Preparation and Properties of $[M\{S_2N_3(SO_2NH_2)\}(PR_3)_2]$ and $[Pt\{SO_2(NH)_2\}(PR_3)_2]$ from Reactions in Liquid Ammonia

Ivan P. Parkin and J. Derek Woollins *
Imperial College of Science, Technology and Medicine, South Kensington, London SW7 2AY

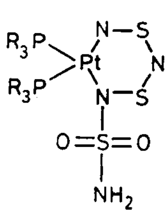
Reaction of $SO_2(NH_2)_2$ or SO_2Cl_2 in liquid ammonia with $[PtCl_2(PR_3)_2]$ gives $[Pt\{SO_2(NH)_2\}(PR_3)_2]$ (PR_3 = PMe_2Ph, $PMePh_2$, PPh_3, PEt_3, or $\frac{1}{2}Ph_2PCH_2CH_2PPh_2$) in good yield (*ca.* 70% isolated). Reaction of $SOCl_2$ in liquid ammonia with $[TiCl_2(C_5H_5)_2]$ or $[PtCl_2(PR_3)_2]$ yields $[Ti(NSO)_2(C_5H_5)_2]$ and $[Pt(NSO)_2(PR_3)_2]$ respectively in *ca.* 60% yield. The compound $S_4N_4O_2$ in liquid ammonia reacts with $[MCl_2(PR_3)_2]$ to produce $[M\{S_2N_3(SO_2NH_2)\}(PR_3)_2]$ (M = Pt, PR_3 = PMe_2Ph, $PMePh_2$, PEt_3, PPr^n_3, or PBu^n_3; M = Pd, PR_3 = $\frac{1}{2}Ph_2PCH_2CH_2PPh_2$) in fair yield (*ca.* 40%). The reactivity of Na_2SO_4, H_2NSO_3H, $SO_3{\cdot}NMe_3$, $S_3N_2(NSO_2CF_3)$, $NaHNSO_2C_6H_4Me$, $(NSOR)_3$, and H_2NSO_2Ph in liquid ammonia has also been investigated. The new compounds were characterised by ^{31}P and ^1H n.m.r., i.r., mass spectroscopy, and microanalyses.

A number of compounds have been synthesized by dissolving sulphur-nitrogen species in liquid ammonia and adding metal complexes.[1-3] Treatment of $[\{PdCl(L)\}_2]$ with $[S_4N_3]Cl$–$NH_3(l)$ gives $[Pd(S_2N_2H)L]$ and reaction of $[PtCl_2(PR_3)_2]$ with $[S_3N_2Cl]Cl$–$NH_3(l)$ produces $[Pt(S_2N_2)(PR_3)_2]$. Several techniques have been employed to investigate the species present in sulphur or sulphur–nitrogen compounds when dissolved in ammonia. Extensive use has been made of Raman and u.v.–visible spectroscopy in attempts at both identifying and quantifying the species present.[4-6] A recent approach to this area has been to use ^{14}N n.m.r. spectroscopy enabling quick and easy product speciation,[7] for example in the identification of $S_3N_3^-$ in the solution formed when adding $[S_3N_2Cl]Cl$ and $[S_4N_3]Cl$ to liquid ammonia.

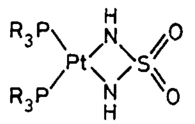
Some attempts have been made to synthesize sulphur–nitrogen–oxygen species. For example, oxygen-co-ordinated $S_4N_4O_2$ has been complexed in $[TiCl_4(S_4N_4O_2)]$.[8] Recently we have shown that reaction of $[PtCl_2(PR_3)_2]$ with $S(NSO)_2$ in liquid ammonia produces $[Pt(NSO)_2(PR_3)_2]$ in good yield.[9-12]

The ^{14}N n.m.r. spectra of $S(NSO)_2$ and $SOCl_2$ show the same peak associated with NSO^- ion (500 p.p.m.) in liquid ammonia.[7] This suggested that $SOCl_2$ could be used instead of $S(NSO)_2$ in the synthesis of $[Pt(NSO)_2(PR_3)_2]$. Furthermore, the unusual ^{14}N n.m.r. spectra of $S_4N_4O_2$ in ammonia initiated attempts to trap the 'SNO' species formed in solution by the addition of $[PtCl_2(PR_3)_2]$; a brief communication of this work has already appeared.[13]

