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## Preparation, Crystal Structure and Fluxional Behaviour of $\sigma$ -S-Bonded Palladium and Platinum Complexes of the Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>R<sup>-</sup> (R = Me or Bu<sup>t</sup>) Anions

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The reaction of the Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>R<sup>-</sup> anions (R = Me or Bu<sub>t</sub>), generated from 1,5-Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub> and the appropriate alkyllithium reagent, with *cis*- or *trans*-[MCl<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>] (M = Pd or Pt) produces the complexes [MCl(PEt<sub>3</sub>)<sub>2</sub>(Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>R)] (R = Me, M = Pd or Pt; R = Bu<sup>t</sup>, M = Pt) shown by X-ray crystallography (M = Pd, R = Me) to involve  $\sigma$ -S bonding of the P<sub>2</sub>N<sub>4</sub>S<sub>2</sub> ring to the metal; variable-temperature <sup>31</sup>P NMR spectra of these complexes indicate a significant energy barrier to rotation about the M-S bond of 41-46 kJ mol<sup>-1</sup>.

The 1,5-diphosphadithiatetrazocines (1,5-dithia-2,4,6,8-tetraaza-3,7-diphosphabicyclo[3.3.0]octanes) 1 (R = alkyl or aryl)<sup>1</sup>exhibit a versatile co-ordination chemistry involving sulfurand/or nitrogen ligation to metals. To date the following $bonding modes have been established: <math>\sigma$ -N,<sup>2</sup>  $\eta$ <sup>2</sup>-S,S',<sup>3</sup>  $\eta$ <sup>2</sup>-S,N- $\mu$ -S'<sup>4</sup> and  $\mu$ , $\eta$ <sup>3</sup>-N,S,S'.<sup>2</sup> In this communication we report that the novel anions Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>R<sup>-</sup> 2a (R = Me) and 2b (R = Bu'), generated by treatment of 1 (R = Ph) with the appropriate alkyllithium, react with *cis*- or *trans*-[MCl<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>] (M = Pd or Pt) to give the complexes 3a-3c, in which the P<sub>2</sub>N<sub>4</sub>S<sub>2</sub> ring is  $\sigma$ -S-bonded to the metal.<sup>+</sup>

Orange crystals of compound 3a were obtained from thfhexane (1:1) at 23 °C.<sup>‡</sup> The molecular geometry and atomic numbering scheme for one of the two independent molecules are shown in Fig. 1. The  $P_2N_4S_2$  ring is attached to the approximately square-planar palladium atom *via* a sulfur atom with d(Pd-S) = 2.253(1) Å, which is comparable to values of

<sup>5</sup> Crystal data for C<sub>37</sub>H<sub>53</sub>ClN<sub>4</sub>P<sub>4</sub>PdS<sub>2</sub>-C<sub>4</sub>H<sub>8</sub>O **3a**: M = 955.86, triclinic, space group PI; at 130 K, a = 12.969(1), b = 17.826(1), c = 20.889(1) Å,  $\alpha = 80.237(4)$ ,  $\beta = 87.438(4)$ ,  $\gamma = 77.626(4)^\circ$ , U = 4648.6(5) Å<sup>3</sup>, Z = 4,  $\mu$ (Mo-K $\alpha$ ) = 7.1 cm<sup>-1</sup>, F(000) = 1992,  $D_c = 1.366$  g cm<sup>-3</sup>. Intensity data were collected at 130 °C on an Enraf-Nonius CAD-4F diffractometer operating in the  $\omega$ -2 $\theta$  mode and using Mo-K $\alpha$  radiation ( $\lambda = 0.710$  73 Å, graphite monochromator). Total number of unique reflections 19 042, of which 15 742 had  $I > 2.5 \sigma(I)$ . Crystal dimensions 0.25 × 0.30 × 0.40 mm. The structure was solved by Patterson methods and subsequent partial structure expansion (SHELX 86)<sup>5</sup> and was refined by full-matrix least-squares techniques with anisotropic thermal parameters for the non-hydrogen atoms to R 0.042 and R' 0.058, with  $w = 1/\sigma(F)^2$ . A correction for secondary extinction was applied. Atomic coordinates, thermal parameters, bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, J. Chem. Soc., Dalton Trans., 1992, Issue 1, pp. xx-xxv.



