Different coordinating behaviour of the imino-phosphoranes $Ph_3P{=}NC(O)CH_2Cl$ and $Ph_3P{=}NC(O)\text{-}2\text{-}NC_5H_4$ towards M^{II} complexes (M = Pd, Pt)

Larry R. Falvello, María M. García, Ignacio Lázaro, Rafael Navarro* and Esteban P. Urriolabeitia

Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza- Consejo Superior de Investigaciones Científicas, 50009 Zaragoza, Spain.
E-mail: rafanava@posta.unizar.es and esteban@posta.unizar.es

Received (in Montpellier, France) 9th September 1998, Accepted 17th November 1998

The coordination behaviour of the iminophosphorane ligands $Ph_3P{=}NC(O)CH_2Cl$ and $Ph_3P{=}NC(O)\text{-}2\text{-}NC_5H_4$ towards different Pd^{II} and Pt^{II} substrates has been explored. The iminophosphorane $Ph_3P{=}NC(O)CH_2Cl$ shows a poor coordination ability, always binding through the iminic N atom. Thus, $Ph_3P{=}NC(O)CH_2Cl$ reacts with $PdCl_2(NCPh)_2$, $[M(C{^\wedge}P)(NCMe)_2]ClO_4$ (M = Pd, Pt) and $[Pd(dmba)(NCMe)_2]ClO_4$ (2 : 1, 1 : 1 and 1 : 1 molar ratio, respectively, $C{^\wedge}P$ = *ortho*-$CH_2C_6H_4P$(*o*-Tol)$_2$-*C*,*P*; dmba = $C_6H_4CH_2NMe_2$-2), resulting in the formation of *trans*-$PdCl_2\{N({=}PPh_3)C(O)CH_2Cl\}_2$, **1**, $[M(C{^\wedge}P)\{N({=}PPh_3)C(O)CH_2Cl\}(NCMe)]ClO_4$ (M = Pd, **2**; Pt, **3**) and $[Pd(dmba)\{N({=}PPh_3)C(O)CH_2Cl\}(NCMe)]ClO_4$, **4**. However, the iminophosphorane $Ph_3P{=}NC(O)\text{-}2\text{-}NC_5H_4$ displays at least three different coordination modes, as a function of the starting material. The reaction of $Ph_3P{=}NC(O)\text{-}2\text{-}NC_5H_4$ with $PdCl_2(NCPh)_2$ or $PtCl_2$ (1 : 1 molar ratio) gives *cis*-$Cl_2M\{N({=}PPh_3)C(O)\text{-}2\text{-}NC_5H_4\}$ (M = Pd, **5**; Pt, **6**) in which the ligand acts as an *N*,*N*-chelate. The reaction with the bis-solvate orthometallated complexes $[M(C{^\wedge}P)(NCMe)_2]ClO_4$ (M = Pd, Pt) and $[Pd(dmba)(NCMe)_2]ClO_4$ (1 : 1 molar ratio) gives the bis-chelate complexes $[M(C{^\wedge}P)\{NC_5H_4\text{-}2\text{-}C(O)N{=}PPh_3\}]ClO_4$ (M = Pd **7**, Pt **8**) and $[Pd(dmba)\{NC_5H_4\text{-}2\text{-}C(O)N{=}PPh_3\}]ClO_4$, **9**, in which the iminophosphorane ligand is coordinated through the pyridinic nitrogen atom and the carbonyl oxygen atom. The X-ray crystal structure of **9** has been determined. The reaction with $[Pd(dmba)(PPh_3)(THF)]ClO_4$ (1 : 1 molar ratio) gives the cationic derivative $[Pd(dmba)(PPh_3)\{NC_5H_4\text{-}2\text{-}C(O)N{=}PPh_3\}]ClO_4$, **10**, in which the iminophosphorane ligand is coordinated only through the pyridinic nitrogen atom. Finally, the iminophosphorane reacts with $[Pd(\mu\text{-}Cl)(dmba)]_2$ (2 : 1 molar ratio) resulting in the cleavage of the chlorine bridging system by the pyridinic N atom and formation of $[Pd(dmba)Cl\{NC_5H_4\text{-}2\text{-}C(O)N{=}PPh_3\}]$, **11**.

Over the last few years our research group has been interested in the coordination chemistry of the α-stabilized phosphorus ylides $Ph_3P{=}C(H)R$ (R = COMe, COPh, COOMe, $CONMe_2$, CN), due to the fact that these ylides can behave as ambidentate ligands.[1–6] The main thrust of this work relates to the reactivity of the aforementioned $Ph_3P{=}C(H)R$ ylides towards several *ortho*-metallated complexes of Pd^{II} and Pt^{II}; we have observed the ambidentate character of the α-stabilized ylides and have also seen that it is possible to predict both the coordination site of the ylide (when there are two possibilities) and the donor atom linked to the metal (*O*- *versus* *C*-coordination, *N*- *versus* *C*-coordination), taking into account as simple an effect as the antisymbiotic behaviour of the metal centre[7,8] and the different electronic and steric requirements of the ylides in their different coordination modes.

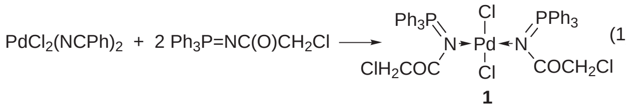
The iminophosphoranes—compounds of general structure $R_3P{=}NR'$—are an interesting class of compounds closely related to the ylides and which show numerous applications to organic synthesis (for instance, the formation of C=N bonds through the Aza–Wittig reaction).[9a] Moreover, they can also behave as ligands towards transition metals through, at least, the lone pair on the N atom. In spite of these similarities, their use as ligands is less developed than that of the ylides,[9] although in the past decade some interesting studies based on the coordinative properties and the reactivity of iminophosphoranes derived from mono- and diphosphines have been reported.[9–23]

Prompted by the results obtained with the α-stabilized ylides, we have undertaken a study of the coordination chemistry of stabilized iminophosphoranes possessing a carbonyl group bonded to the iminic nitrogen[24]—a series of compounds for which there is no precedent in coordination chemistry. The reactivity of two of these derivatives, $Ph_3P{=}NC(O)CH_2Cl$ and $Ph_3P{=}NC(O)\text{-}2\text{-}NC_5H_4$, towards several palladium(II) and platinum(II) substrates has been explored (see Scheme 1). We have chosen complexes with two labile ligands in different arrangements and with different *trans* atoms such as *trans*-$MCl_2(NCPh)_2$ (M = Pd, Pt),[25] $[M(C{^\wedge}P)(NCMe)_2]ClO_4$ (M = Pd,[26] Pt [27]) and $[Pd(dmba)(NCMe)_2]ClO_4$[28] ($C{^\wedge}P$ = *ortho*-$CH_2C_6H_4P$(*o*-Tol)$_2$; dmba = $C_6H_5CH_2NMe_2$-2), complexes with one labile ligand such as $[Pt(C{^\wedge}P)(PPh_3)(NCMe)]ClO_4$ [5] and $[Pd(dmba)(PPh_3)(THF)]ClO_4$[29] and dinuclear complexes such as $[M(\mu\text{-}Cl)(C{^\wedge}P)]_2$ (M = Pd,[30] Pt [27]) and $[Pd(\mu\text{-}Cl)\ (dmba)]_2$[31] in order to explore the coordination properties (nucleophilic ability of the iminic N atom and steric requirements) of these ligands in different environments. In this paper we report the results obtained from this chemistry.

Results

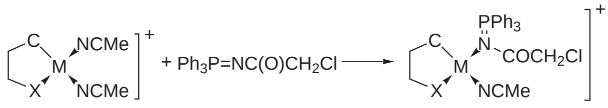
Reactions of $Ph_3P{=}NC(O)CH_2Cl$

The reaction of *trans*-$PdCl_2(NCPh)_2$ with $Ph_3P{=}NC(O)$-CH_2Cl (1:2 molar ratio) in acetone at room temperature results in the precipitation of *trans*-$PdCl_2\{N(=PPh_3)C(O)CH_2Cl\}_2$, **1**, according to its elemental analysis and spectroscopic data [see below and eqn. (1)]. Under the same conditions $PtCl_2(NCPh)_2$ does not react with $Ph_3P{=}NC(O)CH_2Cl$. The same result was observed even under more drastic conditions (refluxing toluene) and when other precursors were used in different solvents and temperatures. It is worth noting that similar reactions between $Na_2[PdCl_4]$ and the iminophosphoranes $(C_6H_4R)_3P{=}NC_6H_4\text{-}R'$ (R = H, R′ = *m*-Me, *p*-Me, *p*-OMe; R = 4-Me, R′ = *p*-OMe) result in the formation of the *ortho*-metallated derivatives[32] $[Pd(\mu\text{-}Cl)\{C_6H_3\text{-}4\text{-}R\text{-}P(C_6H_4R\text{-}4)_2NR'\text{-}2\}]_2$ and that in these reactions complexes of the type L_2PdCl_2 were not isolated.



(1)

The reactions of the iminophosphorane $Ph_3P{=}N(CO)CH_2Cl$ with other bis-solvate complexes show different behaviour from that described for the reaction giving **1**. The reaction of $[M(C^\wedge P)(NCMe)_2]ClO_4$ (M = Pd, Pt) with $Ph_3P{=}NC(O)CH_2Cl$ (1 : 1 molar ratio) in CH_2Cl_2 at room temperature gives the cationic derivatives $[M(C^\wedge P)(NCMe)\{N(=PPh_3)C(O)CH_2Cl\}]ClO_4$ (M = Pd, **2**; Pt, **3**) [see eqn. (2)] as white solids, in analytically pure form according with their elemental analyses and mass spectra. Attempts to displace the remaining NCMe molecule in **2** and **3** by further addition of iminophosphorane resulted in unclear results. If the reaction is performed under the same conditions but using a metal : ligand molar ratio of 1 : 2, a mixture of **2** or **3** and the free iminophosphorane is obtained. Similar results were obtained with the bis-solvate derivative $[Pd(dmba)(NCMe)_2]ClO_4$. Its reaction with 1 equiv. of $Ph_3P{=}NC(O)CH_2Cl$ in CH_2Cl_2 at room temperature gave $[Pd(dmba)(NCMe)\{N(=PPh_3)C(O)CH_2Cl\}]ClO_4$, **4**, as characterized by its elemental analysis and mass spectrum. From **4** it was not possible to displace the NCMe ligand by further addition of iminophosphorane [see eqn. (2)], and the reaction of the starting product with two equivalents of iminophosphorane gave a mixture of **4** and free ligand. The structures of complexes **2**–**4** has been elucidated from their spectroscopic data (see below).



