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Synthesis and characterisation of platinum(II) complexes containing heterobidentate *S*,*N*-chelating ligands: X-ray crystal structure of *cis*-[Pt{$SPPh_2N{=}C(Me)NH$-*S*,*N*}$(PMe_2Ph)_2$]Cl

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Abstract

Deprotonation of the terminal amino group in the *N*-thiophosphoryl compounds $Me_2P(S)N{=}C(NH_2)_2$ (HL^1), $Ph_2P(S)N{=}C(Me)NH_2$ (HL^2) or $Ph_2P(S)N{=}C(NH_2)_2$ (HL^3) using potassium *tert* butoxide in thf, followed by treatment with *cis*-$[PtCl_2(PR_3)_2]$ ($PR_3 = PMe_2Ph$ or $\frac{1}{2}$dppe) generates monocationic complexes *cis*-[Pt(L^n-*S,N*)$(PR_3)_2$]Cl (**1**–**6**), which have been characterised by $^{31}P\{^1H\}$ NMR, IR and FAB$^+$ mass spectroscopies, and for *cis*-[Pt(L^2-*S,N*)$(PMe_2Ph)_2$]Cl (**2**) by single crystal X-ray diffraction. The molecular structure of **2** reveals bidentate coordination of the platinum(II) centre by a bidentate *S,N*-chelating $[Ph_2P(S)N{=}C(Me)NH]^-$ anion, giving a six-membered platinacycle, which adopts a chaise-longue conformation, with a strong hydrogen-bonding interaction between the chloride counterion and the nitrogen-bound proton. ©2000 Elsevier Science Ltd All rights reserved.

Keywords: Thiophosphoryl guanidines; Platinum complexes; Crystal structures

1. Introduction

Ourselves [1,2] and others [3–8] have studied the coordination chemistry of imidodiphosphinate anions $[R_2P(E)NP(E')R'_2]^-$ (R, R$'$ = alkyl, aryl or alkoxy; E, E$'$ = oxygen, sulfur or selenium), generated from the weak acids $HN(R_2PE)(R'_2PE')$, regarded as 'inorganic' analogues of the more ubiquitous β-diketonates such as acetylacetonate. Bidentate *E,E*$'$ chelation of imidodiphosphinate ligands at d- and p-block metal centres produces hexa-atomic metallacycles; crystallographic analyses of several such metal complexes indicate substantial flexibility within the E–P–N–P–E$'$ backbone which enables the adoption of a variety of chelate ring conformations in the solid state, although planarity is rarely observed. The facile construction of imidodiphosphinate ligands, generally by the base-catalysed clipping together of $R_2P(E)NH_2$ and $R'_2P(E')Cl$ precursors or via oxidation of the parent diphosphine $R_2PNHPR'_2$ using elemental chalcogen or hydrogen peroxide, has led to applications for such ligands as metal extraction agents, NMR shift reagents and recently in a catalytic function in the aerobic co-oxidation of alkenes and aldehydes [7–10].

As a class of potentially chelating bidentate ligands, the phosphorus(V) derivatised guanidines and amidines $R_2P(E)N{=}C(X)NH_2$ (R = alkyl or aryl; E = oxygen or sulfur; X = NH_2 or alkyl) have been known for some time, but their coordination chemistry does not appear to have been well explored [11–16]. The presence in these molecules of an ionisable nitrogen-bound proton coupled with the potential for delocalisation of the resulting uninegative charge through the π-system of the anion suggests a high degree of similarity with both imidodiphosphinate and β-diketonate ligands. The combination of chalcogen and nitrogen donor atoms offered by these molecules is, however, rarely encountered in their P–N–P or carbon-backboned counterparts.

Here, we describe our studies on the coordination chemistry of the monoanions derived from $Me_2P(S)N{=}C(NH_2)_2$ (HL^1) and $Ph_2P(S)N{=}C(X)NH_2$ (X = Me (HL^2) or NH_2 (HL^3)) at platinum(II) centres, including one representative crystal structure.

