Hydrolysis Reaction of $[Pt(NSO)_2(PMe_2Ph)_2]$. Crystal Structures of $[Pt(SO_3)(PMe_2Ph)_3]\cdot H_2O$ and $[\{Pt(SO_3)(PMe_2Ph)_2\}_2]\cdot 5CHCl_3$†

Vanessa C. Ginn, Paul F. Kelly, Christos Papadimitriou, Alexandra M. Z. Slawin, David J. Williams and J. Derek Woollins*
Department of Chemistry, Imperial College, South Kensington, London SW7 2AY, UK

The reaction of $[Pt(NSO)_2(PMe_2Ph)_2]$ with water in dichloromethane gives the compounds $[Pt(SO_3)(PMe_2Ph)_3]\cdot H_2O$ **1** and $[\{Pt(SO_3)(PMe_2Ph)_2\}_2]\cdot 5CHCl_3$ **2** which have been characterised by multielement NMR spectroscopy and X-ray crystallography. The mononuclear compound **1** has tetrahedrally distorted square-planar co-ordination of the platinum by three phosphines and the sulfur atom of the sulfite with *trans* angles of 160.4(1) and 161.2(1)°. The binuclear complex **2** contains a six-membered $Pt_2S_2O_2$ ring in a chair conformation with each platinum being co-ordinated by two phosphines and a sulfur and oxygen atom of the different SO_3^{2-} ligands. Phosphorus-31 NMR studies show that the reaction of Ag_2SO_3 with $[PtCl_2(PR_3)_2]$ gives **1** and **2** or simple, O,O′ complexes depending on the nature of PR_3.

We have recently reported[1,2] the preparation of a number of complexes containing the NSO^- ligand. Since SO_2 complexes undergo a number of insertion/addition reactions we have begun investigations into the reactivity of $[Pt(NSO)_2(PMe_2Ph)_2]$ with a variety of reagents. Here, we report the preparation and X-ray crystal structures of $[Pt(SO_3)(PMe_2Ph)_3]\cdot H_2O$ and $[\{Pt(SO_3)(PMe_2Ph)_2\}_2]\cdot 5CHCl_3$ from simple hydrolysis reactions.

Experimental

General experimental procedures were as previously described;[3] unless otherwise stated reactions were performed under N_2 or argon. Phosphorus-31 and ^{195}Pt NMR spectra were recorded in $CDCl_3$ on a JEOL JNM EX270 spectrometer operating at 109.38 and 58 MHz respectively and are referred to 85% H_3PO_4 and Na_2PtCl_6(aq.). IR spectra were recorded as KBr discs using a Perkin Elmer 1720X FT IR spectrometer. Microanalyses were performed by Imperial College Microanalytical Laboratories. The compound $[Pt(NSO)_2(PMe_2Ph)_2]$ was prepared by the literature method[2] and its purity checked by microanalysis and ^{31}P NMR spectroscopy.

$[Pt(SO_3)(PMe_2Ph)_3]\cdot H_2O$ **1**.—A solution of $[Pt(NSO)_2(PMe_2Ph)_2]$ (0.15 g, 0.25 mmol) in CH_2Cl_2 (100 cm^3) was treated with rigorously degassed water (0.1 cm^3) and stirred for 2 d. During this time the solution lightened in colour and gradually precipitated a white solid. After filtration (which yielded 78 mg of white solid) the volume of the solution was reduced to 3 cm^3 *in vacuo* and a $^{31}P\text{-}\{^1H\}$ NMR spectrum recorded. This showed that complete conversion to $[Pt(SO_3)(PMe_2Ph)_3]$ had occurred with the latter being characterised by a doublet at δ −3.4 [$^1J(^{31}P\text{-}^{195}Pt)$ 2976 Hz] and a triplet at δ −25.1 [$^1J(^{31}P\text{-}^{195}Pt)$ 1767 Hz]. The ^{195}Pt NMR spectrum consisted of a triplet of doublets centred around δ −4390. Slow diffusion of Et_2O into this solution gave well formed yellow crystals, yield 60 mg, 35% (based on platinum) {Found: C, 40.3; H, 4.7; N, 0.0; S, 4.1. Calc. for $[Pt(SO_3)(PMe_2Ph)_3]\cdot H_2O$: C, 40.0; H, 4.8; N, 0.0; S, 4.5%}.

