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Synthesis and characterization of complexes of Pd^{II} and Pt^{II} containing the iminophosphorane ligand $Ph_3P{=}NC{\equiv}N$

Larry R. Falvello, Susana Fernández, María M. García, 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; esteban@posta.unizar.es

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The chemistry of the iminophosphorane $Ph_3P{=}NC{\equiv}N$ towards different palladium(II) and platinum(II) subtrates has been investigated. This ligand shows a high selectivity for co-ordination through the terminal N atom (that of the cyanide group), while the phosphoiminic N atom shows very poor nucleophilic ability. The reaction of $[PdCl_2(NCPh)_2]$ with $Ph_3P{=}NCN$ (1 : 2 molar ratio) gives *trans*-$[PdCl_2(NCNPPh_3)_2]$ **1**. The crystal structure of **1** has been determined and shows the iminophosphorane co-ordinated selectively through the nitrilic N atom. The reaction of the cationic derivatives $[M(C\text{–}P)(NCMe)_2][ClO_4]$ [M = Pd or Pt; C–P = *o*-$CH_2C_6H_4P(C_6H_4Me\text{-}o)_2$] with $Ph_3P{=}NCN$ (1 : 2 molar ratio) resulted in the formation of $[M(C\text{–}P)(NCN{=}PPh_3)_2][ClO_4]$ (M = Pd **2** or Pt **3**), for which the same terminal N-co-ordination has been observed. The reaction of $[Pd(dmba)(NCMe)_2][ClO_4]$ (dmba = $C_6H_4CH_2NMe_2$-2) with $Ph_3P{=}NCN$ (1 : 1 molar ratio) gave the dinuclear derivative $[\{Pd(\mu\text{-}NCN{=}PPh_3)(dmba)\}_2][ClO_4]_2$ **4** in which the iminophosphorane acts as an N,N-bridging ligand, while reaction in 1 : 2 molar ratio gave $[Pd(dmba)(NCN{=}PPh_3)_2][ClO_4]$ **5** which possess N-terminal co-ordination. The reaction of this iminophosphorane with monosolvate complexes $[Pd(dmba)(PPh_3)(THF)][ClO_4]$ or $[Pt(C\text{–}P)(PPh_3)(NCMe)][ClO_4]$ (1 : 1 molar ratio) resulted in the formation of $[Pd(dmba)(PPh_3)(NCN{=}PPh_3)][ClO_4]$ **6** or $[Pt(C\text{–}P)(PPh_3)(NCN{=}PPh_3)][ClO_4]$ **7**, and the reaction with the halide bridging derivatives $[\{Pd(\mu\text{-}Cl)(dmba)\}_2]$ or $[\{Pt(\mu\text{-}Cl)(C\text{–}P)\}_2]$ (2 : 1 molar ratio) produced cleavage of the bridging system and formation of $[PdCl(dmba)(NCN{=}PPh_3)]$ **8** and $[PtCl(C\text{–}P)(NCN{=}PPh_3)]$ **9**. The same N-terminal co-ordination mode is observed in complexes **6**–**9**.

Introduction

We have been studying the co-ordination chemistry of α-stabilized phosphorus ylides $Ph_3P{=}C(H)R$ (R = COMe, COPh, COOMe, $CONMe_2$ or CN) and their behaviour as ambidentate ligands.[1–6] The reactivity of these ylides towards several ortho-metallated complexes of Pd^{II} and Pt^{II} has been examined and their ambidentate character observed. Furthermore, we have found that, in many cases, it is possible to predict both the co-ordination site of the ylide and the donor atom linked to the metal (O- *versus* C-bonding, N- *versus* C-bonding) using as simple a concept as the antisymbiotic effect.[7,8]

The iminophosphoranes, compounds of general structure $R_3P{=}NR'$, are an interesting class of compounds closely related to the phosphorus ylides and showing numerous applications to organic synthesis (for instance, the formation of C=N bonds through the Aza–Wittig reaction).[9a] Moreover, they can behave as ligands towards transition metals through, at least, the lone pair on the N atom. In spite of the similarities, their use as ligands is less developed than that of the ylides,[9] although in recent years several groups have focused their interest on the co-ordinative properties and reactivity of iminophosphoranes.[9,10]

Prompted by the results obtained with the α-stabilized ylides, we have decided to explore the co-ordination chemistry of the α-stabilized iminophosphorane $Ph_3P{=}NC{\equiv}N$,[11] a compound for which there is no precedent in co-ordination chemistry. Its reactivity has been explored towards several palladium(II) and platinum(II) substrates (see Scheme 1). We have chosen complexes with two labile ligands in different arrangements and with different *trans* atoms, such as $[MCl_2(NCPh)_2]$ (M = Pd or Pt),[12] $[M(C\text{–}P)(NCMe)_2][ClO_4]$ (M = Pd† or Pt[13]) and $[Pd(dmba)(NCMe)_2][ClO_4]$[16] [C–P = *o*-$CH_2C_6H_4P(C_6H_4\text{-}Me\text{-}o)_2$; dmba = $C_6H_4CH_2NMe_2$-2], complexes with one labile ligand such as $[Pt(C\text{–}P)(PPh_3)(NCMe)][ClO_4]$[5] and $[Pd(dmba)(PPh_3)(THF)][ClO_4]$[17] and dinuclear complexes such as $[\{M(\mu\text{-}Cl)(C\text{–}P)\}_2]$ (M = Pd[14] or Pt[13]) and $[\{Pd(\mu\text{-}Cl)(dmba)\}_2]$[18] in order to explore the co-ordination properties (nucleophilic ability of the iminic N atom and steric requirements) of this ligand in different environments. In this paper we report the results obtained from this chemistry.