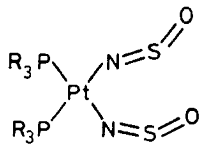
Here, we describe the results of our studies into the synthetic versatility of liquid ammonia solutions of $S_4N_4O_2$, $SOCl_2$, SO_2Cl_2, $SO_2(NH_2)_2$, $NaHNSO_2C_6H_4Me$, and H_2NSO_2Ph with $[PtCl_2(PR_3)_2]$.



(1)–(6)



(7)–(11)



(12)–(14)

Experimental

Manipulations were performed under an inert argon atmosphere. The preparation of $[MCl_2(PR_3)_2]$ was as previously reported;[14] $S_4N_4O_2$, $(SNOCl)_3$, $S_3N_3(OR)_3$, S_3N_2O, S_3N_2N-SO_2CF_3, and $NaNHSO_2C_6H_4Me$ were made by literature methods.[15-20] Ammonia (BOC anhydrous) and the remaining reagents (all Aldrich) were used as supplied. Solvents were dried before use; CH_2Cl_2 from CaH_2, light petroleum (b.p. 60—80 °C) and diethyl ether from sodium–benzophenone. ^{31}P-$\{^1H\}$ N.m.r. spectra were recorded in $CDCl_3$ on a JEOL FX90Q spectrometer operating at 36.21 MHz and are referred to external 85% H_3PO_4, ^1H n.m.r. on a Bruker 250 WM machine operating at 250.21 MHz and referred to internal $CHCl_3$ at δ 7.24. I.r. spectra were obtained as KBr discs using a Perkin-Elmer 1720X spectrometer, mass spectra on a VG 2020 machine using both electron impact (e.i.) and fast atom bombardment (f.a.b.) (thiodiethanol matrix) modes. Microanalyses were carried out by the departmental service at Imperial College.

Preparations.—$[M\{S_2N_3(SO_2NH_2)\}(PR_3)_2]$. The same general procedure was adopted for all compounds, illustrated here for $[Pt\{S_2N_3(SO_2NH_2)\}(PEt_3)_2]$ (**3**). The compound $S_4N_4O_2$ (30 mg, 0.14 mmol) was dissolved in liquid ammonia (5 cm^3) at −78 °C to generate a red solution. The complex $[PtCl_2(PEt_3)_2]$ (70 mg, 0.14 mmol) was added and the suspension stirred for 0.5 h at −78 °C. The ammonia was then allowed to evaporate slowly as the reaction warmed to room temperature leaving a brown-red solid. The residue was extracted with CH_2Cl_2 (5 cm^3), filtered through a glass wool–Celite plug, and complex (**3**) obtained by the addition of light petroleum (20 cm^3). Yield 0.062 mmol (44%).

For $[Pd\{S_2N_3(SO_2NH_2)\}(Ph_2PCH_2CH_2PPh_2)]$ (**4**) the reaction time was reduced to 5 min before the ammonia was allowed to evaporate. If the reaction was left for 0.5 h and worked up as above only $[Pd(S_2N_2)(Ph_2PCH_2CH_2PPh_2)]$ was obtained. Attempted reaction, of $[PtCl_2(PPh_3)_2]$ or $[PtCl_2(Ph_2PCH_2CH_2PPh_2)]$ under the conditions described above, gave only unreacted starting material. However allowing the reaction to warm to room temperature in a sealed vessel for 0.5 h before cooling and allowing the ammonia to evaporate produced $[Pt(S_2N_2)(PPh_3)_2]$ and $[Pt(S_2N_2)(Ph_2PCH_2CH_2PPh_2)]$ in *ca.* 60% yield.

