004) 2008.
[28] T. Hayashi, M. Kawatsura, Y. Uozumi, J. Am. Chem. Soc. 120 (1998) 1681.
[29] (a) C. Lecomte, Y. Dusausoy, J. Protas, J. Tirouflet, A. Dormond, J. Organomet. Chem. 73 (1974) 67;
(b) H. Brunner, Enantiomer 2 (1997) 133;
(c) H. Brunner, Angew. Chem., Int. Ed. Engl. 38 (1999) 1194.
[30] T.E. Sloan, Top. Stereochem. 12 (1981) 1.
[31] (a) P.K. Byers, A.J. Canty, R.T. Honeyman, Adv. Organomet. Chem. 34 (1992) 1;
(b) M.C. Carrión, A. Díaz, A. Guerrero, F.A. Jalón, B.R. Manzano, A. Rodríguez, R.L. Paul, J.C. Jeffery, J. Organomet. Chem. 650 (2002) 210;
(c) N. Arroyo, F. Gómez de la Torre, F.A. Jalón, B.R. Manzano, B. Moreno-Lara, A.M. Rodríguez, J. Organomet. Chem. 603 (2000) 174;
(d) F.A. Jalón, B.R. Manzano, A. Otero, M.C. Rodríguez-Pérez, J. Organomet. Chem. 494 (1995) 179.
[32] (a) K. Vrieze, in: L.M. Jackman, F.A. Cotton (Eds.), Dynamic Nuclear Magnetic Resonance Spectroscopy, Academic Press, New York, 1975;
(b) P.S. Pregosin, R. Salzmann, Coord. Chem. Rev. 155 (1996) 35.
[33] (a) S. Hansson, P.O. Norrby, M.P.T. Sjögren, B. Åkermark, M.E. Cucciolito, F. Giorjuno, A. Vitagliano, Organometallics 12 (1993) 4940;
(b) A. Gogoll, J. Örnebro, J.-E. Bäckvall, J. Am. Chem. Soc. 116 (1994) 3631;
(c) A. Gogoll, H. Grennberg, A. Axén, Organometallics 16 (1997) 1167;
(d) J.G.P. Delis, J.H. Groen, K. Vrieze, P.W.N.M. van Leeuwen, N. Veldman, A.L. Spek, Organometallics 16 (1997) 551;
(e) B. Crociani, S. Antonaroli, G. Bandoli, L. Canovese, F. Visentin, P. Uguagliati, Organometallics 18 (1999) 1137;
(f) Y. Takao, T. Takeda, J.-y. Watanabe, J.-i. Setsune, Organometallics 18 (1999) 2936;
(g) B. Crociani, S. Antonaroli, M. Paci, F. Di Bianca, L. Canovese, Organometallics 16 (1997) 384;
(h) A. Guerrero, F.A. Jalón, B.R. Manzano, A. Rodríguez, R.M. Claramunt, P. Cornago, V. Milata, J. Elguero, Eur. J. Inorg. Chem. (2004) 549;
(i) R.J. van Haaren, K. Goubitz, J. Fraanje, G.P.F. van Strijdonck, H. Oevering, B. Coussens, J.N.H. Reek, P.C.J. Kamer, P.W.N.M. van Leeuwen, Inorg. Chem. 40 (2001) 3363;
(j) F. Gómez-de la Torre, A. de la Hoz, F.A. Jalón, B.R. Manzano, A.M. Rodríguez, Inorg. Chem. 39 (2000) 1152.
[34] (a) A. Albinati, R.W. Kunz, C.W. Ammann, P.S. Pregosin, Organometallics 10 (1991) 1800;
(b) A. Gogoll, C. Johansson, A. Axén, H. Grennberg, Chem. Eur. J. 7 (2001) 396.
[35] (a) T. Hosokawa, Y. Wakabayashi, K. Hosokawa, T. Tsuji, S.-I. Murahashi, Chem. Commun. (1996) 859;
(b) N. Solin, K. Szabó, Organometallics 20 (2001) 5464;
(c) L. Barloy, S. Ramdeehul, J.A. Osborn, C. Carlotti, F. Taulelle, A. de Cian, J. Fischer, Eur. J. Inorg. Chem. (2000) 2523.

