

# The first examples of metal-mediated addition of a phosphorus imine to nitriles; the preparation and X-ray crystal structures of $[\text{PtCl}_4\{\text{NH}=\text{C}(\text{Et})\text{N}=\text{PPh}_3\}_2]$ and $[\text{PtCl}_2(\text{EtCN})\{\text{NH}=\text{C}(\text{Et})\text{N}=\text{PPh}_3\}]$

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Imino(triphenyl)phosphorane,  $\text{Ph}_3\text{P}=\text{NH}$  (**1**), reacts with nitrile complexes of Pt(IV) to generate hydrolytically sensitive  $[\text{PtCl}_4\{\text{NH}=\text{C}(\text{R})\text{N}=\text{PPh}_3\}_2]$  ( $\text{R} = \text{Me}$  **2a**,  $\text{Et}$  **2b**,  $\text{Ph}$  **2c**), and with the Pt(II) complex  $[\text{PtCl}_2(\text{EtCN})_2]$  to give  $[\text{PtCl}_2(\text{EtCN})\{\text{NH}=\text{C}(\text{Et})\text{N}=\text{PPh}_3\}]$  (**3**) and  $[\text{PtCl}_2\{\text{NH}=\text{C}(\text{Et})\text{N}=\text{PPh}_3\}_2]$  (**4**); X-ray crystallography performed upon (**2b**) and (**3**) confirms the presence of an imine/nitrile addition ligand bound by the terminal nitrogen.

The ability of some metal centres to activate nitriles towards nucleophilic attack is now well documented<sup>1</sup> and constitutes an important synthetic route to a diverse range of nitrile/nucleophile addition products, many of which can not be generated by metal-free organic synthetic means. Within such metal-mediated reaction systems, the most commonly employed strategy involves the formation of a C–N bond. Recent examples include addition of ammonia,<sup>2a</sup> amines<sup>2b</sup> and nitrogen heterocycles<sup>2c</sup> to the ligated RCN unit, while metal-mediated nitrile–amine coupling has been identified as a key intermediate step in the formation of imidoylimine(ato) complexes<sup>2d</sup> and phthalocyanines.<sup>2e</sup>

In contrast, examples of nitrile/heteroimine coupling are much rarer; in one such case, part of the current author team showed that N-bound monodentate ligands of the type  $\text{PhR}'\text{C}=\text{N}-\text{C}(\text{R})=\text{NH}$  ( $\text{R}' = \text{Ph}$ ,<sup>3a</sup>  $\text{OAlk}$ <sup>3b</sup>) result from Pt(IV) mediated addition of  $\text{PhR}'\text{C}=\text{NH}$  to RCN. Examples wherein the imine heteroatom originates from Period 3 are so far limited to reactions of the sulfimide  $\text{Ph}_2\text{S}=\text{NH}$  (Fig. 1(a)). Kelly *et al.* observed the formation of both monodentate and bidentate ligands of type  $\text{Ph}_2\text{S}=\text{NC}(\text{R})=\text{NH}$  *via* Pt(II) mediated coupling of the sulfimide to nitriles<sup>4</sup> and subsequent joint work between the two groups extended the latter reactions to Pt(IV) systems

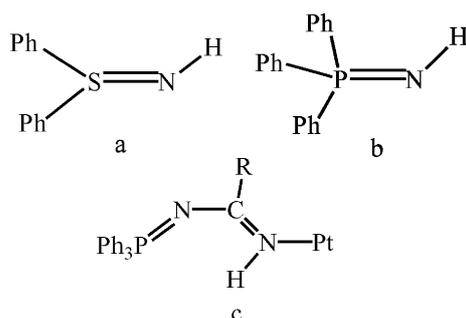


Fig. 1 Structures of  $\text{Ph}_2\text{S}=\text{NH}$  (a) and  $\text{Ph}_3\text{P}=\text{NH}$  (b) together with the new ligands formed in this study (c).

and to derivatised sulfimides, revealing a rich chemistry for the resulting heterodiazadienes, both in ligated and free form.<sup>5</sup>

