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Preparation, Crystal Structure and Fluxional Behaviour of σ-S-Bonded Palladium and Platinum Complexes of the $Ph_4P_2N_4S_2R^-$ (R = Me or Bu^t) Anions

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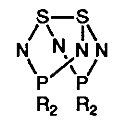
The reaction of the $Ph_4P_2N_4S_2R^-$ anions (R = Me or Bu$_t$), generated from 1,5-$Ph_4P_2N_4S_2$ and the appropriate alkyllithium reagent, with *cis*- or *trans*-$[MCl_2(PEt_3)_2]$ (M = Pd or Pt) produces the complexes $[MCl(PEt_3)_2(Ph_4P_2N_4S_2R)]$ (R = Me, M = Pd or Pt; R = Bu^t, M = Pt) shown by X-ray crystallography (M = Pd, R = Me) to involve σ-S bonding of the $P_2N_4S_2$ ring to the metal; variable-temperature ^{31}P NMR spectra of these complexes indicate a significant energy barrier to rotation about the M–S bond of 41–46 kJ mol^{-1}.



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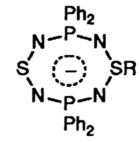
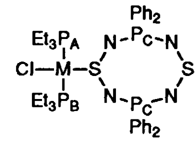


2a R = Me
2b R = Bu^t



M R
3a Pd Me
3b Pt Me
3c Pt Bu^t

The 1,5-diphosphadithiatetrazocines (1,5-dithia-2,4,6,8-tetraaza-3,7-diphosphabicyclo[3.3.0]octanes) **1** (R = alkyl or aryl)[1] exhibit a versatile co-ordination chemistry involving sulfur and/or nitrogen ligation to metals. To date the following bonding modes have been established: σ-N,[2] η^2-S,S′,[3] η^2-S,N-μ-S′[4] and μ,η^3-N,S,S′.[2] In this communication we report that the novel anions $Ph_4P_2N_4S_2R^-$ **2a** (R = Me) and **2b** (R = Bu^t), generated by treatment of **1** (R = Ph) with the appropriate alkyllithium, react with *cis*- or *trans*-$[MCl_2(PEt_3)_2]$ (M = Pd or Pt) to give the complexes **3a**–**3c**, in which the $P_2N_4S_2$ ring is σ-S-bonded to the metal.†

Orange crystals of compound **3a** were obtained from thf–hexane (1:1) at 23 °C.‡ 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 2.266(2)–2.280(2) Å for Pd–S distances *trans* to chlorine.[7] The $P_2N_4S_2$ ring tends towards a chair conformation.

The ^{31}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 δ 14–21 for the inequivalent PEt_3 groups (P_A and P_B) and a single resonance at δ 25–27 for the equivalent PPh_2 groups (P_C) of the heterocyclic ring. The values of *ca.* 390 Hz for $^2J(P_A–P_B)$ in **3a**–**3c** and 2675–2970 Hz for ^1J(Pt–P) in **3b** and **3c** are consistent with a *trans* orientation of the PEt_3 groups.[8] The large three-bond coupling, $^3J(Pt–P_C)$ = 455–465 Hz for **3b** and **3c**, is of similar magnitude to that observed for η^2-S,S′ complexes of **1** (R = Ph, Et or Me) with platinum.[3b]

The AB quartet for the inequivalent PEt_3 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 ^{195}Pt satellites) for P_C remains unchanged and the Pt–PEt_3 couplings are maintained throughout this temperature range. Thus the inequivalent PEt_3 groups must be involved in an *intramolecular* two-site exchange which, we propose, involves a simple rotation of the $P_2N_4S_2$ ligand about the M–S bond. The rate constants, k_r, for this process, determined at various temperatures from the ^{31}P NMR spectra,[9] were used to determine activation energies, E_A, from a plot of ln(k_r) *vs.* T^{-1}. The values of E_A for **3a**–**3c** were in the narrow range 41–46 kJ mol^{-1} indicating that the

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† Addition of a tetrahydrofuran (thf) solution of Li[$Ph_4P_2N_4S_2R$], generated by treatment of **1** (R = Ph, 0.204 mmol) in thf (20 cm^3) at −78 °C with a slight excess of alkyllithium in diethyl ether, to a slurry of *cis*- or *trans*-$[MCl_2(PEt_3)_2]$ (0.204 mmol) in thf (15 cm^3) 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.

‡ Crystal data for $C_{37}H_{53}ClN_4P_4PdS_2{\cdot}C_4H_8O$ **3a**: *M* = 955.86, triclinic, space group $P\bar{1}$; at 130 K, *a* = 12.969(1), *b* = 17.826(1), *c* = 20.889(1) Å, α = 80.237(4), β = 87.438(4), γ = 77.626(4)°, *U* = 4648.6(5) Å^3, *Z* = 4, μ(Mo-Kα) = 7.1 cm^{-1}, *F*(000) = 1992, D_c = 1.366 g cm^{-3}. Intensity data were collected at 130 °C on an Enraf-Nonius CAD-4F diffractometer operating in the ω–2θ mode and using Mo-Kα radiation (λ = 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)[5] 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.

