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Complexation associated rearrangement of iminobiphosphines to diphosphinoamines

Zhaofu Fei, Wee Han Ang, Dongbin Zhao, Rosario Scopelliti, Paul J. Dyson *

Institut des Sciences et Ingénierie Chimiques, Ecole Polytechnique Fédérale de Lausanne, EPFL-BCH, CH-1015 Lausanne, Switzerland

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Dedicated to Professor Brian R. James on the occasion of his 70th birthday.

Abstract

The reaction of the iminobiphosphines RN=PPh_2–PPh_2, where R = C_6H_4(*p*-CN), C_6H_4(*m*-CN), C_6H_4(*o*-C_6H_5), C_6F_5 or C_6H_4(*o*-CF_3), with one molecular equivalent of M(cod)Cl_2 (M = Pd or Pt) results in a rearrangement of the N=P–P unit to the more commonly encountered P–N–P unit, forming mono-chelating complexes of general formula M{RN(PPh_2)$_2$}Cl_2. The related reaction of the same range of iminobiphosphines with Pt(cod)Cl_2 (but not Pd(cod)Cl_2) in 2:1 ratio affords complexes of general formula [Pt{RN(PPh_2)$_2$}$_2$]2Cl. All 15 complexes are isolated in moderate to high yield and they have been fully characterised by spectroscopic methods. Six complexes, viz. [M{C_6H_4(*p*-CN)N(PPh_2)$_2$}Cl_2], [M{C_6H_4(*m*-CN)N(PPh_2)$_2$}Cl_2] and [M{C_6H_4(*o*-C_6H_5)N(PPh_2)$_2$}Cl_2] (M = Pd and Pt), have been characterised in the solid state by single crystal X-ray diffraction analysis.

Keywords: P-Ligands; Diphosphinoamines; Iminophosphines; X-ray crystal structures; Palladium complexes; Platinum complexes

1. Introduction

Iminobiphosphines with PR_2–PR_2=NR′ backbones (**I** in Chart 1) are isoelectronic to the oxobiphosphines with PR_2–PR_2=O skeletons (**II**). They are also isomers of the more commonly encountered diphosphinoamines (**III**) with R_2P–NR′–PR_2 skeletons, and the transformation has been shown to take place on coordination to transition metals [1]. Similarly, oxobiphosphines can also rearrange on coordination to a number of transition metals to give diphosphoxanes PR_2–O–PR_2 (**IV**), which act as bidentate ligands [2]. Diphosphinoamines are widely used as ligands [3], with the ability to chelate to various transition metal centres [4,5], and such compounds have been reviewed in detail [6]. Some diphosphinoamine complexes have been evaluated as catalysts in, for example, asymmetric hydrogenation and hydroformylation reactions [7]. Much of the recent research has focused on chiral systems [8], and functionalised diphosphinoamines with, for example, additional nitrogen and oxygen donor centres [9].

Although iminobiphosphines have also been known for many years [10], they have not been studied to the same extent as oxobiphosphines or diphosphinoamines, presumably because they are generally less stable – some iminobiphosphines are even pyrophoric [11]. However, a series of iminobiphosphines RN=PPh_2–PPh_2 (R = substituted phenyl) recently prepared in our laboratory proved to be stable [12,13], although the cleavage of the P–P bond takes place in the presence of water, leading to the formation of aminophosphines RNHPPh_2 and the oxide derivative RNH–P(O)Ph_2 [1]. Since iminobiphosphines contain a phosphorus(III) centre with a free lone pair of electrons they should be able to complex to transition metal centres. As yet, however, no such compounds have been isolated, although recently, we reported a transition metal associated-rearrangement reaction from iminobiphosphine to

* Corresponding author.
E-mail address: paul.dyson@epfl.ch (P.J. Dyson).

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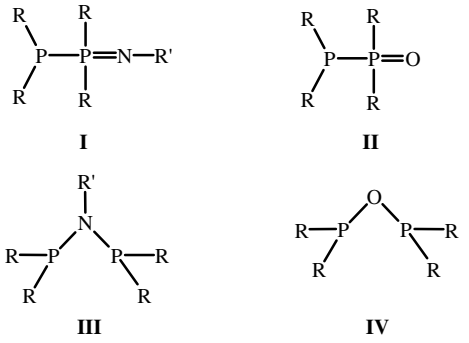
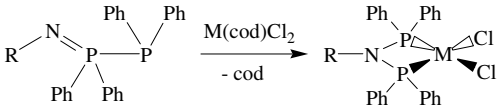


Chart 1.



6 R = C_6H_4(*p*-CN), **a** M = Pd, **b** M = Pt

7 R = C_6H_4(*m*-CN), **a** M = Pd, **b** M = Pt

8 R = C_6H_4(*o*-Ph), **a** M = Pd, **b** M = Pt

9 R = C_6F_5, **a** M = Pd, **b** M = Pt

10 R = C_6H_4(*o*-CF_3), **a** M = Pd, **b** M = Pt

Scheme 1. Reaction of iminobiphosphines **1**–**5** with M(cod)Cl_2 (M = Pd or Pt) in equimolar quantities.

diphosphinoamine [1]. In continuation of our ongoing program in developing and exploring P–N based ligands and their coordination chemistry [14], we report herein a series of reactions between iminobiphosphines and palladium(II) and platinum(II) complexes in which conversion to diphosphinoamines takes place. Based on spectroscopic studies, we are able to comment further on the mechanism of the N=P—P → P–N–P rearrangement.