The observations upon the reactivity of  $\text{Ph}_2\text{S}=\text{NH}$  in such circumstances raises the question of whether other examples of heteroimines bearing atoms from Period 3 can participate in this type of metal-mediated coupling. Though a range of transition-metal complexes of the phosphorus imine  $\text{Ph}_3\text{P}=\text{NH}$  (**1**) (Fig. 1(b)) are known<sup>6</sup> there appear to be no examples of reactions in which the metal mediates addition of the incoming imine to bound nitriles. In order to address this issue we have investigated the reactivity of **1** towards  $[\text{PtCl}_n(\text{RCN})_2]$  ( $n = 2, 4$ ).<sup>†</sup>

Reaction of **1** with  $[\text{PtCl}_4(\text{RCN})_2]$  ( $\text{R} = \text{Me}$ ,  $\text{Et}$ ,  $\text{Ph}$ ) at low temperature readily generates  $[\text{PtCl}_4\{\text{NH}=\text{C}(\text{R})\text{N}=\text{PPh}_3\}_2]$  ( $\text{R} = \text{Me}$  **2a**,  $\text{Et}$  **2b**,  $\text{Ph}$  **2c**). The pale yellow products are moisture sensitive; thus in the case of the most soluble of the complexes, **2b**, after 3 h in solution the formation of  $\text{Ph}_3\text{P}=\text{O}$  can be observed by <sup>31</sup>P NMR and an insoluble precipitate of  $[\text{PtCl}_4\{\text{NH}=\text{C}(\text{Et})\text{NH}_2\}_2]$  results.<sup>5</sup> X-Ray crystallography performed upon **2b** confirms that addition of the phosphorus imine to the original nitrile has taken place, generating the  $\text{HN}=\text{C}(\text{Ph})\text{N}=\text{PPh}_3$  ligand (Fig. 1(c)) (*via* formation of a C–N bond and proton migration) which coordinates to the Pt centre through the terminal nitrogen atom (Fig. 2).<sup>‡</sup> The resulting (triphenylphosphoranylidene)butan-2-imine ligands are situated *trans* to each other (presumably dictated by steric factors) and adopt a *Z*-configuration.

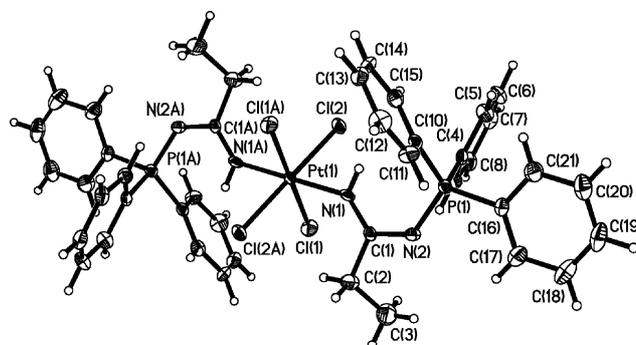


Fig. 2 The crystal structure of **2b**.

Reaction of **1** with the Pt(II) complex  $[\text{PtCl}_2(\text{EtCN})_2]$  also results in imine/nitrile coupling, though in this case the reaction is slower than for Pt(IV) and the product varies with the solvent system. In neat EtCN the result is  $[\text{PtCl}_2(\text{EtCN})\{\text{NH}=\text{C}(\text{Et})\text{N}=\text{PPh}_3\}]$  (**3**), isolated in *ca.* 50% yield, while reaction in

a  $\text{CH}_2\text{Cl}_2$ –EtCN mixture generates a slightly larger yield of  $[\text{PtCl}_2\{\text{NH}=\text{C}(\text{Et})\text{NPPH}_3\}_2]$  (**4**).<sup>†</sup> Both compounds are substantially more stable towards water than (**2**) and X-ray crystallography, performed upon complex (**3**), again confirms the presence of the imine/nitrile addition product as ligand (Fig. 3).<sup>‡</sup> In this case it adopts an *E*-configuration and is located *trans* to an unreacted nitrile group on the square-planar platinum.

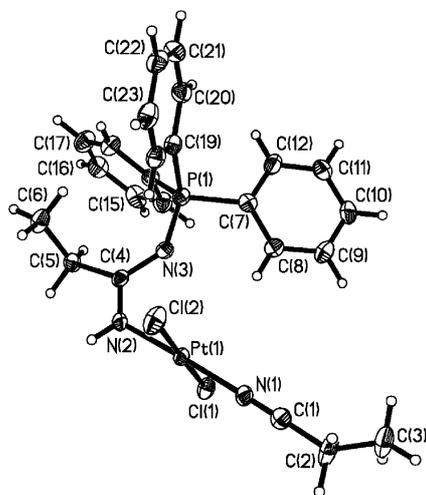


Fig. 3 The crystal structure of **3**.