$[\{Pt(SO_3)(PMe_2Ph)_2\}_2]\cdot 5CHCl_3$ **2**.—A crude unfiltered solution of $[Pt(SO_3)(PMe_2Ph)_3]$ was prepared as above and the solvent removed *in vacuo*. The residue was treated with anhydrous $CHCl_3$ (100 cm^3, Aldrich) and refluxed for 26 h. The resulting clear solution was reduced in volume to 3 cm^3 *in vacuo* and layered with Et_2O to give white crystals, yield 62 mg, 42% (Found: C, 33.7; H, 4.0; N, 0.0; S, 5.4. Calc. for $[\{Pt(SO_3)(PMe_2Ph)_2\}_2]$: C, 34.9; H, 4.0; N, 0.0; S, 5.8%). A closer fit for the microanalytical data could be obtained by including solvate molecules but the degree of solvation was found to be variable. ^{31}P NMR spectrum: AA′XX′ system, δ −21.1 [$^1J(^{31}P\text{-}^{195}Pt)$ 3986, P(2) *trans* to oxygen], −7.5 [$^1J(^{31}P\text{-}^{195}Pt)$ 2329, P(1) *trans* to sulfur]; $^2J(^{31}P\text{-}^{31}P)$ 21.0, $^5J(^{31}P\text{-}^{31}P)$ 4.7 (*trans*), $^5J(^{31}P\text{-}^{31}P)$ 0.4 Hz (*cis*).

X-Ray Crystallography.—Crystal data for **1**. $C_{24}H_{35}O_4P_3PtS$, M = 707.6, monoclinic, space group $P2_1/n$, a = 11.415(4), b = 17.541(6), c = 14.377(5) Å, β = 101.33(3)°, U = 2823 Å^3, Z = 4, D_c = 1.665 g cm^{-3}. Clear yellow block, dimensions 0.40 × 0.40 × 0.50 mm, μ(Mo-Kα) = 52.4 cm^{-1}, λ = 0.710 73 Å, $F(000)$ = 1400.

Data collection and processing. Siemens P4/PC diffractometer, ω-scan method, ($3 \leqslant 2\theta \leqslant 50°$), graphite monochromated Mo-Kα radiation; 4986 independent measured reflections, 3889 observed [$|F_o| > 3\sigma(|F_o|)$], corrected for Lorentz and polarisation factors; empirical absorption correction; maximum and minimum transmission factors 0.117 and 0.090 respectively.

Crystal data for **2**. $C_{37}H_{49}Cl_{15}O_6P_4Pt_2S_2$, M = 1699.6, monoclinic, space group $P2_1/a$, a = 10.917(3), b = 25.499(8), c = 12.229(2) Å, β = 106.10(2)°, U = 3280 Å^3, Z = 2 (the molecule is disposed about a centre of symmetry), D_c = 1.721 g cm^{-3}. White, air-stable needles, dimensions 0.10 × 0.33 × 0.33 mm, μ(Cu-Kα) = 153.07 cm^{-1}, λ = 1.541 78 Å, $F(000)$ = 1644.

Data collection and processing. Siemens P3/PC diffractometer, ω-scan method, ($0 \leqslant 2\theta \leqslant 116°$), graphite monochromated Cu-Kα radiation; 3871 independent measured reflections, 3046 observed [$|F_o| > 4\sigma(|F_o|)$], corrected for Lorentz and polarisation factors; empirical absorption correction; maximum and minimum transmission factors 0.431 and 0.071 respectively.

Structure analysis and refinement. The structures were solved by the heavy-atom method and all the non-hydrogen atoms refined anisotropically. The hydrogen atoms were idealised