Results and discussion

The reaction of $[PdCl_2(NCPh)_2]$ with $Ph_3P{=}NCN$ (1 : 2 molar ratio) in acetone at room temperature results in the precipitation of an orange solid of stoichiometry $[PdCl_2(NCNPPh_3)_2]$ **1** as deduced from its elemental analysis. The reaction of $[PtCl_2(NCPh)_2]$ with $Ph_3P{=}NCN$ (1 : 2 molar ratio) performed under the same conditions (acetone; room temperature, r.t.) gives a mixture of the starting products. If the reaction is performed in refluxing toluene the spectroscopic data of the resulting solid show the presence of both starting materials together with at least three products which appear to contain co-ordinated iminophosphorane. However, the recrystallization of this mixture failed in all attempted cases and we were not able to isolate a $Pt\text{–}NCN{=}PPh_3$ derivative free of the starting

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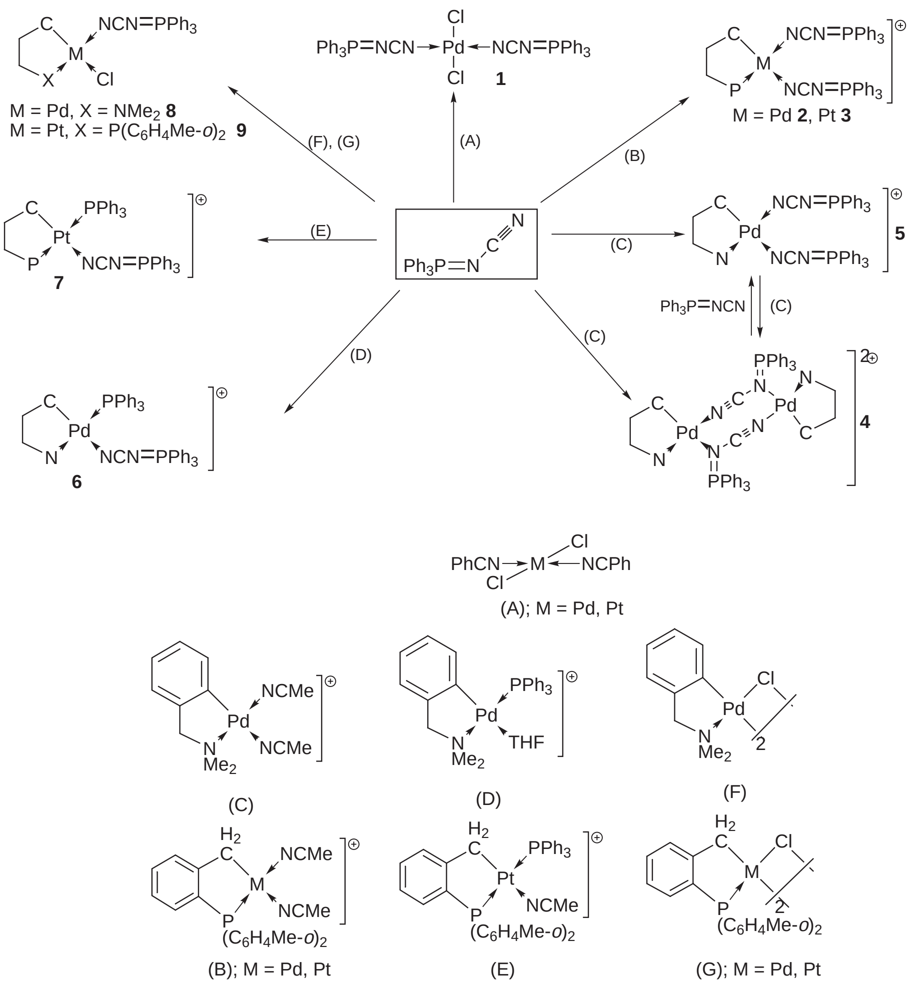
† The complex $[Pd(C\text{–}P)(NCMe)_2][ClO_4]$ was prepared in a way similar to that described in ref. 13 for $[Pt(C\text{–}P)(NCMe)_2][ClO_4]$, with the exception that the reaction was performed starting from $[\{Pd(\mu\text{-}Cl)(C\text{–}P)\}_2]$ (see ref. 14) under a nitrogen atmosphere in dry NCMe (ref. 15).



Scheme 1

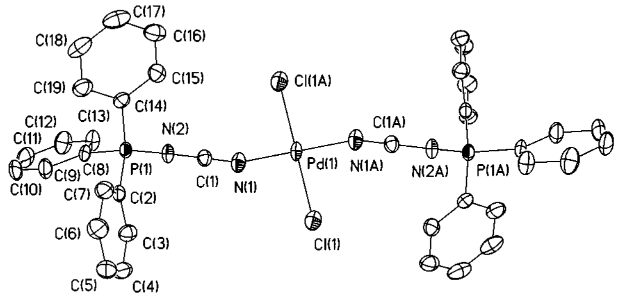


Fig. 1 Thermal ellipsoid plot of *trans*-[PdCl$_2$(NCN=PPh$_3$)$_2$] **1**. Hydrogen atoms have been omitted for clarity. Atoms are drawn at the 50% probability level; Pd(1) lies on a crystallographic inversion center.

Table 1 Selected bond lengths (Å) and angles (°) for complex **1**

Pd(1)–N(1)	1.971(3)	P(1)–C(2)	1.791(3)
Pd(1)–Cl(1)	2.2969(9)	P(1)–C(14)	1.796(3)
P(1)–N(2)	1.609(3)	N(1)–C(1)	1.151(4)
P(1)–C(8)	1.789(3)	C(1)–N(2)	1.292(4)
N(1A)–Pd(1)–N(1)	180.0	N(1A)–Pd(1)–Cl(1)	88.84(9)
N(1)–Pd(1)–Cl(1)	91.16(9)	N(2)–P(1)–C(8)	105.74(14)
N(2)–P(1)–C(2)	111.91(14)	C(8)–P(1)–C(2)	107.65(14)
N(2)–P(1)–C(14)	112.23(14)	C(8)–P(1)–C(14)	108.84(14)
C(2)–P(1)–C(14)	110.22(14)	C(1)–N(1)–Pd(1)	161.9(3)
N(1)–C(1)–N(2)	175.2(3)	C(1)–N(2)–P(1)	122.3(2)

Symmetry transformation used to generate equivalent atoms: A $-x$, $-y$, $-z$.