(2)

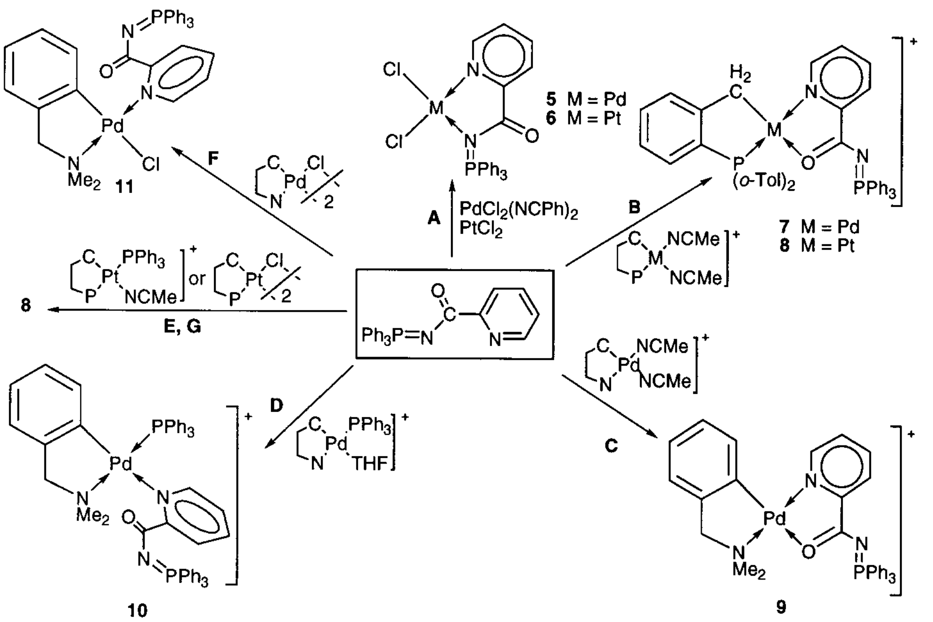
2 X = P(*o*-Tol)$_2$, M = Pd
3 X = P(*o*-Tol)$_2$, M = Pt
4 X = NMe$_2$; M = Pd

The reaction between $[Pt(C^\wedge P)(PPh_3)(NCMe)]ClO_4$ and $Ph_3P{=}NC(O)CH_2Cl$ does not take place even in refluxing THF, and the mixture of the starting compounds is recovered. The same lack of reactivity has been observed in the reaction of the cationic precursor $[Pd(dmba)(PPh_3)(THF)]ClO_4$ with $Ph_3P{=}NC(O)CH_2Cl$. In the same way, $Ph_3P{=}NC(O)CH_2Cl$ is not able to promote the cleavage of the halide bridging system in $[Pd(\mu\text{-}Cl)(dmba)]_2$ or in $[M(\mu\text{-}Cl)(C^\wedge P)]_2$ (M = Pd, Pt).

Reactions of $Ph_3P{=}NC(O)\text{-}2\text{-}NC_5H_4$

The reaction of *trans*-$PdCl_2(NCPh)_2$ with $Ph_3P{=}NC(O)\text{-}2\text{-}NC_5H_4$ (1 : 1 molar ratio) in acetone at room temperature results in the formation of *cis*-$Cl_2Pd\{N(=PPh_3)C(O)\text{-}2\text{-}NC_5H_4\}$, **5** which precipitates as an analytically pure orange solid from the reaction mixture. Under the same conditions, the reaction of $PtCl_2(NCPh)_2$ with $Ph_3P{=}NC(O)\text{-}2\text{-}NC_5H_4$ gives poor yields (about 10%) of *cis*-$Cl_2Pt\{N(=PPh_3)C(O)\text{-}2\text{-}NC_5H_4\}$, **6**, and most of the starting products remain unchanged. This yield is not improved (or only slightly) if the reaction is performed at reflux temperature or if *cis*-$Cl_2Pt(COD)$ is used as starting material. The best yields of the analytically pure product were obtained from the reaction of $PtCl_2$ with $Ph_3P{=}NC(O)\text{-}2\text{-}NC_5H_4$ (1 : 1 molar ratio) in a CH_2Cl_2–acetone mixture at reflux temperature (see Experimental). In both complexes the iminophosphorane ligand is *N*,*N*-bonded to the metal centre, through the pyridinic N atom and through the iminic N atom (see Scheme 1).

A different coordination mode is observed when other bis-solvate derivatives are allowed to react with this ligand. The reaction of $[M(C^\wedge P)(NCMe)_2]ClO_4$ (M = Pd, Pt) with 1 equiv. of $Ph_3P{=}NC(O)\text{-}2\text{-}NC_5H_4$ results in the formation of white solids of stoichiometry $[M(C^\wedge P)\{Ph_3PNC(O)\text{-}NC_5H_4\}]ClO_4$ (M = Pd, **7**; Pt, **8**) as deduced from their elemental analyses and mass spectra (see Experimental). The spectroscopic data (see below) suggest in this case a bonding mode of the iminophosphorane ligand through the pyridinic



Scheme 1 Synthesis of complexes **5**–**11**

N atom and through the carbonyl oxygen, as depicted in Scheme 1.

A behaviour similar to that described for the reactions giving complexes **7**, **8** is observed in the reaction of $[Pd(dmba)(NCMe)_2]ClO_4$ with $Ph_3P{=}NC(O)$-2-NC_5H_4 (1 : 1 molar ratio). The stoichiometry of the reaction product agrees with the formulation $[Pd(dmba)\{Ph_3PNC(O)NC_5H_4\}]ClO_4$, **9**, as indicated by its elemental analysis and mass spectrum, and the spectroscopic data reveal that an N(py) + O(carbonyl) coordination has taken place (see Scheme 1). The determination of the crystal structure of complex **9** shows unambiguously that the iminophosphorane ligand is coordinated through the pyridinic N atom and through the carbonyl oxygen (see below).

On the other hand, the reaction of $[Pt(C^\wedge P)(PPh_3)(NCMe)]ClO_4$ with the iminophosphorane (1 : 1 molar ratio) affords a mixture of products in which it is possible to identify complex **8** as the main product; that is, the chelate effect is strong enough to promote the *N*,*O*-coordination. Similar results were obtained in the reaction of $[Pt(\mu\text{-}Cl)(C^\wedge P)]_2$ with the iminophosphorane (1 : 2 molar ratio). In this case the reaction product was identified as $[Pt(C^\wedge P)\{Ph_3PNC(O)NC_5H_4\}]^+Cl^-$ $[(\mathbf{8}^+)(Cl^-)]$. The palladium complex $[Pd(\mu\text{-}Cl)(C^\wedge P)]_2$ does not react with the iminophosphorane, even in refluxing THF.

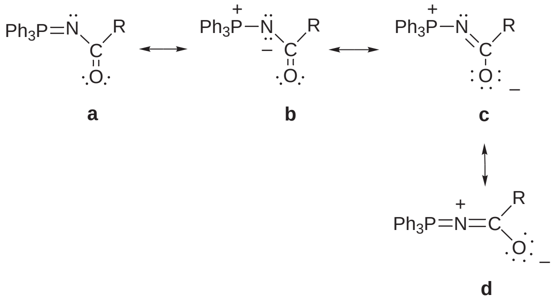
However, the reaction of $[Pd(dmba)(PPh_3)(THF)]ClO_4$ [generated *in situ* from $PdCl(dmba)(PPh_3)$ and $AgClO_4$] with the iminophosphorane (1 : 1 molar ratio) results in the formation of a solid of stoichiometry $[Pd(dmba)(PPh_3)\{Ph_3PNC(O)NC_5H_4\}]ClO_4$, **10**, as deduced from its elemental analysis and mass spectrum. For this complex, the spectroscopic parameters indicate that a different coordination mode is involved; only the pyridinic N atom is bonded to the palladium centre *trans* to the *ortho*-metallated carbon atom of the dmba ligand (see Scheme 1).

The same coordination mode of the ligand is obtained in the reaction of $[Pd(dmba)(\mu\text{-}Cl)]_2$ with the iminophosphorane (1 : 2 molar ratio). A pale yellow solid of stoichiometry $[PdCl(dmba)\{Ph_3PNC(O)NC_5H_4\}]$, **11**, is obtained, as a result of the cleavage of the bridging chlorine system, and it shows similar spectroscopic features as those described for **10**. That is, the iminophosphorane is coordinated selectively through the N(py) atom and is *trans* to the NMe_2 group (see Scheme 1).

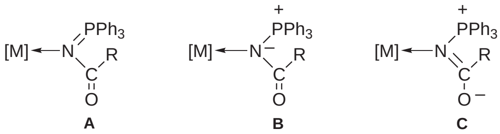
Spectroscopic characterization of complexes 1–11

The IR spectrum of **1** suggests a *trans* arrangement of the ligands since only one Pd—Cl stretch is observed at 319 cm^{-1}. In addition, the P=N absorption undergoes a significant shift to lower energies (1325 cm^{-1}, $\Delta\nu = \nu_{complex} - \nu_{ligand} = -23$ cm^{-1}) compared to the free ligand (1348 cm^{-1}). This low frequency shift indicates that the ligand is coordinated through the lone pair of the N atom[14] [(see eqn. (1)] although the magnitude of the shift is smaller than that described for other *N*-coordinated iminophosphoranes.[14] A more remarkable fact is the sizable increase in the carbonyl stretch energy (1643 cm^{-1} in **1**, 1602 cm^{-1} in the free ligand, $\Delta\nu = 41$ cm^{-1}), probably as a result of the fact that, after coordination, the extensive conjugation of the P=N and C=O bonds[24] is partially blocked and that there is no lone pair delocalization.

