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Conformational Control in $PtS_2(PR_2)_2N$ Metallacycles *via* Ligand-substituent Effects (R = Ph or OPh)

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Two complexes containing the $PtS_2(PR_2)_2N$ ring $[Pt\{R'_2P(S)NP(S)R'_2\}(PR_3)_2]PF_6$ (R = Et, R′ = Ph; R = Me, R′ = OPh), have been synthesised and structurally characterised: changing R from Ph to OPh has a dramatic effect on the ring conformation; whereas a complex with R = Ph has a puckered ring, for R = OPh the S–P–N–P–S portion of the ring is flat.

Systematic studies upon the co-ordination behaviour of $[N(EPPh_2)_2]^-$ (E = S or Se) have, to date, revealed that although this ligand can be regarded as an 'inorganic' analogue of acetylacetonate (acac),[1–3] it invariably adopts a puckered rather than the planar geometry which is observed for acac complexes. Although there is a marked multiple-bond character in $ME_2(PR_2)_2N$ (E = O, S or Se) rings, there does not seem to be any requirement for planarity associated with the π-delocalisation of the $[E\text{–}P\text{–}N\text{–}P\text{–}E]^-$ ligand. This is all the more remarkable given the wealth of planar M–S–N rings.[4]

The majority of the previous studies involved homoleptic complexes with alkyl or aryl groups; the ligand $[Ph_2P(S)NP(S)Ph_2]^-$ has been particularly extensively studied both by ourselves and others[5,6] since it is readily prepared. Here we report on a comparative study of complexes with R = Ph or OPh which reveals dramatic ligand-substituent effects.

Reaction of $[PtCl_2(PEt_3)_2]$ with $[NH(PSPh_2)_2]$ proceeds at room temperature to give complex **1** [equation (1)].

$$[PtCl_2(PEt_3)_2] + Ph_2P(S)NHP(S)Ph_2 + NH_4PF_6 \longrightarrow [Pt(PEt_3)_2\{Ph_2P(S)NP(S)Ph_2\}]PF_6\ \mathbf{1} + HCl + NH_4Cl \quad (1)$$

We obtained $(PhO)_2P(S)NHP(S)(OPh)_2$ by the condensation reaction (2). Reaction with $[PtCl_2(PMe_3)_2]$ proceeded in

$$P(S)(OPh)_2Cl + P(S)(OPh)_2NH_2 \longrightarrow (PhO)_2P(S)NHP(S)(OPh)_2 + HCl \quad (2)$$

a similar fashion to the phenyl derivative in equation (1) to give $[Pt(PMe_3)_2\{(PhO)_2P(S)NP(S)(OPh)_2\}]PF_6$ **2**. Complexes **1** and **2** gave the expected AA′XX′ ^{31}P NMR spectra for the cations and satisfactory microanalysis.[†]

The structure[‡] of **1** (Fig. 1) shows the platinum centre to be co-ordinated by two PEt_3 ligands and the bidentate $[N(SPPh_2)_2]^-$ in slightly distorted (small tetrahedral distortion) square-planar geometry. The complex has crystallographic C_2 symmetry. The co-ordination angles are 81.4(1) [S(1)–Pt–P(3)], 96.1(1) [S(1)–Pt–S(1a)] and 172.4(1)° [S(1)–Pt–P(3a)]. The Pt–P and Pt–S distances [2.288(3) and 2.393(3) Å respectively] are normal. The P–N bond length [1.579(6) Å] shows a characteristic shortening (relative to the neutral ligand)[5] reflecting its partial double-bond character, whilst the P–S bond length [2.021(4) Å] is close to a P–S single bond. The angles within the metallacycle are unexceptional, there being anticipated slight enlargement from ideal tetrahedral and trigonal geometries of the Pt–S–P, S–P–N and P–N–P angles [108.5(1), 114.9(3) and 122.8(7)° respectively]. The conformation of the PtS_2P_2N ring in **1** can best be described as a pseudo-boat and is very similar to that observed in a number of related analogues.[1,5]

In the structure[‡] of **2** (Fig. 2) the platinum centre is co-ordinated to the PMe_3 ligands and the bidentate $[N\{SP(OPh)_2\}_2]^-$ ligand in a slightly (tetrahedrally) distorted square-planar geometry with co-ordination angles in the ranges 86.3(1)–96.6(1) and 171.2(1)–176.7(1)°. The S–Pt–S bite angle in **2** is significantly reduced compared to **1** [87.7(1) *cf.* 96.1(1)° in **1**]. The Pt–S distances in **2** [2.386(3) and 2.401(3) Å] are the same as those in **1**, whilst the Pt–P distances [2.269(3) and 2.270(3) Å] are slightly reduced in **2**. The P–N bond lengths in

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[†] NMR spectra of the cations: $^{31}P\text{-}\{^1H\}$ ($CDCl_3$, 101.4 MHz); **1**, δ_A 36.1 [$^2J(^{31}P\text{–}^{195}Pt)$ 60.5], $\delta_x(PEt_3)$ 12.6 [$^1J(^{31}P\text{–}^{195}Pt)$ 3099.5, $J_{AX'}$ 9.4, $J_{AA'}$ 5.5, $J_{XX'}$ 19.0]; **2**, δ_A 40.2 [$^2J(^{31}P\text{–}^{195}Pt)$ 64.5], δ_x – 19.3 [$^1J(^{31}P\text{–}^{195}Pt)$ 3124 Hz (other couplings not resolved)].