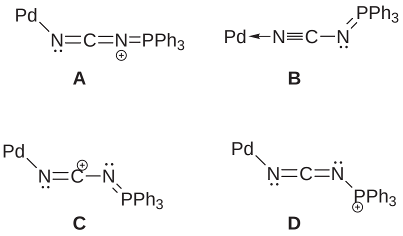
materials, probably due to the similar solubility of the species involved.

The molecular structure of complex **1** has been determined by X-ray diffraction methods. A drawing of the molecule is shown in Fig. 1 and selected bond distances and angles are presented in Table 1. The palladium atom lies on a crystallographic inversion center and has a very slightly distorted square-planar environment. The Pd–Cl bond distance [2.2969(9) Å] falls within the usual range of distances found for this kind of bond,[19] while the Pd–N(1) bond distance [1.971(3) Å] is shorter than other Pd–N (nitrile) bond lengths found in the literature (2.065(14) Å for [(MeNC)PdCl$_2$(μ-dpmp)PdCl$_2$]·NCMe[20] and 2.076(3) Å for [Pd(dmba){P(OMe)$_3$}{NCC(H)=PPh$_3$}][ClO$_4$][2]).

With respect to the internal bond distances and angles of the iminophosphorane ligand, the N(1)–C(1) bond distance [1.151(4) Å] is fairly typical for nitriles.[2,21] The C(1)–N(2) bond distance [1.292(4) Å] is shorter than other distances reported for this kind of bond in iminophosphoranes [ranging from 1.351(6) to 1.461(6) Å],[9,10,21,22] regardless of whether the ligand is co-ordinated or not, and is similar within experimental error to that reported for [Ph$_3$P=NC≡NC$_{10}$H$_{15}$-1][SbCl$_6$][23] [1.25(2) Å] (C$_{10}$H$_{15}$ = adamantyl). The N(2)–P(1) bond [1.609(3) Å] is shorter than that reported for the latter salt [1.64(1) Å], is similar to (within experimental error) or shorter than those found in N-co-ordinated iminophosphoranes [range 1.604(7)–1.627(4) Å], but is longer than those found in free iminophosphoranes [range 1.569(4)–1.585(4) Å].[10] This phosphorus–nitrogen bond is seen to have considerable single bond character if compared to the "true" P=N double bond in [Ph$_3$P=N=PPh$_3$]$^+$ [1.547(2) Å].[24]

Another interesting feature of the structure is the bond angle Pd(1)–N(1)–C(1) [161.9(3)°], the value of which is less than the 180° expected for sp hybridization of the nitrogen atom. The bond angle N(1)–C(1)–N(2) is 175.2(3)° and indicates an almost linear disposition of these bonds, in accord with the presence of a cyanide unit. The environment around the N(2) atom is trigonal planar [C(1)–N(2)–P(1) 122.3(2)°] and that around the phosphorus atom P(1) is tetrahedral.

All of these facts imply that there is an extensive delocalization of the charge density in the P(1)–N(2)–C(1)–N(1) system. The distances and angles taken together suggest participation of the resonance forms **B** and **D** in the bonding description with only small contributions of **A** and **C**. However, the question of why the iminophosphorane co-ordinates selectively through the nitrilic N atom instead of through the iminic N atom remains unanswered. In our experience, the co-ordinative ability of the iminic N atom is worse than those of other donor atoms present in the ligand. For instance, in $Ph_3P{=}NCOC_6H_4N$-2 both the carbonylic oxygen atom and the pyridinic N atom have the same or even a better co-ordination ability than the iminic N atom.[22] This fact would probably be due to the delocalization of the electronic density, which results in a lower charge density at the iminic N atom. It is also worth noting the different behaviour of the phosphoylide $Ph_3P{=}C(H)CN$ and the iminophosphorane $Ph_3P{=}NCN$ towards the same precursor, in this case $[PdCl_2(NCPh)_2]$. While the former ligand co-ordinates selectively through the ylidic carbon atom, giving a mixture of diastereoisomers (*RR*/*SS* and *RS*/*SR*) *trans*-$[PdCl_2\{C(H)(CN)PPh_3\}_2]$, the latter gives **1** which shows selective “end-on” N(nitrile) co-ordination.



Complex **1** was also characterized by spectroscopic methods. The IR spectrum shows a *trans* arrangement of the chloride ligands, and hence of the iminophosphorane ligands, as deduced from the observation of a sharp absorption at 348 cm^{-1}. Moreover, the IR spectrum shows a strong band at 2256 cm^{-1} attributed to the C≡N stretch. This absorption is shifted to higher energy with respect to that of free $Ph_3P{=}NCN$ (2176 cm^{-1}); this shift can be interpreted as a consequence of co-ordination of the iminophosphorane through the iminic N atom, by analogy with the results obtained with the C-co-ordinated phosphoylide $Ph_3P{=}C(H)CN$[2] and N(imine)-bonded keto-stabilized iminophosphoranes $Ph_3P{=}NC(O)R$.[22] The ^{31}P-$\{^1H\}$ NMR spectrum of **1** shows a singlet resonance at δ 27.44 which is shifted to low field by only about 2 ppm with respect to free $Ph_3P{=}NCN$ (δ 25.25). The deshielding of the phosphorus nucleus that would be expected to result from iminic N-bonding is not observed[22] thus suggesting that an “end-on” nitrile co-ordination has taken place, as is depicted in Scheme 1.