2. Results and discussion

Deprotonation of the amine nitrogen atom in $HN(R_2PE)(R'_2PE)$ gives π-delocalised imidodiphosphinate anions $[R_2P(E)NP(E')R'_2]^-$ which have great propen-

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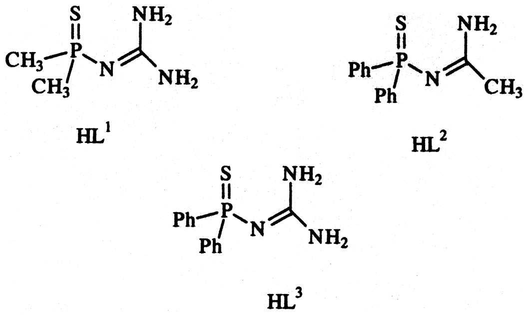

Fig. 1. Structures of the ligands $HL^{1–3}$.

sity towards bidentate *E,E′* chelation at metal centres [1–6]. We believed that the *N*-thiophosphoryl amidine (HL^2) and guanidines ($HL^{1,3}$) (Fig. 1) could in a similar way function as monobasic acids and undergo coordination to metal ions, to give chelates using a heterobidentate *S,N* donor array. To test our hypothesis we attempted to prepare platinum(II) complexes using the anions derived from $HL^{1–3}$.

Treatment of thf solutions of $HL^{1–3}$ with potassium *tert*-butoxide followed by a stoichiometric quantity of *cis*-[$PtCl_2$-$(PR_3)_2$] ($PR_3 = PMe_2Ph$ or $\frac{1}{2}$dppe) proceeds smoothly at reflux with displacement of the chloro ligands from the metal coordination sphere and chelation of the $(L^n)^-$ anion to give cationic complexes *cis*-[Pt(L^n-*S,N*)$(PR_3)_2$]Cl (**1**–**6**) isolable in moderate yields (39–65%) from dichloromethane–diethyl ether, Eq. (1).

$$\begin{aligned} &cis\text{-}[PtCl_2(PR_3)_2]+KL^n \\ &\quad \rightarrow cis\text{-}[Pt(L^n\text{-}S,N)(PR_3)_2]Cl+KCl \end{aligned} \qquad (1)$$

The platinum(II) complexes **1**–**6** are colourless (**1**, **2**) or pale yellow (**3**–**6**) solids, tolerant to air and moisture, and are highly soluble in chlorinated solvents and thf. In their FAB^+ mass spectra all of the complexes give intense peaks which correspond to an ion of composition $[PtL(PR_3)_2]^+$. The $^{31}P\{^1H\}$ NMR spectra for **1**–**6** (Table 1) contain extensive information on $^{195}Pt–^{31}P$ and $^{31}P–^{31}P$ coupling constants and are in accord with their structures; the complexes exhibit first-order AMX spin systems with platinum-195 satellites. The ^1J(Pt–P) coupling constants for the phosphine co-ligands P(2), P(3) lie in the ranges 2917–3004 Hz (P(3) *trans* sulfur) and 3234–3371 Hz (P(2) *trans* nitrogen) in accord with the weaker *trans* influence of N versus S. A similar variation in ^1J(Pt–P) values as a function of the *trans* donor atom has been observed in *cis*-[Pt(S_2N_2)$(PR_3)_2$] and *cis*-[Pt(S_2N_2H)$(PR_3)_2$]$^+$, in which the sulfur–nitrogen anions are *S,N*-bidentate at platinum(II) [17,18]. The ^2J(Pt–P) couplings for the phosphorus(V) atom P(1) of the chelate in **1**–**6** (85–102 Hz) are somewhat larger than the values we have reported in the dithio-imidodiphosphinate complexes *cis*-[Pt{$(SPPh_2)_2N$}$(PR_3)_2$]Cl (60–64 Hz for monodentate phosphines, 79 Hz for dppe) which contain *S,S′*-chelating $[(SPPh_2)_2N]^-$ anions [19]. The *cis* $^2J(P^{III}–Pt–P^{III})$ couplings for the $PhMe_2P$ complexes **1**–**3** (20–25 Hz) are larger in magnitude compared with the dppe complexes (5–10 Hz), in which there is an additional ^3J(P–P) component through the ligand backbone of opposite sign. Each of the *cis* or *trans* $^3J(P^{III}–Pt–S–P^V)$ couplings for **1**–**6** have comparable magnitudes, being between 4 and 11 Hz. Upon deprotonation and chelation the phosphorus atom P(1) of the chelate experiences modest shielding, moving ca. 15 ppm to low frequency from the free ligand value (δ_P 48.3 and 42.2 for HL^1 and HL^2 (*d*-chloroform), 42.5 for HL^3 (d_4-methanol)). Formation of the *S,N* chelate is exclusive in these instances; there is no evidence from $^{31}P\{^1H\}$ NMR spectroscopy for the formation of isomeric complexes of $(L^1)^-$ or $(L^3)^-$ in which the $[R_2P(S)NC(NH_2)NH]^-$ anion functions as an *N,N′* bidentate chelate to platinum(II) by the amino groups at the imine carbon.

