On the Reactivity of the Iminodiphosphane $C_6H_4(o\text{-}CN)N{=}PPh_2{-}PPh_2$: Fragmentation Versus Isomerisation

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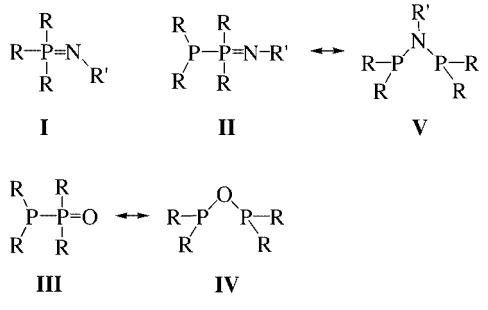
The reactivity of the iminodiphosphane $C_6H_4(o\text{-}CN)N{=}PPh_2{-}PPh_2$, which contains an N=P–P unit, has been investigated. Reaction with small molecules, [viz. H_2O/O_2, H_2O_2, CH_3OH, $C_6H_4(o\text{-}CN)NH_2$] and elemental sulfur result in cleavage of the P–P bond to give aminophosphane-derivatised compounds. The products from these reactions have been characterized spectroscopically, including two by single-crystal X-ray diffraction. The reactivity of the iminodiphosphane towards the transition metal complexes $[M(cod)Cl_2]$ (M = Pd or Pt) has also been investigated. In the reactions, the iminodiphosphane rearranges to form the more common diphosphonylamine (P–N–P) unit which chelates to the metal centres. Three different compounds were isolated from these reactions and they have all been fully characterised by spectroscopy and single-crystal X-ray diffraction.

Introduction

Iminophosphorus compounds such as iminophosphoranes $R_3P{=}NR'$ (I in Scheme 1) act as monodentate ligands using the lone pair at the N-centre.[1] Because the phosphorus centre is formally in the +5 oxidation state, it is rarely involved in coordination to transition metal centres, although the P=N unit has been observed to act as a π-donor.[2] Iminodiphosphanes with $PR_2{-}PR_2{=}NR'$(**II**) backbones are isoelectronic to oxodiphosphanes with $PR_2{-}PR_2{=}O$ (**III**) skeletons. Oxodiphosphanes are useful compounds, since they can rearrange on coordination to transition metals to give diphosphoxanes $PR_2{-}O{-}PR_2$ (**IV**), which act as bidentate ligands.[3] Diphosphoxanes are otherwise difficult to produce due to the Arbuzov rearrangement and their instability towards disproportionation. Iminodiphosphanes are the unstable isomers of diphosphonylamines, which have a $PR_2{-}NR'{-}PR_2$ (**V**) skeleton. Diphosphonylamines are widely used as ligands,[4] with the ability to chelate to various transition metal centres,[5] and such compounds have been reviewed in detail.[6] Some diphosphonylamine complexes have been evaluated as catalysts in, for example, asymmetric hydrogenation and hydroformylation reactions,[7] and much of the recent research has focused on either chiral ligands[8] or functionalized diphosphonylamines with additional donor centres.[9]



Scheme 1

Although iminodiphosphanes have been known for many decades,[10] they have not been studied to the same extent as oxodiphosphanes or diphosphonylamines. This could be because they are generally less stable than these other compounds; some iminodiphosphanes are pyrophoric.[11] Reactivity studies on iminodiphosphanes are essentially concerned with the rearrangement from N=P−P to P−N−P that takes place in the presence of organic bases.[12] Compared to a large number of reports on coordination chemistry of P−O−P and P−N−P ligands, we are not aware of any related studies with iminodiphosphanes, although one could envisage that the phorphorus(III) centre should enable a rich coordination chemistry. Following our recent report on the synthesis of the iminodiphosphane $C_6H_4(o\text{-}CN)N{=}PPh_2{-}PPh_2$ (**1**),[13] which was formed as the major product instead of the diphosphonylamine $C_6H_4(o\text{-}CN)N(PPh_2)_2$, we report herein on the reactivity of **1** towards different reagents ranging from small molecules to transition metal complexes, which lead to very different outcomes as those which we expected.

Results and Discussion

The reaction of **1** with small molecules and transition metal complexes leads to two different outcomes. In all re-

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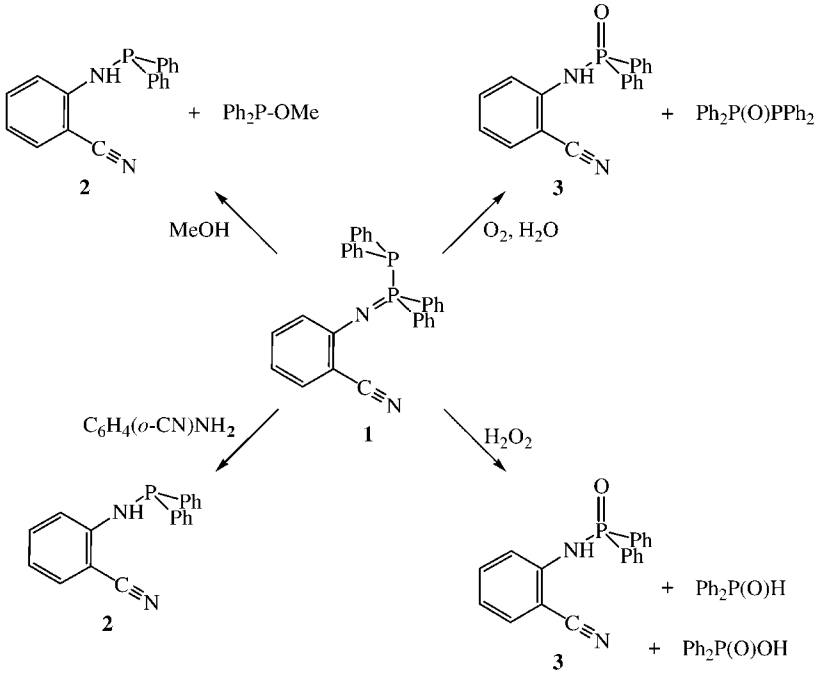
actions cleavage of the P−P bond takes place, but in the reactions with transition metal complexes P−P bond cleavage is accompanied by the formation of a new N−P bond.