[36] (a) M. Kollmar, B. Goldfuss, M. Reggelin, F. Rominger, G. Helmchen, Chem. Eur. J. 7 (2001) 4913;
(b) J. Krause, R. Goddard, R. Mynott, K-R. Pörschke, Organometallics 20 (2001) 1992;
(c) R. Fernández-Galán, F.A. Jalón, B.R. Manzano, J. Rodríguez-de la Fuente, M. Vrahami, B. Jedlicka, W. Weissensteiner, Organometallics 16 (1997) 3758;
(d) P. Barbaro, P.S. Pregosin, R. Salzmann, A. Albinati, R.W. Kunz, Organometallics 14 (1995) 5160;
(e) J. Herrmann, P.S. Pregosin, A. Albinati, Organometallics 14 (1995) 3311.
[37] F. Gómez-de la Torre, A. de la Hoz, F.A. Jalón, B.R. Manzano, A. Otero, A.M. Rodríguez, M.C. Rodríguez-Pérez, Inorg. Chem. 37 (1998) 6606.
[38] (a) J. Elguero, A. Guerrero, F. Gómez-de la Torre, A. de la Hoz, F.A. Jalón, B.R. Manzano, A. Rodríguez, N.J. Chem. 25 (2001) 1050;
(b) J. Elguero, A. Fruchier, A. de la Hoz, F.A. Jalón, B.R. Manzano, A. Otero, F. Gómez-de la Torre, Chem. Ber. 129 (1996) 589.
[39] A.C. Albéniz, P. Espinet, O. López-Cimas, B. Martín-Ruiz, Chem. Eur. J. 11 (2005) 242.
[40] (a) A.J. Deeming, M.N. Meah, P.A. Bates, M.B. Hursthouse, J. Chem. Soc., Dalton Trans. (1988) 235;
(b) R. Goddard, C. Kruger, R. Mynott, M. Neumann, G. Wilke, J. Organomet. Chem. 454 (1993) C20;
(c) P. Hendriks, K. Olie, K. Vrieze, Cryst. Struct. Commun. 4 (1975) 611;
(d) S.C. de Sanctis, N.V. Pavel, L. Toniolo, J. Organomet. Chem. 108 (1976) 409;
(e) F.T. Edelmann, W. Ziegler, V. Behrens, J. Organomet. Chem. 426 (1992) 261;
(f) I. Schwarz, J. Rust, C.W. Lehmann, M. Braun, J. Organomet. Chem. 605 (2000) 109.
[41] P.L. Ruddock, D.J. Williams, P.B. Reese, Steroids 69 (2004) 193.
[42] (a) J. Chatt, L.M. Vallarino, L.M. Venanzi, J. Chem. Soc. (1957) 3413;
(b) D. Drew, J.R. Doyle, Inorg. Synth. 13 (1972) 52.
[43] M.S. Kharasch, R.C. Sailer, F.R. Mayo, J. Am. Chem. Soc. 60 (1938) 882.
[44] R.E. Rülke, J.M. Ernsting, A.L. Speek, C.J. Elsevier, P.W.N. van Leeuwen, R. Vrieze, Inorg. Chem. 32 (1993) 5769.
[45] W.T. Dent, A.J. Wilkinson, J. Chem. Soc. (1964) 1585.
[46] (a) P. Espinet, J.M. Martínez-Ilarduya, C. Pérez-Briso, A.L. Casado, M.A. Alonso, J. Organomet. Chem. 551 (1998) 9;
(b) F. Gómez-de la Torre, A. de la Hoz, F.A. Jalón, B.R. Manzano, A.M. Rodríguez, J. Elguero, M. Martínez-Ripoll, Inorg. Chem. 39 (2000) 1152.
[47] SMART Diffractometer Control Software, Bruker Analytical X-ray Instruments Inc., Madison, WI, 1998.
[48] SAINT Integration Software, Siemens Analytical X-ray Instruments Inc., Madison, WI, 1994.
[49] G.M. Sheldrick, SADABS: A Program for Absorption Correction with the Siemens SMART System, University of Göttingen, Germany, 2001.
[50] SHELXTL Program System Version 5.1; Bruker Analytical X-ray Instruments Inc., Madison, WI, 1998.
[51] International Tables for Crystallography, vol. C., Kluwer, Dordrecht, 1992.