$[Pt(NSO)_2(PR_3)_2]$. The compound $SOCl_2$ (0.10 g, 0.84 mmol) was added dropwise to stirred liquid ammonia (5 cm^3) at −78 °C to generate an orange solution. **CAUTION**: vigorous exothermic reaction. The complex $[PtCl_2(PR_3)_2]$ (0.2 mmol) was added and the suspension stirred for 0.5 h at −78 °C. The ammonia was allowed to evaporate slowly as the reaction warmed to room temperature to leave a yellow-white solid. The solid was extracted with CH_2Cl_2 (5 cm^3), filtered through a Celite–glass wool plug, and mixed with diethyl ether (15 cm^3). The product was obtained as well formed pale yellow crystals on cooling this solution to −20 °C for 12 h. Yield 0.145 mmol (*ca.* 70%).

$[Pt(NSO)_2(PEt_3)_2]$: $\delta(^{31}P) = 1.1$ p.p.m., $J = 3\,070$ Hz; $m/z = 555$ (M^+) and 493 ($M^+ -$ NSO); ν(NSO) 1 242vs, 1 062s, and 567m cm^{-1}. $[Pt(NSO)_2(PMePh_2)_2]$: $\delta(^{31}P) = -8.1$ p.p.m., $J = 3\,120$ Hz; m/z 720 (M^+) and 658 ($M^+ -$ NSO); ν(NSO) 1 242vs, 1 062s, and 569w cm^{-1}.

$[Ti(NSO)_2(C_5H_5)_2]$. The compound $SOCl_2$ (0.30 g, 2.52 mmol) was carefully added dropwise to stirred liquid ammonia (10 cm^3) at −78 °C to generate an orange solution. The complex $[TiCl_2(C_5H_5)_2]$ (0.30 g, 1.22 mmol) was added and the red suspension stirred for 0.5 h at −78 °C. The ammonia was allowed to evaporate as the reaction slowly warmed to room temperature leaving a red-yellow solid. This was extracted with CH_2Cl_2 (20 cm^3), filtered through a Celite–glass wool plug to leave a yellow solution which was pumped to dryness *in vacuo* and washed with diethyl ether (50 cm^3) to leave a yellow solid, $[Ti(NSO)_2(C_5H_5)_2]$ (0.17 g, 0.58 mmol, 48%); m/z 302 (M^+) and 246 ($M^+ -$ NSO); $\delta(^1H)$ 6.37(s).

$[Pt\{SO_2(NH)_2\}(PR_3)_2]$. *Method* (*i*). The compound SO_2Cl_2 (0.10 g, 0.74 mmol) was carefully added dropwise to liquid ammonia (10 cm^3) at −78 °C to generate a red solution. **CAUTION**: care exothermic reaction. Solid $[PtCl_2(PR_3)_2]$ (0.2 mmol) was added and the suspension stirred at −78 °C for 0.5 h. The ammonia was then allowed to evaporate slowly as the reaction warmed slowly to room temperature producing a yellow solid. This was extracted into CH_2Cl_2 (5 cm^3), filtered through a Celite–glass wool plug, and mixed with diethyl ether (15 cm^3). Cooling of this solution to −20 °C produced colourless crystals of $[Pt\{SO_2(NH)_2\}(PR_3)_2]$ (1.1—1.5 mmol, 54—75%).

Method (*ii*). The same quantities and procedures were adopted as above save SO_2Cl_2 was replaced by $SO_2(NH_2)_2$ (0.21 mmol, 0.020 g).

$[Pt(NHSO_2C_6H_4Me)_2(PR_3)_2]$. The compound $Na[NHSO_2C_6H_4Me]$ (0.038 g, 0.2 mmol) was added to liquid ammonia at −78 °C to form a colourless solution; $[PtCl_2(PR_3)_2]$ (0.1 mmol) was added and the suspension stirred for 0.5 h at −78 °C. The ammonia was allowed to evaporate as the solution warmed to room temperature leaving a white solid. This was extracted into CH_2Cl_2 (5 cm^3), filtered through a Celite–glass wool plug, and mixed with diethyl ether (10 cm^3). Cooling of this solution afforded a white solid $[Pt(NHSO_2C_6H_4Me)_2(PR_3)_2]$ (0.042 mmol, 42% yield).

The reaction can be repeated as above using H_2NSO_2Ph instead of $Na[NHSO_2C_6H_4Me]$ to produce $[Pt(NHSO_2Ph)(PMePh_2)_2]$ (**17**) in 38% yield.