[‡] Crystal data: **1**, $C_{36}H_{50}F_6NP_5PtS_2$, monoclinic, space group $C2/c$, $a = 16.670(5)$, $b = 15.529(8)$, $c = 18.108(5)$ Å, $\beta = 111.17(2)°$, $U = 4658$ Å^3, $D_c = 1.46$ g cm^{-3}, $F(000) = 2048$, μ(Mo-Kα) = 3.26 mm^{-1}. Total of 4096 independent reflections collected using a Siemens P4/PC diffractometer with graphite-monochromated Mo-Kα radiation and ω scans. Structure solved by direct methods and refined anisotropically to give $R = 0.052$ and $Rw = 0.053$ (SHELXTL[7]) for 3476 independent observed, absorption-corrected reflections ($F > 4\sigma F$), $w^{-1} = \sigma^2 F + 0.000\,06\,F^2$. **2**, $C_{30}H_{38}F_6NO_4P_5PtS_2$, monoclinic, space group $P2_1/n$, $a = 14.192(2)$, $b = 10.147(2)$, $c = 27.351(3)$ Å, $\beta = 102.74(2)°$, $U = 3842$ Å^3, $D_c = 1.74$ g cm^{-3}, $F(000) = 1984$, μ(Cu-Kα) = 103.9 cm^{-1}. Total of 5350 independent reflections collected using a Siemens P4/PC diffractometer with graphite-monochromated Cu-Kα radiation and ω scans. Structure solved by direct methods and refined anisotropically to give $R = 0.045$ and $Rw = 0.047$ for 4092 (SHELXTL[7]) independent observed, absorption-corrected reflections ($F > 4\sigma F$), $w^{-1} = \sigma^2 F + 0.0005F^2$. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

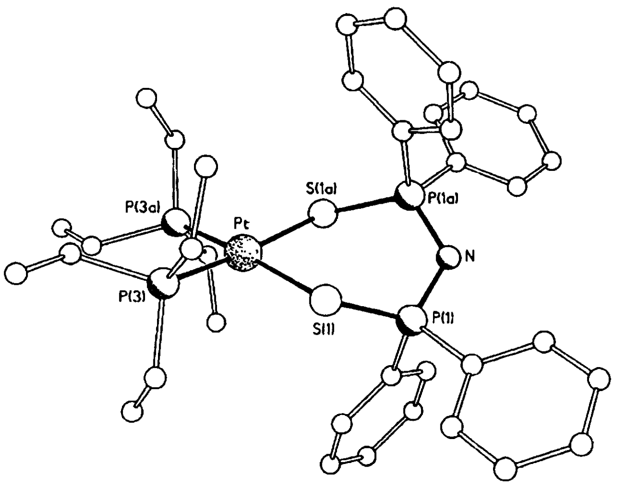

Fig. 1 Structure of the cation in **1**. Selected bond lengths (Å) and angles (°): Pt–S(1) 2.393(3), Pt–P(3) 2.288(3), S(1)–P(1) 2.021(4), P(1)–N 1.579(6); S(1)–Pt–S(1a) 96.1(1), P(3)–Pt–P(3a) 101.9(1), Pt–S(1)–P(1) 108.5(1), S(1)–P(1)–N 114.9(3), P(1)–N–P(1a) 122.8(7)

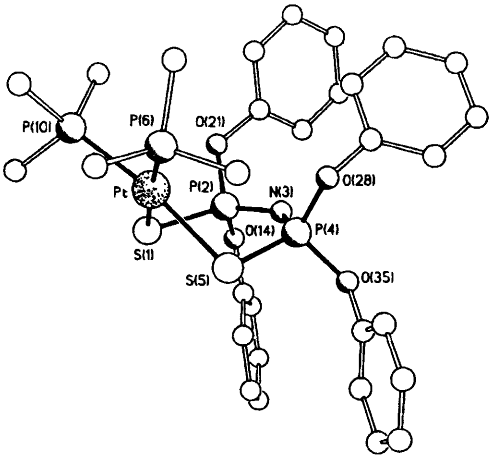

Fig. 2 Structure of the cation in **2**. Selected bond lengths (Å) and angles (°): Pt–S(1) 2.401(3), Pt–S(5) 2.386(3), Pt–P(6) 2.270(3), Pt–P(10) 2.269(3), S(1)–P(2) 1.988(4), P(2)–N(3) 1.548(10), N(3)–P(4) 1.564(10), P(4)–S(5) 1.990(4); S(1)–Pt–S(5) 87.7(1), P(5)–Pt–P(10) 96.6(1), Pt–S(1)–P(2) 100.5(1), S(1)–P(2)–N(3) 120.0(4), P(2)–N(3)–P(4) 132.9(5), N(3)–P(4)–S(5) 120.4(3), P(4)–S(5)–Pt 98.3(1)