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

(C–H = 0.96 Å), assigned isotropic thermal parameters U(H) = $1.2U_{eq}$(C) and allowed to ride on their parent carbons. Refinement was by full-matrix least squares to R = 0.0448 and 0.0822 [$R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$], R' = 0.0450 and 0.0817 [$w^{-1} = \sigma^2(F) + 0.0010$ and $0.0005F^2$] for **1** and **2** respectively. The maximum and minimum residual electron densities in the final ΔF map were 1.91, 3.07 and −0.83, −1.73 e Å^{-3} and the mean and maximum shifts/error in the final refinement cycle were 0.002, 0.062 and 0.000, 0.003 for **1** and **2** respectively. In **2** one chloroform is disordered and was refined with two idealised, distinct orientations of the three chlorine atoms. The other two chloroform molecules were refined with 75% occupancies; the high final R value for **2** is due to the disorder in the solvate chloroform molecules. Computations were carried out on an IBM 386 computer using the SHELXTL PC program system.[4]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Freshly prepared solutions of [Pt(NSO)$_2$(PMe$_2$Ph)$_2$] in CH$_2$Cl$_2$ exhibit the expected ^{31}P-{^{1}H} NMR spectrum [δ −22.1, ^1J(^{31}P–^{195}Pt) 3080 Hz]. However, after several hours the spectrum becomes more complicated with the appearance of a number of extra peaks. Careful exclusion of air and moisture inhibits the change in the spectrum and blank experiments using dry O$_2$ or degassed water show that the reaction is hydrolytic (Fig. 1). The most prominent feature of this new spectrum is the presence of a doublet at δ −3 and a triplet as δ −25 [^1J(^{31}P–^{31}P) = 21 Hz]. The relative intensities of these two resonances implies the presence of a species of the type [PtX(PMe$_2$Ph)$_3$], *i.e.* with platinum bound to three phosphine groups and one other ligand. The ^{195}Pt NMR spectrum of this species consists of a triplet of doublets reflecting the presence of two equivalent and one inequivalent phosphine groups. The magnitude of the ^1J(^{31}P–^{195}Pt) coupling constant for the satellites associated with the triplet resonance is extremely low (1770 Hz) indicating that that 'X' is a species with a strong *trans* influence.[5] At this point the mixture consists of a pale yellow solution together with a white insoluble solid. If the filtered solution is concentrated and layered with Et$_2$O, well formed yellow crystals may be obtained. X-ray crystallography reveals the compound to be [Pt(SO$_3$)(PMe$_2$Ph)$_3$]·H$_2$O **1** containing an SO$_3$$^{2-}$ ligand bound to the metal through sulfur (Tables 1 and 2, Fig. 2).

The geometry about platinum is noticeably distorted from square planar towards tetrahedral with P(1) and S(1) below the co-ordination plane and P(2) and P(3) above this plane. The P(2)–Pt–P(3) and P(1)–Pt–S(1) angles are 160.4(1) and 161.2(1)° respectively. The potential C_s symmetry of the molecule about the P(1)–Pt–S(1) axis is broken by the phenyl group on P(1) [*trans* to S(1)]. The Pt–P distances fall between 2.316(3) [Pt–P(3)] and 2.363(2) Å [Pt–P(1)] with the latter reflecting the strong *trans* influence of the sulfite group; this can be correlated with the low ^1J(^{31}P–^{195}Pt) coupling constant observed for this phosphine. The difference of 0.015 Å between Pt–P(2) and Pt–P(3) is statistically significant but is not readily rationalised. The S–O bond lengths are comparable with those observed[6,7] in species such as Na$_6$[Pd(SO$_3$)$_4$]·2H$_2$O and Na$_2$[Pd(SO$_3$)$_2$(NH$_3$)$_2$]·6H$_2$O, the geometry about the sulfur atom being close to tetrahedral. Compound **1** crystallises with one molecule of water per asymmetric unit. There are no hydrogen-bonding interactions between this water molecule and the oxygen atoms of the sulfite group; indeed there are no significant intermolecular packing interactions.

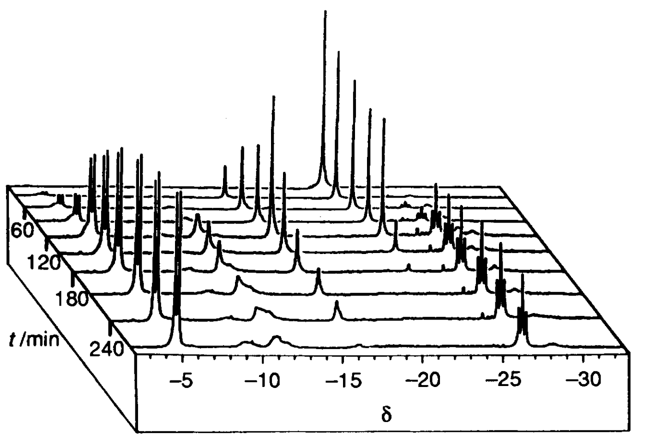

Fig. 1 Stack plot to illustrate the change in the ^{31}P-{^{1}H} NMR spectrum of [Pt(NSO)$_2$(PMe$_2$Ph)$_2$] upon the addition of two drops of water