2. Results and discussion

The reaction of the iminobiphosphines PPh_2–PPh_2=NR, where R = C_6H_4(*p*-CN) (**1**), C_6H_4(*m*-CN) (**2**), C_6H_4(*o*-Ph) (**3**), C_6F_5 (**4**) or C_6H_4(*o*-CF_3) (**5**), with M(cod)Cl_2 (M = Pd or Pt, cod = cycloocta-1,5-diene) in equimolar quantities affords compounds of formula [M{C_6H_4(*p*-CN)N(PPh_2)$_2$}Cl_2] (Pd = **6a**, Pt = **6b**), [M{C_6H_4(*m*-CN)N(PPh_2)$_2$}Cl_2] (Pd = **7a**, Pt = **7b**), [M{C_6H_4(*o*-Ph)N(PPh_2)$_2$}Cl_2] (Pd = **8a**, Pt = **8b**), [M{C_6F_5N(PPh_2)$_2$}Cl_2] (Pd = **9a**, Pt = **9b**) and [M{C_6H_4(*o*-CF_3)N(PPh_2)$_2$}Cl_2] (Pd = **10a**, Pt = **10b**), (see Scheme 1).

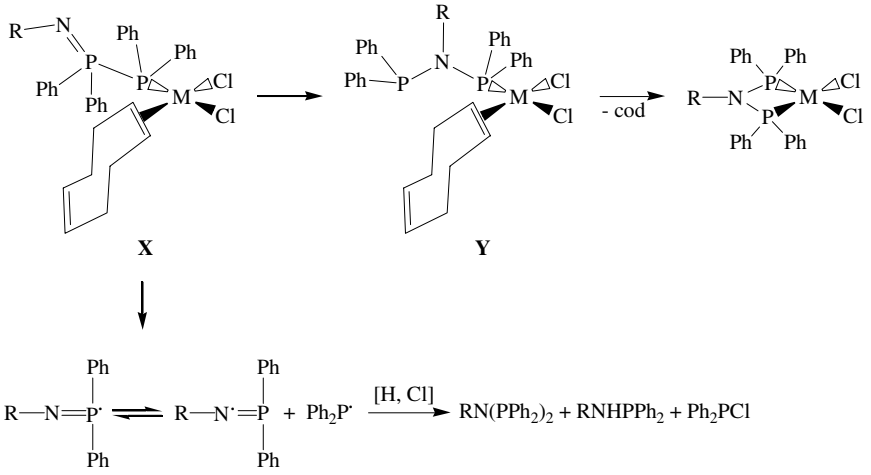
All reactions were followed in situ by ^{31}P NMR spectroscopy, and in the case of the reactions with the palladium(II) complex, the reaction takes place instantaneously at room temperature in dichloromethane, and no evidence for the formation of P–P–Pd intermediates was observed, even on reducing the temperature to ca. −20 °C. As an illustrative example, the reaction of C_6H_4(*p*-CN)N=PPh_2–PPh_2 (**1**) with Pd(cod)Cl_2 in dichloromethane affords, apart from the main signal at 36.0 ppm, corresponding to the formation of [Pd{C_6H_4(*p*-CN)N(PPh_2)$_2$}Cl_2] (**6a**), three other signals at 68.5, 30.5 and 82.0 ppm with low relative intensities. The former two signals probably correspond to the formation of the free ligands C_6H_4(*p*-CN)N(PPh_2)$_2$ and C_6H_4(*p*-CN)N$HPPh_2$, respectively, but due to the low quantity present it was not possible to isolate the compounds responsible for these signals. However, the frequencies of structurally related compounds are similar (cf. C_6H_4(*o*-R)N(PPh_2)$_2$ 64.0–69.0 ppm [13,15] and C_6H_4(*o*-R)N$HPPh_2$ 26.0–31.0 ppm [13,16]). The signal at 82.0 ppm is tentatively assigned to Ph_2PCl [17].

The analogous reactions with Pt(cod)Cl_2 result in same by-products, viz. RN(PPh_2)$_2$, RNHPPh_2 and Ph_2PCl, as indicated by ^{31}P NMR spectroscopy. The formation of P–NH products and Ph_2PCl during the reaction suggests that on coordination of the iminobiphosphine to metal centre (Pd or Pt), an intermediate in which the intact iminobiphosphine coordinates to the Pd or Pt centre (labelled X in Scheme 2) forms initially. This intermediate is presumably short-lived, and rapidly rearranges to the diphosphinoamine, which initially coordinates through just one phosphorus centre (Y in the Scheme) before yielding the final product. Cleavage of the P–P bond in intermediate X would lead to the formation of radicals, which could react to form RN(PPh_2)$_2$, RHNPPh_2 and Ph_2PCl, as indicated by the presence of signals at 65, 30 and 82 ppm in the ^{31}P NMR spectrum. In order to establish the source of the chloride, all the reactions were repeated in a non-chlorinated solvent (thf) but Ph_2PCl is always observed, indicating that the source of the chloride is most probably from the transition metal–chloride starting material. Attempts to quench the reaction in order to analyse the intermediates in more detail failed.

The ^{31}P NMR chemical shifts of the compounds **6**–**10** are in keeping with structurally related complexes [4,9], and there does not appear to be a significant effect of the substituent on the chemical shift. The J_{P-Pt} values in complexes **6b**–**10b** are also normal, with only minor variations compared to the structurally similar compounds [4,9].

The solubility of complexes **6**–**10** is generally quite poor in common solvents such as diethyl ether, dichloromethane or chloroform. However, six of the complexes, [M{C_6H_4(*p*-CN)N(PPh_2)$_2$}Cl_2] (Pd = **6a**, Pt = **6b**), [M{C_6H_4(*m*-CN)N(PPh_2)$_2$}Cl_2] (Pd = **7a**, Pt = **7b**), [M{C_6H_4(*o*-Ph)N(PPh_2)$_2$}Cl_2] (Pd = **8a**, Pt = **8b**), afford crystals from solutions of dichloromethane–diethyl ether or chloroform–diethyl ether (whereas the other complexes form powders under similar conditions). Complexes **9a**, **9b**, **10a** and **10b** do not re-dissolve in $CHCl_3$ or CH_2Cl_2 and are only sparingly soluble in CH_3CN. It is possible that the fluorous-groups are involved in strong hydrogen bonding interactions in the solid state which hinders re-dissolution.

The solid state structures of **6a**, **6b**, **7a**, **7b**, **8a** and **8b** have been established by single crystal X-ray diffraction.