Reactions of $[PtCl_2(PR_3)_2]$ *with* $(SNOCl)_3$, $(SNOR)_3$ (R = Me *or* Pr^i), $S_3N_2(NSO_2CF_3)$, *or* S_3N_2O.—The sulphur–nitrogen–oxygen reagent (0.2 mmol) was dissolved in liquid ammonia at −78 °C. The complex $[PtCl_2(PR_3)_2]$ (0.2 mmol) was added and the suspension stirred for 0.5 h at −78 °C. The ammonia was allowed to evaporate as the reaction warmed slowly to room temperature and the residue extracted with $CDCl_3$ (3 cm^3), filtered through a Celite–glass wool plug and the ^{31}P n.m.r. spectrum recorded.

Results and Discussion

Reaction of $[PtCl_2(PR_3)_2]$ with $S_4N_4O_2$ in liquid ammonia gives $[Pt\{S_2N_3(SO_2NH_2)\}(PR_3)_2]$ in moderate yield [equation (1)]. The products can be regarded as having been formed with

$$S_4N_4O_2 + 3NH_3 + [PtCl_2(PR_3)_2] \longrightarrow 2NH_4Cl + [Pt\{S_2N_3(SO_2NH_2)\}(PR_3)_2] + \text{`SN'} \quad (1)$$

elimination of S^{II} from the $S_4N_4O_2$ as was the case for the formation of NSO^- complexes from $S(NSO)_2$.[9] The ^{31}P n.m.r. spectrum of the crude reaction mixtures reveal the presence of a number of products; $[Pt\{S_2N_3(SO_2NH_2)\}(PR_3)_2]$ accounts for *ca.* 80% by integration. A small amount of $[Pt(S_2N_2)(PR_3)_2]$ (*ca.* 10%) is observed amongst other trace compounds. The products (**1**)—(**6**) crystallise from CH_2Cl_2 as well formed orange-yellow cubes by the addition of n-hexane. Attempts to isolate the product by chromatography (silica and size elution) failed to achieve separation from $[Pt(S_2N_2)(PR_3)_2]$.

The formulation of $[Pt\{S_2N_3(SO_2NH_2)\}(PR_3)_2]$ is justified on the basis of microanalysis, i.r., ^{31}P n.m.r., mass spectroscopy, and in the case of $PR_3 = PMe_2Ph$ by *X*-ray crystallography.[13] The microanalyses (Table 1) indicate that the compounds are crystallised as solvates, with included CH_2Cl_2, as seen in the crystal structure.[13]

The ^{31}P n.m.r. spectra of compounds (**1**)—(**6**) (Table 2) are of the AX type ($^2J = 24$ Hz) with ^{195}Pt satellites (^1J *ca.* = 3 500 and 3 100 Hz) indicating platinum(II) species with inequivalent phosphine ligands. The lower value of ^1J is typical of a phosphine *trans* to a nitrogen donor in a platinum(II) complex.[21,22] The high coupling constant of 3 500 Hz is more consistent with a co-ordinated oxygen,[23] however the close proximity of the electron-withdrawing SO_2NH_2 group to the co-ordinated nitrogen may be an important factor.