Further study of the reactivity of this iminophosphorane ligand gives additional evidence of the poor co-ordinating ability of the iminic N atom. The reaction of $[M(C–P)(NCMe)_2][ClO_4]$ (M = Pd or Pt) with 2 equivalents of $Ph_3P{=}NCN$ results in the formation of white solids of stoichiometry $[M(C–P)(NCN{=}PPh_3)_2][ClO_4]$ (M = Pd **2** or Pt **3**) as indicated by their elemental analyses and mass spectra (see Experimental section). If the reaction is carried out in 1 : 1 molar ratio complex mixtures of **2** or **3** and other unidentified products are obtained. The IR spectra of **2** and **3** show absorptions corresponding to the C≡N group at 2215 and 2228 cm^{-1}, respectively, and the ^{31}P-$\{^1H\}$ NMR spectra show resonances attributed to the phosphorus atom of the C–P ligands [δ 37.54 for **2** and 16.10 for **3** ($^1J_{PtP}$ = 4551 Hz)] together with resonances attributed to the iminophosphorane which appear as two close singlets at δ 27.76 and 29.18 for **2** and at 28.06 and 29.52 for **3**. The close similarity of these resonances to each other and to that of free $Ph_3P{=}NCN$ clearly suggests an N-terminal (nitrile) co-ordination of the ligand, as also deduced for complex **1**. Additional evidence is the absence of coupling between the P atom of the C–P ligand and the P atom of the *trans* $Ph_3P{=}NCN$ ligand. Such coupling is observable when a C-coordinated ylide is *trans* to the P atom of the C–P group[5] and also when an iminophosphorane is co-ordinated through the iminic N atom[22] *trans* to the P atom of the C–P ligand. The structure represented in Scheme 1 accounts for all of these facts.

The observed reactivity contrasts with that reported for the phosphoylide $Ph_3P{=}C(H)CN$[5] and C–P complexes. There, $[Pt(C–P)(NCMe)_2][ClO_4]$ reacts with 1 equivalent of $Ph_3P{=}C(H)CN$ to give $[Pt(C–P)\{C(H)(CN)PPh_3\}(NCMe)][ClO_4]$ which reacts with a second equivalent of the ylide to give $[Pt(C–P)\{C(H)(CN)PPh_3\}\{NCC(H){=}PPh_3\}][ClO_4]$. It is clear that for the phosphoylide there is a high tendency to co-ordinate through the ylidic carbon atom and that the N-co-ordination of the second ylide is driven by the electronic and steric requirements of the first C-co-ordinated ylide. This tendency does not carry over to the iminic N atom of the iminophosphorane and, hence, selective N(nitrile) co-ordination is observed.

The reactivity of the iminophosphorane towards $[Pd(dmba)(NCMe)_2][ClO_4]$ more nearly resembles that reported for the analogous phosphoylide. Thus, $[Pd(dmba)(NCMe)_2][ClO_4]$ reacts with $Ph_3P{=}NCN$ (1 : 1 molar ratio) giving a pale yellow solid of stoichiometry $[Pd(dmba)(NCNPPh_3)][ClO_4]$, as deduced from its elemental analysis. The mass spectrum (positive ion FAB) of this solid shows a peak at *m*/*z* 542 which corresponds to the cationic fragment $[Pd(dmba)(NCNPPh_3)]^+$. The IR spectrum shows a sharp absorption at 2249 cm^{-1}, attributed to the cyano group of the iminophosphorane ligand, and does not show the presence of co-ordinated NCMe which usually appears at higher frequencies. The ^1H NMR spectrum shows the presence of the expected resonances for the Ph, C_6H_4, CH_2N and NMe_2 groups, which integrated as 15 : 4 : 2 : 6, thus confirming the presence of only one iminophosphorane group per dmba ligand. The observation of only one set of signals indicates the presence of only one isomer. Similarly, the ^{31}P-$\{^1H\}$ NMR spectrum shows a singlet resonance at δ 29.16. Excluding the possibility of chelation of the ligand because of the constraint imposed by the nitrile group, we can propose two possible structures for this complex. One is mononuclear with a covalent perchlorate group. This proposition is immediately discarded because the absorptions corresponding to the ClO_4^- group are not split.[2] The other possibility is a dinuclear structure with the iminophosphorane acting as a bridging ligand. This second proposition is supported by two facts: the position of the ν(CN) absorption at 2249 cm^{-1} shifted to high wavenumber with respect to that of $[Pd(dmba)(NCNPPh_3)_2][ClO_4]$ **5** (2211 cm^{-1}, see below) in which both iminophosphorane ligands are N(nitrile)-co-ordinated, and the position of the phosphorus resonance at δ 29.16, shifted downfield with respect to those of **5** (δ 26.60 and 26.41, see below). Both the increase in the ν(CN) wavenumber and the deshielding of the phosphorus resonance strongly suggest that both N atoms of $Ph_3P{=}NCN$ are bonded to the palladium center. A more accurate definition of the nature of the product is given by the measurement of the molar conductance in acetone solution ($c = 5 \times 10^{-4}$ M), which is $\Lambda_M = 268\ \Omega^{-1}\ cm^2\ mol^{-1}$ corresponding to a 2 : 1 electrolyte.[25] Thus, the product can be formulated as the dinuclear complex $[\{Pd(\mu\text{-}NCN{=}PPh_3)(dmba)\}_2][ClO_4]_2$ **4**. The observation of only one set of resonances in the NMR spectra shows that **4** must be a product of high symmetry and that of the two highest symmetry isomers only one is present. The ^1H–^1H NOESY spectrum of complex **4** shows a strong NOE interaction between the *ortho* protons of phenyl groups and the methyl protons of the NMe_2 group, showing their mutually *cis* disposition. The dimeric structure depicted in Scheme 1 accounts for these observations.

