

## Facile Synthesis of SN and S–N–O Complexes in Liquid Ammonia; X-Ray Structure of Pt[(HN)<sub>2</sub>SO<sub>2</sub>](PPh<sub>2</sub>Me)<sub>2</sub>

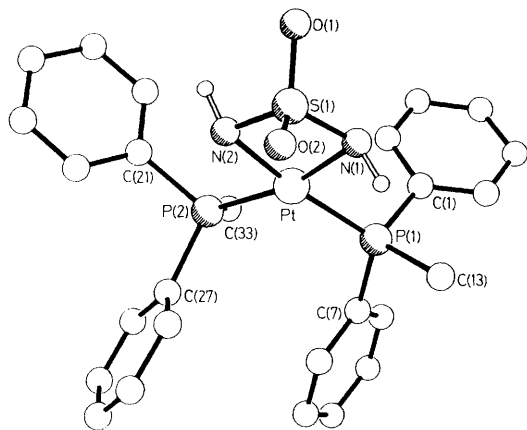
Ivan P. Parkin, Alexandra M. Z. Slawin, David J. Williams, and J. Derek Woollins\*

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

Addition of SCl<sub>2</sub>, SOCl<sub>2</sub>, SO<sub>2</sub>Cl<sub>2</sub>, or SeCl<sub>4</sub> to liquid ammonia followed by Pt(PR<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> gives complexes of the type Pt(S<sub>2</sub>N<sub>2</sub>)(PR<sub>3</sub>)<sub>2</sub>, Pt(NSO)<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub>, Pt[(HN)<sub>2</sub>SO<sub>2</sub>](PR<sub>3</sub>)<sub>2</sub>, and Pt(Se<sub>2</sub>N<sub>2</sub>)(PR<sub>3</sub>)<sub>2</sub> respectively; the X-ray structure of Pt[(HN)<sub>2</sub>SO<sub>2</sub>](PPh<sub>2</sub>Me)<sub>2</sub> is reported.

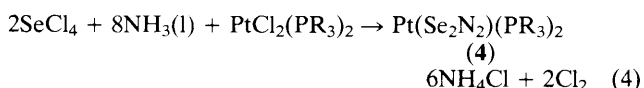
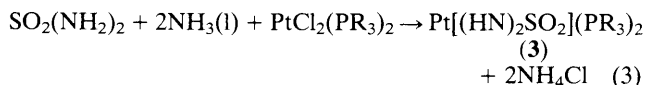
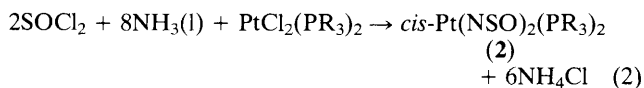
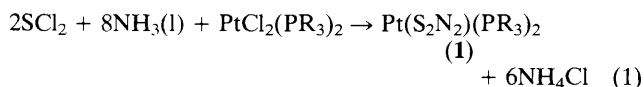
A number of groups are involved in the synthesis of metalla-sulphur–nitrogen compounds.<sup>1,2</sup> These compounds are of interest since the metal centres stabilise otherwise unknown SN anions and some of the materials possess interesting solid state structures. The majority of the prepara-

tive routes involve a number of stages, typically including the isolation of one or more sulphur–nitrogen precursors. For example, we have described the synthesis of Pt(S<sub>2</sub>N<sub>2</sub>)(PR<sub>3</sub>)<sub>2</sub> (**1**) from reactions<sup>3,4</sup> involving Na[S<sub>3</sub>N<sub>3</sub>] or S<sub>4</sub>N<sub>4</sub>H<sub>4</sub>. Although these reactions proceed in good yield Na[S<sub>3</sub>N<sub>3</sub>] is explosive



**Figure 1.** The X-ray structure of Pt[(HN)<sub>2</sub>SO<sub>2</sub>](PPh<sub>2</sub>Me)<sub>2</sub> (**3**). Selected bond lengths and angles: Pt–N(1) 2.073(5), Pt–N(2) 2.061(5), N(1)–S(1) 1.614(5), S(1)–N(2) 1.636(5), Pt–P(1) 2.250(1), Pt–P(2) 2.249(1), S(1)–O(1) 1.436(5), S(1)–O(2) 1.454(6) Å; N(1)–Pt–N(2) 71.9(2), N(1)–Pt–P(1) 95.0(1), P(1)–Pt–P(2) 100.0(1), P(2)–Pt–N(2) 93.2(1), Pt–N(1)–S(1) 95.8(2), N(1)–S(1)–N(2) 96.6(2), S(1)–N(2)–Pt 95.5(2), O(1)–S(1)–O(2) 114.1(3)°.