Selected i.r. vibrations due to the co-ordinated $[S_2N_3(SO_2NH_2)]^{2-}$ ligand are shown in Table 3. In the N–H stretching region two vibrations occur at *ca.* 3 300 and 3 220 cm^{-1}. The lower-frequency vibration is slightly broader than the higher frequency suggesting some degree of hydrogen bonding. The exocyclic SO_2NH_2 group has SO_2 vibrations at *ca.* 1 325 and 1 150 cm^{-1} compared to those attributable to the same group in $S_4N_4O_2$ at 1 330 and 1 139 cm^{-1}. The δ(OSO) rock and δ(OSO) bend of compounds (**1**)—(**4**) were assigned by comparison with the observed vibrations of $S_4N_4O_2$. The crystal structure[13] of (**1**) indicates that the PtS_2N_3 ring can be regarded as a $Pt(S_2N_2)$ ring with a $N(SO_2NH_2)$ group inserted into the Pt–S bond. The ring contains a planar PtS_2N_2 unit with the $N(SO_2NH_2)$ nitrogen displaced below this plane. The observed ν(N–S) bands at *ca.* 1 120, 870, 800, and 640 cm^{-1} are similar to those observed for $[Pt(S_2N_2H)(PR_3)_2]$ (1 040, 875, and 640 cm^{-1}) complexes.[14] The band observed at 800 cm^{-1}, although not observed for the PtS_2N_2H and PtS_2N_2 rings, is typical of many observed SN stretches. The low-frequency vibrations at 491, 401, and 341 cm^{-1} are assigned as δ(NS) modes by analogy with those of $[Pt(S_2N_2H)(PR_3)_2]$ and $[Pt(S_2N_2)(PR_3)_2]$ complexes.[14,21] However the existence of Pt–S or Pt–N vibrations could account for some of the observed bands in this region.

The mass spectra of compound (**1**)—(**6**) consist principally of the parent ion $[M\{S_2N_3(SO_2NH_2)\}(PR_3)_2]^+$, and fragmentation ions due to $[M\{S_2N_3(SO_2)\}(PR_3)_2]^+$ and $[M(S_2N_3)(PR_3)_2]^+$, consistent with the proposed structure.

On varying the phosphine, unlike the $[PtCl_2(PR_3)_2]$–S_4N_3Cl system,[3] the product distribution in the $S_4N_4O_2$–$[PtCl_2(PR_3)_2]$ reaction is altered. With $[PtCl_2(PPh_3)_2]$ and $[PtCl_2(Ph_2PCH_2CH_2PPh_2)]$ no reaction occurred unless the mixture was allowed to warm to room temperature in a pressure tube. In this case $[Pt(S_2N_2)(PPh_3)_2]$ and $[Pt(S_2N_2)(Ph_2PCH_2CH_2PPh_2)]$ were the main products

Table 1. Microanalytical data (calculated values in parentheses) and yields

	Compound	Analysis/% C	Analysis/% H	Analysis/% N	Yield/%
(1)	$[Pt\{S_2N_3(SO_2NH_2)\}(PMe_2Ph)_2]\cdot CH_2Cl_2$	27.40 (27.45)	3.45 (3.35)	7.50 (7.55)	40
(2)	$[Pt\{S_2N_3(SO_2NH_2)\}(PMePh_2)_2]\cdot CH_2Cl_2$	36.95 (37.40)	3.70 (3.50)	6.90 (6.45)	43
(3)	$[Pt\{S_2N_3(SO_2NH_2)\}(PEt_3)_2]$	23.25 (23.35)	5.25 (5.20)	9.00 (9.05)	43
(4)	$[Pd\{S_2N_3(SO_2NH_2)\}(Ph_2PCH_2CH_2PPh_2)]\cdot CH_2Cl_2$	41.25 (41.90)	3.45 (3.40)	7.10 (7.25)	48
(5)	$[Pt\{S_2N_3(SO_2NH_2)\}(PPr^n{}_3)_2]$	25.90 (26.70)	6.30 (5.75)	8.00 (7.05)	35
(7)	$[Pt\{SO_2(NH)_2\}(PMe_2Ph)_2]$	33.95 (34.00)	3.85 (4.25)	5.05 (4.95)	34
(8)	$[Pt\{SO_2(NH)_2\}(PMePh_2)_2]$	45.30 (45.15)	4.05 (4.05)	3.95 (4.05)	65
(9)	$[Pt\{SO_2(NH)_2\}(PPh_3)_2]$	51.50 (51.20)	3.95 (3.85)	3.85 (3.30)	54
(10)	$[Pt\{SO_2(NH)_2\}(Ph_2PCH_2CH_2PPh_2)]\cdot 0.5CH_2Cl_2$	44.00 (43.60)	3.65 (3.45)	3.00 (3.80)	63
(11)	$[Pt\{SO_2(NH)_2\}(PEt_3)_2]$	26.25 (26.45)	6.10 (5.80)	5.20 (4.95)	75
(12)	$[Pt(NSO)_2(PEt_3)_2]\cdot 0.5CH_2Cl_2$	24.55 (25.10)	5.75 (5.20)	4.75 (4.70)	71
(13)	$[Pt(NSO)_2(PMePh_2)_2]\cdot CH_2Cl_2$	39.80 (40.30)	3.85 (3.50)	3.25 (3.45)	65
(14)	$[Ti(NSO)_2(C_5H_5)_2]\cdot 0.5CH_2Cl_2$	36.55 (36.85)	3.20 (3.35)	8.75 (8.15)	48
(15)	$[Pt(NHSO_2C_6H_4Me)_2(PMe_2Ph)_2]$	44.35 (44.40)	3.85 (3.95)	3.30 (3.45)	42
(16)	$[Pt(NHSO_2C_6H_4Me)_2(PEt_3)_2]$	40.50 (40.50)	6.00 (5.95)	3.80 (3.65)	42
(17)	$[Pt(NHSO_2Ph)_2(PMePh_2)_2]\cdot 0.5CH_2Cl_2$	48.50 (48.75)	3.80 (3.90)	2.35 (2.95)	38