When the reaction between $[Pd(dmba)(NCMe)_2][ClO_4]$ and $Ph_3P{=}NCN$ is performed in 1:2 molar ratio a solid of stoichiometry $[Pd(dmba)(NCNPPh_3)_2][ClO_4]$ **5** is obtained as deduced from its elemental analysis and mass spectrum. The characterization of complex **5** follows the same key features as those reported for **1**–**4**. The ν(CN) of **5** appears at 2211 cm^{-1}, shifted to high frequencies with respect to free $Ph_3P{=}NCN$, and the $^{31}P\text{-}\{^1H\}$ NMR spectrum shows two close singlet resonances (δ 26.60 and 26.41), very similar to the resonance of free $Ph_3P{=}NCN$. All of these facts mean that both iminophosphorane ligands are N(nitrile)-co-ordinated, as depicted in Scheme 1.

Complexes **4** and **5** can also be obtained by mutual interconversion (see Scheme 1). Thus, **4** reacts with an additional equivalent of $Ph_3P{=}NCN$ to give **5** while **5** reacts with 1 equivalent of the solvate $[Pd(dmba)(NCMe)_2][ClO_4]$ to give **4**.

The reactivity observed for the iminophosphorane is in this case somewhat similar to that reported for the phosphoylide towards C,N-orthometallated derivatives of Pd^{II}.[2] Thus, $Ph_3P{=}C(H)CN$ reacted with $[Pd(dmba)(NCMe)_2][ClO_4]$ (1:1 molar ratio) to give the dimer $[\{Pd[\mu\text{-}NCC(H)PPh_3](dmba)\}_2][ClO_4]_2$. To this point the behaviour of the two ligands is analogous. However, the dinuclear complex further reacts with the ylide giving $[Pd(dmba)\{C(H)(CN)PPh_3\}\{NCC(H){=}PPh_3\}][ClO_4]$ in which the two ylides are co-ordinated in different ways, one through the C atom and the other through the N atom. Its analogous derivative **5** possess the two iminophosphorane ligands co-ordinated in the same way as a result, once again, of the poor nucleophilicity of the iminic N atom.

The reaction of the monosolvate complexes $[Pd(dmba)(PPh_3)(THF)][ClO_4]$ or $[Pt(C\text{–}P)(PPh_3)(NCMe)][ClO_4]$ with $Ph_3P{=}NCN$ (1:1 molar ratio) gives the corresponding cationic derivatives $[Pd(dmba)(PPh_3)(NCN{=}PPh_3)][ClO_4]$ **6** and $[Pt(C\text{–}P)(PPh_3)(NCN{=}PPh_3)][ClO_4]$ **7**, as deduced from their elemental analyses and mass spectra. The IR spectra of **6** and **7** show a strong absorption at 2239 cm^{-1} in both cases, and their $^{31}P\text{-}\{^1H\}$ NMR spectra show the expected resonances for the presence of the PPh_3 (**6**) and C–P and PPh_3 in *trans* positions (**7**) together with the signals attributed to the iminophosphorane (δ 27.69 for **6** and 27.27 for **7**). As discussed in the preceding paragraphs, these data imply an N(nitrile) co-ordination of the $Ph_3P{=}NCN$ ligand. Similar results (N-co-ordination) have been obtained with the ylide $Ph_3P{=}C(H)CN$ and the same precursors.[2,5]

Finally, the iminophosphorane $Ph_3P{=}NCN$ is able to promote the cleavage of the halide bridging systems in the dinuclear complexes $[\{Pd(\mu\text{-}Cl)(dmba)\}_2]$ and $[\{Pt(\mu\text{-}Cl)(C\text{–}P)\}_2]$. Thus, the reaction of these compounds with $Ph_3P{=}NCN$ (1:2 molar ratio) results in the formation of solids of stoichiometry $[PdCl(dmba)(NCN{=}PPh_3)]$ **8** and $[PtCl(C\text{–}P)(NCN{=}PPh_3)]$ **9** in accord with their elemental analyses. However, the reaction of $[\{Pd(\mu\text{-}Cl)(C\text{–}P)\}_2]$ with $Ph_3P{=}NCN$ (1:2 molar ratio) under the same conditions does not promote cleavage and the starting products are recovered. The IR spectrum of **8** shows the $\nu(C{\equiv}N)$ absorption at 2243 cm^{-1} and the Pd–Cl stretch at 305 cm^{-1}, while that of **9** shows the $\nu(C{\equiv}N)$ absorption at 2233 cm^{-1} and the Pt–Cl stretch at 292 cm^{-1}. Both facts, the increase in energies of the $\nu(C{\equiv}N)$ absorption and the shift to higher frequency of the M–Cl stretch, point to the presence of a terminal chloride ligand and an N-bonded iminophosphorane ligand as a result of the cleavage of the halide bridging system. That is, these products are not simply mixtures of the starting materials. The NMR spectra of **8** and **9** (see Experimental section) show the expected resonances for all groups present in these molecules and also show only one set of resonances; that is, only one isomer (of the two possible) is present in solution. The sterochemistry of this isomer has been assigned as Cl-*trans*-to-C, as depicted in Scheme 1, on the basis of the spectroscopic data and by analogy to the splitting of the $M(\mu\text{-}Cl)_2M$ (M = Pd or Pt) system by N-donor ligands.[5,17]

Conclusion

The iminophosphorane $Ph_3P{=}NCN$ behaves as an N(nitrile)-donor ligand towards complexes of Pd^{II} and Pt^{II}, regardless of the electronic and steric requirements of the other ligands around the metal centre. Only in one case we have been able to co-ordinate this ligand through both the iminic N atom and the nitrilic N atom, in a bridging mode. No examples have been found with selective iminic N-co-ordination. This behaviour could be due to an extensive delocalization of the electron density along the P–NC–N system, which reduces the charge density, and thus the coordinating ability, of the iminic N atom.

Experimental

CAUTION: perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of these materials should be prepared and handled with great caution. See ref. 26.

