## PREPARATION AND LIGAND PROPERTIES OF BIS-THIONYLIMINO COMPLEXES OF THE TYPE M(NSO)<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub>. X-RAY STRUCTURE OF Pt(NSO)<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>

# IVAN P. PARKIN, ALEXANDRA M. Z. SLAWIN, DAVID J. WILLIAMS and J. DEREK WOOLLINS\*

Department of Chemistry, Imperial College of Science and Technology, South Kensington, London SW7 2AY, U.K.

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Abstract—Reaction of  $S(NSO)_2$  with *cis*-MCl<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub> (M = Pt, PR<sub>3</sub> = PMe<sub>3</sub>, PEt<sub>3</sub>, PPr<sub>3</sub><sup>n</sup>, PBu<sub>3</sub><sup>n</sup>, PPh<sub>3</sub>, PMePh<sub>2</sub>, PMe<sub>2</sub>Ph and dppe; M = Pd, PR<sub>3</sub> = dppe) in liquid ammonia gives *cis*-M(NSO)<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub> quantitatively by <sup>31</sup>P NMR and in 60% isolated yield. The new compounds have been characterized by microanalyses, IR, <sup>1</sup>H and <sup>31</sup>P NMR, mass spectrometry and in the case of Pt(NSO)<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>, X-ray crystallography. The molecule has *cis* square-planar geometry with approximate  $C_2$  symmetry.

Compounds containing the NSO- ligand have been the subject of recent work;<sup>1,2</sup> reaction of Rh(CO)H(PPh<sub>3</sub>)<sub>3</sub> with CsNSO<sub>2</sub> gives Rh  $(NSO)(CO)(PPh_3)_2$ , whilst treatment of  $Ti(Cp)_2$  $Cl_2$  with KNSO yields the bis compound Ti(Cp)<sub>2</sub>(NSO)<sub>2</sub>.<sup>3</sup> The cis and trans isomers of  $Pt(NSO)_2(PPh_3)_2$ have been made from  $Pt(C_2H_4)(PPh_3)_2$ ; reaction with  $Hg(NSO)_2$  gives the trans product<sup>4</sup> whilst with PhAs(NSO)<sub>2</sub> the cis isomer is obtained.<sup>5</sup> Reaction of Hg(NSO)<sub>2</sub> with cis-PtCl<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub> has also been claimed<sup>4</sup> to give cis- $Pt(NSO)_2(PR_3)_2$  on the basis of <sup>31</sup>P NMR only, but there are discrepancies between the data reported in refs 4 and 5. In the light of these problems we have now developed a general synthetic route for the formation of  $M(NSO)_2(PR_3)_2$ .

We are currently investigating the synthetic potential of various sulphur–nitrogen reagents with metal complexes using liquid ammonia as solvent.<sup>6,7</sup> Here, we report the synthesis and spectroscopic characterization of the new complexes,  $M(NSO)_2(PR_3)_2$  and  $Ti(Cp)_2(NSO)_2$  from the reaction of  $S(NSO)_2$  in liquid ammonia. The X-ray crystal structure of  $Pt(NSO)_2(PMe_3)_2$  is also reported.

### **EXPERIMENTAL**

All manipulations were performed under an inert atmosphere (argon or nitrogen). Solvents were dried before use:  $CH_2Cl_2$  was distilled from  $CaH_2$ and petroleum ether (60–80) distilled from sodium benzophenone. The <sup>31</sup>P NMR and some <sup>1</sup>H NMR were recorded using a JEOL FX90Q spectrometer operating at 36.21 and 89.55 MHz, and referenced to external 85% H<sub>3</sub>PO<sub>4</sub> and internal SiMe<sub>4</sub>, respectively. The other <sup>1</sup>H NMR were obtained on a Bruker WM 250 MHz operating at 250.13 MHz referenced to CHCl<sub>3</sub> at 7.24 ppm. IR spectra were obtained from KBr discs using a Perkin–Elmer 1720 spectrophotometer. Mass spectra were obtained both by EI and FAB (using thiodiethanol matrix) on a VG 2020 machine. Microanalyses were performed by the departmental service.