Table 2. ^{31}P N.m.r. data in $CDCl_3$ and referred to 85% H_3PO_4

Compound	δ_a	δ_b	^1J_a	^1J_b	$^2J_{ab}$
(1)	−16.0	−19.1	3 539	3 178	24
(2)	−5.1	−1.9	3 594	3 265	24
(3)	4.0	1.4	3 476	3 152	24
(4)	54.3	48.6	—	—	40
(5)	−5.4	−6.3	3 478	3 178	22
(6)	−3.3	−5.5	3 480	3 168	22
	δ		J		
(7)	−22.2		3 308		
(8)	−7.0		3 342		
(9)	10.9		3 454		
(10)	35.4		3 336		
(11)	0.9		3 276		
(15)	−17.5		3 301		
(16)	2.7		3 270		
(17)	−4.9		3 364		

Table 3. Selected i.r. vibrations (cm^{-1}) of $[M\{S_2N_3(SO_2NH_2)\}(PR_3)_2]$ (pressed KBr discs)

Compound **(1)**	**(2)**	**(3)**	**(4)**	$S_4N_4O_2$	Assignment
3 303s		3 301s	3 360s		ν(N–H)
	3 209s				ν(N–H)
3 232m		3 233s	3 216s		ν(N–H)
1 404m	1 410w		1 410m		δ(N–H)
1 327s	1 316m	1 325m	1 342m	1 330vs	ν_{asym}(S–O)
1 149vs	1 148s	1 150vs	1 150vs	1 139vs	ν_{sym}(S–O)
1 126s	1 108s	1 099s	1 123(sh)	1 115vs	ν_{asym}(S–O)
880s	878(sh)	868s	863m		ν(S–N)
816s		799s	795s		ν(S–N)
657m	647m	640m	630m	620s	ν(S–N)
604m	607m	608m		602m	δ(OSO) rock
584w	584w	583w	579m		
548m	545w	547m	548(sh)	557m	δ(OSO) bend
491w	494w	497w	486w		δ(S–N)
401w		401w	401w		
341w		358w	360w	376, 320	δ(N–S)/ν(Pt–S)

isolated in 60% yield. The ^{14}N n.m.r. spectrum of $S_4N_4O_2$ in liquid ammonia[7] is temperature and time dependent, such that with time the peak associated with $S_3N_3^-$ increases. We have shown previously[21] that $S_3N_3^-$ reacts with $[PtCl_2(PR_3)_2]$ to give $[Pt(S_2N_2)(PR_3)_2]$. The low solubility of $[PtCl_2(PPh_3)_2]$ and $[PtCl_2(Ph_2PCH_2CH_2PPh_2)]$ in liquid ammonia at −78 °C means that no reaction can occur until the system is allowed to warm up; on warming (and with time) more $S_3N_3^-$ is present and thus the product distribution is altered with $[Pt(S_2N_2)(PR_3)_2]$ formation favoured.