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 cm^{-1}) were recorded on a Perkin-Elmer 883 spectrophotometer in Nujol mulls between polyethylene sheets, ^1H (300.13 MHz) and $^{31}P\text{-}\{^1H\}$ (121.49 MHz) NMR spectra from $CDCl_3$ or CD_2Cl_2 solutions at room temperature (unless otherwise stated) on a Bruker ARX-300 spectrometer; ^1H spectra were referenced using the solvent signal as an internal standard and $^{31}P\text{-}\{^1H\}$ spectra were externally referenced to H_3PO_4 (85%). The two dimensional $^1H\text{–}^1H$ NOESY experiment for complex **4** was performed at a measuring frequency of 300.13 MHz. The data were acquired into a 512 × 1024 matrix, and then transformed into 1024 × 1024 points using a sine window in each dimension. The mixing time was 400 ms. Mass spectra (positive ion FAB) were recorded on a V.G. Autospec. spectrometer from CH_2Cl_2 solutions. Electrical conductivity measurements were performed in acetone solutions with concentrations of about 5×10^{-4} M using a Philips PW 9509 conductivity cell. The ligand $Ph_3P{=}NC{\equiv}N$[11] and the complexes $[MCl_2(NCPh)_2]$ (M = Pd or Pt),[12] $[M(C\text{–}P)(NCMe)_2][A]$ (M = Pd[15] or Pt[13]), $[Pd(dmba)(NCMe)_2][A]$,[16] $[Pd(dmba)(PPh_3)(THF)][A]$,[17] $[Pt(C\text{–}P)(PPh_3)(NCMe)][A]$[5] ($A = ClO_4^-$), $[\{M(\mu\text{-}Cl)(C\text{–}P)\}_2]$ (M = Pd,[14] or Pt[13]) and $[\{Pd(\mu\text{-}Cl)(dmba)\}_2]$[18] were prepared according to published methods.

Preparations

***trans*-$[PdCl_2(N{\equiv}CN{=}PPh_3)_2]$ 1.** To a solution of $[PdCl_2(NCPh)_2]$ (0.100 g, 0.260 mmol) in 20 cm^3 of acetone the iminophosphorane $Ph_3P{=}NC{\equiv}N$ (0.157 g, 0.521 mmol) was added. After a few minutes an orange solid precipitated which was collected, washed with additional acetone (10 cm^3), Et_2O (25 cm^3), air-dried and identified as complex **1**, 0.117 g (58% yield). The acetone solution was evaporated to dryness and the residue treated with Et_2O (25 cm^3), giving a second fraction of **1**, 0.035 g (17% yield, net yield 75%) (Found: C, 57.98; H, 3.86; N, 7.13. Calc. for $C_{38}H_{30}Cl_2N_4P_2Pd$: C, 58.37; H, 3.87; N, 7.16%). IR ($\tilde{\nu}/cm^{-1}$): 2256 (ν_{NC}), 348 ($\nu_{Pd\text{–}Cl}$). ^1H NMR ($CDCl_3$): δ 7.63–7.48 (m, Ph). $^{31}P\text{-}\{^1H\}$ NMR ($CDCl_3$): δ 27.44 (s, $NPPh_3$).

$[Pd(C\text{–}P)(N{\equiv}CN{=}PPh_3)_2][ClO_4]$ 2. To a solution of $[Pd(C\text{–}P)(NCMe)_2][ClO_4]$ (0.100 g, 0.169 mmol) in 20 cm^3 of CH_2Cl_2 the iminophosphorane $Ph_3P{=}NC{\equiv}N$ (0.102 g, 0.338 mmol) was added, and the resulting solution stirred at room temperature for 30 min. The solvent was then evaporated to dryness and the residue washed with Et_2O (25 cm^3), giving complex **2** as a white solid which was collected and air-dried, 0.104 g (55% yield) (Found: C, 63.79; H, 4.18; N, 5.00. Calc. for $C_{59}H_{50}ClN_4O_4P_3Pd$: C, 63.62; H, 4.52; N, 5.03%). IR ($\tilde{\nu}$/cm^{-1}): 2215 (ν_{NC}). Mass spectrum (FAB$^+$) [*m*/*z*, (%)]: 1013 (15, M^+) and 711 (55% $[M - NCNPPh_3]^+$). ^1H NMR ($CDCl_3$, 213 K): δ 7.69–6.64 (m, 42H, Ph + *o*-MeC_6H_4), 2.95 (s, broad, 2H, CH_2Pd), 2.44 and 2.16 (2s, 6H, 2*o*-MeC_6H_4). ^{31}P-{^1H} NMR ($CDCl_3$, 213 K): δ 37.54 (s, C–P), 29.18 (s, $NPPh_3$) and 27.76 (s, $NPPh_3$).

[Pt(C–P)(N≡CN=PPh$_3$)$_2$][ClO$_4$] 3. Complex **3** was synthesized in the same way as **2**: [Pt(C–P)(NCMe)$_2$][ClO$_4$] (0.100 g, 0.147 mmol) was treated with $Ph_3P{=}NC{\equiv}N$ (0.088 g, 0.29 mmol) in CH_2Cl_2 to give **3** as a white solid, 0.117 g (66% yield) (Found: C, 58.63; H, 3.85; N, 4.63. Calc. for $C_{59}H_{50}ClN_4O_4P_3Pt$: C, 58.93; H, 4.19; N, 4.66%). IR ($\tilde{\nu}$/cm^{-1}): 2228 (ν_{NC}). Mass spectrum (FAB$^+$) [*m*/*z*, (%)]: 1102 (35%, M^+) and 800 (100, $[M - NCNPPh_3]^+$). ^1H NMR ($CDCl_3$, 213 K): δ 7.72–6.61 (m, 42H, Ph + *o*-MeC_6H_4), 2.99, 2.77 (AB spin system, 2H, CH_2Pt, $^2J_{HH} = 16.4$ Hz), 2.45 and 2.10 (2s, 6H, 2*o*-MeC_6H_4). ^{31}P-{^1H} NMR ($CDCl_3$, 213 K): δ 29.52 (s, $NPPh_3$), 28.06 (s, $NPPh_3$) and 16.10 (s, C–P, $^1J_{Pt-P} = 4551$ Hz).