The bond distances within the new ligands in **2b** and **3** are broadly consistent with a localised  $\text{N}(\text{I})=\text{C}(\text{I})-\text{N}(\text{II})=\text{P}(\text{I})$  bonding arrangement within the ligand backbone. The most significant difference in bond lengths between the two structures is associated with the metal-bound nitrogen atoms of the new ligands. In the case of **3**  $\text{Pt}-\text{N}$  is significantly shorter than for **2b**, consistent with the nitrile possessing a weaker *trans* labilising ability than the imine/nitrile adduct.

Free species of the type  $\text{Ph}_3\text{P}=\text{NC}(\text{R})=\text{NH}$  are known (though no coordination chemistry has been reported), but may only be prepared by direct reaction of imine with nitrile when the latter is activated by a very electron-withdrawing R group (such as  $\text{CCl}_3$  or  $\text{CF}_3$ ).<sup>7</sup> Formation of other examples uses more involved techniques, typically the reaction of *N*-chlorobenzamides ( $\text{ArC}(\text{=NCl})\text{NH}_2$ ) with  $\text{PPh}_3$  and base; this of course requires prior preparation of the *N*-chlorobenzamides.<sup>8</sup> The resulting heterodiazadienes have become the subject of some considerable interest thanks to their ability to act as sources of  $\text{Ar}-\text{C}(\text{N})\text{N}$  moieties during cyclisation reactions. By way of example, Rossi *et al.* have shown that  $\text{Ph}_3\text{P}=\text{NC}(\text{Ph})=\text{NH}$  is an effective reagent for the one-pot synthesis of dihydropyrimidines and pyrimidines *via* reaction with both acyclic and cyclic  $\alpha,\beta$ -unsaturated aldehydes.<sup>9</sup>

The platinum-mediated reactions thus provide novel and very facile routes to potential synthons—and platinum does appear key to the success of the technique, as identical reactions involving  $[\text{PdCl}_2(\text{EtCN})_2]$  result simply in the substitution product  $[\text{PdCl}_2(\text{HN}=\text{PPh}_3)_2]$ . Furthermore, the results of the study confirm that heteroimine/nitrile coupling using imines containing heavier (*i.e.* Period 3) atoms is not just limited to the sulfimides and suggests that further work in this area will be fruitful.

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K. and A. J. L. P. are grateful to the FCT and the POCTI program (POCTI/QUI/43415/2001 project)(FEDER funded) for financial support of their studies. We are grateful to Johnson Matthey for loans of precious metals.