With $[PdCl_2(Ph_2PCH_2CH_2PPh_2)]$ if the reaction time is much greater than 5 min only $[Pd(S_2N_2)(Ph_2PCH_2CH_2PPh_2)]$ is formed. With shorter times the expected product **(4)** is obtained.

Reaction of SO_2Cl_2 or $SO_2(NH_2)_2$ with $[PtCl_2(PR_3)_2]$ in liquid ammonia gives $[Pt\{SO_2(NH)_2\}(PR_3)_2]$ **(7)**—**(11)** [equation (2)]. The SO_2Cl_2 provides an *in situ* source of

$$SO_2(NH_2)_2 + [PtCl_2(PR_3)_2] + 2NH_3 \longrightarrow 2NH_4Cl + [Pt\{SO_2(NH)_2\}(PR_3)_2] \quad (2)$$

Table 4. Selected i.r. vibrations (cm^{-1}) of [Pt{$SO_2(NH)_2$}$(PR_3)_2$] (pressed KBr discs)

Compound	ν(N-H)	$\nu_{sym}(SO_2)$	$\nu_{asym}(SO_2)$	δ(OSO) rock
(**7**)	3 255vs	1 265vs	1 118s, 1 159m	588m
(**8**)	3 264vs	1 261vs	1 137vs, 1 117vs	578m
(**9**)	3 236vs	1 270vs	1 110vs, 1 171m	584m
(**10**)	3 236vs	1 272vs	1 113vs	578m
(**11**)	3 245vs	1 262vs	1 115vs, 1 170m	582m

Table 5. Mass spectral data

Compound	M^+	$M^+ - SO_2NH_2$	$M^+ - NSO_2NH_2$
(**1**)	658	577	523
(**2**)	748*	705	691
(**3**)	617	537	523
	M^+	$M^+ - O_2$	$M^+ - SO_2$
(**8**)		657	625
(**9**)	813		745
(**11**)	526	494	461

Mass spectra of (**3**) and (**11**) in the e.i. mode, the rest as f.a.b. spectra in a thiodiethanol matrix.
* $M^+ - O_2H$

$$SO_2Cl_2 + 4NH_3 \longrightarrow 2NH_4Cl + SO_2(NH_2)_2 \quad (3)$$

$SO_2(NH_2)_2$ [equation (3)]. The reaction proceeds cleanly with isolated yields of *ca.* 75%. The reaction type of chloride extraction from [$PtCl_2(PR_3)_2$] in liquid ammonia with simultaneous addition of SN species to the platinum is now quite well established.[3,6,13] Compounds (**7**)—(**11**) are isoelectronic with the well known sulphato complex [$Pt(SO_4)(PR_3)_2$].

The ^{31}P n.m.r. spectra of compounds (**7**)—(**11**) consist of a singlet with a $^1J(^{195}Pt-^{31}P)$ coupling constant of *ca.* 3 300 Hz suggesting that the ligands *trans* to the phosphine groups are likely to be nitrogen donors because oxygen donors would give a larger coupling constant. The chemical shifts show typical variation with phosphine. The ^1H n.m.r. spectra have a peak at *ca.* δ 3 of relative integral 2 due to the N–H protons.

The e.i. mass spectra of compounds (**7**)—(**11**) give the molecular ion with the expected isotopic cluster abundance. The fragmentation ions are consistent with nitrogens co-ordinated to the platinum with peaks due to [Pt{$S(NH)_2$}$(PR_3)_2$]$^+$ and [$Pt(NH)_2(PR_3)_2$]$^+$ being observed. The i.r. spectra show a ν(NH) vibration at *ca.* 3 240 cm^{-1}, the expected $\nu(SO_2)$ symmetric and asymmetric stretches, as well as the SO_2 rock and bend modes. These modes are similar to those observed for (**1**)—(**4**). The existence of these vibrations coupled with the other information suggests that nitrogen rather than oxygens are bound to the platinum centre.