[{Pd(dmba)(μ-N≡CN=PPh$_3$)}$_2$][ClO$_4$]$_2$ 4. Complex **4** was synthesized in the same way as **2**: [Pd(dmba)(NCMe)$_2$][ClO$_4$] (0.084 g, 0.20 mmol) was treated with $Ph_3P{=}NC{\equiv}N$ (0.060 g, 0.20 mmol) in CH_2Cl_2 to give **4** as a pale yellow solid, 0.104 g (82% yield) (Found: C, 51.85; H, 4.17; N, 6.43. Calc. for $C_{28}H_{27}ClN_3O_4PPd$: C, 52.35; H, 4.23; N, 6.54%). IR ($\tilde{\nu}$/cm^{-1}): 2249 (ν_{NC}). Mass spectrum (FAB$^+$) [*m*/*z*, (%)]: 542 [100, $(M/2)^+$]. $\Lambda_M/\Omega^{-1}\ cm^2\ mol^{-1} = 268$ (5×10^{-4} M in acetone solution). ^1H NMR ($CDCl_3$, 223 K): δ 7.71–7.61 (m, 15 H, Ph), 6.94 (m, 1H, C_6H_4), 6.85 (m, 1H, C_6H_4), 6.72 (m, 2H, C_6H_4), 3.81 (s, 2H, CH_2) and 2.72 (s, 6H, NMe_2). ^{31}P-{^1H} NMR ($CDCl_3$): δ 29.16 (s, $NPPh_3$).

[Pd(dmba)(N≡CN=PPh$_3$)$_2$][ClO$_4$] 5. Complex **5** was synthesized in the same way as **2**: [Pd(dmba)(NCMe)$_2$][ClO$_4$] (0.200 g, 0.474 mmol) was treated with $Ph_3P{=}NC{\equiv}N$ (0.286 g, 0.948 mmol) in CH_2Cl_2 to give **5** as a white solid, 0.307 g (69% yield) (Found: C, 58.90; H, 4.18; N, 7.08. Calc. for $C_{47}H_{42}ClN_5O_4P_2Pd$: C, 59.76; H, 4.48; N, 7.41%). IR ($\tilde{\nu}$/cm^{-1}): 2211 (ν_{NC}). Mass spectrum (FAB$^+$) [*m*/*z*, (%)]: 844 (60, M^+). ^1H NMR ($CDCl_3$): δ 7.69–7.55 (m, 30H, Ph), 6.88–6.80 (m, 3H, C_6H_4), 6.56 (m, 1H, C_6H_4), 3.79 (s, 2H, CH_2) and 2.52 (s, 6H, NMe_2). ^{31}P-{^1H} NMR ($CDCl_3$): δ 26.60 and 26.41 (2s, $NPPh_3$).

[Pd(dmba)(PPh$_3$)(N≡CN=PPh$_3$)][ClO$_4$] 6. To a solution of [Pd(dmba)Cl(PPh$_3$)] (0.100 g, 0.186 mmol) in THF (20 cm^3), $AgClO_4$ (0.038 g, 0.19 mmol) was added. The resulting suspension was stirred in the dark at room temperature for 20 min and then filtered. To the freshly obtained solution of [Pd(dmba)(THF)(PPh$_3$)][ClO$_4$] (0.186 mmol) the iminophosphorane $Ph_3P{=}NC{\equiv}N$ (0.056 g, 0.19 mmol) was added and the resulting solution stirred at room temperature for 15 min. The solvent was evaporated to dryness and the oily residue treated with Et_2O (25 cm^3), giving complex **6** as a white solid, 0.143 g (85% yield) (Found: C, 60.77; H, 4.29; N, 4.65. Calc. for $C_{46}H_{42}ClN_3O_4P_2Pd$: C, 61.07; H, 4.68; N, 4.64%). IR ($\tilde{\nu}$/cm^{-1}): 2239 (ν_{NC}). Mass spectrum (FAB$^+$) [*m*/*z* (%)]: 804 (40, M^+), 542 (45, $[M - PPh_3]^+$) and 502 (100, $[M - NCNPPh_3]^+$). ^1H NMR ($CDCl_3$): δ 7.74–7.29 (m, 30 H, Ph), 6.96 (d, 1H, C_6H_4, $^3J_{HH} = 6.5$), 6.80 (t, 1H, C_6H_4, $^3J_{HH} = 7.2$), 6.34 (t, 1H, C_6H_4, $^3J_{HH} = 7.2$), 6.19 (t, 1H, C_6H_4, $^3J_{HH} \approx {}^4J_{PH} = 6.8$), 4.00 (d, 2H, CH_2, $^4J_{PH} = 1.9$) and 2.50 (d, 6H, NMe_2, $^4J_{PH} = 2.6$ Hz). ^{31}P-{^1H} NMR ($CDCl_3$): δ 42.11 (s, Pd–PPh_3) and 27.69 (s, $NPPh_3$).

[Pt(C–P)(PPh$_3$)(N≡CN=PPh$_3$)][ClO$_4$] 7. Complex **7** was synthesized in the same way as **2**: [Pt(C–P)(PPh$_3$)(NCMe)][ClO$_4$] (0.100 g, 0.111 mmol) was treated with $Ph_3P{=}NC{\equiv}N$ (0.034 g, 0.11 mmol) in CH_2Cl_2 to give **7** as a white solid, 0.089 g (69% yield) (Found: C, 59.56; H, 4.23; N, 2.34. Calc. for $C_{58}H_{50}ClN_2O_4P_3Pt$: C, 59.92; H, 4.33; N, 2.41%). IR ($\tilde{\nu}$/cm^{-1}): 2353, 2340 (ν_{NCMe}), 2239 (ν_{NC}). Mass spectrum (FAB$^+$) [*m*/*z* (%)]: 1062 (100, M^+), 800 (25, $[M - PPh_3]^+$), 760 (65, $[M - NCNPPh_3]^+$). ^1H NMR ($CDCl_3$, 213 K): δ 7.71–6.76 (m, 42 H, Ph + *o*-MeC_6H_4), 3.14, 2.21 (AX spin system, 2H, CH_2Pt, $^2J_{HH} = 15.9$ Hz), 2.38, 2.26 (2s, 6H, 2*o*-MeC_6H_4). ^{31}P-{^1H} NMR ($CDCl_3$, 213 K): δ 31.55, 27.22 (AB spin system, C–P + PPh_3, $^1J_{PtP} = 3005$, $^1J_{PtP'} = 2968$, $^2J_{PP'} = 408$ Hz) and 27.27 (s, $NPPh_3$).