2.266(2)–2.280(2) Å for Pd–S distances *trans* to chlorine.<sup>7</sup> The  $P_2N_4S_2$  ring tends towards a chair conformation. The <sup>31</sup>P NMR spectra for compounds **3a–3c** at 223 K are

The <sup>31</sup>P NMR spectra for compounds **3a–3c** at 223 K are consistent with the solid-state structure (see Table 1). The spectra consist of two resonances (AB quartets) at  $\delta$  14–21 for the inequivalent PEt<sub>3</sub> groups (P<sub>A</sub> and P<sub>B</sub>) and a single resonance at  $\delta$  25–27 for the equivalent PPh<sub>2</sub> groups (P<sub>C</sub>) of the heterocyclic ring. The values of *ca.* 390 Hz for <sup>2</sup>J(P<sub>A</sub>–P<sub>B</sub>) in **3a–3c** and 2675–2970 Hz for <sup>1</sup>J(Pt–P) in **3b** and **3c** are consistent with a *trans* orientation of the PEt<sub>3</sub> groups.<sup>8</sup> The large threebond coupling, <sup>3</sup>J(Pt–P<sub>C</sub>) = 455–465 Hz for **3b** and **3c**, is of similar magnitude to that observed for  $\eta^2$ -S,S' complexes of 1 (**R** = Ph, Et or Me) with platinum.<sup>3b</sup>

The AB quartet for the inequivalent PEt<sub>3</sub> groups collapses to give a single resonance { $\delta = \delta(P_A) + [\delta(P_B)/2]$ } when toluene solutions of compounds **3a-3c** are warmed from 223 to 363 K (see Fig. 2). The reverse of these changes is observed on cooling to 223 K. The singlet (with <sup>195</sup>Pt satellites) for P<sub>C</sub> remains unchanged and the Pt-PEt<sub>3</sub> couplings are maintained throughout this temperature range. Thus the inequivalent PEt<sub>3</sub> groups must be involved in an *intramolecular* two-site exchange which, we propose, involves a simple rotation of the P<sub>2</sub>N<sub>4</sub>S<sub>2</sub> ligand about the M-S bond. The rate constants, k<sub>r</sub>, for this process, determined at various temperatures from the <sup>31</sup>P NMR spectra,<sup>9</sup> were used to determine activation energies, E<sub>A</sub>, from a plot of ln(k<sub>r</sub>) vs. T<sup>-1</sup>. The values of E<sub>A</sub> for **3a-3c** were in the narrow range 41-46 kJ mol<sup>-1</sup> indicating that the

<sup>&</sup>lt;sup>†</sup> Addition of a tetrahydrofuran (thf) solution of Li[Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>R], generated by treatment of 1 (R = Ph, 0.204 mmol) in thf (20 cm<sup>3</sup>) at -78 °C with a slight excess of alkyllithium in diethyl ether, to a slurry of *cis*- or *trans*-[MCl<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>] (0.204 mmol) in thf (15 cm<sup>3</sup>) at -78 °C gave air-stable, orange-yellow (**3a**) or pale yellow (**3b** and **3c**) crystals in 50-60% yields. Satisfactory C,H,N analyses were obtained.