## Notes and references

<sup>†</sup> *Synthesis of 2b*: A solution of **1** (0.25 mmol) in  $\text{CH}_2\text{Cl}_2$  (0.78 mL) was added dropwise, with stirring, to a suspension of  $[\text{PtCl}_4(\text{EtCN})_2]$  (0.10 mmol) in EtCN (1 mL) cooled with liquid  $\text{N}_2$ . After being allowed to warm to ambient temperature the reaction mixture was stirred for a further 20 min before the pale yellow product was obtained by filtration; an additional yield of the product was obtained by addition of  $\text{Et}_2\text{O}$  (*ca.* 0.3 mL) to the filtrate. Yield 60–70%. Anal. Calc. for  $\text{C}_{24}\text{H}_{26}\text{N}_4\text{Cl}_4\text{Pt}$ : C, 50.36; H, 4.23; N, 5.59. Found: C, 49.89; H, 4.46; N, 5.36%.  $\text{FAB}^+\text{-MS}$ ,  $m/z$  1025  $[\text{M} + \text{Na}]^+$ , 1001  $[\text{M}]^+$ , 929  $[\text{M} - 2\text{HCl}]^+$ . IR spectrum in KBr, selected bands,  $\text{cm}^{-1}$ : 3425w br  $\nu(\text{O}-\text{H})$ , 3339m  $\nu(\text{N}-\text{H})$ , 1528s  $\nu(\text{C}=\text{N}$  and  $\text{C}=\text{C}$  from Ar), 1115ms  $\nu(\text{P}=\text{N})$ .  $^1\text{H}$  NMR in  $\text{CDCl}_3$ ,  $\delta$  7.73–7.50 (m, 15H, Ph), 5.78 (s + d,  $J_{\text{P-H}}$  37.7 Hz, 1H, NH), 2.92 (m, 2H,  $\text{CH}_2\text{CH}_3$ ) and 1.25 (t, 3H,  $\text{CH}_2\text{CH}_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR in  $\text{CDCl}_3$ ,  $\delta$  8.91 (s + d,  $J_{\text{P-P}}$  41.6 Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR was not measured because of fast decomposition in the non-dried solvent. Compounds **2a** and **2c** were prepared in similar manner, with full precipitation occurring during the course of the reaction thanks to their lower solubility. *Synthesis of 3 and 4*: A solution of **1** (0.25 mmol) in  $\text{CH}_2\text{Cl}_2$  (0.78 mL) was added dropwise, with stirring, to a solution of  $[\text{PtCl}_2(\text{EtCN})_2]$  (37.5 mg, 0.10 mmol) in EtCN (1 mL) at ambient temperature. After 15 min the resulting pale yellow precipitate was filtered off, washed with EtCN (0.3 mL) and dried in air resulting in a *ca.* 50% yield of **3**. An alternative synthesis performed in identical fashion using Pt starting material resulted in a lemon-yellow solution after 1 h of reaction. After reduction of volume and addition of  $\text{Et}_2\text{O}$  (2 mL) the precipitated yellow powder was filtered off, washed with  $\text{CH}_2\text{Cl}_2$ – $\text{Et}_2\text{O}$  (1 mL; 1 : 1, v/v) and twice with  $\text{Et}_2\text{O}$  (1 mL) and dried in air to give a *ca.* 65% yield of **4**. When the reaction was performed in  $\text{CH}_2\text{Cl}_2$  only, a broad mixture of products, including both the addition and substitution products was obtained. **3**: Anal. Calc. for  $\text{C}_{24}\text{H}_{26}\text{N}_4\text{Cl}_4\text{PtP}$ : C, 44.17; H, 4.02; N, 6.44. Calc. for  $\text{C}_{24}\text{H}_{26}\text{N}_4\text{Cl}_4\text{PtP}\cdot\text{H}_2\text{O}$ : C, 42.98; H, 4.21; N, 6.27. Found: C, 43.00; H, 4.11; N, 6.22%.  $\text{FAB}^+\text{-MS}$ ,  $m/z$  598  $[\text{M} + \text{H}]^+$ , 562  $[\text{M} - \text{Cl}]^+$ , 525  $[\text{M} - 2\text{HCl}]^+$ . IR spectrum in KBr, selected bands,  $\text{cm}^{-1}$ : 3435m br  $\nu(\text{O}-\text{H})$ , 3281ms  $\nu(\text{N}-\text{H})$ , 1564ms  $\nu(\text{C}=\text{N}$  and  $\text{C}=\text{C}$  from Ar), 1112ms  $\nu(\text{P}=\text{N})$ .  $^1\text{H}$  NMR in  $\text{CDCl}_3$ ,  $\delta$  7.67–7.52 (m, 15H, Ph), 5.05 (s, br, 1H, NH), 3.02 (dq,  $^4J_{\text{P-H}}$  2.50 Hz, 2H,  $\text{CH}_2$ ) and 2.70 (q, 2H,  $\text{CH}_2$ ), 1.31 and 1.29 (two t, 6H, two  $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR in  $\text{CDCl}_3$ ,  $\delta$  173.14 (br,  $\text{C}=\text{N}$ ), 128.68 (*p*-Ph), 128.20 (d,  $^2J_{\text{C-P}}$  28.24 Hz) and 124.90 (d,  $^3J_{\text{C-P}}$  12.50 Hz) (*o*- and *m*-Ph's), 29.72 (d,  $^3J_{\text{C-P}}$  13.85) and 7.72 (Et), 8.30 and 5.39 (Et).  $^{31}\text{P}\{^1\text{H}\}$  NMR in  $\text{CDCl}_3$ ,  $\delta$  8.53.  $^{195}\text{Pt}$  NMR in  $\text{CDCl}_3$ ,  $\delta$  2158.8 (788 Hz). **4**: Anal. Calc. for  $\text{C}_{42}\text{H}_{42}\text{N}_4\text{Cl}_4\text{PtP}_2$ : C, 54.24; H, 4.55; N, 6.03. Found: C, 54.15; H, 5.01; N, 5.84%.  $\text{FAB}^+\text{-MS}$ ,  $m/z$  931  $[\text{M}]^+$ , 894  $[\text{M} - \text{HCl}]^+$ , 858  $[\text{M} - 2\text{HCl}]^+$ . IR spectrum in KBr, selected bands,  $\text{cm}^{-1}$ : 3425m br  $\nu(\text{O}-\text{H})$ , 3327ms  $\nu(\text{N}-\text{H})$ , 1541s  $\nu(\text{C}=\text{N}$  and  $\text{C}=\text{C}$  from Ar), 1113s  $\nu(\text{P}=\text{N})$ .  $^1\text{H}$  NMR in  $\text{CDCl}_3$ ,  $\delta$  7.69–7.49 (m, 15H, Ph), 5.44 (s, br, 1H, NH), 3.06 (dq,  $^4J_{\text{P-H}}$  2.34 Hz, 2H,  $\text{CH}_2$ ), 1.29 (t, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR in  $\text{CDCl}_3$ ,  $\delta$  176.31 ( $\text{C}=\text{N}$ ), 132.53 (m, *p*-Ph and *m*-Ph), 129.72 (*o*-Ph), 33.60 (d,  $^3J_{\text{C-P}}$  12.89) and 12.12 (Et).  $^{31}\text{P}\{^1\text{H}\}$  NMR in  $\text{CDCl}_3$ ,  $\delta$  6.24.  $^{195}\text{Pt}$  NMR in  $\text{CDCl}_3$ ,  $\delta$  –1901.9 (455 Hz).