Reactions of $C_6H_4(o\text{-CN})N{=}PPh_2{-}PPh_2$ (1) with Small Molecules

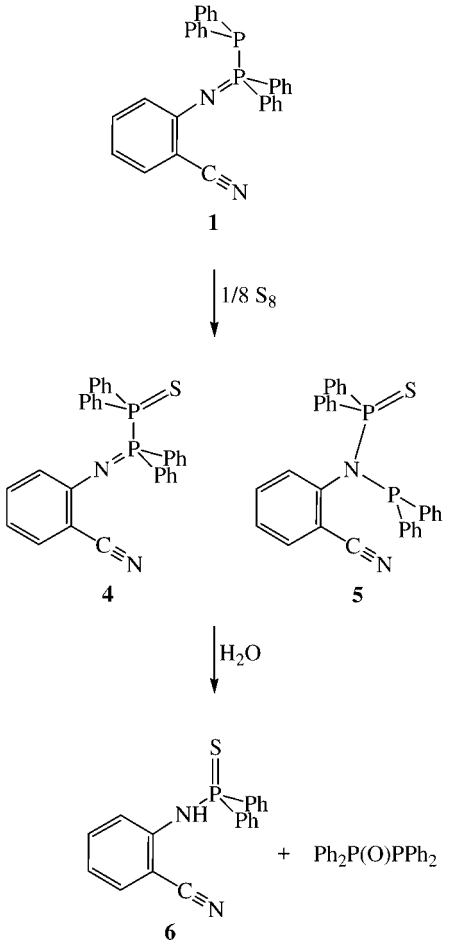
The iminodiphosphane **1** is stable in the solid state, but in solution it decomposes rapidly on exposure to air or moisture. In methanol, **1** decomposes immediately to form the aminophosphane precursor **2** and $Ph_2P{-}OMe$, as indicated by ^{31}P NMR spectroscopy which exhibits characteristic resonances at δ = 29.5 and 117.6 ppm, respectively.[14] Over a prolonged period, the only remaining phosphorus containing compound that is observed is $Ph_2P{-}OMe$ (Scheme 2). If a sample of **1** in CH_2Cl_2 is exposed to air or moisture, it slowly hydrolyses to the aminophosphane **2**, which reacts further to form the oxide [$C_6H_4(o$-CN)$NHPPh_2(O)$] (**3**). The other product observed in the reaction is $Ph_2P(O)PPh_2$, as evidenced by ^{31}P NMR spectroscopy, which exhibits two doublets centred at δ = −21.1 and 36.0 ppm ($^1J_{P,P}$ = 225 Hz).[14] The reaction of **1** with H_2O_2 is somewhat more complicated. In addition to the aminophosphane **2** and the oxide **3**, the ^{31}P NMR spectrum shows the presence of $Ph_2P(O)H$ and $Ph_2P(O)OH$ as indicated by signals at δ = 20 and 34 ppm, respectively.[14] Compound **1** also reacts with $C_6H_4(o\text{-CN})NH_2$ in $CDCl_3$ to form the aminophosphane **2** in quantitative yield; in this case, traces of HCl from the solvent may serve as catalysts leading to the cleavage of the P−P bond; a similar reaction has been previously reported.[12]

The reaction of **1** with elemental sulfur gave mixtures of several products. Attempts to isolate a pure product afforded [$C_6H_4(o$-CN)$NHPPh_2(S)$] (**6**; Scheme 3). Since it has previously been reported that treatment of iminodiphosphanes with elemental sulfur give N=P−P=S derivatives,[10] it is not unreasonable to assume that **6** and $Ph_2P(O)PPh_2$ could form via intermediates **4** or **5** (Scheme 3) by hydrolysis. The reaction was monitored by ^{31}P NMR spectroscopy over 24 hours. At the start of the reaction, two doublets at δ = 6.0 and 32.5 ppm ($^1J_{P,P}$ = 73.5 Hz) are observed. The coupling value is between that of an N=P−P=S intermediate similar to **4**, (ca. 30 Hz),[10] and that of type **5** compounds (ca. 100 Hz).[15] Few examples of related compounds are known[16] and it is therefore difficult to interpret the NMR spectroscopic data more fully. The intermediate could not be isolated. We must therefore speculate that while both could be involved, analogues of **5** are quite stable, and hence, **4** is more likely. It is worth noting that both **3** and **6** can be obtained in quantitative yield by reaction of **2** with H_2O_2 or elemental sulfur, respectively, using literature methods.[17]

The solid-state structures of **3** and **6** have been established by single-crystal X-ray diffraction and details of the structure determination are given in Table 1. Crystals of **3** were grown from diethyl ether and crystals of **6** were grown from dichloromethane/diethyl ether by slow evaporation. The structures of **3** and **6** are illustrated in Figures 1 and 2,



Scheme 2. Reaction of **1** with MeOH, O_2/H_2O, H_2O_2 and $C_6H_4(o\text{-CN})NH_2$



Scheme 3. Reaction of **1** with elemental sulfur showing the possible intermediates

respectively, and key bond parameters are given in the captions.