Scheme 2 shows the proposed resonance forms **a**–**d** for the free iminophosphorane. Using these forms as a point of departure, we suggest the canonical forms **A**–**C** in Scheme 3 for the coordinated iminophosphorane. It is clear that the forms **c** and **d** in Scheme 2 could not contribute to the description of the bonding, since a decrease in the energy of the CO stretch should then be observed (for instance, in form **C** in Scheme 3). Thus, the bonding in compound **1** should be described in terms of the resonance forms **a** and **b** which result in forms **A** and **B**. It has been proposed previously[13] that the bond orders can be conveniently described by the presence of the double bond form **A** and the dipolar form **B**, with a higher participation of **A** than of **B**. Thus, it is sensible to assume that the decrease in the energy of the P=N absorption could be due to the presence of the canonical form **B** and the increase in the CO absorption energy can be rationalized on the basis of the existence of both forms **A** and **B**. Additional evidence for the *N*-coordination of the iminophosphorane ligand can be found in the $^{31}P\{^1H\}$ NMR spectrum of **1**. It displays a single resonance at 37.50 ppm—that is, shifted downfield by more than 16 ppm with respect to the free ligand (21.36 ppm). This deshielding of the P atom is in good agreement with the weakening of the P—N bond in form **B**, and it has been previously proposed as a proof of *N*-bonding.[13–15]



Scheme 2 Proposed resonance forms for the iminophosphoranes $Ph_3P{=}NC(O)R$ (R = CH_2Cl, NC_5H_4-2).



Scheme 3 Proposed resonance forms for the coordinated iminophosphoranes $Ph_3P{=}NC(O)R$ (R = CH_2Cl, NC_5H_4-2).

Complexes **2**–**4** show in their IR spectra absorptions attributable to the presence of coordinated NCMe (about 2200 cm^{-1}) and characteristic absorptions of the $C^\wedge P$ [27] and dmba[28] ligands. Moreover, the IR spectra of **2**–**4** also show features similar to those described for complex **1**, namely a decrease in the energy of the P=N absorption and an increase for that of the carbonyl with respect to the free ligand. These facts allow us to propose for **2**–**4** the same coordination mode as in **1**. The $^{31}P\{^1H\}$ NMR spectrum of **2** at low temperature ($CDCl_3$, 213 K) shows two close singlets at about 38 ppm, while the spectrum of **3** shows a broad resonance at about 16 ppm with ^{195}Pt satellites ($^1J_{PtP} = 4334$ Hz) that is attributed to the $C^\wedge P$ ligand, and a doublet resonance at about 40 ppm with ^{195}Pt satellites ($^2J_{PtP} = 62.2$ Hz) that is assigned to the iminophosphorane ligand. These facts mean that the P nucleus of the iminophosphorane ligand is deshielded with respect to the free ligand, as we have described for **1**, and again points to *N*-coordination for this ligand. In addition, the appearance of the latter resonance as a doublet ($^3J_{PP} = 5.9$ Hz) and the magnitude of the coupling constant suggest a mutually *trans* arrangement of the P atom of the $C^\wedge P$ ligand and the P=N ligand around the platinum centre[5] as depicted in eqn. (2). The broad signal at 16 ppm for **3** is not resolved on further cooling (CD_2Cl_2, 183 K) and the spectrum of **2** in CD_2Cl_2 at 183 K shows a broadening of the resonances (compared with that at 213 K), but is not resolved, either. Although for complex **2** we have not seen a complete splitting of the resonances, we propose for both complexes (**2** and **3**) the same structure [see eqn. (2)]. The ^1H NMR spectra of **2** and **3** show the expected resonances for all of the groups present in the molecule and do not show any unusual features. The observed P=N-*trans*-P geometry is similar to that observed with phosphoylides[5] and could be due to a minimization of the steric interactions.

The spectroscopic characterization of **4** reveals features similar to those described for **2** and **3** (see Experimental). Both the ^{1}H and the ^{31}P{^{1}H} NMR spectra show the expected resonances, and we have proposed the Me$_2$N-*trans*-N=P geometry [see eqn. (2)] by analogy with the results obtained with phosphorus ylides.[2,3,6]

The IR spectra of **5** and **6** show similar features. The *cis* geometry of these complexes can be inferred from the presence of two absorptions in the 330 cm^{-1} region (see Experimental). On the other hand, the carbonyl absorption appears as a sharp band at 1652 cm^{-1} for **5** and at 1659 cm^{-1} for **6**, shifted to higher frequencies with respect to the free ligand, which shows a set of several close resonances in this region (1606, 1590, 1580 and 1559 cm^{-1}). The ν_{PN} absorption appears at about 1315 cm^{-1}, while in the free ligand it appears at 1366 cm^{-1}. As described for the IR spectrum of complex **1**, these two facts together mean that the iminic N atom is bonded to the metal centre.

In both cases, the conclusion that the iminophosphorane acts as an *N*,*N*-chelating ligand in **5** and **6** comes from the analysis of their NMR spectra. The ^{1}H NMR spectrum of complex **6** shows the resonance attributed to the H$_6$ proton of the pyridinic fragment as a doublet with ^{195}Pt satellites ($^3J_{PtH} = 38$ Hz) and its ^{31}P{^{1}H} NMR spectrum shows a single resonance at 34.62 ppm with ^{195}Pt satellites ($^2J_{PtP} = 146$ Hz). This last resonance is deshielded, as expected, with respect to the free ligand, which appears at 23.89 ppm, and confirms the IR observations. The close similarity between the NMR spectra of **5** and **6** allows us to propose the same structure for these complexes, as depicted in Scheme 1.

The IR spectra of **7** and **8** do not show the presence of coordinated NCMe, in good agreement with the analytical data, and indicate that the iminophosphorane ligand acts as a chelate. In addition, the carbonyl absorption is found at 1537 (**7**) and 1538 (**8**) cm^{-1}, notably shifted to lower frequencies with respect to the free ligand. The ν_{PN} absorption appears at about 1378 cm^{-1}, that is, shifted 10 cm^{-1} to higher frequency with respect to the free ligand. Both shifts suggest strongly that the ligand is no longer acting as an *N*,*N*-chelate but that the carbonyl oxygen is now implicated in the bonding. More structural information can be inferred from the ^{31}P{^{1}H} NMR spectra of **7** and **8**. In these spectra, the resonances attributed to the iminophosphorane moiety appear at 23.56 (**7**) and 23.75 (**8**) ppm as singlet signals. This position lies very close to that observed in the free ligand (23.89 ppm), suggesting that now the P=N fragment is not *N*-coordinated to the metal centre, which is in good agreement with the IR data. Moreover, the resonance attributed to the iminophosphorane ligand in the spectrum of **8** does not show Pt satellites. From these data, it is sensible to conclude that the iminophosphorane ligand is coordinated through the pyridinic N atom and the carbonyl oxygen. This coordination mode (*N*,*O*-chelating) would result in the formation of two geometric isomers, but only one is observed in solution; that is, the reaction is stereoselective. The ^{1}H NMR spectra of **7** and **8** show a similar pattern of resonances for both complexes and do not show unusual features. However, the ^{1}H-^{1}H NOESY experiment performed on compound **8** gives structural information. The clear NOE interaction between the signal at 8.79 ppm (attributed to the H$_6$ pyridinic proton) and the AB spin system of the Pd—CH$_2$ protons (about 3.6 and 3.9 ppm) clearly indicates the *cis* disposition of these fragments. The structure depicted in Scheme 1 accounts for all of the experimental findings described.

The IR spectrum of **9** shows the carbonyl absorption at 1538 cm^{-1} and the P=N absorption at 1378 cm^{-1}, both in the same range as those described for **7** and **8**. The ^{31}P{^{1}H} NMR spectrum shows a singlet signal at 26.04 ppm, slightly shifted to low field compared to the free ligand, but far from the position of the phosphorus resonance in complex **5**. The ^{1}H NMR spectrum shows the expected set of resonances and both the ^{31}P{^{1}H} NMR and the ^{1}H NMR spectra show the presence of a single isomer. The ^{1}H-^{1}H NOESY spectrum of complex **9** shows an intense NOE interaction between the H$_6$ *ortho* proton of the dmba ligand and the H$_6$ *ortho* proton of the pyridine fragment, indicating their mutually *cis* disposition (see Scheme 1).

The IR spectrum of **10** shows interesting differences with respect to those described for **5**–**9**. The carbonyl stretching region shows the presence of four bands (1607, 1585, 1565 and 1538 cm^{-1}) with a pattern of absorptions very similar to that of the free ligand. Moreover, these absorptions are found at energies very close to those observed for the free ligand. The ν_{PN} absorption appears at 1350 cm^{-1}, also very close to the corresponding absorption in the free ligand. The ^{31}P{^{1}H} NMR spectrum of **10** shows the presence of two singlet resonances, one at 42.57 ppm, attributed to the PPh$_3$ ligand, and the other at 23.52 ppm, assigned to the iminophosphorane ligand and which has a very similar chemical shift to that of the free ligand. The IR and ^{31}P{^{1}H} NMR data imply that in complex **10** the iminophosphorane is coordinated only through the pyridinic nitrogen. This coordination mode leaves the fragment —C=O—N=PPh$_3$ unchanged with respect to the free ligand, and this could be the responsible for the similar pattern of absorptions in the IR spectra and also for the similarities in the phosphorus NMR resonances, when comparing **10** and the free ligand. For instance, in complexes **5** and **6** the —N=PPh$_3$ fragment was implicated in the binding, and in complexes **7**–**9** the CO group also participated in the coordination, resulting in a significant change in the pattern of absorptions on going from the free ligand to the coordinated ligand. The ^{1}H NMR spectrum of **10** shows the expected resonances for the presence of the dmba and the iminophosphorane ligands and gives information about the stereochemistry of the complex. Thus, the CH$_2$N protons and the methyl groups of the dmba ligand are split into doublets, suggesting that the PPh$_3$ ligand is located *trans* to the NMe$_2$ unit and that the reaction occurs with retention of configuration at the palladium atom. Additional evidence is found in the ^{1}H-^{1}H NOESY spectrum of **10**, in which it is possible to observe an intense NOE interaction between the H$_6$ proton of the pyridinic fragment and the NMe$_2$ groups. Moreover, the pyridine group should have a restricted rotation around the Pd—N bond since in the spectrum at room temperature the CH$_2$N protons of the dmba ligand appear as diastereotopic hydrogens (AB spin system) and the methyl groups of the NMe$_2$ unit as a broad singlet that is resolved into two sharp singlets on cooling. This means that the molecular plane is no longer a plane of symmetry due to the asymmetry introduced by the *N*-coordination of the ligand. The structure depicted in Scheme 1 accounts for all of these observations.