The compounds  $PtCl_2(PR_3)_2$  (PR<sub>3</sub> = PMe<sub>3</sub>, PEt<sub>3</sub>, PPr<sub>3</sub><sup>n</sup>, PBu<sub>3</sub><sup>n</sup>, PMe<sub>2</sub>Ph, PMePh<sub>2</sub>, PPh<sub>3</sub> and dppe) and PdCl<sub>2</sub>(dppe) were made as previously described.<sup>8</sup> Ti(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Cl<sub>2</sub> (Aldrich) and anhydrous ammonia (BOC) were used as supplied. S(NSO)<sub>2</sub> was prepared by the literature method.<sup>9</sup>

### Preparation of $M(NSO)_2(PR_3)_2$

All these complexes (Table 1) were made by the same general method illustrated here for  $Pt(NSO)_2$  (PPr<sub>3</sub>)<sub>2</sub> (3). *cis*-PtCl<sub>2</sub>(PPr<sub>3</sub>)<sub>2</sub> (0.080 g, 0.137 mmol) was added to a stirred red solution of  $S(NSO)_2$  (0.021 g, 0.137 mmol) in liquid ammonia at  $-78^{\circ}$ C. The resultant suspension was stirred for 30 min at  $-78^{\circ}$ C and then the ammonia blown off by a stream of argon. The resultant yellow solid was

<sup>\*</sup>Author to whom correspondence should be addressed.

Compound	С	Н	N	Melting point (°C)	Yield (%)
$Pt(NSO)_2(PMe_3)(1)$	14.8	4.5	5.7	154-157	62
	(15.3)	(3.8)	(5.9)		
$Pt(NSO)_{2}(PEt_{3})_{2}$ (2)	25.9	5.4	5.0	124-125	54
	(25.9)	(5.4)	(5.0)		
$Pt(NSO)_{2}(PPr_{3}')_{2}$ (3)	33.5	6.6	4.3	110113	50
	(33.8)	(6.6)	(4.4)		
$Pt(NSO)_2(PMe_2Ph)_2$ (4)	32.3	4.5	4.9	107-110	65
	(32.3)	(3.7)	(4.7)		
$Pt(NSO)_2(PMePh_2)_2$ (5)	42.9	3.5	3.9	121-123	57
	(43.4)	(3.6)	(3.9)		
$Pt(NSO)_{2}(PPh_{3})_{2}$ (6)	46.7	3.3	3.2		62
	(46.7)	(3.3)	(3.0)		
$Pt(NSO)_2(dppe) \cdot CDCl_3(7)$	38.3	3.8	3.6		43
	(38.6)	(3.4)	(3.4)		
$Pd(NSO)_2(dppe)(8)$	48.9	4.2	4.5		32
	(49.6)	(4.5)	(4.7)		
$Ti(Cp)_{2}(NSO)_{2}$ (9)	39.1	3.2	9.3		75
	(39.7)	(3.3)	(9.3)		

Table 1. Microanalytical data

extracted into  $CH_2Cl_2$  (5 cm<sup>3</sup>), filtered through a celite/glass wool plug and layered with petroleum ether 60-80 (50 cm<sup>3</sup>). Cooling of the solution to  $-20^{\circ}C$  yielded crystals of (3) (0.044 g, 0.068 mmol,

59%). Microanalytical data are given in Table 1, NMR data in Table 2, and MS and selected IR data in Table 3.