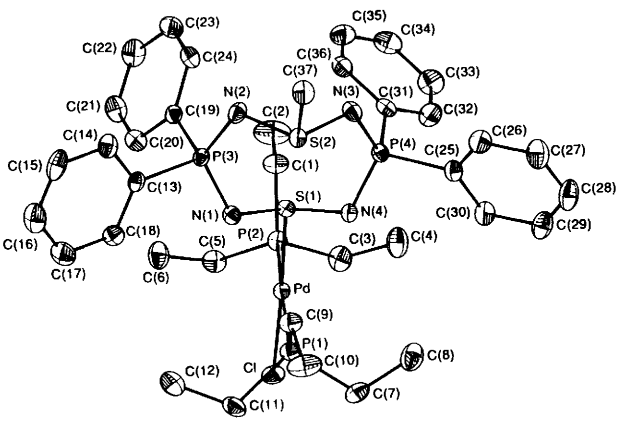

Fig. 1 An ORTEP[6] plot (50% probability ellipsoids) for molecule A of [$PdCl(PEt_3)_2(Ph_4P_2N_4S_2Me)$] **3a** (solvated thf molecule is not shown). Selected bond lengths (Å) and angles (°): Pd–Cl 2.364(1), Pd–S(1) 2.253(1), Pd–P(1) 2.334(1), Pd–P(2) 2.334(1), S(1)–N(1) 1.651(3), S(1)–N(4) 1.664(4), 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 $^{31}P-\{^1H\}$ NMR parameters for [$MCl(PEt_3)_2(Ph_4P_2N_4S_2R)$] **3a** (M = Pd, R = Me), **3b** (M = Pt, R = Me) and **3c** (M = Pt, R = Bu^t)[a]

	3a	3b	3c
$\delta(P_A)^b$	20.1	21.4	20.2
$\delta(P_B)^b$	16.8	15.5	14.2
$\delta(P_C)^c$	24.8	27.1	27.0
$^2J(P_A–P_B)$	388	388	389
$^4J(P_A–P_C)$	17.5	≈0	≈0
$^4J(P_B–P_C)$	11	≈0	≈0
$^1J(Pt–P_A)$		2963	2969
$^1J(Pt–P_B)$		2676	2683
$^3J(Pt–P_C)$		464	456

[a] Chemical shifts are quoted in ppm relative to 85% H_3PO_4, coupling constants in Hz. Spectra were recorded at *ca.* 223 K in [$^2H_8$]toluene. The inequivalent phosphorus atoms P_A, P_B and P_C are identified in the structural drawing. [b] The resonances for P_A and P_B appear as an AB quartet. [c] The resonance for P_C in compound **3a** is an overlapping doublet of doublets due to coupling to both P_A and P_B; 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 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 σ-S complexes described herein. The variable-temperature ^{31}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 fluxional behaviour of **2a** and **2b** will be provided in the full account of this work.

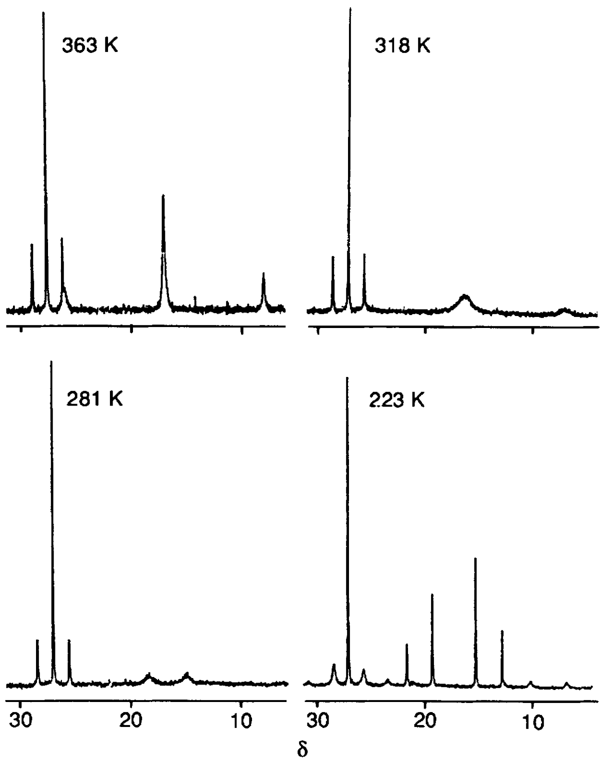

Fig. 2 Variable-temperature ^{31}P NMR spectra for *trans*-[$PtCl(PEt_3)_2(Ph_4P_2N_4S_2Bu^t)$] **3c** in toluene

Acknowledgements

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