The IR spectrum of **11** shows a pattern of absorptions in the carbonyl region similar to that of the free ligand and of **10**. Moreover, we also observe the Pd—Cl stretch at 281 cm^{-1}, the characteristic absorptions of the dmba ligand, and the P—N band at 1348 cm^{-1}. The position of the Pd—Cl absorption is found at higher frequencies than in the starting dimer, which is typical for Cl-*trans*-to-C arrangements.[33] The NMR spectra provide more structural information. The ^{1}H NMR spectrum shows the resonance attributed to the H$_6$ of the dmba ligand shifted strongly upfield, appearing now at 6.55 ppm. This is also observed in [PdCl(dmba)py][29] and the reason for this shift is the anisotropic shielding of this proton due to the *cis* pyridine ligand. We have established the mutual *cis* disposition of the pyridine group and the aromatic ring of the dmba ligand by the observation of a strong NOE interaction between the H$_6$ (dmba) and the H$_6$ (py) protons in the 1H-1H NOESY spectrum of **11**. The ^{31}P{^{1}H} NMR spectrum

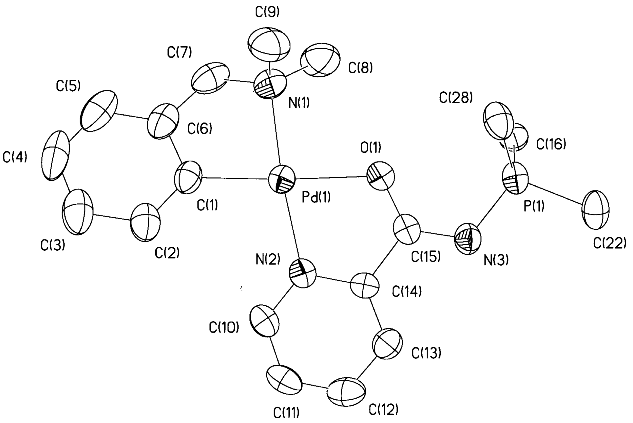


Fig. 1 Thermal ellipsoid plot of the $[\text{Pd(dmba)}\{\text{Ph}_3\text{PNC(O)-2-NC}_5\text{H}_4\}]^+$ cation. H atoms and phenyl groups have been omitted for clarity. Atoms are drawn at the 50% probability level.

of **11** shows a singlet resonance at 23.14 ppm. With these data, it is reasonable to propose for complex **11** a structure such as that depicted in Scheme 1 in which the iminophosphorane is coordinated only through the pyridinic nitrogen atom.

Crystal structure of complex 9

Crystals of adequate quality for X-ray measurements were grown by slow diffusion of *n*-hexane into a solution of **9** in CH_2Cl_2 at −30 °C. A drawing of the organometallic cationic fragment is shown in Fig. 1, relevant crystallographic parameters are presented in Table 1 and selected bond distances and angles are collected in Table 2.

The palladium atom is located in a slightly distorted square planar environment, surrounded by the C and N atoms of the dmba ligand and by the pyridinic N atom and the carbonyl oxygen of the iminophosphorane ligand, with the latter showing its *N*,*O*-chelating coordination mode.

The structural parameters of the dmba ligand and the pyridine fragment of the iminophosphorane ligand are similar to those found in other complexes containing these groups.[1–4,6] The C(14)—C(15) bond distance [1.502(5) Å] corresponds to a C—C single bond and the C(15)—O(1) bond distance [1.266(5) Å] indicates largely double bond character. This C═O bond distance is similar within experimental error to that found in the free stabilized iminophosphoranes $\text{Ph}_3\text{P{=}NC(O)Ph}$ [1.245(5) Å] [34] or $\text{RPh}_2\text{P{=}NC(O)Ph}$ (R = conjugated diolefinic group) [1.263(6) or 1.247(4) Å],[35] in *O*-coordinated ylides such as $[\text{Pd(dmba)(py)}\{\text{OC(Me){=}C(H)PPh}_3\}]\text{ClO}_4$ [1.275(4) Å][1] or *trans*-$[\text{SnMe}_3\text{Cl}\{\text{OC(Me){=}C(H)PPh}_3\}]$ (1.27 Å) [36] and is shorter than that observed in *trans*-$\text{TiCl}_4[\text{OC(Me){=}C(H)PPh}_3](\text{THF})\cdot\text{THF}$ [1.332(8) Å],[37] although it is still longer than the C═O bond distances found in *C*-bound ylides.[3,6] The Pd—O(1) bond distance [2.105(3) Å] is shorter than that found in the *O*-bonded ylide $[\text{Pd(dmba)(py)}\{\text{OC(Me){=}C(H)PPh}_3\}]\text{ClO}_4$ [2.154(2) Å].[1]

Table 1 Crystal data and structure refinement for **9**

Empirical formula	$\text{C}_{33}\text{H}_{31}\text{ClN}_3\text{O}_5\text{PPd}$
Formula weight	722.43
Temperature	150(1) K
Wavelength/Å	0.71073
Crystal system, space group	$P2_1/c$, Monoclinic
a/Å	10.5939(6)
b/Å	24.5212(15)
c/Å	12.1504(9)
β/°	95.004(6)
Volume/Å^3	3144.3(4)
Z, Calcd density/Mg m^{-3}	4, 1.526
Absorption coefficient/mm^{-1}	0.772
Reflections collected/unique	5821/5515 [$R_{\text{int}} = 0.0314$]
Max. and min. transmission	0.8364 and 0.7130
Data/restraints/parameters	5515/0/399
Goodness-of-fit on F^2	1.023
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0435$, $wR_2 = 0.0984$
Largest diff. peak and hole/e Å^{-3}	0.589 and −0.468

$R_1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$. $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$. Goodness-of-fit $= [\Sigma w(F_o^2 - F_c^2)^2/(n_{\text{obs}} - n_{\text{param}})]^{1/2}$.

Table 2 Selected bond lengths (Å) and angles (°) for **9**

Pd(1)—C(1)	1.972(4)	Pd(1)—N(2)	2.056(3)
Pd(1)—N(1)	2.056(4)	Pd(1)—O(1)	2.105(3)
C(14)—C(15)	1.502(5)	C(15)—O(1)	1.266(5)
C(15)—N(3)	1.313(5)	N(3)—P(1)	1.624(4)
P(1)—C(22)	1.792(4)	P(1)—C(28)	1.794(4)
P(1)—C(16)	1.800(4)		
C(1)—Pd(1)—N(2)	103.56(16)	C(1)—Pd(1)—N(1)	82.44(17)
N(2)—Pd(1)—N(1)	170.97(13)	C(1)—Pd(1)—O(1)	173.66(14)
N(2)—Pd(1)—O(1)	79.57(12)	N(1)—Pd(1)—O(1)	95.14(13)
N(2)—C(14)—C(15)	115.3(3)	C(13)—C(14)—C(15)	122.2(4)
O(1)—C(15)—N(3)	125.1(4)	O(1)—C(15)—C(14)	117.2(4)
N(3)—C(15)—C(14)	117.7(4)	C(15)—O(1)—Pd(1)	114.2(3)
C(15)—N(3)—P(1)	118.4(3)	N(3)—P(1)—C(22)	105.2(2)
N(3)—P(1)—C(28)	112.31(19)	C(22)—P(1)—C(28)	108.7(2)
N(3)—P(1)—C(16)	113.7(2)	C(22)—P(1)—C(16)	108.2(2)
C(28)—P(1)—C(16)	108.4(2)		