Reaction of Na[$NHSO_2C_6H_4Me$] or NH_2SO_2Ph with [$PtCl_2(PR_3)_2$] gives [$Pt(NHSO_2R')_2(PR_3)_2$] (R′ = Ph or C_6H_5Me) (**15**)—(**17**) in good yield. The ^{31}P n.m.r. spectra are very similar to those of (**7**)—(**11**) with the coupling constants being *ca.* 30 Hz different and the chemical shifts *ca.* +3 p.p.m. greater. This is not surprising because both sets of species are nitrogen donors on a platinum(II) centre with effectively the same co-ordinated groups [$(NH)_2SO_2$ compared to $(NHSO_2R)_2$].

We have synthesized [$Pt(NSO)_2(PR_3)_2$] from reaction of [$PtCl_2(PR_3)_2$] with $S(NSO)_2$ in liquid ammonia.[9] The compound $S(NSO)_2$ is difficult to prepare and handle although its use in the formation of [$Pt(NSO)_2(PR_3)_2$] is effectively quantitative. The ^{14}N n.m.r. spectra of $S(NSO)_2$ and $SOCl_2$ in liquid ammonia have the same peak at 500 p.p.m. previously assigned as NSO^- ion. This, coupled with the reactivity of SO_2Cl_2 in liquid ammonia, prompted an investigation of the reactivity of $SOCl_2$–NH_3(l) with [$PtCl_2(PR_3)_2$] [equation (5)]. The reaction was found to proceed cleanly and the products (**12**)—(**14**) easily isolated as before. This route has the significant advantage of generating the NSO^- ion without having to isolate[9] $S(NSO)_2$ or a reactive salt such as KNSO or KNSNR[11,12] [equation (4)].

$$SOCl_2 + 4NH_3 \longrightarrow 2NH_4Cl + [NH_4][NSO] \quad (4)$$

$$2NSO^- + [PtCl_2(PR_3)_2] \longrightarrow [Pt(NSO)_2(PR_3)_2] + 2Cl^- \quad (5)$$

Reaction of $(SNOCl)_3$ with [$PtCl_2(PR_3)_2$] in liquid ammonia gives a mixture of products (by ^{31}P n.m.r. spectroscopy), of which [$Pt(NSO)_2(PR_3)_2$] accounts for *ca.* 20% and [$Pt(S_2N_2)(PR_3)_2$] *ca.* 15% by integration. The large number of products made isolation of [$Pt(NSO)_2(PR_3)_2$] difficult. The ^{14}N n.m.r. spectrum of $(SNOCl)_3$ does not show a peak due to NSO^-, but only a broad singlet[7] at 98 p.p.m. Thus the reaction with [$PtCl_2(PR_3)_2$] is surprisingly complicated.

Another SNO reagent, $S_3N_2(NSO_2CF_3)$ (five-membered S_3N_2 ring with an exocyclic NSO_2CF_3 group) reacts in liquid ammonia with [$PtCl_2(PR_3)_2$] to give exclusively [$Pt(S_2N_2)(PR_3)_2$]. No platinum compound with an exocyclic SO_2CF_3 group analogous to SO_2NH_2 in compound (**1**)—(**6**) was found. This is probably because in ammonia $S_3N_2(NSO_2CF_3)$ dissociates the exocyclic group [equation (6)]. The generated

$$S_3N_2(NSO_2CF_3) + NH_3 \longrightarrow S_3N_3^- + H_3NSO_2CF_3^+ \quad (6)$$

$S_3N_3^-$ ion is known[18] to react with [$PtCl_2(PR_3)_2$] to give [$Pt(S_2N_2)(PR_3)_2$] [equation (7)].

$$S_3N_3^- + [PtCl_2(PR_3)_2] + 3NH_3 \longrightarrow 2NH_4Cl + [Pt(S_2N_2)(PR_3)_2] + \text{`}NSNH^-\text{'} \quad (7)$$

Like $S_3N_2(NSO_2CF_3)$, the reaction of S_3N_2O in ammonia with [$PtCl_2(PR_3)_2$] failed to lead to a compound containing oxygen but yielded [$Pt(S_2N_2)(PR_3)_2$]. In liquid ammonia S_3N_2O probably reacts to form $S_3N_3^-$ [equation (8)].

$$S_3N_2O + 2NH_3 \longrightarrow [NH_4][S_3N_3] + H_2O \quad (8)$$

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