Preparation of Ti(Cp)<sub>2</sub>(NSO)<sub>2</sub> was carried out

	<sup>31</sup> P N	IMR	MR				
Compound	$\delta$ (ppm)	<sup>1</sup> <i>J</i> (Hz)		ΙΗ	NMR		
1	-32.6	3027	1.17 [d, Hz]	² <i>J</i> (P—H)	10.8, <sup>3</sup> J	(Pt—H)	34.1
2	1.1	3070	1.15 [d of Hz (18H)	t, <sup>3</sup> <i>J</i> (P	H) 17.4, 1, 12H)	² <i>J</i> (HH	) 7.1
3	-7.8	3069	1.61 (m, 2 (18H)]	24H), 1.0	0 [t, <sup>2</sup> <i>J</i> (H	—H) 7.0	Hz,
4	-22.1	3088	1.48 [d, Hz, (12H	<sup>2</sup> <i>J</i> ( <b>P</b> — <b>H</b> ) )], 7.42 (n	10.9, <sup>3</sup> J n, 10H)	(Pt—H)	32.3
5	-8.1	3119	1.76 [d, <sup>2</sup> . (6H)], 7.4	/(PH) 1 (m, 20H	0.2, ${}^{3}J(P-$	—H) 33.0	Hz,
6	8.8	3190	7.3 (m)		/		
7	33.9	3112	7.8 (m, 8	H), 7.4 (n	n, 12H), 2	2.28 (m, 4	H)
8	53.4		7.6 (m, 8	H), 7.3 (n	1, 12H), 2	2.4 (m, 4I	T)
9			6.37 (s)		. ,.	•	
<b>10</b> <sup>a</sup>	-7.0	3072					
			<sup>31</sup> P NMR				
		$\delta_{a}$	$\delta_{x}$	${}^{i}J_{a}$	${}^{1}J_{x}$	${}^{2}J_{ax}$	
$Pt(NSO)Cl(PEt_3)_2$ (11) 7.4		0.2	3640	2734	20		
$\begin{array}{llllllllllllllllllllllllllllllllllll$		-0.6	-6.3	3695	2944	20	
		39.8	33.8	3700	3003	8	

Table 2.  $^{31}P$  and  $^{1}H$  NMR data for compounds of the type  $ML_2(NSO)_2$  and  $Pt(NSO)Cl(PR_3)_2$ 

<sup>a</sup>(10) =  $Pt(NSO)_2(PBu_3^n)_2$ .

Compound	V <sub>asym</sub>	$v_{sym}$	Def.	<b>M</b> +	M <sup>+</sup> —NSO	M <sup>+</sup> (NSO) <sub>2</sub>
1	1245s	1061m	567w	471	409	346
	1230vs	1047vs				
2	1243vs	1057s	567m	555	493	
	1228vs	1050s	554m			
3	1249vs	1058vs	545m	639	576	513
	1221m					
4	1242vs	1055vs	555w	596	533	
		1020m				
5	1242vs	1062s	569w	720	658	596
6	1243vs	1062m	547m			
	1228s	1092m				
7	1239vs	1057s	562w			
		1012m				
8	1250vs	1054s				
		1010m				
9	1235vs	1075s	525m	302	246	

Table 3. Mass spectral and selected NSO IR vibrations

under the same experimental conditions as above except that the crystals were grown by slow diffusion of *n*-hexane (15 cm<sup>3</sup>) into a  $CH_2Cl_2$  (5 cm<sup>3</sup>) solution at room temperature.

Crystal data.  $C_6H_{18}N_2O_2P_2S_2Pt$ , M = 471.4, monoclinic, a = 9.963(2), b = 13.903(2), c = 11.406(2) Å,  $\beta = 109.85(2)^\circ$ , U = 1486 Å<sup>3</sup>, space group  $P2_1/n$ , Z = 4,  $D_c = 2.11$  g cm<sup>-3</sup>. Yellow, airstable prisms, dimensions  $0.03 \times 0.20 \times 0.23$  mm,  $\mu$ (Cu- $K_{\alpha}$ ) = 225 cm<sup>-1</sup>,  $\lambda = 1.54178$  Å, F(000) = 896.