With respect to the iminophosphorane fragment, the C(15)—N(3) bond distance is 1.313(5) Å and the N(3)—P(1) bond distance is 1.624(4) Å. The P—N bond distance is similar within experimental error to those found in other uncoordinated stabilized iminophosphoranes [1.626(3) Å for $\text{Ph}_3\text{P{=}NC(O)Ph}$,[34] 1.603(5) and 1.607(3) Å for $\text{RPh}_2\text{P{=}NC(O)Ph}$],[35] while the C—N bond distance is similar within experimental error or slightly shorter than those found in the same derivatives [1.353(5) Å for $\text{Ph}_3\text{P{=}NC(O)Ph}$,[34] and 1.326(7) and 1.350(4) Å for $\text{RPh}_2\text{P{=}NC(O)Ph}$][35] as can be expected for a non-coordinating disposition of this fragment. The comparison of these bond distances in our complex with those found in other coordinated and uncoordinated non-stabilized iminophosphoranes reveals that in our case there is extensive delocalization of the charge density through the P—N—C—O system, which results in an elongation of the P═N bond and in a shortening of the C—N bond. Thus, the C(15)—N(3) bond distance is shorter than those found in the complexes $[\text{PtCl(PPhMe}_2)\{\text{CH(PPh}_2{=}\text{NC}_6\text{H}_4\text{CH}_3\text{-4)}_2\}]$ [1.396(7) Å for the uncoordinated fragment and 1.418(6) Å for the coordinated one],[22a] *trans*-$[\text{PtCl}_2\{\text{N(=PPh}_3)\text{C(C}_6\text{F}_5){=}\text{CHCO}_2\text{Et}\}\{E\text{-NH}{=}\text{C(C}_6\text{F}_5)\text{C(=PPh}_3)\text{CO}_2\text{Et}\}]$ [1.399(5) Å],[22b] $[\text{PtCl(PPhMe}_2)\{\text{CH(PPh}_2{=}\text{NC}_6\text{H}_4\text{CH}_3\text{-4)(PPh}_2\text{NHC}_6\text{H}_4\text{-4-Me)}\}]$ [1.388(10) Å],[18] $[\text{PtCl(PEt}_3)\{\text{CH (PPh}_2{=}\text{NC}_6\text{H}_4\text{CH}_3\text{-4)(PPh}_2\text{N}'\text{HC}_6\text{H}_4\text{-4-Me)-}C,N\}][\text{PtCl}_3(\text{PEt}_3)]$ [1.405(9) Å],[18] in the adducts $\text{Ph}_3\text{P{=}N(Me)BH}_3$ [1.456(5) Å] [20] or $[\text{Ph}_3\text{P{=}N(Me)}_2]^+$ [1.425(7)–1.461(6) Å] [20] or even in free ligands such as $4,6\text{-(CN)}_2\text{C}_6\text{F}_2\text{-1,3-bis(N{=}PPh}_2\text{CH}_2\text{PPh}_2)$ [1.356(5) and 1.358(5) Å][21] and $4,6\text{-(CN)}_2\text{C}_6\text{F}_2\text{-1-(N{=}PPh}_2\text{CH}_2\text{PPh}_2)\text{-3-(N{=}PPh}_3)$ [1.351(6) and 1.364(6) Å].[21] On the other hand, the N(3)—P(1) bond distance is 1.624(4) Å, which is similar within experimental error or longer than those reported for the complexes, adducts or free ligands described above (it should be kept in mind that the P—N bond in phosphazenes, where the bond order is formally 1.5, has been found to average 1.560(12) Å for 26 values reported recently).[38] These phosphorus–nitrogen bond distances are 1.555(4) and 1.612(4) Å for $[\text{PtCl(PPhMe}_2)\{\text{CH(PPh}_2{=}\text{NC}_6\text{H}_4\text{CH}_3\text{-4)}_2\}]$,[22a] 1.643(3) Å for *trans*-$[\text{PtCl}_2\{\text{N(=PPh}_3)\text{C(C}_6\text{F}_5){=}\text{CHCO}_2\text{Et}\}\{E\text{-NH}{=}\text{C(C}_6\text{F}_5)\text{C(=PPh}_3)\text{CO}_2\text{Et}\}]$,[22b] 1.613(6) Å for $[\text{PtCl(PPhMe}_2)\{\text{CH(PPh}_2{=}\text{NC}_6\text{H}_4\text{CH}_3\text{-4) (PPh}_2\text{NHC}_6\text{H}_4\text{-4-Me)}\}]$,[18] 1.604(7) Å for $[\text{PtCl(PEt}_3)\{\text{CH(PPh}_2{=}\text{NC}_6\text{H}_4\text{CH}_3\text{-4)(PPh}_2\text{N}'\text{HC}_6\text{H}_4\text{-4-Me)-}C,N\}][\text{PtCl}_3(\text{PEt}_3)]$,[18] 1.605(3) and 1.627(4), 1.624(4) Å for adducts $\mathrm{Ph_3P{=}N(Me)BH_3}$[20] and $[\mathrm{Ph_3P{=}N(Me)_2}]\mathrm{BF_4}$,[20] 1.581(3) and 1.569(4) Å for 4,6-$\mathrm{(CN)_2C_6F_2}$-1,3-bis-($\mathrm{N{=}PPh_2CH_2PPh_2}$)[21] and 1.585(4), 1.578(4) for 4,6-$\mathrm{(CN)_2C_6F_2}$-1-($\mathrm{N{=}PPh_2CH_2PPh_2}$)-3-($\mathrm{N{=}PPh_3}$).[21] Thus, it is clear that the P=N bond distance is longer and the N—C one shorter, not only when compared with other free iminophosphoranes but also when the comparison is made with *N*-coordinated iminophosphoranes. This gives proof of the extensive delocalization of the electron density along the O—C—N—P system and could be related to the low tendency of the iminic N atom to behave as a nucleophile, as we have seen in complexes **1**–**4**. Finally, the environment around the phosphorus atom is tetrahedral with P—C bond distances similar to those found in ylide complexes.[1,4–6]

Discussion

The observed reactivity of $\mathrm{Ph_3P{=}NC(O)CH_2Cl}$ towards bis-solvate complexes of palladium shows a close resemblance to those described by us[2,3,5,6] and others[39] for the chemistry of the same precursors with phosphorus ylides; that is, the displacement of the two NCPh ligands from $\mathrm{PdCl_2(NCPh)_2}$ giving a bis-iminophosphorane derivative, and the replacement of only one NCMe ligand from $[\mathrm{M(C^{\wedge}P)(NCMe)_2}]\mathrm{ClO_4}$ or $[\mathrm{Pd(dmba)(NCMe)_2}]\mathrm{ClO_4}$. This would seem to imply that the iminophosphorane $\mathrm{Ph_3P{=}NC(O)CH_2Cl}$ behaves similarly to the phosphorus ylides $\mathrm{Ph_3P{=}C(H)COR}$ (R = Me, Ph, OMe, $\mathrm{NMe_2}$) and that the nucleophilic ability of the iminic N atom is similar to that of the ylidic carbon. Further reactivity studies of this iminophosphorane with the other reported precursors shows that the iminic N atom is in fact less nucleophilic than the ylidic C atom and that this iminophosphorane cannot behave as an ambidentate ligand.

For instance, the reaction between $[\mathrm{Pt(C^{\wedge}P)(PPh_3)(NCMe)}]\mathrm{ClO_4}$ and $\mathrm{Ph_3P{=}NC(O)CH_2Cl}$ does not take place even in refluxing THF, and the mixture of starting compounds is recovered; the same lack of reactivity has been observed in the reaction of $[\mathrm{Pd(dmba)(PPh_3)(THF)}]\mathrm{ClO_4}$ with $\mathrm{Ph_3P{=}NC(O)CH_2Cl}$. Towards the same precursors, the ylides $\mathrm{Ph_3P{=}C(H)COR}$ react giving *O*-coordinated ylides.[3,5] In the same way, $\mathrm{Ph_3P{=}NC(O)CH_2Cl}$ is not able to promote cleavage of the halide bridging system in $[\mathrm{Pd(\mu\text{-}Cl)(dmba)}]_2$ or in $[\mathrm{M(\mu\text{-}Cl)(C^{\wedge}P)}]_2$ (M = Pd, Pt), whereas the ylides do, resulting in the formation of $[\mathrm{PdCl(dmba)\{C(H)CONMe_2(PPh_3)\}}]$ [6] or $[\mathrm{MCl(C^{\wedge}P)\{C(H)COR(PPh_3)\}}]$ [5,6] (M = Pd, Pt). In conclusion, the N atom of the resonance-stabilized iminophosphorane $\mathrm{Ph_3P{=}NC(O)CH_2Cl}$ is a poor nucleophile, even when compared with its homologous α-stabilized phosphoylides, probably due to the negative influence of the C=O group on the N(imine) donor ability. However, under certain conditions it is able to displace weakly coordinated ligands, giving the corresponding iminophosphorane derivatives.

With respect to the different coordination modes observed in complexes **5**–**11**, there are two interesting questions to be answered. First, what drives the adoption of the *N*,*N*-chelating, the *N*,*O*-chelating or the *N*(py)-unidentate mode towards a given substrate? Second, why is a single isomer observed in all cases?

It seems that, in this ligand, the N(py) is more strongly coordinated to Pd or Pt than N(imine), and this more than O(carbonyl). Thus, one can expect that the preferred coordination mode for $\mathrm{Ph_3P{=}NC(O)\text{-}2\text{-}NC_5H_4}$ would be the *N*,*N*-chelating mode, and this is, in fact, the observed mode in **5** and **6**. On the other hand, the higher tendency of the N(py) atom to coordinate could explain the binding observed in complexes **10** and **11**. The known reluctance[40] of the $\mathrm{PPh_3}$ ligand to be *trans* to the *ortho*-metallated carbon atom of the dmba ligand explains the geometry proposed for **10** in Scheme 1, while in the absence of phosphine ligands, the pyridinic fragment of the iminophosphorane behaves as a 'free' pyridine and coordinates *trans* to the $\mathrm{NMe_2}$ group (**11**).[29] In fact, this tendency of the pyridine to coordinate *trans* to the $\mathrm{NMe_2}$ group could be the starting point for a reasonable explanation of the *N*,*O*-coordination in **9**. The reactivity of a number of *N*-donor ligands (including pyridines) towards $[\mathrm{Pd(\mu\text{-}Cl)(dmba)}]_2$—and other *C*,*N*-cyclometallated palladium complexes—has been reported[29] and in all cases these ligands were coordinated *trans* to the $\mathrm{NMe_2}$ unit, showing a certain reluctance to be coordinated *trans* to the *ortho*-metallated carbon atom. Thus, the selective N(py) coordination *trans* to the $\mathrm{NMe_2}$ group gives the explanation for the observation of a single isomer. Now, there are two possible donor atoms to be coordinated—the carbonyl oxygen and the iminic N atom—and the *O*-coordination resides probably on the consideration of steric factors—the large volume of the $\mathrm{-N{=}PPh_3}$ unit would prevent its coordination *cis* to the $\mathrm{NMe_2}$ group and thus *O*-coordination is preferred. Similar arguments can be considered for complexes **7** and **8**; the reluctance of the pyridine to coordinate *trans* to the carbon atom being responsible for the existence of a single isomer, and the presence of a bulky P(*o*-Tol)$_2$ group responsible for the *cis* *O*-coordination.[41]

In conclusion, the iminophosphorane $\mathrm{Ph_3P{=}NC(O)\text{-}2\text{-}NC_5H_4}$ shows very interesting chemical behaviour and displays at least three different coordination modes towards the same metals (palladium and platinum). We think that this versatility could permit the deliberate variation of the coordination mode as a function of the metal-containing precursor and that this modulation could, moreover, result in different chemical properties and different reactivity. Further studies on the reactivity of these iminophosphoranes are now in progress.

Experimental

Safety Note: *Caution*! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of these materials should be prepared and they should be handled with great caution. See ref. 42.