Fig. 1 An ORTEP<sup>6</sup> plot (50% probability ellipsoids) for molecule A of  $[PdCl(PEt_3)_2(Ph_4P_2N_4S_2Me)]$  3a (solvated thf molecule is not shown). Selected bond lengths (Å) and angles (°): Pd-Cl 2.364(1), Pd-S(1) 2.253(1), Pd-P(1) 2.334(1), Pd-P(2) 2.334(1), S(1)-N(1) 1.651(3), S(1)-N(4) 1.664(4), S(2)-N(2) 1.626(4), S(2)-N(3) 1.624(3), P(3)-N(1) 1.616(3), P(3)-N(2) 1.615(3), P(4)-N(3) 1.617(3), P(4)-N(4) 1.618(3), S(2)-C(37) 1.773(4); Cl-Pd-P(1) 85.91(3), Cl-Pd-P(2) 87.56(3), S(1)-Pd-P(1) 91.18(3), S(1)-Pd-P(2) 95.43(3), Pd-S(1)-N(1) 102.3(1), Pd-S(1)-N(4) 104.1(1), N(1)-S(1)-N(4) 109.3(2), N(2)-S(2)-N(3) 108.1(1), N(2)-S(2)-C(37) 99.4(2), N(3)-S(2)-C(37) 98.5(2), N(1)-P(3)-N(2) 120.1(2), N(3)-P(4)-N(4) 119.7(1), S(1)-N(1)-P(3) 116.8(1), S(2)-N(2)-P(3) 115.6(2), S(2)-N(3)-P(4) 116.7(1), S(1)-N(4)-P(4) 115.3(2). The structural parameters for molecule B are not significantly different from those of A

Table 1 <sup>31</sup>P-{<sup>1</sup>H} NMR parameters for [MCl(PEt<sub>3</sub>)<sub>2</sub>(Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>R)] 3a (M = Pd, R = Me), 3b (M = Pt, R = Me) and 3c (M = Pt, R = Bu')<sup>a</sup>

	3a	3b	3c
$\delta(\mathbf{P}_{\mathbf{A}})^{b}$	20.1	21.4	20.2
$\delta(P_B)^b$	16.8	15.5	14.2
$\delta(\mathbf{P}_{\mathbf{C}})^{c}$	24.8	27.1	27.0
$^{2}J(\dot{P}_{A}-P_{B})$	388	388	389
$^{4}J(P_{A}-P_{C})$	17.5	$\approx 0$	$\approx 0$
$^{4}J(P_{B}-P_{C})$	11	$\approx 0$	$\approx 0$
$^{1}J(Pt-P_{A})$		2963	2969
$^{1}J(\text{Pt}-\text{P}_{B})$		2676	2683
$^{3}J(\text{Pt}-\text{P}_{\text{C}})$		464	456

<sup>a</sup> Chemical shifts are quoted in ppm relative to 85% H<sub>3</sub>PO<sub>4</sub>, coupling constants in Hz. Spectra were recorded at *ca.* 223 K in [<sup>2</sup>H<sub>8</sub>]toluene. The inequivalent phosphorus atoms P<sub>A</sub>, P<sub>B</sub> and P<sub>C</sub> are identified in the structural drawing. <sup>b</sup> The resonances for P<sub>A</sub> and P<sub>B</sub> appear as an AB quartet. <sup>c</sup> The resonance for P<sub>C</sub> in compound **3a** is an overlapping doublet of doublets due to coupling to both P<sub>A</sub> and P<sub>B</sub>; these couplings are not resolved in the signals for **3b** and **3c**.

barrier to rotation is not affected significantly by the nature of R or M.

In summary, the facile generation of the novel anion  $Ph_4P_2N_4S_2R^-$  ( $R = Me \text{ or } Bu^t$ ) provides a new approach for the preparation of metal complexes of the  $P_2N_4S_2$  ring, as illustrated by the first examples of  $\sigma$ -S complexes described herein. The variable-temperature <sup>31</sup>P NMR spectra of compounds 2a and 2b provide evidence for the presence of either conformational isomers or of both *S*- and *N*-alkylated isomers. However, only *S*-alkylated products are isolated in the reactions of 2a or 2b with electrophiles. Further details of the



Fig. 2 Variable-temperature  ${}^{31}P$  NMR spectra for *trans*-[PtCl-(PEt<sub>3</sub>)<sub>2</sub>(Ph<sub>4</sub>P<sub>2</sub>N<sub>4</sub>S<sub>2</sub>Bu<sup>t</sup>)] 3c in toluene

fluxional behaviour of **2a** and **2b** will be provided in the full account of this work.

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