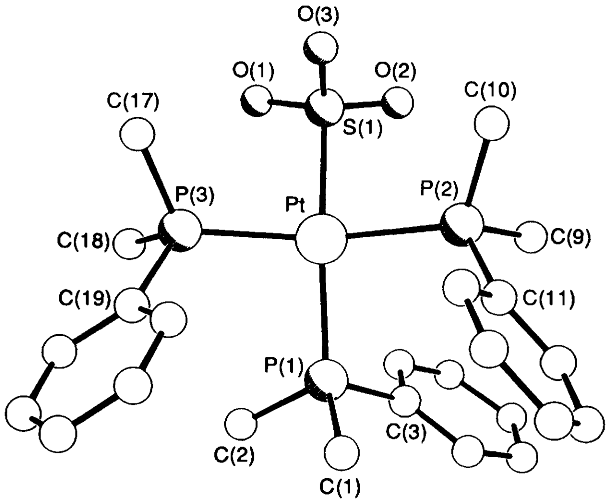

Fig. 2 X-Ray crystal structure of [Pt(SO$_3$)(PMe$_2$Ph)$_3$]·H$_2$O

In the pure state [Pt(SO$_3$)(PMe$_2$Ph)$_3$] is thermally stable and no change is seen in its ^{31}P-{^{1}H} NMR spectrum obtained after refluxing for several hours in CHCl$_3$. However, if this reflux is performed using the unpurified compound (*i.e.* in the presence of the insoluble solid) then ^{31}P-{^{1}H} NMR spectroscopy shows a gradual decrease in the intensity of the peaks due to the starting material and the appearance of an entirely new set of resonances. Fig. 3. shows the spectrum after refluxing for 26 h; at this point the solution is totally clear with all of the original solid having been dissolved. The most intense feature of the spectrum appears, at normal resolution, as an AX pair of doublets. There is a notable disparity in the magnitude of the two ^1J(^{31}P–^{195}Pt) coupling constants associated with each resonance; for that at δ −21 the coupling is 3986 Hz whilst the resonance at δ −7.5 shows a coupling of 2329 Hz. Careful examination of a resolution-enhanced spectrum reveals it to be of the AA'XX' rather than the AX type. As Fig. 3 shows, two other resonances are also observed in the spectrum of the crude product at δ −14.9 [^1J(^{31}P–^{195}Pt) 2466] and −18.0 [^1J(^{31}P–^{195}Pt) 3848 Hz].

Slow diffusion of diethyl ether into the above solution yields white needles and X-ray crystallography reveals the compound to be [{Pt(SO$_3$)(PMe$_2$Ph)$_2$}$_2$]·5CHCl$_3$ **2** (Tables 3 and 4, Fig. 4). In contrast to **1** where the platinum atom is co-ordinated by three phosphines and one sulfite ligand here a dimeric structure is formed with two bidentate sulfite bridging ligands. Although this binding mode has been postulated for sulfite groups[8] (on the basis of IR data) this is the first X-ray crystallographic evidence for such an arrangement. The molecule has crystallographic C_i symmetry, with distorted square-planar geometry at the platinum atoms [maximum deviation 0.06 Å