<sup>‡</sup> The X-ray diffraction data were collected with a Nonius KappaCCD diffractometer using Mo- $K\alpha$  radiation ( $\lambda = 0.71073$  Å). The structures were solved by direct (SHELXS) and refined by SHELXL program. A multiscan absorption correction based on equivalent reflections (XPREF in SHELXTL v. 6.14) was applied to all of the data. The NH hydrogens were located from the difference Fourier map. Other hydrogens were placed in idealized position and constrained to ride on their parent atom. *Crystal data for 2b*:  $\text{C}_{24}\text{H}_{26}\text{Cl}_4\text{N}_4\text{PtP}$ ,  $M = 653.44$  g  $\text{mol}^{-1}$ , monoclinic, space group  $C2/c$  (no. 15),  $a = 22.0217(3)$ ,  $b = 8.7854(5)$ ,  $c = 24.7704(10)$  Å,  $\beta = 93.0890(10)^\circ$ ,  $V = 4792.3(3)$  Å<sup>3</sup>,  $T = 120$  K,  $Z = 8$ ,  $D_c = 1.811$  g  $\text{cm}^{-3}$ ,  $\mu(\text{Mo-K}\alpha) = 6.163$  mm<sup>−1</sup>, 14991 reflections collected, 4744 unique ( $R_{\text{int}} = 0.0582$ ). The final  $R_1$  was 0.0325 [ $I > 2\sigma(I)$ ] and  $wR_2(F^2) = 0.0625$  [ $I > 2\sigma(I)$ ]. *Crystal data for 3*:  $\text{C}_{42}\text{H}_{42}\text{Cl}_4\text{N}_4\text{P}_2\text{Pt}$ ,  $M = 1001.63$  g  $\text{mol}^{-1}$ , triclinic, space group  $P\bar{1}$  (no. 2),  $a = 10.1210(2)$ ,  $b = 13.7987(4)$ ,  $c = 15.6217(4)$  Å,  $\alpha = 73.8900(10)$ ,  $\beta = 86.897(2)$ ,  $\gamma = 89.625(2)^\circ$ ,  $V = 2092.85(9)$  Å<sup>3</sup>,  $T = 100$  K,  $Z = 2$ ,  $D_c = 1.589$  g  $\text{cm}^{-3}$ ,  $\mu(\text{Mo-K}\alpha) = 3.719$  mm<sup>−1</sup>, 12933 reflections collected, 7363 unique ( $R_{\text{int}} = 0.0294$ ). The final  $R_1$  was 0.0301 [ $I > 2\sigma(I)$ ] and  $wR_2(F^2) = 0.0695$  [ $I > 2\sigma(I)$ ]. CCDC reference numbers 264823 and 264824. See <http://www.rsc.org/suppdata/dt/b5/b502970h/> for crystallographic data in CIF or other electronic format.

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