Data collection and processing. A Nicolet R3m diffractometer,  $\omega$ -scan method,  $(2\theta \le 100^\circ)$ , graphite-monochromated Cu- $K_{\alpha}$  radiation; 1523 independent measured reflections of which 1387 were observed  $[|F_o| > 3\sigma(|F_o|)]$ , corrected for Lorentz and polarization factors; empirical absorption correction based on 362 azimuthal measurements (laminar correction (100) prominent). Minimum and maximum transmission factors were 0.018 and 0.097.

Structure analysis and refinement. The structure was solved by the heavy atom method and all the non-hydrogen atoms refined anisotropically. The hydrogen atoms were idealized (C-H = 0.96 Å), assigned isotropic thermal parameters U(H) $= 1.2U_{eq}(C)$  and allowed to ride on their parent carbons. The methyl groups were refined as rigid bodies. Refinement was by block-cascade full-R = 0.052, matrix least-squares to (R = $\Sigma[|F_{\rm o}| - |F_{\rm c}|]/\Sigma|F_{\rm o}|],$  $R_{\rm w} = 0.055$  $(\mathbf{w}^{-1} = \sigma^2(F))$  $+0.00130F^2$ ). The maximum and minimum residual electron density in the final  $\Delta F$  map were 1.47 and -1.46 eÅ<sup>-3</sup>, respectively. The mean and maximum shifts/error in the final refinement cycle were 0.004 and 0.052, respectively. Computations were carried out on an Eclipse S140 computer using the SHELXTL program system<sup>10</sup> and published scattering factors.

#### **RESULTS AND DISCUSSION**

Reaction between  $PtCl_2(PR_3)_2$  and  $S(NSO)_2$ gives  $Pt(NSO)_2(PR_3)_2$  in good yield, *ca* 60% [eq. (1)]

$$Pt(PR_3)_2Cl_2 + S(NSO)_2 \longrightarrow$$

 $Pt(NSO)_2(PR_3)_2 + SCl_2.$  (1)

<sup>31</sup>P NMR shows that the reaction proceeds almost quantitatively with the only other observable phosphorus-containing species being  $PtS_2N_2(PR_3)_2$  (*ca* 5%). The observed disulphurdinitrido complex is probably formed from the products of the reaction between the eliminated SCl<sub>2</sub> and liquid ammonia [eq. (2)]

$$6SCl_{2} + 18NH_{3} \longrightarrow 3S_{2}N_{2}^{2^{-}} + 12NH_{4}Cl + 6H^{+}$$

$$S_{2}N_{2}^{2^{-}} + PtCl_{2}(PR_{3})_{2} \longrightarrow$$

$$Pt(S_{2}N_{2})(PR_{3})_{2} + 2Cl^{-}.$$
 (2)

We have shown previously that reaction of an ammonia solution of SCl<sub>2</sub> with PtCl<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub> gives exclusively Pt(S<sub>2</sub>N<sub>2</sub>)(PR<sub>3</sub>)<sub>2</sub>.<sup>11</sup> When a slight excess of PtCl<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub> to S(NSO)<sub>2</sub> is used (1.2:1.0 molar ratio), *ca* 25% Pt(S<sub>2</sub>N<sub>2</sub>)(PR<sub>3</sub>)<sub>2</sub> is observed by <sup>31</sup>P NMR. Further increasing the molar ratio to (2:1) gives Pt(NSO)<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub> (25%), Pt(NSO)Cl(PR<sub>3</sub>)<sub>2</sub> (50%) and Pt(S<sub>2</sub>N<sub>2</sub>)(PR<sub>3</sub>)<sub>2</sub> (25%).