Table 1 Atomic coordinates (× 10^4) for $[Pt(SO_3)(PMe_2Ph)_3]\cdot H_2O$

Atom	*x*	*y*	*z*
Pt	669(1)	227(1)	2913(1)
P(1)	1000(2)	1553(1)	3099(2)
C(1)	863(9)	2213(5)	2104(7)
C(2)	111(9)	2036(5)	3846(7)
C(3)	2506(8)	1670(5)	3798(6)
C(4)	3384(9)	2106(5)	3514(6)
C(5)	4531(9)	2121(6)	4068(7)
C(6)	4799(8)	1723(6)	4897(7)
C(7)	3907(11)	1325(7)	5220(8)
C(8)	2797(9)	1285(6)	4655(7)
P(2)	2359(2)	21(1)	2264(2)
C(9)	3818(10)	−10(6)	3043(8)
C(10)	2297(10)	−853(5)	1577(9)
C(11)	2477(8)	725(5)	1365(6)
C(12)	1531(9)	728(6)	571(7)
C(13)	1553(11)	1258(7)	−156(8)
C(14)	2478(11)	1787(7)	−80(8)
C(15)	3379(10)	1781(7)	715(8)
C(16)	3382(8)	1250(5)	1410(7)
P(3)	−1315(2)	269(1)	3058(2)
C(17)	−2192(9)	−537(6)	2561(8)
C(18)	−1666(11)	352(6)	4237(7)
C(19)	−2086(8)	1051(5)	2361(6)
C(20)	−2914(9)	1520(6)	2690(7)
C(21)	−3444(10)	2107(7)	2133(8)
C(22)	−3172(9)	2247(6)	1284(8)
C(23)	−2392(9)	1792(6)	922(7)
C(24)	−1855(9)	1189(6)	1484(7)
S(1)	678(2)	−1081(1)	3243(2)
O(1)	−54(6)	−1185(4)	3983(4)
O(2)	1924(6)	−1268(4)	3615(6)
O(3)	187(4)	−1502(3)	2376(3)
O(30)	−5148(4)	599(3)	−762(3)

Table 2 Selected bond lengths (Å) and angles (°) for the complex $[Pt(SO_3)(PMe_2Ph)_3]\cdot H_2O$

Pt–P(1)	2.363(2)	Pt–P(2)	2.331(3)
Pt–P(3)	2.316(3)	Pt–S(1)	2.342(2)
S(1)–O(1)	1.486(8)	S(1)–O(2)	1.456(7)
S(1)–O(3)	1.463(5)		
P(1)–Pt–P(2)	94.1(1)	P(1)–Pt–P(3)	95.5(1)
P(2)–Pt–P(3)	160.4(1)	P(1)–Pt–S(1)	161.2(1)
P(2)–Pt–S(1)	87.6(1)	P(3)–Pt–S(1)	88.7(1)
Pt–S(1)–O(1)	106.6(3)	Pt–S(1)–O(2)	105.1(3)
O(1)–S(1)–O(2)	110.8(4)	Pt–S(1)–O(3)	109.7(2)
O(1)–S(1)–O(3)	111.9(4)	O(2)–S(1)–O(3)	112.4(4)

for O(1′)]. There is, however, a small tetrahedral distortion although it is significantly reduced compared to **1** [*trans* angles of 170.6(2) and 173.5(3)°, *cf.* 160.4(1) and 161.2(1)° in **1**]. As Fig. 4 highlights, the core of the molecule adopts a chair conformation with the planar O(1)–S(1)–O(1′)–S(1′) unit being inclined by 124° with respect to the Pt–O(1)–S(1′) and Pt′–O(1′)–S(1) planes. Within the six-membered rings the O(1)–Pt–S(1′) angle is slightly reduced at 82.8(3)° whereas that at S(1) is close to tetrahedral [Pt–S(1)–O(1) 103.2(4)°] and that at oxygen is enlarged [S(1)–O(1)–Pt′ 125.0(9)°]. The transannular S ··· S′ and Pt ··· Pt′ distances are 3.6 and 4.3 Å respectively. The different Pt–P bond distances reflect the nature of the atom *trans* to the phosphorus, with Pt–P(1) (*trans* to S) being longer. The geometries at the sulfur atoms are approximately tetrahedral, and as expected the bridging S(1)–O(1) bond length [1.538(13) Å] is longer than the exocyclic S–O bond lengths (average 1.45 Å); the latter are comparable to those in **1**. As in **1** there are no significant intermolecular contacts in the structure of **2**.