There are two independent molecules in the asymmetric unit of **3**. The P−N distances average 1.652(6) and 1.6773(15) Å in **3** and **6**, respectively, which is within the range usually found in related compounds.[18] The O-atom forms strong intermolecular N−H···O hydrogen bonds [N1A···O1B 2.788(7), N1B···O1AA 2.804(8) Å; N1A−H1A···O1B 161°, N1B−H1B···O1AA 152°], which, by symmetry, gives a polymeric one-dimensional chain along the base vector [1 0 1]. Interestingly, the N-atom of the CN group in **3** forms weak hydrogen bonds with the hydrogen atoms of a phenyl ring. In **6**, the hydrogen bond network similar to that observed in compound **2** (previously reported),[13] leads to a dimeric structure obtained through N−H···NC interactions [N···N, 3.098(2) Å; N−H···N, 151°]. The CN triple bond lengths in **3** and **6** are the same [1.140(10) versus 1.149(2) Å], and not significantly different from the free aminophosphane **2** [1.152(2) Å].

Reactions of C_6H_4(*o*-CN)N=PPh_2−PPh_2 (1) with Transition Metal Complexes

The reaction of **1** with [M(cod)Cl_2] (M = Pd or Pt, cod = cycloocta-1,5-diene) in equimolar quantities affords [M{C_6H_4(*o*-CN)N(PPh_2)$_2$}Cl_2], M = Pd (**7**), M = Pt (**8**), as the main products (Scheme 4). The synthesis of compounds **7** and **8** was followed by ^{31}P NMR spectroscopy, and in the reaction of **1** with [Pd(cod)Cl_2] in dichloromethane, for example, besides the main signal at δ = 39 ppm, another signal at δ = 64.2 ppm with low intensity was also observed. This peak probably corresponds to the free diphosphonylamine C_6H_4(*o*-CN)N(PPh_2)$_2$ (cf. the chemical shift of C_6H_4(*o*-OCH_3)N(PPh_2)$_2$ is δ = 65.6 ppm,[15] and C_6H_5N(PPh_2)$_2$ is δ = 67.7 ppm[19]). The ^{31}P NMR spectrum of **8** exhibits a signal at δ = 27.0 ppm ($^1J_{P,Pt}$ = 3377 Hz) typical of similar compounds, and there does not appear to be a significant influence on the chemical shift by virtue of the CN group.[20] The reaction of [M(cod)Cl_2] (M = Pd or Pt) with a series of iminodiphosphanes with electron-withdrawing groups[13b] have been followed by ^{31}P NMR spectroscopy. In one case, in the reaction between [Pt(cod)Cl_2] and C_6H_4(*o*-CF_3)N=PPh_2−PPh_2, the rate is sufficiently slow to reveal two doublets centred at δ = 65.0 ($J_{P\text{-}P}$ = 68 Hz) and 30.5 ($J_{P\text{-}P}$ = 68 Hz) ppm, which are tentatively ascribed to an intermediate in which the intact iminodiphosphane coordinates to the platinum. This assignment is based on the low value of the $J_{P\text{-}P}$ coupling constant and the short liftime, presumably because the coordinated iminodiphosphane rapidly rearranges to the diphosphonylamine, which initially coordinates through just one phosphorus centre before yielding the final product. Efforts to quench the reaction in order to analyse the intermediates in more detail failed. After 24 hours at room temperature the signals of the starting material and the two doublets at δ = 65.0 ppm and 30.5 ppm disappeared and only one main signal at δ = 25.5 ppm corresponding to the diphosphonylamine product remained.

The reaction of [Pt(cod)Cl_2] with two equivalents of **1** affords the cationic complex [Pt{C_6H_4(*o*-CN)N(PPh_2)$_2$}$_2$]Cl_2 (**9**) in high yield. ^{31}P NMR spectroscopy suggests that in the reaction complex, **8** forms initially, and reacts with further ligand to form **9**. The $^1J_{P\text{-}Pt}$ value of **9** is much lower than that of **8** and other mono-chelated platinum complexes, but is in keeping with structurally related bis-chelated compounds.[21] In the reaction mixture, low intensity signals at δ = 27.0 and 29.0 ppm are present, which correspond to **8** and the aminophosphane **2**. An additional signal at δ = 82.0 ppm with very low intensity is present, and possibly corresponds to Ph_2PCl. This would suggest that $Ph_2P^{\cdot}$ radicals are formed, which can be treated with [Pt(cod)Cl_2] starting material or CH_2Cl_2 solvent. The source of the chloride is more likely from [Pt(cod)Cl_2] as Ph_2PCl is also observed when the reaction is carried out in THF. The analogous reaction of **1** with [Pd(cod)Cl_2] does not give an analogous compound to **9**, possibly due to the smaller size of the palladium metal ion or the weaker Pd−P bond relative to platinum. Although we speculate that complexes **7**−**9** could be formed through the N=P−P−Pd or N=P−P−Pt intermediate, we were unable to obtain any evidence for their formation, even when the reactions were carried out at −20 °C.