Scheme 2. Proposed reaction mechanism of **1**–**5** with M(cod)Cl_2 (M = Pd or Pt).

Table 1
Crystallographic data for **6a**, **6b**, **7a**, **7b**, **8a** and **8b**

	6a	**6b**	**7a**	**7b**	**8a**	**8b**
Chemical formula	$C_{33}H_{28}Cl_6N_2P_2Pd$	$C_{33}H_{28}Cl_6N_2P_2Pt$	$C_{32}H_{26}Cl_4N_2P_2Pd$	$C_{32}H_{26}Cl_4N_2P_2Pt$	$C_{36}H_{29}Cl_2NP_2Pd$	$C_{39}H_{32}Cl_{11}NP_2Pt$
F_w	833.61	922.30	748.69	837.38	714.84	1161.64
Crystal system	orthorhombic	orthorhombic	monoclinic	monoclinic	triclinic	triclinic
Space group	*Pbcn*	*Pbcn*	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a (Å)	11.4007(8)	11.318(3)	12.990(3)	12.9553(7)	10.4419(6)	12.0399(5)
b (Å)	21.1544(14)	21.213(3)	14.7846(14)	14.8941(5)	11.9054(9)	13.8676(10)
c (Å)	14.7294(10)	14.7099(9)	17.130(3)	17.2375(9)	13.3373(10)	13.9204(10)
α (°)	90	90	90	90	91.543(6)	82.787(6)
β (°)	90	90	103.657(19)	104.105(5)	109.875(6)	87.218(5)
γ (°)	90	90	90	90	91.405(6)	77.646(5)
Volume (Å^3)	3552.4(4)	3534.7(10)	3196.6(11)	3225.8(3)	1557.71(18)	2251.9(3)
Z	4	4	4	4	2	2
D_{calc} (g cm^{-3})	1.559	1.733	1.556	1.724	1.524	1.713
F(000)	1672	1800	1504	1632	724	1136
μ (mm^{-1})	1.090	4.541	1.041	4.806	0.897	3.869
Temperature (K)	140(2)	140(2)	140(2)	140(2)	140(2)	140(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Measured reflections	20449	19912	18710	18234	9518	13484
Unique reflections	2995	3030	5653	5382	4830	6992
Unique reflections [$I > 2\sigma(I)$]	2466	2565	4086	4484	3844	6184
Number of data/restraints/ parameters	2995/6/221	3030/0/222	5653/0/371	5382/0/371	4830/0/380	6992/18/487
R^a [$I > 2\sigma(I)$]	0.0379	0.0808	0.0591	0.0224	0.0288	0.0485
$wR_2{}^a$ (all data)	0.0846	0.1858	0.1826	0.0550	0.0541	0.1275
Goodness-of-fit[b]	1.117	1.333	1.085	0.972	0.947	1.040

[a] $R = \sum\|F_o| - |F_c\|/\sum|F_o|$, $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.
[b] Goodness-of-fit $= \{\sum[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$ where *n* is the number of data and *p* is the number of parameters refined.

Crystal data and details of the structure determination are summarised in Table 1 and their structures are shown in Figs. 1–3 together with key bond parameters summarised in Tables 2 and 3.

There are close similarities between the solid state structures of **6**–**8** with all the compounds having the same overall features, viz. a chelating P–N–P ligand and two chloride ligands forming a square planar geometry. The M–P bond distances and M–Cl bond distances are typical for such compounds [4,9]. Notably, larger P1–M–P2 angles are observed in the platinum complexes compared to the palladium complexes, while smaller Cl1–M–Cl2 angles are found for each pair of the diphosphinoamine–metal complexes. The larger P1–M–P2 angles required for the platinum complexes originate from the greater size of the platinum centre, as compared to palladium. Consequently, the phenyl groups on the diphosphinoamine ligands bonded to the platinum centres are spread out more widely, resulting in greater steric interactions with the chloro ligands and smaller Cl–M–Cl angles. The metal–ligand bond parameters for the complexes are compared in Table 2.

The different substituents on the amino-phenyl rings also affect the planarity of the trigonal P1–N1–(C13)–P2

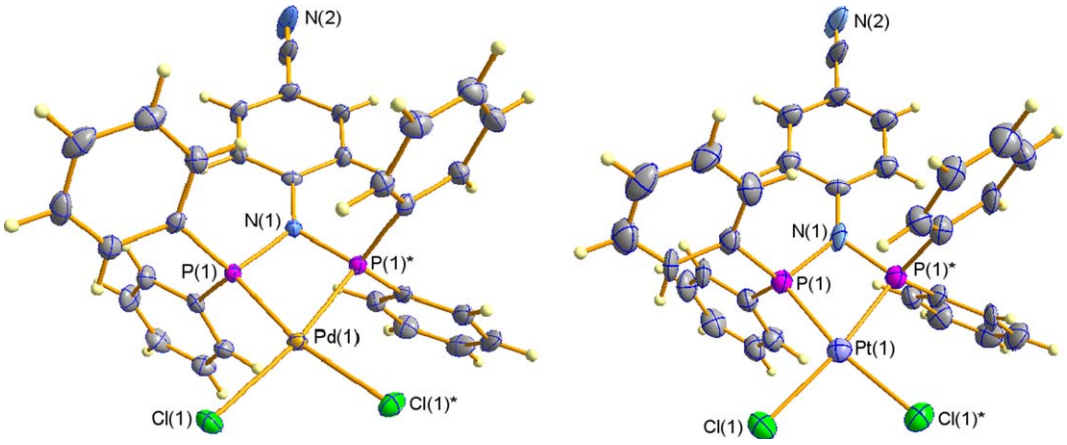


Fig. 1. ORTEP representation of **6a** (left) and **6b** (right); thermal ellipsoids are drawn at 50% equiprobability envelopes, with hydrogen atoms as spheres of arbitrary diameter. C and H atoms are not labelled for clarity and solvent molecules are also omitted.