General procedures

Solvents were dried and distilled by standard methods prior to use. Elemental analyses of C, H, N were carried out on a Perkin–Elmer 2400 microanalyser. Infrared spectra (4000–200 $\mathrm{cm^{-1}}$) were recorded on a Perkin–Elmer 883 infrared spectrophotometer in Nujol mulls between polyethylene sheets. ^{1}H (300.13 MHz) and $^{31}\mathrm{P}\{^1\mathrm{H}\}$ (121.49 MHz) NMR spectra were recorded from $\mathrm{CDCl_3}$, $\mathrm{CD_2Cl_2}$ or $\mathrm{(CD_3)_2CO}$ solutions at room temperature (unless otherwise stated) on a Bruker ARX-300 spectrometer; ^{1}H NMR spectra were referenced using the solvent signal as an internal standard and $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectra were externally referenced to $\mathrm{H_3PO_4}$ (85%). The two dimensional ^{1}H-^{1}H NOESY experiments for complexes **8**–**11** were performed at a measuring frequency of 300.13 MHz. The data were acquired in a phase sensitive mode into a 512 × 1024 matrix, and then transformed into 1024 × 1024 points using a sine window in each dimension. The mixing time was in all cases 400 ms. Mass spectra (positive ion FAB) were recorded on a VG Autospec spectrometer from $\mathrm{CH_2Cl_2}$ solutions. The starting products $\mathrm{MCl_2(NCPh)_2}$ (M = Pd, Pt),[25] $[\mathrm{M(C^{\wedge}P)(NCMe)_2}](\mathrm{ClO_4})$ (M = Pd,[26] Pt [27]), $[\mathrm{Pd(dmba)(NCMe)_2}](\mathrm{ClO_4})$,[28] $[\mathrm{Pt(C^{\wedge}P)(PPh_3)(NCMe)}](\mathrm{ClO_4})$,[5] $[\mathrm{Pd(dmba)(PPh_3)(THF)}]\mathrm{ClO_4}$,[29] $[\mathrm{M(\mu\text{-}Cl)(C^{\wedge}P)}]_2$ (M = Pd,[30] Pt [27]), $[\mathrm{Pd(\mu\text{-}Cl)(dmba)}]_2$[31] and $\mathrm{Ph_3P{=}NC(O)R}$ (R = $\mathrm{CH_2Cl}$, 2-py)[24] were prepared according to published methods.

Syntheses

***trans*-$PdCl_2\{N(=PPh_3)C(O)CH_2Cl\}_2$, 1.** To a solution of $PdCl_2(NCPh)_2$ (0.200 g, 0.521 mmol) in 20 mL of acetone the iminophosphorane $Ph_3P{=}NC(O)CH_2Cl$ (0.369 g, 1.04 mmol) was added. In a few seconds an orange precipitate of **1** appeared, which was stirred at room temperature for 5 min, filtered, washed with acetone (10 mL) and Et_2O (25 mL) and air-dried. Obtained: 0.329 g (71% yield). Anal. calcd for $C_{40}H_{34}Cl_4N_2O_2P_2Pd$ (884.88 g mol^{-1}): C, 54.29; H, 3.87; N, 3.16. Found: C, 54.36; H, 3.70; N, 3.19. IR (ν, cm^{-1}): 1643 (ν_{CO}), 1325 (ν_{PN}), 319 (ν_{PdCl}). ^1H NMR (CD_2Cl_2): δ 7.88–7.58 (m, 15H, Ph), 4.25 (s, 2H, CH_2). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 37.50 (s, $-NPPh_3$).

$[Pd(C^\wedge P)\{N(=PPh_3)C(O)CH_2Cl\}(NCMe)](ClO_4)$, 2. To a solution of $[Pd(C^\wedge P)(NCMe)_2](ClO_4)$ (0.200 g, 0.338 mmol) in 20 mL of CH_2Cl_2 the iminophosphorane $Ph_3P{=}NC(O)CH_2Cl$ (0.120 g, 0.338 mmol) was added, and the resulting solution was stirred at room temperature for 30 min. The solvent was then evaporated to dryness and the residue was washed with Et_2O (25 mL) giving **2** as a white solid, which was collected and air-dried. Obtained: 0.155 g (51% yield). Anal. calcd for $C_{43}H_{40}Cl_2N_2O_5P_2Pd$ (904.06 g mol^{-1}): C, 57.13; H, 4.46; N, 3.10. Found: C, 56.63; H, 4.41; N, 2.92. IR (ν, cm^{-1}): 2306, 2278 (ν_{NCMe}), 1647 (ν_{CO}), 1321 (ν_{PN}). Mass spectrum (FAB+) [m/z, (%)]: 762 (15%) $[M-ClO_4-NCMe]^+$. ^1H NMR ($CDCl_3$, 213 K): δ 7.73–6.38 (m, 27H, Ph + o-MeC_6H_4), 4.93 (s, 2H, CH_2Cl), 3.24, 2.88 (AB spin system, 2H, $CH_2{-}Pd$, $^2J_{HH} = 14.1$ Hz), 2.71, 2.10, 1.94 (3s, 9H, 2 o-MeC_6H_4 + NCMe). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 213 K): δ 38.01, 37.56 (2s, $-NPPh_3$ + $C^\wedge P$).

$[Pt(C^\wedge P)\{N(=PPh_3)C(O)CH_2Cl\}(NCMe)](ClO_4)$, 3. Complex **3** was synthesized in the same way as **2**: $[Pt(C^\wedge P)(NCMe)_2](ClO_4)$ (0.200 g, 0.294 mmol) was reacted in CH_2Cl_2 with $Ph_3P{=}NC(O)CH_2Cl$ (0.104 g, 0.294 mmol) to give **3** as a white solid. Obtained: 0.212 g (73% yield). Anal. calcd for $C_{43}H_{40}Cl_2N_2O_5P_2Pt$ (992.75 g mol^{-1}): C, 52.02; H, 4.06; N, 2.82. Found: C, 51.97; H, 3.73; N, 2.62. IR (ν, cm^{-1}): 2310, 2282 (ν_{NCMe}), 1651 (ν_{CO}), 1318 (ν_{PN}). Mass spectrum (FAB+) [m/z, (%)]: 852 (40%) $[M-ClO_4-NCMe]^+$. ^1H NMR ($CDCl_3$, 213 K): δ 7.82–6.31 (m, 27H, Ph + o-MeC_6H_4), 4.92 (s, 2H, CH_2Cl), 3.09, 3.01 (AB spin system, 2H, $CH_2{-}Pt$, $^2J_{HH} = 16.2$ Hz), 2.72, 2.19, 1.87 (3s, 9H, 2 o-MeC_6H_4 + NCMe). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 213 K): δ 40.30 (d, 1P, $-NPPh_3$, $^2J_{PtP} = 62.2$ Hz, $^3J_{PP} = 5.9$ Hz), 16.41 (br s, $C^\wedge P$, $^1J_{PtP} = 4334$ Hz).

$[Pd(dmba)\{N(=PPh_3)C(O)CH_2Cl\}(NCMe)](ClO_4)$, 4. Complex **4** was synthesized in the same way as **2**: $[Pd(dmba)(NCMe)_2](ClO_4)$ (0.200 g, 0.474 mmol) was reacted in CH_2Cl_2 with $Ph_3P{=}NC(O)CH_2Cl$ (0.168 g, 0.474 mmol) to give **4** as a white solid. Obtained: 0.236 g (68% yield). Anal. calcd for $C_{31}H_{32}Cl_2N_3O_5PPd$ (734.89 g mol^{-1}): C, 50.66; H, 4.39; N, 5.72. Found: C, 49.99; H, 4.25; N, 5.29. IR (ν, cm^{-1}): 2329 (ν_{NCMe}), 1636 (ν_{CO}), 1332 (ν_{PN}). Mass spectrum (FAB+) [m/z, (%)]: 595 (45%) $[M-ClO_4-NCMe]^+$. ^1H NMR ($CDCl_3$): δ 7.76–7.69 (m, 6H, Ph), 7.67–7.61 (m, 3H, Ph), 7.53–7.47 (m, 6H, Ph), 6.94 (td, 1H, C_6H_4, $^3J_{HH} = 7.3$ Hz, $^4J_{HH} = 1.2$ Hz), 6.90–6.74 (m, 3H, C_6H_4), 5.45, 5.39 (AB spin system, 2H, CH_2Cl, $^2J_{HH} = 15.7$ Hz), 3.69, 3.32 (AB spin system, 2H, CH_2N, $^2J_{HH} = 13.7$ Hz), 2.70, 2.31 (2s, 6H, NMe_2), 1.93 (s, 3H, NCMe). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 38.18 ($-NPPh_3$).

***cis*-$Cl_2Pd\{N(=PPh_3)C(O)$-2-$NC_5H_4\}$, 5.** To a solution of $[PdCl_2(NCPh)_2]$ (0.200 g, 0.521 mmol) in 20 mL of acetone the iminophosphorane $Ph_3P{=}NC(O)$-2-NC_5H_4 (0.199 g, 0.521 mmol) was added. After a few minutes, an orange solid precipitated, which was collected, washed with additional acetone (10 mL), Et_2O (25 mL), air-dried and identified as **5**. Obtained: 0.128 g (44% yield). The acetone solution was evaporated to dryness and the residue treated with Et_2O (25 mL), giving a second fraction of **5**. Obtained: 0.107 g (37% yield, total yield 81%). Anal. calcd for $C_{24}H_{19}Cl_2N_2OPPd$ (559.71 g mol^{-1}): C, 51.50; H, 3.42; N, 5.00. Found: C, 50.99; H, 3.16; N, 4.81. IR (ν, cm^{-1}): 1652 (ν_{CO}), 1316 (ν_{PN}), 350, 328 (ν_{PdCl}). ^1H NMR (CD_2Cl_2): δ 9.20 (d, 1H, H_6, NC_5H_4, $^3J_{HH} = 5.7$ Hz), 8.11–8.00 (m, 7H, Ph + NC_5H_4), 7.80 (d, 1H, H_3, NC_5H_4, $^3J_{HH} = 6.6$ Hz), 7.73–7.68 (m, 3H, Ph), 7.63–7.57 (m, 7H, Ph + NC_5H_4). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 33.72 (s, $-NPPh_3$).

***cis*-$Cl_2Pt\{N(=PPh_3)C(O)$-2-$NC_5H_4\}$, 6.** Finely ground $PtCl_2$ (0.300 g, 1.13 mmol) was suspended in 35 mL of a mixture of CH_2Cl_2–acetone (9 : 1) and the iminophosphorane $Ph_3P{=}NC(O)$-2-NC_5H_4 (0.431 g, 1.13 mmol) was added. The resulting mixture was refluxed for 48 h. During this time, most of the platinum salt dissolved and gave an orange-brown suspension. Once cooled this suspension was filtered over Celite and the resulting yellow-orange solution was evaporated to dryness. The residue was treated with Et_2O (50 mL), giving **6** as a deep-yellow solid, which was filtered, washed with additional Et_2O (20 mL) and air-dried. Obtained: 0.333 g (45% yield). Anal. calcd for $C_{24}H_{19}Cl_2N_2OPPt$ (648.40 g mol^{-1}): C, 44.46; H, 2.95; N, 4.32. Found: C, 44.31; H, 2.96; N, 4.13. IR (ν, cm^{-1}): 1659 (ν_{CO}), 1311 (ν_{PN}), 346, 310 (ν_{PtCl}). ^1H NMR (CD_2Cl_2): δ 9.52 (d, 1H, H_6, NC_5H_4, $^3J_{HH} = 5$ Hz, $^3J_{PtH} = 38$ Hz), 8.11–7.17 (m, 18H, Ph + NC_5H_4). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 34.62 (s, $-NPPh_3$, $^2J_{PtP} = 146$ Hz).