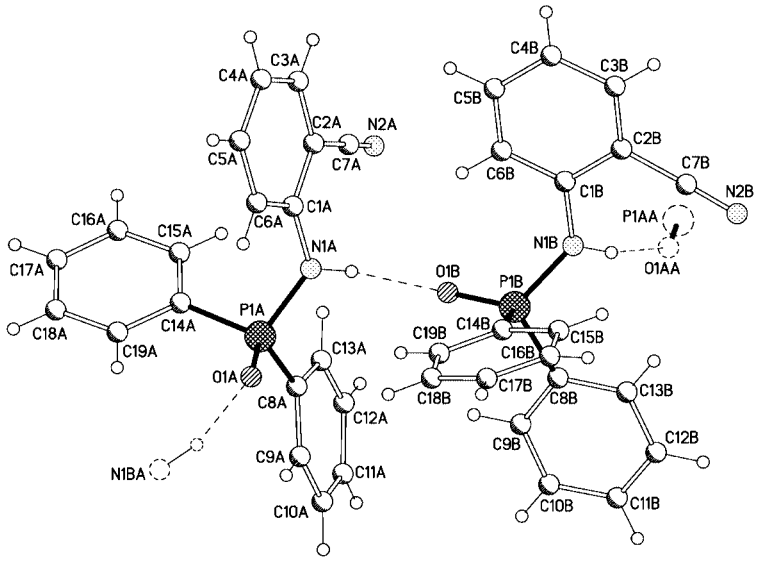


Figure 1. Molecular structure of **3** in the solid state; key bond lengths (Å) and angles (°) include: P1A−O1A 1.496(5), P1A−N1A 1.653(6), N1A−C1A 1.413(9), N2A−C7A 1.140(10), P1B−O1B 1.491(5), P1B−N1B 1.651(6), N1B−C1B 1.430(9), N2B−C7B 1.143(10); O1A−P1A−N1A 117.6(3), C1A−N1A−P1A 124.1(5), O1B−P1B−N1B 117.8(3), C1B−N1B−P1B 124.2(5); the second letter in the numbering scheme concerns the following symmetry transformation: $x - 1/2, -y + 1/2, z - 1/2$

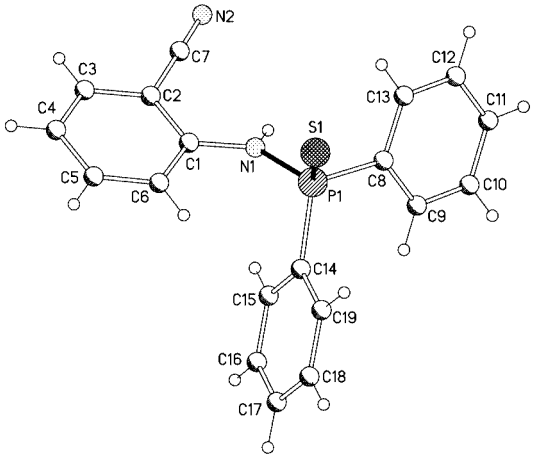
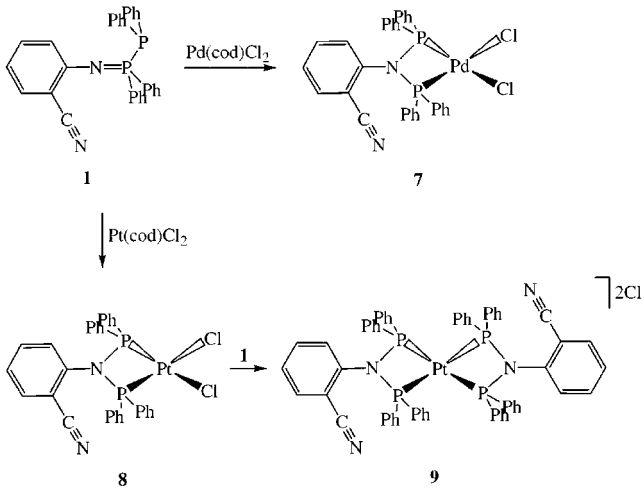


Figure 2. Molecular structure of **6** in the solid-state; key bond lengths (Å) and angles (°) include: S1−P1 1.9390(7), P1−N1 1.6773(15), N1−C1 1.399(2), N2−C7 1.149(2); N1−P1−S1 115.08(6), C1−N1−P1 126.84(13)



Scheme 4. Reaction of **1** with $[M(cod)Cl_2]$ (M = Pd or Pt)

Complex **7** forms good quality crystals suitable for X-ray determination from dichloromethane/thf solution at 0 °C. Crystals of complex **8** were obtained from dichloromethane/diethyl ether solution at 0 °C. Though the two structures could be isotypical, they have different space groups due to the cocrystallisation of different solvents with **7**. Two independent molecules lie within the asymmetric unit of **8**. There are close similarities between **7** and **8** shown in Figures 3 and 4, respectively. Both structures have a *cis*-chelating $C_6H_4(o\text{-}CN)N(PPh_2)_2$ ligand and two chloride ligands around the metal centres. The Pd−Cl/Pt−Cl and Pd−P/Pt−P bond lengths are all normal,[15,18,20] and the P1−N1−P2, and P1−Pd1−P2 angles as well as the P1···P2 distance in the palladium complex **7** compare very well with those found for **8** (see captions for details) and they are all within the range usually found in the related complexes.[15,18,20]