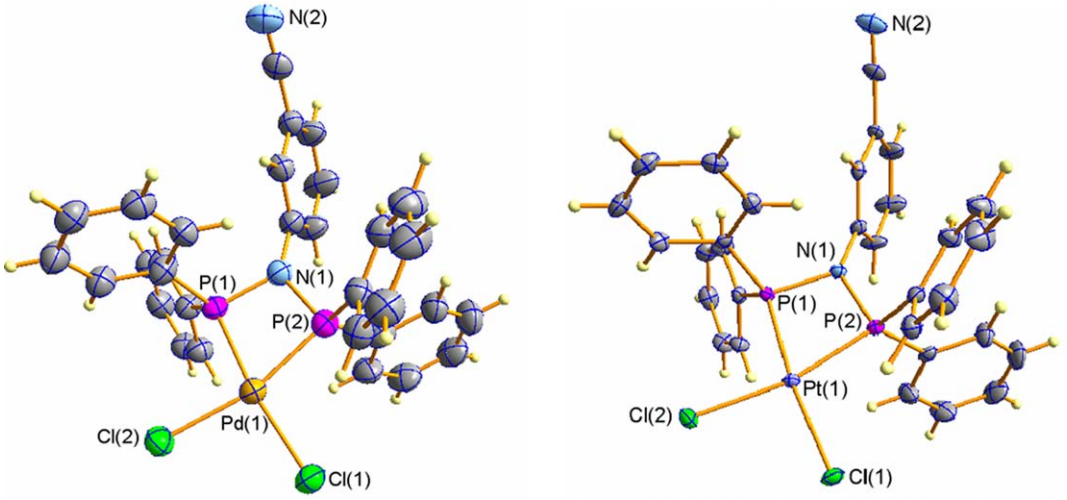


Fig. 2. ORTEP representation of **7a** (left) and **7b** (right); thermal ellipsoids are drawn at 50% equiprobability envelopes, with hydrogen atoms as spheres of arbitrary diameter. C and H atoms are not labelled for clarity and solvent molecules are also omitted.

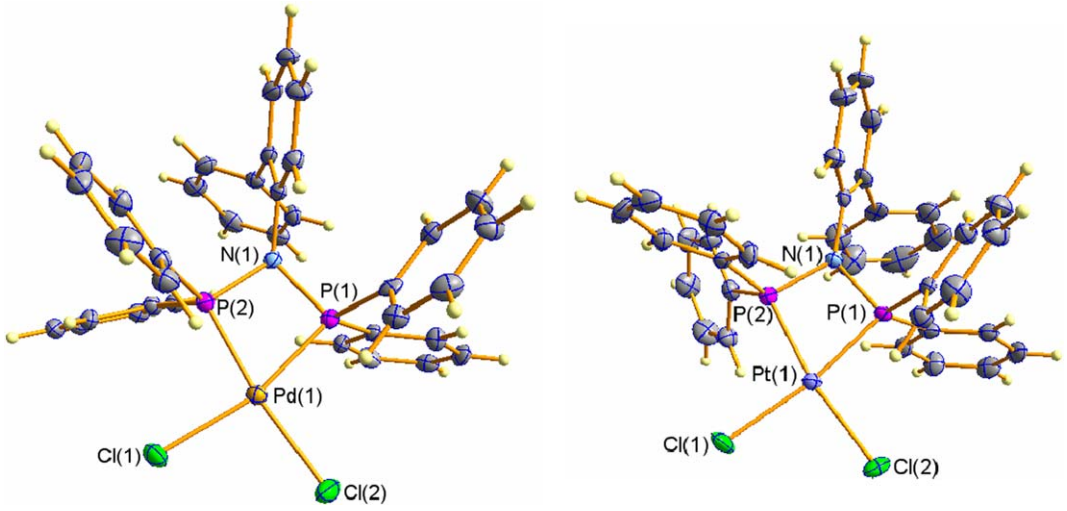


Fig. 3. ORTEP representation of **8a** (left) and **8b** (right); thermal ellipsoids are drawn at 50% equiprobability envelopes, with hydrogen atoms as spheres of arbitrary diameter. C and H atoms are not labelled for clarity and solvent molecules are also omitted.

Table 2
Key metal–ligand bond parameters in **6a**, **6b**, **7a**, **7b**, **8a** and **8b**

	Ligand	M–P_{ave} (Å)	M–Cl_{ave} (Å)	P1–M–P2 (°)	Cl1–M–Cl2 (°)
6a	C_6H_4(*p*-CN)N(PPh_2)$_2$	2.2211(8)	2.3667(8)	72.62(4)	95.18(4)
6b		2.201(3)	2.352(3)	73.38(14)	91.23(15)
7a	C_6H_4(*m*-CN)N(PPh_2)$_2$	2.219(3)	2.355(3)	72.29(5)	95.31(5)
7b		2.212(2)	2.360(2)	72.77(3)	92.03(3)
8a	C_6H_4(*o*-phenyl)N(PPh_2)$_2$	2.216(2)	2.360(2)	72.23(3)	92.39(3)
8b		2.117(4)	2.353(4)	72.95(7)	91.84(7)

Table 3
Key bond parameters of iminophosphine ligands in **6a**, **6b**, **7a**, **7b**, **8a** and **8b**

	P–N_{ave} (Å)	N1–C13[a] (Å)	P1–N1–P2 (°)	P1···P2 (Å)	*d*(N1)[b] (Å)	Σ(N1)[c] (°)
1	1.727(6)	1.434(4)	114.49(14)			
6a	1.715(2)	1.434(5)	100.1(2)	2.631	0.000	359.96
6b	1.733(10)	1.400(19)	98.7(7)	2.630	0.000	360.10
2	1.746(2)	1.449(6)	112.7(2)			
7a	1.706(8)	1.440(7)	100.2(2)	2.618	0.076	359.30
7b	1.713(6)	1.445(4)	99.99(13)	2.625	0.093	358.99
8a	1.735(5)	1.458(4)	97.70(13)	2.613	0.311	348.60
8b	1.712(12)	1.460(10)	99.9(3)	2.621	0.156	357.10

[a] C13 refers to the C-atom on the phenyl ring adjacent to the N1-atom.
[b] *d*(N1) refers to the perpendicular distance of the N1-atom from the plane formed by P1, P2 and C13 atoms. The distances were measured using CCDC Mercury 1.4 [18].
[c] Σ(N1) refers to the total angular displacement about the N1-atom subtended by the P1, P2 and C13 atoms.