Table 3 Atomic coordinates (× 10^4) for $[\{Pt(SO_3)(PMe_2Ph)_2\}_2]\cdot 5CHCl_3$

Atom	*x*	*y*	*z*
Pt	1607(1)	379(1)	1164(1)
P(1)	2106(6)	1252(2)	1053(5)
C(1)	3750(23)	1434(8)	1226(25)
C(2)	1367(27)	1510(9)	−325(19)
C(3)	1575(24)	1657(8)	2022(16)
C(4)	327(26)	1563(8)	2131(19)
C(5)	−194(28)	1869(10)	2813(24)
C(6)	484(31)	2264(10)	3394(28)
C(7)	1666(40)	2376(9)	3261(27)
C(8)	2210(25)	2089(8)	2589(22)
P(2)	2771(5)	245(2)	2959(4)
C(9)	3859(24)	−318(8)	3028(20)
C(10)	1753(25)	95(10)	3851(20)
C(11)	3796(20)	749(7)	3761(15)
C(12)	3396(23)	1088(8)	4411(19)
C(13)	4152(29)	1470(10)	5074(23)
C(14)	5364(33)	1496(11)	5048(26)
C(15)	5835(29)	1160(13)	4445(29)
C(16)	4993(27)	780(10)	3779(21)
S(1)	868(5)	−483(2)	982(4)
O(1)	−587(11)	−418(4)	539(11)
O(2)	1116(15)	−788(5)	2007(12)
O(3)	1310(14)	−728(5)	77(13)
C(20)	−45(7)	−1522(3)	3527(5)
Cl(1)	291	−1109	4737
Cl(2)	−1630	−1752	3254
Cl(3)	1006	−2064	3830
C(30)	1880(10)	3331(3)	−691(8)
Cl(4)	1651	3029	538
Cl(5)	370	3463	−1647
Cl(6)	2719	2896	−1349
C(40)	7661(10)	137(5)	1734(10)
Cl(7)	6160	275	765
Cl(8)	8073	658	2722
Cl(9)	7526	−443	2485
Cl(7′)	6808	738	1527
Cl(8′)	8494	77	3192
Cl(9′)	6577	−388	1330

Table 4 Selected bond lengths (Å) and angles (°) for the complex $[\{Pt(SO_3)(PMe_2Ph)_2\}_2]\cdot 5CHCl_3$

Pt–P(1)	2.305(5)	Pt–P(2)	2.236(5)
Pt–S(1)	2.330(5)	Pt–O(1′)	2.074(12)
S(1)–O(1)	1.538(13)	S(1)–O(2)	1.435(15)
S(1)–O(3)	1.464(17)		
P(1)–Pt–P(2)	97.2(2)	P(1)–Pt–S(1)	170.6(2)
P(2)–Pt–S(1)	92.1(2)	P(1)–Pt–O(1′)	87.9(3)
P(2)–Pt–O(1′)	173.5(3)	S(1)–Pt–O(1′)	82.8(3)
Pt–S(1)–O(1)	103.2(4)	Pt–S(1)–O(2)	116.8(6)
O(1)–S(1)–O(2)	107.0(9)	Pt–S(1)–O(3)	107.3(6)
O(1)–S(1)–O(3)	107.7(8)	O(2)–S(1)–O(3)	114.0(9)
S(1)–O(1)–Pt′	125.0(9)		

Given the structure of **2** it is possible tentatively to assign the other resonances seen at δ −14.9 and δ −18.0 in Fig. 3. The $^1J(^{31}P-^{195}Pt)$ coupling constants associated with these two peaks (2466 and 3848 Hz respectively) are similar to those for P *trans* to S (2329 Hz) and P *trans* to O (3986 Hz) observed in **2**. It is therefore likely that these resonances are due to the head-to-head dimer rather than the observed crystallised head-to-tail dimer. Although this structure is only speculative it should be noted that whenever these two peaks occur they are always present as a pair of equal intensity which lends weight to the suggestion that they result from one molecule.

The IR spectra of **1** and **2** contain characteristic bands due to the phosphine groups. The 12 strong vibrations occur in the