In their IR spectra **1**–**6** exhibit several strong bands in the region 1400–1700 cm^{-1}; the ν_{NH} vibrations (broad bands of medium intensity between 3400–3100 cm^{-1}) and the ν_{PS} bands (ca. 562 cm^{-1} for **1** and **4**, ca. 588 cm^{-1} for **2**, **3**, **5** and **6**) are shifted only marginally from the values in the uncomplexed molecules $HL^{1–3}$ (HL^1 3377, 3142 (ν_{NH}) and 558 (ν_{PS}); HL^2 3361, 3285, 3230 (ν_{NH}) and 575 (ν_{PS}); HL^3 3437, 3350, 3299, 3201 (ν_{NH}) and 586 (ν_{PS})).

The molecular structure of *cis*-[Pt{$SPPh_2N{=}C(Me)NH$-*S,N*}$(PMe_2Ph)_2$]Cl (**2**) has been determined by single crystal X-ray diffraction, Fig. 2. The coordination sphere at the metal atom Pt(1) comprises two mutually *cis* dimethylphenylphosphine ligands, bound through P(2) and P(3), and $(L^2)^-$ ligand bound via the terminal sulfur and nitrogen atoms S(1) and N(14) to form a six-membered Pt(1)–

Table 1
$^{31}P\{^1H\}$ NMR spectral data for [Pt(L^n-*S,N*)$(PR_3)_2$]Cl (**1**–**6**) [a]

	δ_P			^1J(Pt–P)/Hz			J(P–P)/Hz		
	P(1)	P(2)	P(3)	Pt–P(1)	Pt–P(2)	Pt–P(3)	P(1)–P(2)	P(1)–P(3)	P(2)–P(3)
[Pt(L^1-*S,N*)$(PMe_2Ph)_2$]Cl (**1**)	32.2	−7.7	−22.6	92	3273	2930	11	4	22
[Pt(L^2-*S,N*)$(PMe_2Ph)_2$]Cl (**2**)	25.2	−7.7	−23.5	88	3371	2913	10	6	20
[Pt(L^3-*S,N*)$(PMe_2Ph)_2$]Cl (**3**)	28.2	−7.6	−22.5	102	3332	2938	10	[b]	25
[Pt(L^1-*S,N*)(dppe)]Cl (**4**)	48.9	38.5	30.3	3234	2997	85	6	6	10
[Pt(L^2-*S,N*)(dppe)]Cl (**5**)	52.1	37.8	24.0	3247	3003	87	10	5	5
[Pt(L^3-*S,N*)(dppe)]Cl (**6**)	50.4	38.8	26.7	3262	3004	90	8	8	8

[a] $CDCl_3$ solutions. P(1) = PS, P(2) *trans* nitrogen and P(3) *trans* sulfur.

[b] Not resolved.

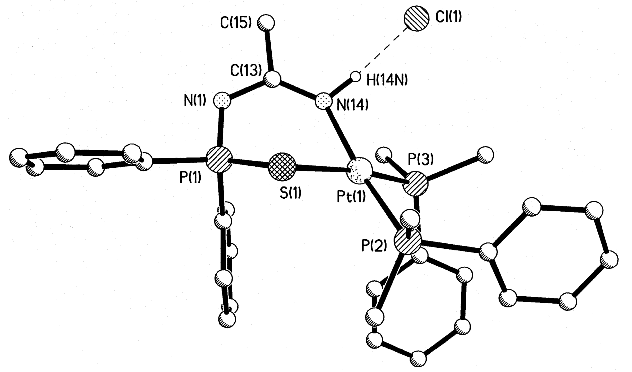

Fig. 2. X-ray crystal structure of *cis*-[Pt{SPPh$_2$N=C(Me)NH-*S,N*}-(PMe$_2$Ph)$_2$]Cl (**2**) (hydrogen atoms bound to carbon omitted for clarity). Selected bond lengths (Å) and angles (°): Pt(1)–S(1) 2.403(2), Pt(1)–P(2) 2.284(2), Pt(1)–P(3) 2.289(2), Pt(1)–N(14) 2.060(8), P(1)–S(1) 2.036(4), P(1)–N(1) 1.604(8), N(1)–C(13) 1.335(12), C(13)–N(14) 1.314(12); P(3)–Pt–P(2) 96.17(9), P(2)–Pt(1)–S(1) 85.57(9), S(1)–Pt(1)–N(14) 90.8(3), N(14)–Pt(1)–P(3) 89.1(3), Pt(1)–S(1)–P(1) 91.75(12), P(1)–N(1)–C(13) 121.5(7), S(1)–P(1)–N(1) 115.3(3), N(1)–C(13)–N(14) 127.5(9), C(13)–N(14)–Pt(1) 134.5(7).