and S<sub>4</sub>N<sub>4</sub>H<sub>4</sub> is obtained by reduction of S<sub>4</sub>N<sub>4</sub> which is also difficult to handle. There have been some reports on the preparation of NSO<sup>−</sup> complexes. We have<sup>5</sup> used Hg(NSO)<sub>2</sub> whilst Heberhold<sup>6</sup> and Roesky<sup>7</sup> used potassium salts of NSO<sup>−</sup> and RNSN<sup>−</sup> which are very air sensitive and explode violently on contact with chlorinated solvents. Recently,<sup>8–10</sup> we have found that a number of SN compounds [e.g. S<sub>4</sub>N<sub>4</sub>, S<sub>4</sub>N<sub>4</sub>O<sub>2</sub>, S(NSO)<sub>2</sub>] dissolve and react to form metal complexes in liquid ammonia. Here, we report on simple ‘one-pot’ routes which do not require the isolation of any SN or SNO starting materials or special handling precautions (equations 1–3). Furthermore, we have also been able to apply this methodology to the synthesis of the first examples of complexes containing the bidentate O<sub>2</sub>S(NH)<sub>2</sub><sup>2−</sup> or Se<sub>2</sub>N<sub>2</sub><sup>2−</sup> ligands (equations 3 and 4).



In a typical reaction the sulphur halide or oxyhalide (1–2.5 mmol) is carefully added to NH<sub>3</sub>(l) (10 ml) at −78 °C. After stirring for ca. 30 min PtCl<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub> (0.5–1.25 mmol) is added and the reaction is then allowed to warm slowly to room temperature with the ammonia being blown off under a stream of nitrogen. The final products are obtained by recrystallisation from CH<sub>2</sub>Cl<sub>2</sub>–petroleum ether. Yields are in the range 50–75%.

The products gave satisfactory microanalyses, and for (**1**) and (**2**) their spectroscopic properties are identical to those previously reported.<sup>3,10</sup> Compounds (**3**) and (**4**) have the expected n.m.r. properties† and in the case of (**3**; PR<sub>3</sub> = PPh<sub>2</sub>Me) we have determined the X-ray structure.‡ The molecule (Figure 1) has the expected square planar geometry with Pt–P and Pt–N bond lengths that are typical for Pt<sup>II</sup>. The PtN<sub>2</sub>S ring is essentially planar (max. deviation 0.03 Å) with the oxygen atoms lying equidistant above and below the plane. The ring is rotated ca. 5° with respect to the P(1)–Pt–P(2) plane. The sulphamido ligand has slightly lengthened S=O bonds compared to sulphamide<sup>11</sup> and SO<sub>4</sub><sup>2−</sup> whilst the S–N bond lengths are intermediate between single and double and comparable to those in sulphamide. Both the sulphur and the nitrogen atoms are pyramidal, and within the four-membered ring the angles, of necessity, are reduced from their normal value; those at nitrogen and sulphur are ca. 96° whilst the N(1)–Pt–N(2) angle is appreciably reduced at 71.9(2)°. The Pt...S distance is 2.75 Å and the N(1)...N(2) distance is 2.43 Å. There is a weak intermolecular H-bond between N(1) and O(2) [3.10 Å, N(1)–H...O(2) 142°].

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† <sup>31</sup>P N.m.r. data for (**3**; PR<sub>3</sub> = PPh<sub>2</sub>Me) δ −7.0 p.p.m. [<sup>1</sup>J(<sup>31</sup>P–<sup>195</sup>Pt) 3342 Hz]; (**4**; PR<sub>3</sub> = PPh<sub>2</sub>Me) δ 45.7, 37.1 p.p.m. [<sup>2</sup>J(<sup>31</sup>P–<sup>31</sup>P) 10, <sup>1</sup>J 2817, 2627 Hz].

‡ *Crystal data* for (**3**; PR<sub>3</sub> = PPh<sub>2</sub>Me): C<sub>26</sub>H<sub>28</sub>N<sub>2</sub>P<sub>2</sub>O<sub>2</sub>PtS, *M* = 689.6, triclinic, *a* = 10.645(2), *b* = 10.823(2), *c* = 12.132(3) Å, α = 83.31(2), β = 88.36(2), γ = 68.22(2)°; *U* = 1289 Å<sup>3</sup>, space group *P* $\bar{1}$ , *Z* = 2, *D*<sub>c</sub> = 1.78 g cm<sup>−3</sup>, μ(Cu–Kα) = 124 cm<sup>−1</sup>. Crystal dimensions 0.13 × 0.15 × 0.20 mm. Data were measured on a Nicolet R3m diffractometer with graphite monochromated Cu–Kα radiation using ω-scans. The structure was solved by the heavy atom method and refined using anisotropic thermal parameters and absorption corrected data, to give *R* = 0.032, *R*<sub>w</sub> = 0.034 for 3416 independent observed reflections [|*F*<sub>o</sub>| > 3σ(|*F*<sub>c</sub>|), θ ≤ 58°]. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.