Compound **9** crystallises within a few minutes in a solvent mixture of dichloromethane and diethyl ether at −22 °C. The crystal architecture is composed of the dication, two chloride anions and eight dichloromethane molecules which form a *pseudo*-crown topology around the cation (Figure 5). The Pt metal centre lies on the inversion centre and this, in turn, imposes exact planar geometry at the metal centre although the bite angle of 71.51(3)° required by the chelating diphosphonylamine ligands causes a slight deviation from the idealised geometry. The phosphorus centres within each ligand are also close, the P1···P2 distance being 2.6919(11) Å, significantly longer than in **7** and **8**. The Pt−P bond lengths in **9** are equivalent with an aver-

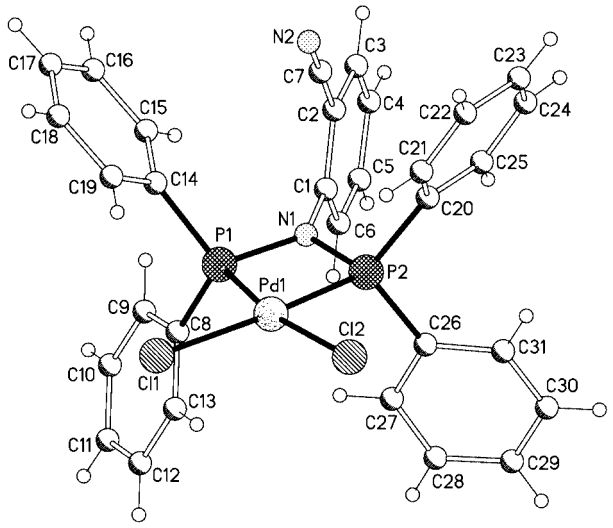


Figure 3. Molecular structure of **7** in the solid state; key bond lengths (Å) and angles (°) include: Pd1−P2 2.211(2), Pd1−P1 2.225(2), Pd1−Cl2 2.344(2), Pd1−Cl1 2.349(2), P1···P2 2.624(3), P1−N1 1.705(5), P2−N1 1.709(6), N1−C1 1.442(8), N2−C7 1.134(9); P2−Pd1−P1 72.53(8), Cl2−Pd1−Cl1 94.04(9), P1−N1−P2 100.4(3), C1−N1−P1 131.6(5), C1−N1−P2 127.9(5)

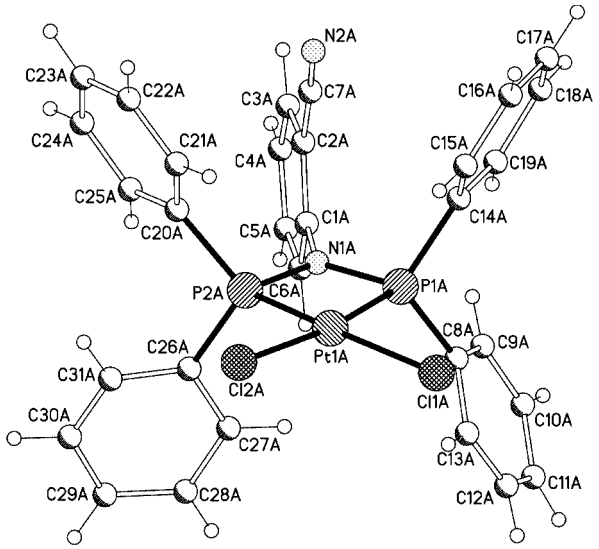


Figure 4. Molecular structure of **8** in the solid-state (showing one of the two independent molecules); key bond lengths (Å) and angles (°) include: Pt1A−P2A 2.208(5), Pt1A−P1A 2.217(4), Pt1A−Cl2A 2.325(4), Pt1A−Cl1A 2.357(5), P1A···P2A 2.639(6), P1A−N1A 1.716(15), P2A−N1A 1.692(14), N1A−C1A 1.45(3), N2A−C7A 1.16(2), Pt1B−P2B 2.200(5), Pt1B−P1B 2.205(5), Pt1B−Cl2B 2.336(5), Pt1B−Cl1B 2.345(5), P1B···P2B 2.620(7), P1B−N1B 1.709(15), P2B−N1B 1.687(15), N1B−C1B 1.42(2), N2B−C7B 1.14(2); P2A−Pt1A−P1A 73.24(17), Cl2A−Pt1A−Cl1A 91.8(2), P2A−N1A−P1A 101.5(8), C1A−N1A−P2A 126.9(11), C1A−N1A−P1A 131.4(11), P2B−Pt1B−P1B 73.00(18), Cl2B−Pt1B−Cl1B 91.48(19), P2B−N1B−P1B 101.0(8), C1B−N1B−P2B 126.4(12), C1B−N1B−P1B 132.2(12)

age length of 2.3035(9) Å. There is an extensive network of hydrogen-bonding interactions; the most important seem to comprise those between the chloride anions and dichloromethane solvent. Intra- and intermolecular hydrogen-bond-