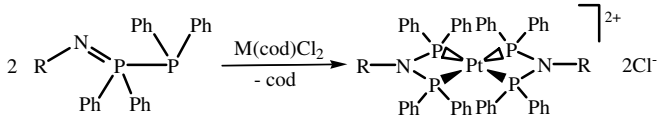
moieties in the coordinated diphosphinoamine complexes (Table 3). This is in keeping with our previous observations based on complexes derived from C_6H_4(*o*-CN)N=PPh_2–PPh_2 [1a], and other functionalised diphosphinoamine complexes [4,9]. In a planar environment, N1 would lie within the plane formed by P1, P2 and C13 and the angles subtended at N1 by P1, P2 and C13 should sum up to 360°, as observed in **6a** and **6b**. In **7a** and **7b**, the displacement distances of N1 from planarity are significantly larger, 0.076 and 0.093 Å, respectively, and the total angular displacements about N1 are slightly lower than 360°, i.e., 359.30° and 358.99°, respectively. However, the largest deviations were observed in complexes derived from iminophosphine, **3**. In **8a** and **8b**, the displacement distances are 0.311 and 0.156 Å, respectively, while the total angular displacements about N1 are only 348.60° and 357.10°, indicating significant deviation from planarity. A plausible explanation for these structural differences is the participation of the amino-phenyl group in the π-delocalisation framework between the P1–N1–P2 atoms. For **6a** and **6b**, the amino-phenyl rings were oriented such that they are coplanar to the trigonal P1–N1–(C13)–P2 moieties, while in **7a**, **7b**, **8a** and **8b**, the amino-phenyl rings are almost perpendicular. Therefore, it is possible that in **6a** and **6b**, extended delocalisation within the P1–N1–[C_6H_4(*p*-CN)]–P2 system is present, stabilising the planar framework, which is not present in **7a**, **7b**, **8a** and **8b**. In addition for **8a** and **8b**, the bulky *o*-phenyl groups create further steric hindrances resulting in greater deviations.

Since all the complexes discussed here are derived from N=P–P ligands following a rearrangement reaction, it makes little sense to compare the structural features between the complexes and the N=P–P ligands before and after coordination. However, since the P–N–P ligands [C_6H_4(*p*-CN)N(PPh_2)$_2$, C_6H_4(*m*-CN)N(PPh_2)$_2$] have also been analysed by X-ray [13], it is worth comparing the effect of coordination on the structural features on the P–N–P ligand. The bond lengths of the C≡N group are only marginally different from the parent ligand. Notably, the average P–N distances in complexes **6a**, **7a** and **7b** are 1.715(2), 1.706(8) and 1.713(6) Å, respectively, which are somewhat shorter than in the free diphosphinoamine ligands derived from **1** and **2** [1.727(6) and 1.746(2) Å, respectively]. In addition, despite coordination of the phosphorus centres to the transition metal, the N1–C13 distance in **6a** 1.434(5) Å, **7a** 1.440(7) Å and **7b** 1.445(4) Å, remains essentially unchanged compared to the corresponding parent ligands, i.e., 1.434(4) and 1.449(6) Å. In **6b**, however, the reverse was observed, i.e., the average P–N distance [1.733(10) Å] remains unchanged while the N1–C13 distance [1.400(19) Å] is significantly smaller. The most significant changes are observed in the P–N–P angles. In the diphosphinoamine ligands derived from **1** and **2**, the P–N–P angles are 114.49(14)° and 112.70(2)°, respectively. In order to accommodate the transition metal centres, these angles are reduced to between 98° and 100° in **6a**, **6b**, **7a** and **7b**, corresponding to a 10% decrease in angular displacement between the P1–N1 and P2–N1 bonds.

Not surprisingly, the nature of the crystal packing of **6a**, **6b**, **7a**, **7b**, **8a** and **8b** in the solid state is strongly dependent on the nature of the substituent attached to the diphosphinoamine ligand, rather than transition metal. For **6a** and **6b**, both complexes are packed into the orthorhombic lattice with the *Pbcn* space group, for **7a** and **7b** the monoclinic lattice with the $P2_1/n$ space group, and **8a** and **8b** the triclinic lattice with the $P\bar{1}$ space group (Table 1). The presence of the dichloromethane (or chloroform) solvate appears to have little influence on the structural motif and such solvates in related molecules are not uncommon [14,19].

The reaction of $[Pt(cod)Cl_2]$ with two equivalents of the iminobiphosphines **1**–**5** affords the cationic platinum complexes $[Pt\{C_6H_4(p\text{-}CN)N(PPh_2)_2\}_2]2Cl$ (**6c**), $[Pt\{C_6H_4(m\text{-}CN)N(PPh_2)_2\}_2]2Cl$ (**7c**), $[Pt\{C_6H_4(o\text{-}Ph)N(PPh_2)_2\}_2]2Cl$ (**8c**), $[Pt\{C_6F_5N(PPh_2)_2\}_2]2Cl$ (**9c**) and $[Pt\{C_6H_4(o\text{-}CF_3)N(PPh_2)_2\}_2]2Cl$ (**10c**), as the major products (Scheme 3). The analogous reaction with $[Pd(cod)Cl_2]$ leads to the formation of **6a**–**10a** and unreacted starting materials along with some impurities. Cationic platinum(II) complexes with two diphosphinoamine ligands have been prepared previously from diphosphinoamine ligands [20]. The reaction of $[Pt(cod)Cl_2]$ with two molar equivalents of the diphosphinoamines $C_6H_4(p\text{-}CN)N(PPh_2)_2$, $C_6H_4(m\text{-}CN)N(PPh_2)_2$ or $C_6H_4(p\text{-}Ph)N(PPh_2)_2$ in dichloromethane gave quantitatively the bis-chelating complexes **6c**–**8c**. In each case, the ^{31}P NMR spectrum of the reaction mixture gave rise to only a singlet with characteristic P–Pt satellites. The products isolated from the reaction using iminobiphosphines **1**, **2** or **3** as starting materials gave identical signals, however, impurities similar to those observed in the 1:1 reactions were also present. The yield is thus correspondingly lower compared to the reaction with the P–N–P ligands, even when the reaction is conducted in a non-chlorinated solvent such as thf. It is not unreasonable to assume that the formation of **6c**–**10c** follows a similar mechanism as illustrated above in Scheme 2.