The <sup>31</sup>P NMR spectra of 1–7 (Table 2) consist of singlets with platinum satellites indicating that the

phoshines are equivalent. The magnitude of the <sup>31</sup>P-<sup>195</sup>Pt coupling constant (ca 3100 Hz) is appropriate for platinum(II) and suggests nitrogen rather than oxygen bound NSO<sup>-</sup> ligands. (2850 Hz for phosphorus *trans* to nitrogen in  $Pt(S_2N_2)(PR_3)_2$ , 3250 Hz in Pt(S<sub>2</sub>N<sub>2</sub>H)(PR<sub>3</sub>) $_{2}^{+}$ X<sup>-</sup>.)<sup>8,11</sup> An oxygen bound ligand would be expected to have a greater coupling constant. Detailed analysis of the fragmentation pattern of the mass spectra shows peaks corresponding to  $Pt(NSO)(NS)(PR_1)^+_2$  and  $Pt(NS)_2(PR_3)_2^+$ , both of which could not be readily accounted for if the complex was oxygen bound. Finally, nitrogen bound NSO<sup>-</sup> ligands are more likely, as nitrogen is expected to formally carry the negative charge. The  ${}^{31}P$  chemical shifts and  ${}^{1}J$ couplings are dependant on the phosphine. The observed shifts in the complexes mirror the shifts in the uncoordinated phosphine. For example, on increasing the number of methyl groups from PPh<sub>3</sub> through to PMe<sub>3</sub> the chemical shift becomes more negative and the magnitude of  ${}^{1}J$  is reduced. Methyl groups are better  $\sigma$ -donors than phenyl groups and poorer  $\pi$ -acceptors. Thus, increasing the number of methyl groups results in greater electron density on the phosphorus atoms, better shielding and more negative chemical shifts.

The <sup>31</sup>P NMR spectra of **11–13** are of the AX type with <sup>2</sup>J <sup>31</sup>P—<sup>31</sup>P couplings of 20 Hz, typical for platinum(II).<sup>8,11</sup> The <sup>195</sup>Pt–<sup>31</sup>P coupling constants of 3650 and 2850 Hz are typical of phosphorus *trans* to chlorine and nitrogen in platinum(II) complexes, leading us to postulate the existence of these PtCl(NSO)(PR<sub>3</sub>)<sub>2</sub> complexes (N.B. no solid compounds of this formula have

been isolated to date). Further evidence for our formulation comes from the position of the resonances in 11. For example, phosphorus *trans* to nitrogen occurs at 0.2 ppm compared to 1.5 ppm in 2, and phosphorus *trans* to chlorine occurs at 7.4 ppm compared to 9.1 ppm in  $PtCl_2(PEt_3)_2$ .

<sup>1</sup>H NMR (Table 2) for 1, 4 and 5 reveal methyl resonances split by both  ${}^{2}J_{P-H}$  of 11 Hz and  ${}^{3}J_{Pt-H}$  of *ca* 34 Hz. This again indicates identical phosphine groups in a symmetric environment. For the other complexes (2, 3, 6, 7) the small differences in chemical shifts hide the couplings.

Compounds 1 and 9 exhibit characteristic NSO vibrations in the regions 1250-1200 cm<sup>-1</sup> and 1090-1040  $\text{cm}^{-1}$  corresponding to the asymmetric and symmetric stretching modes, respectively. Previous IR studies of RNSO compounds suggest that these two modes are not strongly coupled. Individual modes were assigned to v(NS) or v(SO) although the subject of disagreement in these compounds has been largely resolved with the higher frequency mode being assigned as the v(NS). In this study compounds 1 and 2 both show two  $v_{asym}$  and  $v_{sym}$ vibrations and in the absence of coupled modes suggests two inequivalent NSO groups. This cannot be reconciled with the crystal structure which shows a symmetric environment and similarly with the  ${}^{31}P$ NMR. For compounds 4, 5, 7 and 8 only one band for the  $v_{asym}$  is observed although this is broadened relative to the  $v_{asym}$  observed in 1 and 2. However, the  $v_{svm}$  shows two modes although these are partially covered by ligand modes.