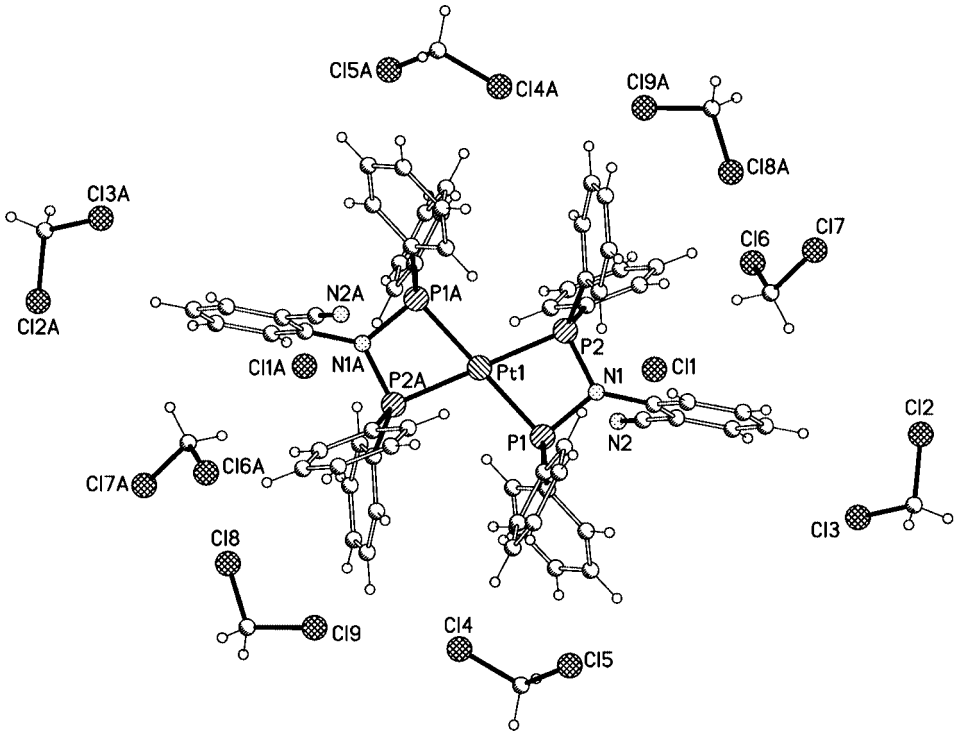


Figure 5. Molecular structure of **9**·8CH_2Cl_2 in the solid-state; key bond lengths (Å) and angles (°) include: Pt1−P1 2.3046(8), Pt1−P2 2.3025(8), P1−N1 1.718(2), P2−N1 1.713(3), N1−C1 1.445(4), N2−C7 1.148(4); P2A−Pt1−P1 108.49(3), P2−Pt1−P1 71.51(3), N1−P1−Pt1 92.33(9), N1−P2−Pt1 92.54(9), C1−N1−P2 126.95(19), C1−N1−P1 128.3(2), P2−N1−P1 103.34(14); letter A indicates the following symmetry transformation: $-x, -y, -z$

ing interactions in a number of related platinum and palladium phosphane complexes have been reported previously.[22]

Concluding Remarks

In conclusion, we have examined the reactivity of $C_6H_4(o\text{-CN})N{=}PPh_2{-}PPh_2$ (**1**) towards small molecules and transition metal complexes. All the reactions carried out show that the P−P bond is easily cleaved. The reactions with small molecules give products with a P−NH backbone. In the presence of transition metals, rearrangements forming a P−N−P skeleton take place, a new type of reaction in this intensively explored field.

Experimental Section

All manipulations were performed under an inert atmosphere of dry nitrogen using standard Schlenk techniques. The iminodiphosphane $C_6H_4(o\text{-CN})N{=}PPh_2{-}PPh_2$ (**1**) and $C_6H_4(o\text{-CF}_3)N{=}PPh_2{-}PPh_2$ were prepared by the literature methods[13] and all other reagents were purchased from Aldrich and used as received. Solvents were dried using the appropriate reagents and distilled prior to use. 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 Thermo-Finnigan LCQ™ Deca XP Plus quadrupole ion-trap instrument using literature methods[23] with samples infused directly into the source at 5 μL min^{-1} with a syringe pump. The spray voltage was set at 5 kV and the capillary temperature at 50 °C. Elemental analysis was carried out by the Institute of Molecular and Biological Chemistry (EPFL).

Reaction of 1 with MeOH: 1 (58 mg, 0.12 mmol) was added to MeOH (2.0 mL) at room temp. The ^{31}P NMR spectrum of the solution immediately showed the presence of two signals at δ = 29.5 and 117.6 ppm with equal intensity, corresponding to **2** and $Ph_2P{-}OMe$. After 24 h the signal at δ = 29.5 ppm disappeared leaving only the signal at δ = 117.6 ppm.

Reaction of 1 with O_2/H_2O: A sample containing **1** (195 mg, 0.40 mmol) in CH_2Cl_2 (5.0 mL) was exposed to air for two days. The resulting solid was then washed with diethyl ether (2 × 5.0 mL). The filtrates were collected and solvent was removed in vacuo. The remaining solid was washed with diethyl ether (2 × 2.0 mL). After slow evaporation of solvent, crystals of **3** were obtained, which were suitable for X-ray structure analysis. Yield 21 mg, 18 %. M.p. 168 °C. ^1H NMR (ppm in $CDCl_3$): δ = 6.70−8.15 (m, aromatic H), 5.50 (1 H, broad signal, NH) ppm. ^{31}P NMR (ppm in $CDCl_3$): δ = 20.5 (s) ppm. ESI-MS: *m/z*: 319 $[M + H]^+$. $C_{19}H_{15}N_2OP$ (318.3): calcd. C 71.69, H 4.75, N 8.80; found C 71.63, H 4.87, N 8.79.