The δ ^{31}P chemical shift of complexes **6c**–**10c** lies within the range of related known complexes [1a,20], with similar J_{P-Pt} values. Compared to **6**(**a** and **b**)–**10**(**a** and **b**), which



1 - 5

6c: $C_6H_4(p\text{-}CN)$

7c: $C_6H_4(m\text{-}CN)$

8c: $C_6H_4(o\text{-}Ph)$

9c: C_6F_5

10c: $C_6H_4(o\text{-}CF_3)$

Scheme 3. Reaction of iminobiphosphine **1**–**5** with $Pt(cod)Cl_2$ in 2:1 ratio.

are air stable in the solid state and in solution, the cationic complexes **6c**–**10c** are very sensitive to moisture, decomposing to the mono-chelating complexes **6b**–**10b**. The other components from the decomposition are the appropriate aminophosphine $RNHPPh_2$ and $Ph_2P(O)H$, as evidenced by ^{31}P NMR spectroscopy. Complexes **6c**–**10c** are reasonably soluble in common solvents such as dichloromethane, chloroform and acetonitrile. Crystals of **6c** and **7c** have been obtained from a dichloromethane–diethyl ether solution upon cooling to 0 °C, unfortunately the quality of the crystals was not adequate for single crystal X-ray diffraction analysis.

Unlike the reaction of **1**–**5** with $[Pt(cod)_2Cl_2]$ in 2:1 ratio, by which the bis-chelating complexes are formed as main products, the 2:1 reaction with $[Pd(cod)_2Cl_2]$ is somewhat more complicated. The ^{31}P NMR spectra of all the reaction mixtures in dichloromethane contain several signals in the ranges 25.0–45.0 and 64.0–67.0 ppm as well as a peak at 81 ppm. Following recrystallization, only the mono-chelating products **6a**–**10a** could be isolated in low yield.

2.1. Concluding remarks

The transition metal mediated rearrangement of iminobiphosphines (N=P–P) to diphosphinoamines (P–N–P) has been described in some detail. This kind of rearrangement is analogous to the transformation from O=P–P to P–O–P, and has potential use in synthesis of chelating and bis-chelating transition metal complexes, since not all diphosphinoamines are available [13] using the commonly used synthetic methods.

3. Experimental

All manipulations were performed under an inert atmosphere of dry nitrogen using standard Schlenk techniques using solvents dried using the appropriate reagents and distilled prior to use. Iminobiphosphines **1**–**5** were prepared according to the previously published method [13]. NMR spectra were obtained at 20 °C on a Bruker DMX 200 instrument using $SiMe_4$ for ^1H and 85% H_3PO_4 for ^{31}P as external standards. ESI-MS spectra were recorded on a ThermoFinnigan LCQ™ Deca XP Plus quadrupole ion trap instrument using the literature procedure [21]. Samples were infused directly into the source at 5 μL min^{-1} using a syringe pump. The spray voltage was set at 5 kV and the capillary temperature at 50 °C. Elemental analysis was carried out at the EPFL.

3.1. Reaction of *1–5* with *Pd(cod)Cl₂* in a 1:1 mole ratio, synthesis of *6a–10a*

A typical procedure. $Pd(cod)Cl_2$ (14.3 mg, 0.05 mmol) in dichloromethane (5.0 ml) was added to a solution of **1**–**5** (0.05 mmol) in dichloromethane (5.0 ml) at 0 °C. After the addition was complete, the reaction mixture was allowed to warm to room temperature. The reaction was

followed by ^{31}P NMR spectroscopy which showed that the starting material had been consumed after 5 min. After this time the reaction was stopped, the solvent was removed under reduced pressure and thf or diethyl ether (2.0 ml) was added and the sample was stored at 2 °C. After 24 h the precipitate that had formed was collected by filtration. Crystals of **6a**, **7a** and **8a** suitable for X-ray diffraction analysis were grown from a solution of dichloromethane–diethyl ether at −21 °C.

*3.1.1. [Pd{C$_6$H$_4$(p-CN)N(PPh$_2$)$_2$}Cl$_2$] (**6a**)*

Yield: 70%; m.p. > 285 °C (decomp.). ^1H NMR (ppm in CD_2Cl_2): 6.65–8.15 (m, aromatic H); ^{31}P NMR (ppm in CD_2Cl_2): 36.07 (s), ESI-MS *m/z*: 662 $[M + H]^+$, *Anal*. Calc. for $C_{31}H_{24}Cl_2N_2P_2Pd$: H, 3.64; C, 56.09; N, 4.22. Found: H, 3.67; C, 56.50; N, 4.18%.

*3.1.2. [Pd{C$_6$H$_4$(m-CN)N(PPh$_2$)$_2$}Cl$_2$] (**7a**)*

Yield: 61%; m.p. > 285 °C. ^1H NMR (ppm in CD_2Cl_2): 6.65–8.20 (m, aromatic H); ^{31}P NMR (ppm in CD_2Cl_2): 37.85 (s), ESI-MS *m/z*: 662 $[M + H]^+$. *Anal*. Calc. for $C_{31}H_{24}Cl_2N_2P_2Pd$: H, 3.64; C, 56.09; N, 4.22. Found: H, 3.66; C, 56.41; N, 4.15%.