The X-ray structure of 1 is shown in Fig. 1 with bond lengths and angles in Table 4. The molecule

Pt—P(1)	2.262(3)	Pt—P(2)	2.264(4)
Pt - N(1)	2.049(11)	Pt—N(2)	2.049(10)
<b>P</b> (1)— <b>C</b> (1)	1.788(26)	P(1)—C(2)	1.796(16)
P(1)C(3)	1.797(18)	P(2)C(4)	1.763(23)
P(2)—C(5)	1.786(25)	P(2)—C(6)	1.818(19)
N(1)—S(1)	1.492(13)	S(1)—O(1)	1.456(19)
N(2)—S(2)	1.465(14)	S(2)O(2)	1.442(18)
P(1) - Pt - P(2)	96.3(1)	P(1)— $Pt$ — $N(1)$	88.5(3)
P(2) - Pt - N(1)	174.7(3)	P(1) - Pt - N(2)	173.1(4)
P(2) - Pt - N(2)	90.2(4)	N(1)— $Pt$ — $N(2)$	85.1(5)
Pt - P(1) - C(1)	113.1(7)	Pt—P(1)—C(2)	119.8(5)
C(1) - P(1) - C(2)	2) 105.5(11)	Pt-P(1)-C(3)	113.1(7)
C(1) - P(1) - C(3)	s) 103.2(11)	C(2)-P(1)-C(3	) 100.3(8)
Pt - P(2) - C(4)	116.9(7)	Pt—P(2)—C(5)	116.4(8)
C(4) - P(2) - C(5)	5) 103.2(12)	PtP(2)C(6)	113.6(7)
C(4) - P(2) - C(6)	5) 102.0(11)	C(5)-P(2)-C(6	) 102.8(11)
Pt-N(1)-S(1)	129.5(9)	N(1) - S(1) - O(1)	) 123.3(8)
Pt-N(2)-S(2)	132.6(8)	N(2) - S(2) - O(2)	2) 121.4(8)

Table 4. Bond lengths and angles for  $Pt(NSO)_2(PMe_3)_2$  (1)



Fig. 1. The X-ray structure of 1.

has slightly distorted *cis* square-planar geometry with local non-crystallographic  $C_2$  symmetry and the expected bond lengths and angles. The Pt—N(1)—N(2) and Pt—P(1)—P(2) planes are rotated *ca* 3° with respect to each other about an axis bisecting the P(1)—Pt—P(2) angle. The two Pt—N—S—O planes are rotated 85° from the coordination plane. There is no crystallographic evidence to explain the complexity of the IR spectrum; there are no significant intermolecular contacts.

#### REFERENCES

- 1. H. W. Roesky, K. K. Pandey, B. Krebs and M. J. Dartmann, J. Chem. Soc., Dalton Trans. 1984, 2271.
- H. Dieno, H. W. Roesky, M. Noltemeyer and G. M. Sheldrick, J. Chem. Soc., Chem. Commun. 1987, 1483.
- 3. M. Hebberhold, F. Neumann, G. S. Fink and U. Thewalt, *Inorg. Chem.* 1987, 26, 3612.
- R. Short, M. B. Hursthouse, T. G. Purcell and J. D. Woollins, J. Chem. Soc., Chem. Commun. 1987, 407.
- 5. T. Chivers, K. S. Dhathathreyan, C. Lensink and J. F. Richardson, *Inorg. Chem.* 1988, 27, 1570.
- 6. I. P. Parkin, P. S. Belton, J. D. Woollins and D. J. Williams, J. Chem. Soc., Chem. Commun., submitted.
- 7. I. P. Parkin, J. D. Woollins and D. J. Williams, J. Chem. Soc., Dalton Trans., submitted.
- R. Jones, C. P. Warrens, D. J. Williams and J. D. Woollins, J. Chem. Soc., Dalton Trans. 1987, 907.
- 9. D. A. Armitiage and A. W. Sinder, *Inorg. Chem.* 1972, 11, 1151.
- G. M. Sheldrick, SHELXTL, An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data. University of Göttingen, F.R.G. (1978) (revision 4.1 1983).
- 11. I. P. Parkin, unpublished results.