S(1)–P(1)–N(1)–C(13)–N(14) platinacycle. There is a hydrogen-bonding interaction between the chloride counter-ion Cl(1) and the remaining amine proton H(14n) at N(14) (H(14n)···Cl(1) 2.34 Å, N(14)–H(14n)···Cl(1) 164°). Within the chelate ring, the atoms of the Pt(1)–N(14)–C(13)–N(1)–P(1) chain are coplanar, S(1) being displaced by 1.27 Å from this plane. There are deviations from square planarity at the metal centre; the angles between *cis* atoms are in the range 85.6–96.2°, moreover the P(2)–Pt(1)–P(3) and N(14)–Pt(1)–S(1) planes are twisted by 13° relative to each other. The Pt–P and Pt–N distances in **2** (Pt(1)–P(2) 2.284(2), Pt(1)–P(3) 2.289(2) and Pt(1)–N(14) 2.060(8) Å) correspond closely with the parameters for [Pt(S$_2$N$_2$)(PMe$_2$Ph)$_2$] (Pt–P 2.271(4) and 2.265(3) Å, Pt–N 2.081(8) Å) although the Pt–S distance is somewhat longer in the (L^2)$^-$ complex (Pt–S 2.403(2) Å in **2**, c.f. 2.270(5) Å for the (S$_2$N$_2$)$^{2-}$ complex) [17].

In summary *S,N* bidentate chelates can be readily formed at platinum(II) by *N*-thiophosphoryl derivatives of guanidines and amidines upon prior deprotonation using potassium *tert*-butoxide. Efforts are underway to extend the range of metal complexes which can be obtained using the anions derived from HL$^{1–3}$.

3. Experimental

Complexation reactions were performed under an atmosphere of oxygen-free nitrogen; subsequent work-up and recrystallisations were in air. Dichloromethane and thf were dried and distilled from calcium hydride and sodium respectively, *cis*-[PtCl$_2$(PR$_3$)$_2$] (PR$_3$ = PMe$_2$Ph or $\frac{1}{2}$dppe) was prepared by the addition of stoichiometric quantities of PR$_3$ to *cis*-[PtCl$_2$(cycloocta-1,5-diene)] in dichloromethane, potassium *tert*-butoxide (Aldrich) and other solvents employed were unpurified. ^{31}P{^{1}H} NMR (36.2 MHz, referenced to external 85% phosphoric acid (δ 0)) and IR spectra (pressed KBr discs) were recorded on JEOL FX90Q NMR and Perkin-Elmer System 2000 NIR FT-Raman spectrometers respectively. Elemental analyses (PE 2400 CHN elemental analyser) were performed by the University of Loughborough Analytical Service, FAB mass spectra (positive ionisation mode, 3-nitrobenzyl alcohol matrix) were carried out by the EPSRC National Mass Spectrometry Service Centre, Swansea.

The platinum(II) complexes *cis*-[Pt(L^n-*S,N*)(PR$_3$)$_2$]Cl (**1**–**6**) were prepared by the same general procedure.

To a solution of the ligand HL^n (0.2 mmol) and potassium *tert*-butoxide (0.25 mmol) in thf (5 cm^3) was added *cis*-[PtCl$_2$(PR$_3$)$_2$] (0.2 mmol) as a solid in one portion. The resulting yellow mixture was heated at reflux for 2 h and then cooled to room temperature. The solvent was removed in vacuo, the crude product was extracted in dichloromethane (5 cm^3) and the solution filtered through a plug of glass wool-Celite. The dichloromethane filtrate was concentrated under reduced pressure to ca. 2 cm^3; vapour diffusion of diethyl ether into the solution over several days gave the complexes *cis*-[Pt(L^n-*S,N*)(PR$_3$)$_2$]Cl (**1**–**6**) as either colourless (**1**, **2**) or pale yellow (**3**–**6**) solids. Conversion is quantitative by ^{31}P{^{1}H} NMR spectroscopy, isolated yields of the complexes were typically 39–65% based on Pt.