Reaction of 1 with H_2O_2: An excess of H_2O_2 (0.20 mL, 30 %) was added at 0 °C to a solution of **1** (195 mg, 0.40 mmol) in CH_2Cl_2 (5.0 mL). The solvent was then removed and the resulting solid was recrystallised from dichloromethane and diethyl ether to give **3**. Yield 25.0 mg, 20 %.

Reaction of 1 with C_6H_4(o-CN)NH_2: A solution of **1** (486 mg, 1.0 mmol) and C_6H_4(o-CN)NH_2 (118 mg, 1.0 mmol) in $CDCl_3$ (5.0 mL) was stirred at room temp for 24 h. The ^{31}P NMR spectrum shows the full conversion of **1** into **2**. The solvent was removed in vacuo to give **2**. Yield 602 mg, 99 %. Spectroscopic data were in excellent agreement with that reported in ref.[13a]

Reaction of 1 with S_8: A sample containing **1** (195 mg, 0.40 mmol) and elemental sulfur (13 mg, 0.40 mmol) in CH_2Cl_2 (5.0 mL) was stirred at room temp for 24 h and then exposed to the air for 24 h. The resulting oily product was washed with diethyl ether (2 × 5.0 mL) to give a colourless solid. Recrystallisation from dichloromethane and diethyl ether gave compound **6** as colourless crystals suitable for X-ray analysis. Yield 50.0 mg, 15 %. M.p. 201 °C. ^1H NMR ($CDCl_3$): δ = 6.60−8.10 (m, aromatic H), 5.5 (1 H, broad signal, NH) ppm. ^{31}P NMR ($CDCl_3$): δ = 53.9 (s) ppm. ESI-MS: *m/z*: 335 $[M + H]^+$. $C_{19}H_{15}N_2PS$ (334.4): calcd. C 68.25, H 4.52, N 8.38; found C 68.63, H 4.57, N 8.29.

Reaction of 1 with [Pd(cod)Cl_2] in 1:1 Ratio: Pd(cod)Cl_2 (14.3 mg, 0.05 mmol) was added to a solution of **1** (24.3 mg, 0.05 mmol) in dichloromethane (5.0 mL) at room temp and stirred for 30 minutes. Thf (2.0 mL) was added and the sample was placed in a freezer at 0 °C. Crystals of **7** were collected by filtration. Yield 23.5 mg, 72 %. M.p. > 285 °C (decomp.). ^1H NMR ($CDCl_3$): δ = 6.65−8.15 (m, aromatic H) ppm. ^{31}P NMR ($CDCl_3$): δ = 39.0 (s) ppm. ESI-MS: *m/z*: 664 $[M - H + Li]^+$, $C_{31}H_{24}Cl_2N_2P_2Pd$ (663.8): calcd. C 56.09, H 3.64, N 4.22; found C 56.63, H 3.69, N 4.11.

An analogous procedure was used with $C_6H_4(o\text{-CF}_3)N{=}PPh_2{-}PPh_2$. Yield 68%. M.p. 220 °C. ^1H NMR (CD_3CN): δ = 6.65−8.15 (m, aromatic H) ppm. ^{31}P NMR (CD_3CN): δ = 44.80 (s) ppm. ESI-MS: *m/z*: $[M + H]^+$. $C_{31}H_{24}Cl_2F_3NP_2Pd$ (706.8): calcd. C 52.68, H 3.42, N 1.98; found C 52.73, H 3.49, N 2.00.

Reaction of 1 with [Pt(cod)Cl_2] in 1:1 Ratio: Pt(cod)Cl_2 (17.2 mg, 0.05 mmol) was added to a solution of **1** (24.3 mg, 0.05 mmol) in dichloromethane (5.0 mL) at room temp and stirred for 30 minutes. Thf (2.0 mL) was added and the sample was placed in a freezer at 0 °C. Crystals of **8** were collected by filtration. Yield 29.3 mg, 78 %. M.p. > 285 °C (decomp.). ^1H NMR ($CDCl_3$): δ = 6.60−8.10 (m, aromatic H) ppm. ^{31}P NMR $CDCl_3$): δ = 27.0 (s, ^1J(PPt) = 3377 Hz) ppm. ESI-MS: *m/z*: 754 $[M - H + Li]^+$. $C_{31}H_{24}Cl_2N_2P_2Pt$ (752.5): calcd. C 49.48, H 3.21, N 3.72; found H C 49.63, 3.30, N 3.68.

An analogous procedure was used with $C_6H_4(o\text{-CF}_3)N{=}PPh_2{-}PPh_2$. Yield 78 %. M.p. > 285 °C. ^1H NMR ($CDCl_3$): δ = 6.65−8.15 (several multiples, aromatic H) ppm. ^{31}P NMR ($CDCl_3$): δ = 25.43 (s, ^1J(PPt) = 3350.0 Hz) ppm. ESI-MS: *m/z*: 793 $[M + H]^+$. $C_{31}H_{24}Cl_2F_3NP_2Pt$ (795.5): calcd. C 46.81, H 3.04, N 1.76; found C 46.92, H 3.08, N 1.73.

