The Preparation and Crystal Structure of *cis*-Bis(trimethylsilylsulphurdiimido)bis(triphenylphosphine)platinum(II)

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Reaction of (η^2-ethene)bis(triphenylphosphine)platinum(0) with bis(trimethylsilyl)sulphurdiimide yields *cis*-[Pt(NSNSiMe$_3$)$_2$(PPh$_3$)$_2$] the first example of a complex containing the RNSN$^-$ ligand, in this case sigma bonded to platinum *via* nitrogen.

Currently there are few examples of transition metal complexes containing simple sulphur–nitrogen ligands and generally the known compounds have been prepared *via* thermodynamically unstable sulphur–nitrogen species such as tetrasulphurtetranitride.[1—3] It is important to establish routes to novel sulphur–nitrogen complexes since complexation may stabilise reactive SN fragments which otherwise would not be observed (*c.f.* metalla-boron-hydrides[4]) and also in the light of the unusual electrical properties of polymeric sulphur-nitride, (SN)$_x$. We have undertaken a systematic investigation of routes to metal–sulphur–nitrogen species, with particular interest in the use of stable sulphur–nitrogen starting materials. Herein we report that reaction of bis(trimethylsilyl)sulphurdiimide with (η^2-ethene)bis(triphenylphosphine)platinum(0) yields the title complex which contains the first example of a sulphurdiimido ligand, which is isoelectronic with SO_2.

In a typical experiment $(Me_3SiN)_2S$ (0.027 mmol) was added to a solution of $Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2$ (0.027 mmol) in 5 cm^3 of benzene. After stirring for 2 h the reaction mixture was reduced to dryness *in vacuo,* extracted in 10 cm^3 of benzene and filtered through Celite. Crystals of $[Pt(NSNSiMe_3)_2(PPh_3)_2]$ (0.012 mmol) suitable for *X*-ray analysis† were obtained by reducing the above solution to *ca.* 3 cm^3 and treating it with light petroleum. Satisfactory C, H, and N microanalyses were obtained whilst $^{31}P\text{-}\{^1H\}$ n.m.r. spectroscopy (C_6D_6) gave a 1:4:1 triplet, δ 11.76 p.p.m., ^1J(Pt-P) 3098 Hz (relative to external 85% H_3PO_4).

The structure of the molecule is shown in Figure 1. As expected from the Pt-P coupling constant the complex is square planar with Pt-P distances which are appropriate to Pt^{II}. The anionic Me_3SiNSN^- ligands are sigma bonded to the platinum *via* their nitrogen atoms with the Pt-N distances being similar to those reported[5] for $Pt(S_2N_2H)_2$. The S-N distances within the planar ligand indicate SN double bonds and although there is some difference in the Pt-N-S angle between the two ligands in the solid state, in solution the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum shows only one phosphorus resonance. The Me_3SiNSN^- ligand is isoelectronic with SO_2, however the co-ordination mode reported here is unique in that there are no examples of SO_2 groups terminally bonded to transition metals.

The present compound is the first of a potentially large class of complexes containing the (unstable) $RNSN^-$ group and also offers scope for the formation of novel cyclic SN species *via* replacement of its labile Me_3Si groups.

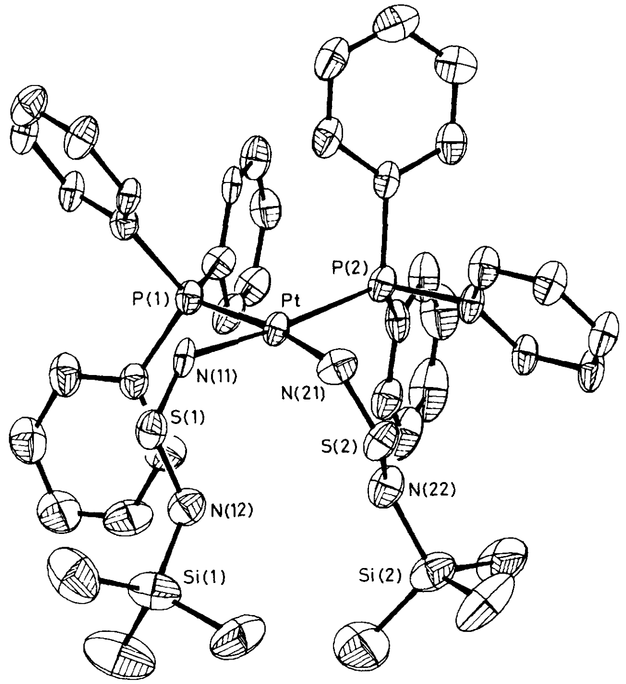

Figure 1. The molecular structure of *cis*-$[Pt(NSNSiMe_3)_2(PPh_3)_2]$. The bond distances and angles (e.s.d.s in parentheses) are: Pt-N(11) 2.015(10), Pt-N(21) 2.036(10), Pt-P(1) 2.284(5), Pt-P(2) 2.265(5), S(1)-N(11) 1.508(10), S(1)-N(12) 1.503(12), S(2)-N(21) 1.497(10), S(2)-N(22) 1.542(10), Si(1)-N(12) 1.749(11), Si(2)-N(22) 1.721(11) Å; N(11)-Pt-N(21) 85.4(4), Pt-N(11)-S(1) 138.1(5), Pt-N(21)-S(2) 123.8(5), N(11)-S(1)-N(12) 121.1(6), N(21)-S(2)-N(22) 118.5(6), S(1)-N(12)-Si(1) 124.8(8), S(2)-N(22)-Si(2) 125.4(7)°.

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† *Crystal data:* $C_{42}H_{48}N_4P_2S_2Si_2Pt$, $M = 985.3$, triclinic, $a = 10.935(1)$, $b = 11.155(1)$, $c = 19.673(2)$ Å, $\alpha = 105.28(1)$, $\beta = 102.21(1)$, $\gamma = 89.31(1)°$, $U = 2260.0$ Å^3, space group $P\bar{1}$, $Z = 2$, $D_c = 1.448$ g cm^{-3}, $\lambda(Cu\text{-}K_\alpha) = 1.5418$ Å, $\mu(Cu\text{-}K_\alpha) = 80.6$ cm^{-1}. The structure was solved by heavy atom techniques and refined by full-matrix least-squares using intensity data {6594 unique reflections recorded of which 5359 were considered observed $[I \geqslant 1.5\sigma(I)]$} measured on a CAD4 diffractometer giving $R = 0.059$. Anisotropic thermal parameters were used for all non-hydrogen atoms; hydrogens were only included for the phenyl rings and were fixed with idealised geometry to their respective carbon atoms. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW. Any request should be accompanied by the full literature citation for this communication.