2 are slightly shorter [1.584(10), 1.564(10) Å] than their counterparts in **1** [1.579(6) Å]. Furthermore, there is a small reduction in the P–S bond length in **2** with respect to **1** [1.988(4) and 1.990(4) *cf.* 2.021(4) Å]. The gross effect of these bond-length changes is to produce an overall contraction of the ring in **2** *versus* **1**.

Accompanying the bond length changes which indicate extended delocalisation in the S–P–N–P–S portion of **2** there are dramatic changes in the ring angles [Fig. (3)]. The angles at S are relaxed [Pt–S(5)–P(4) 98.3(1), Pt–S(1)–P(2) 100.5(1)°], whilst those at phosphorus and nitrogen are dramatically enlarged with angles at P of 120.0(4), 120.4(3)° and a P(2)–N(3)–P(4) angle of 132.9(5)°, respectively. Accompanying these significant changes is a flattening of the S–P–N–P–S chain (maximum deviation from planarity 0.035 Å) with resulting hinging of this fragment about the S(1)–S(5) axis with respect to the co-ordination plane (fold angle 68°).

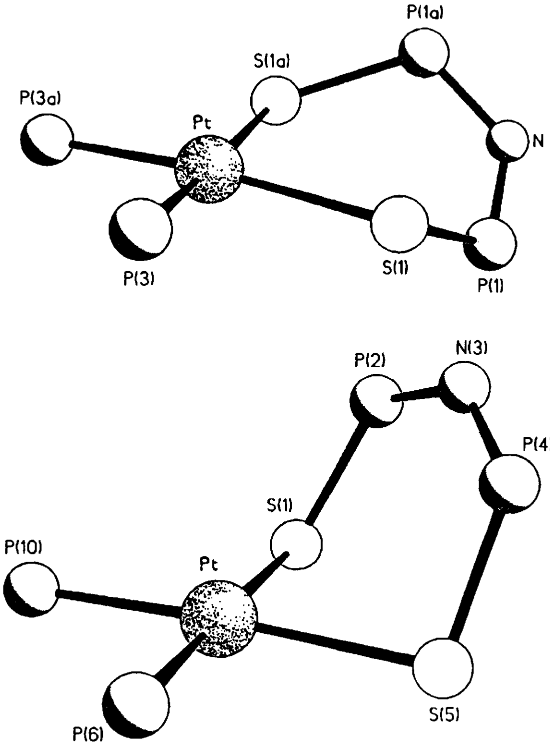

Fig. 3 Comparison of the core geometries of the cations in **1** (upper) and **2** (lower)

Given the relationship between the ligand used here and acac, the geometry that we observe in **2** is more reasonable than the puckered geometry observed for **1** (although still substantially different from the geometry observed for acac complexes) and the previous examples of this ligand. It is interesting to speculate on the factors responsible for the different geometries of **1** and **2**. There do not appear to be any steric factors which favour either geometry and so the difference in the electron-withdrawing ability of Ph and OPh must be significant. One explanation is that the OPh group as a better electron-withdrawing group than a Ph group increases the extent of π-electron donation from the N and S atoms in a similar fashion to the observation that the P–N bond lengths in $(NPF_2)_3$ are shorter than those in $(NPCl_2)_3$ *via* changes in the extent of π bonding.[4] Further theoretical studies as well as the synthesis of related systems are underway.

References

1 I. Haiduc, C. Silvestru, H. W. Roesky, H.-G. Schmidt and M. Noltemeyer, *Polyhedron*, 1993, **12**, 69.

2 J. S. Casa, A. Castineiras, I. Haiduc, A. Sanchez, J. Sordo and E. M. Vasquez-Lopez, *Polyhedron*, 1994, **13**, 2873.

3 R. Rossi, A. Marchi, L. Marvelli, L. Magon, M. Peruzzini, U. Casellato and R. Graziani, *J. Chem. Soc., Dalton Trans.*, 1993, 723.

4 H. G. Heal, *The Inorganic Heterocyclic Chemistry of Sulfur, Nitrogen and Phosphorus*, Academic Press, London, 1980.

5 P. Bhattacharyya, J. Novosad, J. Phillips, A. M. Z. Slawin, D. J. Williams and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 1995, 1607.

6 M. S. Balakrishna, B. D. Santarsiero and R. G. Cavell, *Inorg. Chem.*, 1994, **33**, 3079.

7 G. M. Sheldrick, SHELXTL, Siemens Analytical Instruments, Madison, WI, 1990.

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