*3.1.3. [Pd{C$_6$H$_4$(o-C$_6$H$_5$)N(PPh$_2$)$_2$}Cl$_2$] (**8a**)*

Yield: 75%; m.p. 275 °C (decomp.). ^1H NMR (ppm in $CDCl_3$): 6.60–8.25 (m, aromatic H); ^{31}P NMR (ppm in $CDCl_3$): 39.99 (s), ESI-MS *m/z*: 712 $[M + 1]^+$. *Anal*. Calc. for $C_{36}H_{29}Cl_2NP_2Pd$: H, 4.09; C, 60.48; N, 1.96. Found: H, 4.13; C, 60.53; N, 1.91%.

*3.1.4. [Pd{C$_6$F$_5$N(PPh$_2$)$_2$}Cl$_2$] (**9a**)*

Yield: 62%; m.p. > 285 °C. ^1H NMR (ppm in $CDCl_3$): 6.80–8.30 (m, aromatic H); ^{31}P NMR (ppm in $CDCl_3$): 45.0 (s), ESI-MS *m/z*: 727 $[M + 1]^+$. *Anal*. Calc. for $C_{30}H_{20}Cl_2F_5NP_2Pd$: H, 2.77; C, 49.44; N, 1.92. Found: H, 2.80; C, 49.53; N, 1.89%.

*3.1.5. [Pd{C$_6$H$_4$(o-CF$_3$)N(PPh$_2$)$_2$}Cl$_2$] (**10a**)*

Yield: 61%; m.p. 220 °C. ^1H NMR (ppm in CD_3CN): 6.65–8.15 (m, aromatic H); ^{31}P NMR (ppm in CD_3CN): 44.80 (s), ESI-MS *m/z*: 703 $[M + 1]^+$. *Anal*. Calc. for $C_{31}H_{24}Cl_2F_3NP_2Pd$: H 3.42, C 52.68, N 1.98; Found: H 3.49, C 52.73, N 2.00%.

*3.2. Reaction of **1–5** with Pt(cod)Cl$_2$ in a 1:1 mole ratio, synthesis of **6b–10b***

A typical procedure. Pt(cod)Cl_2 (17.2 mg, 0.05 mmol) in dichloromethane (5.0 ml) was added to a solution of **1–5** (0.05 mmol) in dichloromethane (5.0 ml) at 0 °C. After the addition was complete, the reaction mixture was allowed to warm to room temperature and stirred for 30 min. The solvent was removed under reduced pressure and the solid residue was washed with diethyl ether (2 × 5.0 ml). To the solid, dichloromethane (2.0 ml) and diethyl ether (10.0 ml) were added. The precipitate that formed after cooling the sample at 0 °C for 1–2 days was collected by filtration and washed with diethyl ether (2 × 2.0 ml). Crystals of **6b** and **7b** suitable for X-ray diffraction analysis were grown from a solution of dichloromethane–diethyl ether solution at −21 °C, and crystals of **8b** were grown from a solution of chloroform–diethyl ether.

*3.2.1. [Pt{C$_6$H$_4$(p-CN)N(PPh$_2$)$_2$}Cl$_2$] (**6b**)*

Yield: 72%; m.p. 249 °C. ^1H NMR (ppm in $CDCl_3$): 6.60–8.10 (m, aromatic H); ^{31}P NMR (ppm in $CDCl_3$): 22.41 (s, ^1J(PPt) = 3342.82 Hz), ESI-MS *m/z*: 751 $[M + H]^+$. *Anal*. Calcd for $C_{31}H_{24}Cl_2N_2P_2Pt$: H 3.21, C 49.48, N 3.72; Found: H 3.28, C 49.64, N 3.66%.

*3.2.2. [Pt{C$_6$H$_4$(m-CN)N(PPh$_2$)$_2$}Cl$_2$] (**7b**)*

Yield: 69%; m.p. 270 °C. ^1H NMR (ppm in $CDCl_3$): 6.65–8.15 (m, aromatic H); ^{31}P NMR (ppm in $CDCl_3$): 23.69 (s, ^1J(PPt) = 3350.25 Hz), ESI-MS *m/z*: 751 $[M + H]^+$. *Anal*. Calc. for $C_{31}H_{24}Cl_2N_2P_2Pt$: H, 3.21; C, 49.48; N, 3.72. Found: H, 3.26; C, 49.59; N, 3.67%.

*3.2.3. [Pt{C$_6$H$_4$(o-C$_6$H$_5$)N(PPh$_2$)$_2$}Cl$_2$] (**8b**)*

Yield: 71%; m.p. > 285 °C. ^1H NMR (ppm in CD_2Cl_2): 6.65–8.15 (m, aromatic H); ^{31}P NMR (ppm in CD_2Cl_2): 26.52 (s, ^1J(PPt) = 3371.04 Hz), ESI-MS *m/z*: 801 $[M + H]^+$. *Anal*. Calc. for $C_{36}H_{29}Cl_2NP_2Pt$: H, 3.64; C, 53.81; N, 1.74. Found: H, 3.73; C, 53.92; N, 1.76%.

*3.2.4. [Pt{C$_6$F$_5$N(PPh$_2$)$_2$}Cl$_2$] (**9b**)*

Yield: 52%; m.p. > 285 °C. ^1H NMR (ppm in CD_2Cl_2): 6.65–8.15 (m, aromatic H); ^{31}P NMR (ppm in CD_2Cl_2): 31.14 (s, ^1J(PPt) = 3392.61 Hz), ESI-MS *m/z*: 815 $[M + H]^+$. *Anal*. Calc. for $C_{30}H_{20}Cl_2F_5NP_2Pt$: H, 2.47; C, 44.08; N, 1.71. Found: H, 2.74; C, 44.21; N, 1.69%.