[Pt(L^1-*S,N*)(PMe$_2$Ph)$_2$]Cl (**1**). *Anal.* Found: C, 33.40; H, 4.70; N, 6.10. Calc. for C$_{19}$H$_{31}$N$_3$P$_3$ClPtS: C, 34.73; H, 4.76; N, 6.40%. FAB$^+$ MS: *m/z* 621 ($M^+ - $Cl). IR (cm^{-1}): 3302, 3156 (ν_{NH}), 562 (ν_{PS}).

[Pt(L^2-*S,N*)(PMe$_2$Ph)$_2$]Cl (**2**). *Anal.* Found: C, 45.51; H, 4.58; N, 3.49. Calc. for C$_{30}$H$_{36}$N$_2$P$_3$ClPtS: C, 46.18; H, 4.65; N, 3.59%. FAB$^+$ MS: *m/z* 744 ($M^+ - $Cl). IR (cm^{-1}): 3123 (ν_{NH}), 588 (ν_{PS}).

[Pt(L^3-*S,N*)(PMe$_2$Ph)$_2$]Cl (**3**). *Anal.* Found: C, 45.78; H, 4.78; N, 5.75. Calc. for C$_{29}$H$_{35}$N$_3$P$_3$ClPtS: C, 44.59; H, 4.52; N, 5.38%. FAB$^+$ MS: *m/z* 746 ($M^+ - $Cl). IR (cm^{-1}): 3439, 3264, 3203 (ν_{NH}), 588 (ν_{PS}).

[Pt(L^1-*S,N*)(dppe)]Cl (**4**). *Anal.* Found: C, 39.41; H, 4.69; N, 6.17. Calc. for C$_{29}$H$_{34}$N$_3$P$_3$ClPtS: C, 44.64; H, 4.39; N, 5.39%. FAB$^+$ MS: *m/z* 743 ($M^+ - $Cl). IR (cm^{-1}); 3329, 3163 (ν_{NH}), 562 (ν_{PS}).

[Pt(L^2-*S,N*)(dppe)]Cl (**5**). *Anal.* Found: C, 50.96; H, 4.77; N, 3.06. Calc. for C$_{40}$H$_{39}$N$_2$P$_3$ClPtS: C, 53.19; H, 4.35; N, 3.10%. FAB$^+$ MS: *m/z* 866 ($M^+ - $Cl). IR (cm^{-1}): 3340 (ν_{NH}), 585 (ν_{PS}).

[Pt(L^3-*S,N*)(dppe)]Cl (**6**). *Anal.* Found: C, 50.57; H, 4.42; N, 4.98. Calc. for C$_{39}$H$_{38}$N$_3$P$_3$ClPtS: C, 51.80; H, 4.24; N, 4.65%. FAB$^+$ MS: *m/z* 867 ($M^+ - $Cl). IR (cm^{-1}); 3346, 3148 (ν_{NH}), 588 (ν_{PS}).

3.1. X-ray crystallography

X-ray diffraction studies on crystals of *cis*-[Pt(L^2-*S,N*)(PMe$_2$Ph)$_2$]Cl (**2**) grown from dichloromethane–hexane by solvent diffusion, were performed using a Bruker SMART diffractometer with graphite-monochromated Mo

Kα radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods, the non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms bound to carbon were idealised and fixed (C–H 0.95 Å); the NH proton H(14n) associated with N(14) was located by a ΔF map and allowed to refine anisotropically. Structural refinements were by the full-matrix least-squares method on F^2 using the program SHELXTL-PC [20]. $C_{30}H_{36}N_2P_3ClPtS$, colourless needles, $0.08 \times 0.12 \times 0.15$ mm, $M = 780.12$, monoclinic, $a = 9.9790(2)$, $b = 29.4825(4)$, $c = 10.9449(2)$ Å, $\beta = 90.835(1)°$, $U = 3219.7(1)$ Å^3, $T = 293$ K, space group $P2_1/n$, $Z = 4$, $\mu(\text{Mo K}\alpha) = 4.677$ mm^{-1}. Of 13959 measured data 4587 were unique reflections ($R_{\text{int}} = 0.0421$) to give $R_1 = 0.0414$ ($I > 2\sigma(I)$, 3680 observed) and $wR_2 = 0.0881$.

Supplementary data

Full lists of structure refinement data, atomic coordinates, bond lengths and angles, anisotropic displacement parameters and hydrogen atom parameters have been deposited as supplementary material, no. 137216, at the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

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