Reaction of 1 with [Pt(cod)Cl_2] in 2:1 Ratio: Pt(cod)Cl_2 (18.7 mg, 0.05 mmol) was added to a solution of **1** (48.6 mg, 0.10 mmol) in dichloromethane (5.0 mL)and stirred for 30 min at room temp. Diethyl ether (2.0 mL) was added and the reaction mixture was placed in a freezer at −22 °C. X-ray suitable crystals of **9** were obtained within a few minutes. The crystals were collected by filtration. Yield 81.0 mg, 86 %. ^1H NMR ($CDCl_3$): δ = 6.60−8.10 (m, aromatic H), 5.32 (s, CH_2Cl_2) ppm. ^{31}P NMR ($CDCl_3$): δ = 39.5 (s, $^1J_{P,Pt}$ = 2399 Hz) ppm. ESI-MS^+ *m/z* = 1167 $[M]^+$. $C_{70}H_{64}Cl_{18}N_4P_4Pt$ (1918.4): calcd. C 43.83, H 3.36, N 2.92; found H 3.40, C 43.94, N 2.89.

An analogous procedure was used with $C_6H_4(o\text{-CF}_3)N{=}PPh_2{-}PPh_2$. Yield 51 %. M.p. 260 °C. ^1H NMR ($CDCl_3$): δ = 6.65−8.15 (m, aromatic H) ppm. ^{31}P NMR ($CDCl_3$): δ = 44.0 (s, ^1J(PPt) = 2400.0 Hz) ppm. ESI-MS: *m/z*: 1252 $[M]^+$. $C_{62}H_{48}Cl_2F_6N_2P_4Pt$ (1325.0): calcd. C 56.20, H 3.65, N 2.11; found C 56.32, H 3.68, N 2.13.

X-ray Characterization: X-ray measurements were performed on a 4-circle kappa goniometer equipped with an Oxford Diffraction KM4 Sapphire CCD (**3**, **6**, **9**) and on a marresearch mar345 IPDS (**7**, **8**) at 140 K; **7** was collected at room temp. A summary of the crystallographic data and the structure refinements is listed in Table 1 and relevant geometrical parameters, including bond lengths and angles are included into the figure captions. Data reduction was carried out with CrysAlis RED, release 1.6.9.[24] Absorption correction[25] was applied to all data sets but **6**. Structure solutions of **3**, **8** and **9** by SIR92,[26] **6** by SHELXS-97[27] and **7** by SIR97.[28] Structure refinement as well as molecular graphics and geometrical calculations were performed for all structures with the SHELXTL software package, release 5.1.[29] The structures were refined using the full-matrix least-squares on F^2 with all non-H atoms anisotropically defined. H atoms were placed in calculated positions using the "riding model'. Some disorder problems were encountered during the refinement of **7** and **8**. In the case of **7**, THF molecules were disordered over the inversion centre with 50 % occupation and in order to get reasonable parameters some geometrical restraints were employed, whereas for **8** the whole structure has undergone "rigid bond'' restraints. CCDC-201872 (**9**) and -209134 ... -209137 (**3**, **6**, **7**, **8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033: E-mail: deposit@ccdc.cam.ac.uk].

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Table 1. Crystal data and details of the structure determination for **3**, **6**, **7**·2thf, **8** and **9**·8CH_2Cl_2

	3	**6**	**7**·2thf	**8**	**9**·8CH_2Cl_2
Chemical formula	$C_{19}H_{15}N_2OP$	$C_{19}H_{15}N_2PS$	$C_{39}H_{40}Cl_2N_2O_2P_2Pd$	$C_{31}H_{24}Cl_2N_2P_2Pt$	$C_{70}H_{64}Cl_{18}N_4P_4Pt$
Molecular weight	318.30	334.36	807.97	752.45	1918.32
Crystal system	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$I2/a$	$P\bar{1}$	$P2_1$	$P2_1/n$
a (Å)	14.0346(18)	15.3909(12)	11.456(5)	10.957(4)	13.0331(6)
b (Å)	16.758(4)	9.3846(8)	11.481(4)	14.671(6)	21.2595(11)
c (Å)	14.748(3)	23.2452(13)	16.953(9)	17.6483(18)	15.7534(8)
α (°)	90	90	79.94(4)	90	90
β (°)	101.477(14)	95.181(6)	74.77(4)	96.912(19)	109.556(5)
γ (°)	90	90	61.87(5)	90	90
V (Å^3)	3399.4(12)	3343.7(4)	1893.9(15)	2816.4(15)	4113.1(3)
Z	8	8	2	4	2
$D_{calcd.}$ (g·cm^{-3})	1.244	1.328	1.417	1.775	1.549
F(000)	1328	1392	828	1464	1912
μ (mm^{-1})	0.167	0.289	0.751	5.310	2.410
T (K)	140	140	293	140	140
Wavelength (Å)	0.71073	0.71073	0.71070	0.71070	0.71073
Measured reflections	20002	9267	11515	16532	23617
Unique reflections	5686	2936	6262	9241	6869
Unique reflections [$I > 2\sigma(I)$]	1907	2462	2635	6194	5681
Data/parameters	5686/415	2936/208	6262/443	9241/686	6869/439
R_1 [a] [$I > 2\sigma(I)$]	0.0851	0.0354	0.0470	0.0571	0.0254
wR_2 [a] (all data)	0.1368	0.0957	0.1100	0.1522	0.0729
GooF[b]	0.943	1.072	0.812	1.053	1.102

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$. [b] GooF $= [\Sigma w(F_o^2 - F_c^2)^2/(n\text{-}p)]^{1/2}$ where n is the number of data and p is the number of parameters refined.

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