$[Pd(C^\wedge P)\{N(=PPh_3)C(O)$-2-$NC_5H_4\}](ClO_4)$, 7. Complex **7** was synthesized in the same way as **2**: $[Pd(C^\wedge P)(NCMe)_2](ClO_4)$ (0.200 g, 0.338 mmol) was reacted with $Ph_3P{=}NC(O)$-2-NC_5H_4 (0.129 g, 0.338 mmol) in CH_2Cl_2 to give **7** as a white solid. Obtained: 0.231 g (77% yield). Anal. calcd for $C_{45}H_{39}ClN_2O_5P_2Pd$ (891.62 g mol^{-1}): C, 60.62; H, 4.41; N, 3.14. Found: C, 59.93; H, 4.19; N, 2.97. IR (ν, cm^{-1}): 1537 (ν_{CO}), 1379 (ν_{PN}). Mass spectrum (FAB+) [m/z, (%)]: 791 (75%) $[M-ClO_4]^+$. ^1H NMR ($CDCl_3$, 213 K): δ 8.78 (d, 1H, H_6, NC_5H_4, $^3J_{HH} = 8$ Hz), 8.57 (d, 1H, H_3, NC_5H_4, $^3J_{HH} = 4$ Hz), 8.32 (t, 1H, H_5, NC_5H_4, $^3J_{HH} = 8$ Hz), 7.92 (t, 1H, H_4, NC_5H_4, $^3J_{HH} = 4$ Hz), 7.68–6.69 (m, 27H, Ph + o-MeC_6H_4), 3.76, 3.63 (AB spin system, 2H, $CH_2{-}Pd$, $^2J_{HH} = 13$ Hz), 2.36, 1.58 (2s, 6H, 2 o-MeC_6H_4). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 213 K): δ 32.73 (s, $C^\wedge P$), 23.56 (s, $-NPPh_3$).

$[Pt(C^\wedge P)\{N(=PPh_3)C(O)$-2-$NC_5H_4\}](ClO_4)$, 8. Complex **8** was synthesized in the same way as **2**: $[Pt(C^\wedge P)(NCMe)_2](ClO_4)$ (0.100 g, 0.147 mmol) was reacted with $Ph_3P{=}NC(O)$-2-NC_5H_4 (0.056 g, 0.15 mmol) in CH_2Cl_2 to give **8** as a white solid. Obtained: 0.109 g (76% yield). Anal. calcd for $C_{45}H_{39}ClN_2O_5P_2Pt$ (980.31 g mol^{-1}): C, 55.13; H, 4.01; N, 2.86. Found: C, 55.17; H, 3.68; N, 2.88. IR (ν, cm^{-1}): 1538 (ν_{CO}), 1378 (ν_{PN}). Mass spectrum (FAB+) [m/z, (%)]: 880 (100%) $[M-ClO_4]^+$. ^1H NMR ($CDCl_3$, 213 K): δ 8.79 (d, 1H, H_6, NC_5H_4, $^3J_{HH} = 7.5$ Hz), 8.46 (t, 1H, H_5, NC_5H_4, $^3J_{HH} = 8$ Hz), 7.98 (m, 2H, $H_4 + H_3$, NC_5H_4), 7.68–6.65 (m, 27H, Ph + o-MeC_6H_4), 3.91, 3.58 (AB spin system, 2H, $CH_2{-}Pt$, $^2J_{HH} = 15$ Hz), 2.39, 1.60 (2s, 6H, 2 o-MeC_6H_4). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 213 K): δ 23.75 (s, $-NPPh_3$), 14.63 (s, $C^\wedge P$, $^1J_{PtP} = 4251$ Hz).

$[Pd(dmba)\{N(=PPh_3)C(O)$-2-$NC_5H_4\}](ClO_4)$, 9. Complex **9** was synthesized in the same way as **2**: $[Pd(dmba)(NCMe)_2](ClO_4)$ (0.100 g, 0.237 mmol) was reacted in CH_2Cl_2 with $Ph_3P{=}NC(O)$-2-NC_5H_4 (0.091 g, 0.24 mmol) to give **9** as a white solid. Obtained: 0.148 g (87% yield). Anal. calcd for $C_{33}H_{31}ClN_3O_5PPd$ (722.43 g mol^{-1}): C, 54.86; H, 4.32; N, 5.81. Found: C, 54.62; H, 4.21; N, 5.71. IR (ν, cm^{-1}): 1538 (ν_{CO}), 1378 (ν_{PN}). Mass spectrum (FAB+) [m/z, (%)]: 622

(100%) $[M - ClO_4]^+$. ^1H NMR ($CDCl_3$): δ 8.69 (d, 1H, H_3, NC_5H_4, $^3J_{HH} = 5$ Hz), 8.64 (dd, 1H, H_6, NC_5H_4, $^3J_{HH} = 8$ Hz, $^4J_{HH} = 1.2$ Hz), 8.28 (td, 1H, H_5, NC_5H_4, $^4J_{HH} = 1.4$ Hz), 7.77–7.68 (m, 10H, Ph + NC_5H_4), 7.63–7.59 (m, 6H, Ph), 7.07–6.74 (m, 4H, C_6H_4), 3.95 (s, 2H, CH_2N), 2.41 (s, 6H, NMe_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 26.04 ($-NPPh_3$).

[Pd(dmba)(PPh$_3$){N(=PPh$_3$)C(O)-2-*N*C$_5$H$_4$}](ClO$_4$), 10. To a THF solution (25 mL) of PdCl(dmba)(PPh_3) (0.200 g, 0.371 mmol), $AgClO_4$ (0.077 g, 0.37 mmol) was added. The resulting suspension was stirred at room temperature in the dark for 30 min, then filtered. To the freshly obtained solution of [Pd(dmba)(PPh_3)(THF)](ClO_4) the iminophosphorane $Ph_3P{=}NC(O)$-2-NC_5H_4 (0.131 g, 0.371 mmol) was added, and the resulting pale yellow solution was stirred at room temperature for 30 min. The solvent was then evaporated to half-volume, resulting in the precipitation of **10**, which was filtered, washed with Et_2O (25 mL) and air-dried. Obtained: 0.309 g (84% yield). Anal. calcd for $C_{51}H_{46}ClN_3O_5P_2Pd$ (984.75 g mol^{-1}): C, 62.20; H, 4.71; N, 4.27. Found: C, 61.97; H, 5.01; N, 4.34. IR (ν, cm^{-1}): 1607, 1585, 1565, 1538 (ν_{CO}), 1350 (ν_{PN}). Mass spectrum (FAB+) [*m*/*z*, (%)]: 884 (10%) $[M - ClO_4]^+$, 622 (100%) $[M - ClO_4 - PPh_3]^+$. ^1H NMR ($CDCl_3$, 213 K): δ 8.80 (d, 1H, H_3, NC_5H_4, $^3J_{HH} = 5$ Hz), 8.34 (d, 1H, H_6, NC_5H_4, $^3J_{HH} = 8$ Hz), 7.93–7.40 (m, 17H, Ph + NC_5H_4), 6.98 (d, 1H, C_6H_4, $^3J_{HH} = 7.2$ Hz), 6.82 (t, 1H, C_6H_4, $^3J_{HH} = 7.8$ Hz), 6.35 (t, 1H, C_6H_4, $^3J_{HH} = 7.8$ Hz), 6.27 (t, 1H, C_6H_4, $^3J_{HH} \cong {}^4J_{PH} = 6$ Hz), 4.16, 3.53 (AB spin system, 2H, CH_2N, $^2J_{HH} = 13.2$ Hz), 2.65, 1.88 (2s, 6H, NMe_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 213K): δ 42.57 (s, $Pd-PPh_3$), 23.52 (s, $-NPPh_3$).

[Pd(dmba)Cl{N(=PPh$_3$)C(O)-2-*N*C$_5$H$_4$}], 11. To a solution of $[Pd(\mu\text{-}Cl)(dmba)]_2$ (0.100 g, 0.181 mmol) in CH_2Cl_2 (25 mL) the iminophosphorane $Ph_3P{=}NC(O)$-2-NC_5H_4 (0.138 g, 0.362 mmol) was added, and the resulting solution was stirred at room temperature for 1 h. The solvent was then evaporated to dryness and the oily residue treated with Et_2O (30 mL), giving **11** as a pale yellow solid. Obtained: 0.198 g (83% yield). Anal. calcd for $C_{33}H_{31}ClN_3OPPd$ (658.46 g mol^{-1}): C, 60.19; H, 4.74; N, 6.38. Found: C, 59.78; H, 4.45; N, 6.24. IR (ν, cm^{-1}): 1604, 1588, 1562, 1538 (ν_{CO}), 1348 (ν_{PN}), 281 (ν_{PdCl}). ^1H NMR ($CDCl_3$): δ 8.86 (d, 1H, H_3, NC_5H_4, $^3J_{HH} = 5$ Hz), 8.35 (d, 1H, H_6, NC_5H_4, $^3J_{HH} = 7.5$ Hz), 8.11 (t, 1H, H_5, NC_5H_4, $^3J_{HH} = 7.5$ Hz), 7.81–7.68 (m, 7H, Ph + NC_5H_4), 7.63–7.55 (m, 3H, Ph), 7.52–7.42 (m, 6H, Ph), 6.98–6.76 (m, 3H, C_6H_4), 6.55 (d, 1H, H_6, C_6H_4, $^3J_{HH} = 6.6$ Hz), 3.74 (s, 2H, CH_2N), 2.44 (s, 6H, NMe_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 23.14 ($-NPPh_3$).