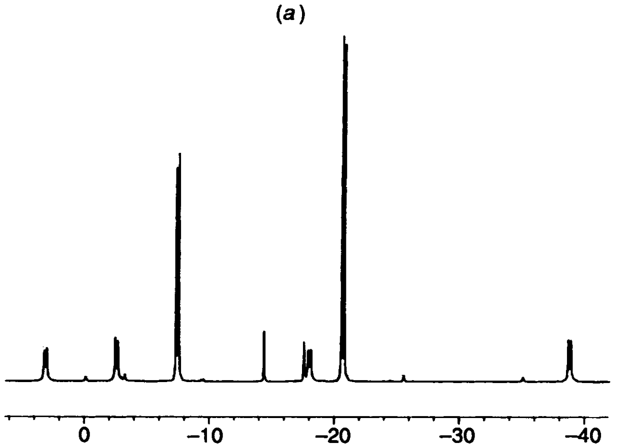

Fig. 3 $^{31}P-\{^1H\}$ NMR spectrum obtained after refluxing impure **1** in $CDCl_3$ for 26 h: (*a*) full spectrum recorded at 109.38 MHz and (*b*) selected parts of the spectrum recorded at 202 MHz and resolution enhanced

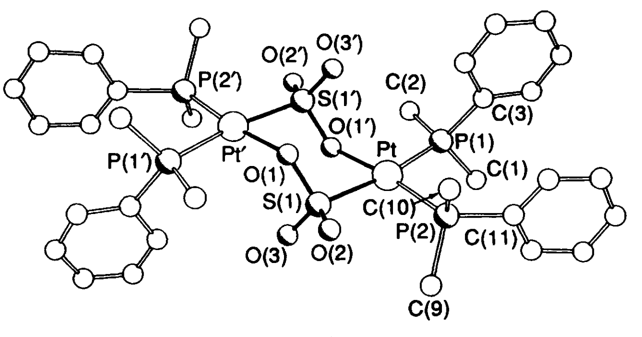

Fig. 4 X-Ray crystal structure of $[\{Pt(SO_3)(PMe_2Ph)_2\}_2]\cdot 5CHCl_3$

region (1100–400 cm^{-1}) where bands due to the sulfite ligand are also expected. Despite this, however, most of the predicted bands for the SO_3^{2-} ligands are observed in each case. In **1** co-ordination is *via* the sulfur atom and the compound thus retains the C_{3v} symmetry elements of the SO_3^{2-} anion; all four expected vibrational modes (two stretching and two bending) are observed at 1131s, 991s, 637s and 504w cm^{-1}. These values compare well with those observed for complexes such as $[Co(SO_3)(NH_3)_5]Cl$ (1110, 985, 633 and 519 cm^{-1}) where the ligand is also bound to the metal *via* the sulfur atom.[9]

The bidentate sulfite ligand has reduced symmetry and thus more bands are expected in the 1200–940 cm^{-1} (stretching) region. For $[\{Pt(SO_3)(PMe_2Ph)_2\}_2]$ vibrations are seen at 1168/1156m, 1048s and 1004m cm^{-1} with the highest frequency band being split. The observed[8] stretching vibrations for $Pd(SO_3)(phen)$ (phen = 1,10-phenanthroline), which is believed to have the same bridging co-ordination mode, are at 1175, 1067 and 939 cm^{-1} in the S–O stretching region.

The overall reaction can be summarised in equation (1). It is

$$[Pt(NSO)_2(PMe_2Ph)_2] + H_2O \longrightarrow [Pt(SO_3)(PMe_2Ph)_3] + \text{solid}$$

$$[Pt(SO_3)(PMe_2Ph)_3] + \text{solid} \xrightarrow{\Delta} [\{Pt(SO_3)(PMe_2Ph)_2\}_2] \quad (1)$$

clear that the nature of the insoluble solid formed is of crucial importance. The IR spectrum is dominated by peaks at 3177 and 1401 cm^{-1} which are characteristic of $[NH_4]^+$. The presence of this cation is also suggested by the high hydrogen content revealed by microanalysis (C, 14.7; H, 4.0; N, 6.10; Cl, 2.2; S, 8.8%) which give a ratio of 4.4C:14.2H:1.6N:1S (note that the chlorine content probably represents a small amount of $CHCl_3$ of solvation). The high carbon content suggests that it is a platinum–phosphine species; as Fig. 1 shows no formation of free PMe_2Ph (or of its sulfide or oxide) the production of a tris(phosphine) species must be balanced by the production of an insoluble mono(phosphine–platinum) species. However, to date we have been unable to characterise the insoluble solid which we obtain.