*3.2.5. [Pt{C$_6$H$_4$(o-CF$_3$)N(PPh$_2$)$_2$}Cl$_2$] (**10b**)*

Yield: 58%; m.p. > 285 °C.^1H NMR (ppm in $CDCl_3$): 6.65–8.15 (several multiples, aromatic H); ^{31}P NMR (ppm in $CDCl_3$): 25.50 (s, ^1J(PPt) = 3350.0 Hz), ESI-MS *m/z*: 793 $[M + H]^+$. *Anal*. Calc. for $C_{31}H_{24}Cl_2F_3NP_2Pt$: H, 3.04; C, 46.81; N, 1.76. Found: H, 3.08; C, 46.92; N, 1.73%.

*3.3. Reaction of **1–5** with Pt(cod)Cl$_2$ in a 2:1 mole ratio, synthesis of **6c–10c***

A typical procedure. Pt(cod)Cl_2 (18.7 mg, 0.05 mmol) in dichloromethane (5.0 ml) was added to a solution of **1–5** (0.10 mmol) in dichloromethane (5.0 ml) at 0 °C. After the addition was complete, the reaction mixture was allowed to warm to room temperature and stirred for 4 h. The ^{31}P NMR spectra of the reaction mixture showed that the starting materials have been consumed. The solvent was then removed under reduced pressure and the remaining solid was washed with diethyl ether (3 × 5.0 ml). The collected solid was suspended in diethyl

ether (10.0 ml) and dichloromethane (2.0 ml) was added. The samples were placed in a freezer at −21 °C. The solid formed after 1–2 days was collected by filtration.

*3.3.1. [Pt{C$_6$H$_4$(p-CN)N(PPh$_2$)$_2$}$_2$·2Cl] (**6c**)*

Yield: 63%; m.p. > 285 °C. ^{1}H NMR (ppm in $CDCl_3$): 6.60–8.10 (m, aromatic H); ^{31}P NMR (ppm in $CDCl_3$): 34.73 (s, ^1J(PPt) = 2438.43 Hz); ESI-MS$^+$ *m/z* 1166 [cation]$^+$. *Anal.* Calc. for $C_{62}H_{48}Cl_2N_4P_4Pt$: H, 3.90; C, 60.10; N, 4.52. Found: H, 3.95; C, 60.14; N, 4.46%.

*3.3.2. [Pt{C$_6$H$_4$(m-CN)N(PPh$_2$)$_2$}$_2$·2Cl] (**7c**)*

Yield: 58%; m.p. > 285 °C. ^{1}H NMR (ppm in $CDCl_3$): 6.60–8.10 (m, aromatic H), ^{31}P NMR (ppm in $CDCl_3$): 36.80 (s, ^1J(PPt) = 2429.52 Hz); ESI-MS$^+$ *m/z* 1166 [cation]$^+$. *Anal.* Calc. for $C_{62}H_{48}Cl_2N_4P_4Pt$: H, 3.90; C, 60.10; N, 4.52. Found: H, 3.97; C, 60.21; N, 4.50%.

*3.3.3. [Pt{C$_6$H$_4$(o-C$_6$H$_5$)N(PPh$_2$)$_2$}$_2$·2Cl] (**8c**)*

Yield: 61%; m.p. > 285 °C. ^{1}H NMR (ppm in $CDCl_3$): 6.65–8.15 (m, aromatic H); ^{31}P NMR (ppm in CD_2Cl_2): 39.26 (s, ^1J(PPt) = 2343.40 Hz), ESI-MS *m/z*: 1268 [cation]$^+$. *Anal.* Calc. for $C_{72}H_{58}Cl_2N_2P_4Pt$: H, 4.36; C, 64.48; N, 2.09. Found: H, 4.33; C, 64.50; N, 2.10%.

*3.3.4. [Pt{C$_6$F$_5$N(PPh$_2$)$_2$}$_2$·2Cl] (**9c**)*

Yield: 56%; m.p. 275 °C. ^{1}H NMR (ppm in CD_2Cl_2): 6.65–8.15 (m, aromatic H); ^{31}P NMR (ppm in CD_2Cl_2): 41.90 (s, ^1J(PPt) = 2480.02 Hz), ESI-MS *m/z*: 1295 [cation]$^+$. *Anal.* Calc. for $C_{60}H_{40}Cl_2F_{10}N_2P_4Pt$: H, 2.95; C, 52.65; N, 2.05. Found: H, 2.99; C, 52.73; N, 2.01%.

*3.3.5. [Pt{C$_6$H$_4$(o-CF$_3$)N(PPh$_2$)$_2$}$_2$·2Cl] (**10c**)*

Yield: 51%; m.p. 260 °C. ^{1}H NMR (ppm in $CDCl_3$): 6.65–8.15 (m, aromatic H); ^{31}P NMR (ppm in $CDCl_3$): 44.0 (s, ^1J(PPt) = 2400.0 Hz), ESI-MS *m/z*: 1252 [cation]$^+$. *Anal.* Calc. for $C_{62}H_{48}Cl_2F_6N_2P_4Pt$: H, 3.65; C, 56.20; N, 2.11. Found: H, 3.68; C, 56.32; N, 2.13%.

3.4. Crystallographic structure determination

Data collection for **6a**, **6b**, **7a**, **7b**, **8a** and **8b** was performed on a four-circle Kappa goniometer equipped with an Oxford Diffraction KM4 Sapphire CCD or MAR345 IPDS at 140 K. Data reduction was performed using CrysAlis RED [22]. Structure solution of **6a**, **7a** and **8a** was performed using SHELXS [23], **6b** and **8b** using SIR-92 [24], and **7b** using DIRDIF [25]. Structures were refined by full-matrix least-squares refinement (against F^2) with all non-hydrogen atoms refined anisotropically. Hydrogen atoms were placed in their geometrically generated positions and refined isotropically. Empirical absorption corrections were applied to **6b**, **7a**, **8a** and **8b** using DELABS [26], and semi-empirical adsorption corrections to **7b** using MULABS [27]. Graphical representations of the structures were made with DIAMOND [28]. Relevant crystallographic data are compiled in Table 1 and key bond parameters in Tables 2 and 3. The CIF files have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 281091–281096. Copies of these information may be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

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