Crystallography

X-ray data collection. A pale yellow crystal of **9** was mounted on a quartz fibre and covered with epoxy. Normal procedures were used for the determination of the unit cell constants and for the measurement of intensity data. After preliminary indexing and transformation of the cell to a conventional setting, axial photographs were taken of the *a*, *b*, *c* and [1 1 1] axes to verify the lattice dimensions and Laue group. Unit cell dimensions were determined from 25 centred reflections in the range $21.9 \leqslant 2\theta \leqslant 33.7°$. For intensity data collection, pure ω-scans were used with $\Delta\omega = 1.15 + 0.35 \tan \theta$. Three monitor reflections were measured after every 30 min of beam time, and the orientation of the crystal was checked after every 500 intensity measurements. Absorption corrections[43] were based on azimuthal scans of 15 reflections. The reflections used for this purpose had their bisecting position χ values distributed in the range of 5–90°.

Solution and refinement. The structure was solved and developed by Patterson and Fourier methods using SHELX-86.[44] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms bonded to the aromatic carbon atoms, and of the CH_2 and CH groups were constrained to idealized geometries, and the isotropic displacement parameter of each of these hydrogen atoms was set to a value of 1.2 times the equivalent isotropic displacement parameter of its parent carbon atom. The hydrogen atoms of the CH_3 groups were also constrained to idealized geometries and the isotropic displacement parameter of each of these hydrogen atoms was set to a value of 1.5 times the equivalent isotropic displacement parameter of its parent carbon atom. The data-to-parameter ratio in the final refinement was 13.8. The structure was refined on $F_0{}^2$, and all reflections were used in the least squares calculation.[45] The residuals and other pertinent parameters are summarized in Table 1. Crystallographic calculations were done on a Local Area VAXCluster (VAX/VMS V5.5-2). Data reduction was done by the program XCAD4B.[46]

CCDC reference number 440/082. See http://www.rsc.org/suppdata/nj/1999/227/ for crystallographic files in .cif format.

Acknowledgements

We would like to thank the Dirección General de Enseñanza Superior (Spain) for financial support (Projects PB95-0792 and PB95-0003-C02-01) and Prof. J. Forniés for his invaluable logistical support.

Notes and references

1 L. R. Falvello, S. Fernández, R. Navarro and E. P. Urriolabeitia, *Inorg. Chem.*, 1996, **35**, 3064.

2 L. R. Falvello, S. Fernández, R. Navarro and E. P. Urriolabeitia, *Inorg. Chem.*, 1997, **36**, 1136 and references therein.

3 L. R. Falvello, S. Fernández, R. Navarro, I. Pascual and E. P. Urriolabeitia, *J. Chem. Soc., Dalton Trans.*, 1997, 763 and references therein.

4 L. R. Falvello, S. Fernández, R. Navarro and E. P. Urriolabeitia, *New J. Chem.*, 1997, **21**, 909.

5 S. Fernández, M. M. García, R. Navarro and E. P. Urriolabeitia, *J. Organomet. Chem.*, 1998, **561**, 67.

6 I. C. Barco, L. R. Falvello, S. Fernández, R. Navarro and E. P. Urriolabeitia, *J. Chem. Soc., Dalton Trans.*, 1998, 1699.

7 R. G. Pearson, *Inorg. Chem.*, 1973, **12**, 712.

8 J. A. Davies and F. R. Hartley, *Chem. Rev.*, 1981, **81**, 79.

9 (*a*) A. W. Johnson, W. C. Kaska, K. A. O. Starzewski and D. A. Dixon, *Ylides and Imines of Phosphorus*, Wiley, New York, 1993, ch. 13 and references given therein. (*b*) J. Vicente, M. T. Chicote, J. Fernández-Baeza, F. J. Lahoz and J. A. López, *Inorg. Chem.*, 1991, **30**, 3617 and references given therein.

10 K. A. O. Starzewski and H. T. Dieck, *Inorg. Chem.*, 1979, **18**, 3307.

11 K. V. Katti and R. G. Cavell, *Inorg. Chem.*. 1989, **28**, 413.

12 K. V. Katti and R. G. Cavell, *Organometallics*, 1989, **8**, 2147.

13 K. V. Katti, R. J. Batchelor, F. W. B. Einstein and R. G. Cavell, *Inorg. Chem.*, 1990, **29**, 808.

14 P. Imhoff, R. van Asselt, C. J. Elsevier, M. C. Zoutberg and C. H. Stam, *Inorg. Chim. Acta*, 1991, **184**, 73.

15 K. V. Katti and R. G. Cavell, *Organometallics*, 1991, **10**, 539.

16 K. V. Katti, B. D. Santarsiero, A. A. Pinkerton and R. G. Cavell, *Inorg. Chem.*, 1993, **32**, 5919.

17 M. S. Balakrishna, B. D. Santarsiero and R. C. Cavell, *Inorg. Chem.*, 1994, **33**, 3079.

18 M. W. Avis, K. Vrieze, H. Kooijman, N. Veldman, A. Spek and C. J. Elsevier, *Inorg. Chem.*, 1995, **34**, 4092.

19 A. Mahieu, A. Igau, J. Jaud and J. P. Majoral, *Organometallics*, 1995, **14**, 944.

20 W. K. Holley, G. E. Ryschkewitsch, A. E. Koziol and G. J. Palenik, *Inorg. Chim. Acta*, 1995, **239**, 171.

21 J. Li, R. McDonald and R. G. Cavell, *Organometallics*, 1996, **15**, 1033.

22 (*a*) M. W. Avis, K. Vrieze, J. M. Ernsting, C. J. Elsevier, N. Veldman, A. Spek, K. V. Katti and C. L. Barnes, *Organometallics*, 1996, **15**, 2376. (*b*) J. Vicente, M. T. Chicote, M. A. Beswick and M. C. Ramírez de Arellano, *Inorg. Chem.*, 1996, **35**, 6592. For other new iminophosphorane complexes, see: (*c*) P. Molina, A. Arques, A. García and M. C. Ramírez de Arellano, *Tetrahedron Lett.*, 1997, **38**, 7613. (*d*) J. Vicente, A. Arcas, D. Bautista and M. C. Ramírez de Arellano, *Organometallics*, 1998, **17**, 1564.

23 R.-Z. Ku, D.-Y. Chen, G.-H. Lee, S.-M. Peng and S.-T. Liu, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2631.

24 S. Bittner, Y. Assaf, P. Krief, M. Pomerantz, B. T. Ziemnicka and C. G. Smith, *J. Org. Chem.*, 1985, **50**, 1712.

25 G. K. Anderson and M. Lin, *Inorg. Synth.*, 1990, **28**, 60.

26 The complex $[Pd(C^\wedge P)(NCMe)_2]ClO_4$ was prepared in a way similar to that described in ref. 27 for $[Pt(C^\wedge P)(NCMe)_2]ClO_4$, with the exception that the reaction was performed starting from $[Pd(\mu\text{-}Cl)(C^\wedge P)]_2$ (see ref. 30) under nitrogen atmosphere in dry NCMe: P. Villarroya, Ph.D. Thesis, University of Zaragoza, 1998.

27 J. Forniés, A. Martín, R. Navarro, V. Sicilia and P. Villarroya, *Organometallics*, 1996, **15**, 1826.

28 J. Forniés, R. Navarro and V. Sicilia, *Polyhedron*, 1988, **7**, 2659.

29 A. J. Deeming, I. P. Rothwell, M. B. Hursthouse and L. New, *J. Chem. Soc., Dalton Trans.*, 1978, 1490.

30 (*a*) W. A. Herrmann, C. Brossmer, K. Öfele, C.-P. Reisinger, T. Priermeier, M. Beller and H. Fischer, *Angew. Chem., Int. Ed. Engl.* 1995, **34**, 1844. (*b*) L. R. Falvello, J. Forniés, A. Martín, R. Navarro, V. Sicilia and P. Villarroya, *Inorg. Chem.*, 1997, **36**, 6166.

31 A. C. Cope and E. C. Friedrich, *J. Am. Chem. Soc.* 1968, **90**, 909.

32 H. Alper, *J. Organomet. Chem.* 1977, **127**, 385.

33 (*a*) E. L. Weinberg, B. K. Hunter and M. C. Baird, *J. Organomet. Chem.*, 1982, 240, **95**. (*b*) B. Crociani, T. Boschi, R. Pietropaolo and U. Belluco, *J. Chem. Soc.* (*A*), 1970, 531.

34 I. Bar and J. Bernstein, *Acta Crystallogr., Sect. B*, 1980, **36**, 1962.

35 F. López-Ortiz, E. Peláez-Arango, F. Palacios, J. Barluenga, S. García-Granda, B. Tejerina and A. García-Fernández, *J. Org. Chem.*, 1994, **59**, 1984.

36 J. Buckle, P. G. Harrison, T. J. King and J. A. Richards, *J. Chem. Soc., Chem. Comm.*, 1972, 1104.

37 J. A. Albanese, D. A. Staley, A. L. Rheingold and J. L. Burmeister, *Inorg. Chem.*, 1990, **29**, 2209.

38 H. R. Allock, A. A. Dembek, M. N. Mang, G. H. Riding, M. Parzev and K. B. Visscher, *Inorg. Chem.*, 1992, **31**, 2734.

39 See, for instance: (*a*) E. T. Weleski, J. L. Silver, M. D. Jansson and J. L. Burmeister, *J. Organomet. Chem.*, 1975, **102**, 365. (*b*) J. Vicente, M. T. Chicote and J. Fernández-Baeza, *J. Organomet. Chem.*, 1989, **364**, 407 and references cited in ref. 3.

40 J. Vicente, A. Arcas, D. Bautista and P. G. Jones, *Organometallics*, 1997, **16**, 2127 and references therein.

41 We thank one of the referees for stimulating suggestions and helpful discussions.

42 W. C. Wolsey, *J. Chem. Educ.*, 1973, **50**, A335.

43 Absorption corrections and molecular graphics were done using the commercial package SHELXTL-PLUS, Release 4.21/V: © 1990, Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin.

44 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.

45 G. M. Sheldrick, *SHELXL-97: FORTRAN Program for the Refinement of Crystal Structures from Diffraction Data*, Göttingen University, Göttingen, Germany, 1997.

46 K. Harms, private communication.

Paper 8/07066K