Mechanistically, the first stage of the reaction must involve attack on the NSO^- sulfur by one (or more) water molecules. One may envisage this leading to a complex of the type Pt–NH–S(OH)O as the first product. At what point the ligand changes from N- to S-co-ordination is unclear although a π-bonded intermediate is possibly involved. Such species are well known[10] for complexes of RNSO, and indeed it is interesting that the π-bonded $[Pt(PhNSO)(PPh_3)_2]$ has been shown to decompose to $[Pt(SO_4)(PPh_3)_2]$ in 'incompletely dried and deoxygenated solvent'.

Clearly the intermediate seen at δ −14.5 in Fig. 1 plays a vital role in the overall reaction and some clues as to its identity may be obtained from the NMR data. The $^1J(^{31}P-^{195}Pt)$ coupling constant in this case is 2503 Hz which is consistent with P being *trans* to S and is only slightly higher than that observed for **2**. Indeed both the coupling constant and the δ value are very similar to those observed for the P atom *trans* to S in the proposed isomer of the latter [δ −14.9, $^1J(^{31}P-^{195}Pt)$ 2466 Hz]. This would imply that the species may contain the SO_3 unit with one inequivalent oxygen, possibly in the form of OH. Almost certainly all the nitrogen has been removed from the ligand at this point since when this species is observed as a decomposition product of $[Pt(^{15}NSO)_2(PMe_2Ph)_2]$ no splittings due to ^{15}N can be seen [AA′XX′ system, δ (^{31}P) −21.6, δ(^{15}N) 382.7, $^2J(^{31}P-^{31}P)$ 23.02, $^2J(^{15}N-^{15}N)$ 0, $^2J(^{31}P-^{15}N)$ −1.7 (*cis*) and 28.6 Hz (*trans*)]. If at this stage of the reaction the ligand does still contain nitrogen it is not directly bonded to the metal.

It has been reported that reaction of Ag_2SO_3 with *cis*-$[PtCl_2(PPh_3)_2]$ gives $[Pt(SO_3)(PPh_3)_2]$ which was postulated as being monomeric with bidentate O,O′ co-ordination on the basis of IR studies. We have repeated this reaction as well as the analogous reactions using PMe_2Ph and PMe_3. Interestingly the reactions involving the smaller phosphines give rise to mixtures containing **1** and **2** (by ^{31}P NMR) whereas the reaction with PPh_3 gives a compound which has a simple ^{31}P NMR spectrum, δ 6.0 [s, $^{1}J(^{195}Pt-^{31}P)$ 4021 Hz], which is compatible with simple bidentate O,O′ co-ordination of the SO_3^{2-} ligand. The sensitivity of this reaction to the nature of the phosphine suggests that the co-ordination chemistry of the SO_3^{2-} anion is even more complex than was previously assumed.

Acknowledgements

We are grateful to the SERC for the provision of the diffractometer and to Johnson Matthey for loans of precious metals.

References

1 I. P. Parkin, A. M. Z. Slawin, D. J. Williams and J. D. Woollins, *J. Chem. Soc., Chem. Commun.*, 1989, 1060.
2 I. P. Parkin and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 1990, 519.
3 R. Jones, C. P. Warrens, D. J. Williams and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 1987, 907.
4 SHELXTL, Version 4.2, Siemens X-Ray Analytical Instruments, Madison, WI, 1990.
5 *Transition Metal Nuclear Magnetic Resonance*, ed. P. S. Pregosin, Elsevier, Amsterdam, 1991.
6 D. Messer, D. K. Breitinger and W. Haegler, *Acta Crystallogr., Sect. B*, 1981, **37**, 19.
7 M. V. Capparelli and L. N. Becka, *J. Chem. Soc. A*, 1969, 260.
8 R. Eskenazi, J. Raskovan and R. Levitus, *J. Inorg. Nucl. Chem.*, 1965, **27**, 371.
9 G. Newman and D. B. Powell, *Spectrochim. Acta*, 1963, **19**, 213.
10 R. Meij, D. J. Stufkens, K. Vrieze, E. Roosendaal and H. Schenk, *J. Organomet. Chem.*, 1978, **155**, 323.
11 S. Bhaduri, B. F. G. Johnson, A. Khair, I. Ghatak and D. M. P. Mingos, *J. Chem. Soc., Dalton Trans.*, 1979, 1572.

Received 5th *January* 1993; *Paper* 3/00048F