[PdCl(dmba)(N≡CN=PPh$_3$)] 8. To a solution of [{Pd(μ-Cl)(dmba)}$_2$] (0.100 g, 0.181 mmol) in CH_2Cl_2 (20 cm^3) the iminophosphorane $Ph_3P{=}NC{\equiv}N$ (0.109 g, 0.362 mmol) was added, and the resulting solution stirred at room temperature for 15 min. The solvent was evaporated to dryness and the oily residue treated with Et_2O (25 cm^3), giving complex **8** as a yellow solid, 0.170 g (81% yield) (Found: C, 57.88; H, 4.49; N, 7.19. Calc. for $C_{28}H_{27}ClN_3PPd$: C, 58.15; H, 4.70; N, 7.26%). IR ($\tilde{\nu}$/cm^{-1}): 2243 (ν_{NC}) and 305 (ν_{PdCl}). ^1H NMR ($CDCl_3$): δ 7.70–7.52 (m, 15 H, Ph), 6.94–6.84 (m, 3H, C_6H_4), 6.69 (m, 1H, C_6H_4), 3.84 (d, 2H, CH_2) and 2.84 (s, 6H, NMe_2). ^{31}P-{^1H} NMR ($CDCl_3$): δ 26.78 (s, $NPPh_3$).

[PtCl(C–P)(N≡CN=PPh$_3$)] 9. To a suspension of [{Pt(μ-Cl)(C–P)}$_2$] (0.100 g, 0.094 mmol) in 20 cm^3 of CH_2Cl_2 the iminophosphorane $Ph_3P{=}NC{\equiv}N$ (0.057 g, 0.19 mmol) was added. The original suspension gradually dissolved and after 30 min stirring at room temperature a colorless solution was obtained. The solvent was then evaporated to dryness and the residue washed with Et_2O (25 cm^3), giving complex **9** as a white solid which was collected and air dried, 0.124 g (79% yield) (Found: C, 57.39; H, 4.02; N, 3.28. Calc. for $C_{40}H_{35}ClN_2P_2Pt$: C, 57.45; H, 4.22; N, 3.35%). IR ($\tilde{\nu}$/cm^{-1}): 2233 (ν_{NC}) and 292 (ν_{PtCl}). ^1H NMR ($CDCl_3$, 213 K): δ 7.65–6.66 (m, 27H, Ph + *o*-MeC_6H_4), 3.42, 3.33 (AB spin system, 2H, CH_2Pt, $^2J_{HH} = 16.7$ Hz), 2.59, 2.31 (2s, 6H, 2*o*-MeC_6H_4). ^{31}P-{^1H} NMR ($CDCl_3$, 213 K): δ 27.07 (s, $NPPh_3$) and 19.00 (s, C–P, $^1J_{PtP} = 4743$ Hz).

Crystallography

Data collection. Crystals of complex **1** of adequate quality for X-ray purposes were grown from slow diffusion of *n*-hexane into a CH_2Cl_2 solution of **1** kept at −30 °C. An orange crystal was mounted on a quartz fiber and covered with epoxy. Normal procedures were used on a Enraf-Nonius CAD4 diffractometer 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* and *c* axes to verify the Laue symmetry and lattice dimensions. Accurate unit cell dimensions were determined from 25 centered reflections in the range $22.4 \le 2\theta \le 31.2°$. For intensity data collection, ω–2θ scans were used with $\Delta\omega = 1.12 + 0.35\tan\theta$. Three monitor reflections were measured after 3 h of beam time, and the orientation of the crystal was checked after every 400 intensity measurements. Absorption corrections[27] were based on azimuthal scans of 11 reflections, 4 of which had the Eulerian angle χ near 90°. The other reflections used for this purpose had their bisecting-position χ values distributed in the range 12–70°.

Structure solution and refinement. The structure was solved and developed by Patterson and Fourier methods.[28] All non-hydrogen atoms were assigned anisotropic displacement parameters. The hydrogen atoms of the aromatic carbon atoms

Table 2 Crystal data and structure refinement for complex **1**

Formula	$C_{38}H_{30}Cl_2N_4P_2Pd$
Formula weight	781.90
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	9.5452(7)
b/Å	12.9923(5)
c/Å	13.8799(7)
β/°	93.862(6)
V/Å^3	1717.4(2)
Z	2
D_c/Mg m^{-3}	1.512
μ/mm^{-1}	0.823
Reflections collected	3226
Unique reflections	3022, $R_{int} = 0.0399$
Data/restraints/parameters	3022/0/214
Goodness of fit	1.045
Final $R1$, $wR2$ indices [$I > 2\sigma(I)$]	0.0349, 0.0937
T/K	150(2)
λ(Mo-Kα)/Å	0.71073

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 data-to-parameter ratio in the final refinement was 14.1. The structure was refined on F_o^2, and all reflections were used in the least-squares calculations.[29] The residuals and other pertinent parameters are summarized in Table 2. Crystallographic calculations were done on a Local Area VAXCluster computer (VAX/VMS V5.5-2). Data reduction was done by the program XCAD4B.[30]

CCDC reference number 186/1184.

See http://www.rsc.org/suppdata/dt/1998/3745/ for crystallographic files in .cif format.

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