

## Platinum Dithiocarbonimidato Complexes *via* Abstraction of Sulphur from Organic Isothiocyanates

By FRANK L. BOWDEN, ROBERT GILES, and ROBERT N. HASZELDINE\*

(Chemistry Department, University of Manchester Institute of Science and Technology, Manchester M60 1QD)

**Summary** Dithiocarbonimidatoplatinum(II) complexes,  $\text{Pt}(\text{S}_2\text{C}:\text{NR})\text{L}_2$ , are obtained from  $\text{Pt}(\text{allene})\text{L}_2$ ,  $\text{PtL}_4$ , or  $\text{Pt}(\text{PhNCS})\text{L}_2$  by a reaction with organic isothiocyanates that involves a novel sulphur abstraction.

ONLY three neutral transition metal complexes of the dithiocarbonimidate ligand,  $\text{S}_2\text{C}=\text{NR}^{2-}$  are known; these are  $\text{M}(\text{S}_2\text{C}=\text{NR})\text{L}_2$ , ( $\text{M}=\text{Ni}, \text{Pd}, \text{Pt}$ ;  $\text{R}=\text{CN}$ ,  $\text{L}=\text{Ph}_3\text{P}$ ) prepared from  $(\text{NH}_4)_2(\text{S}_2\text{C}=\text{NCN})$  and  $\text{MCl}_2\text{L}_2$ .<sup>1</sup> We now report that the platinum complexes  $\text{Pt}(\text{allene})\text{L}_2$  (Ia, allene =  $\text{CH}_2:\text{C}:\text{CH}_2$ ; Ib, allene =  $\text{CF}_3\cdot\text{CH}:\text{C}:\text{CH}_2$ ),  $\text{PtL}_4$  (II), or  $\text{Pt}(\text{PhNCS})\text{L}_2$  (III) ( $\text{L}=\text{Ph}_3\text{P}$ ) react with an excess of a liquid organic isothiocyanate (*e.g.*,  $\text{PhNCS}$  or  $\text{MeNCS}$ ) at room temperature to give red solutions from which white crystals of the dithiocarbonimidato complexes  $\text{Pt}(\text{S}_2\text{C}:\text{NR})\text{L}_2$  (IVa,  $\text{R}=\text{Ph}$ ; IVb,  $\text{R}=\text{Me}$ ) are isolated (30–60%). The formation of phenyl isocyanide by sulphur abstraction from phenyl isothiocyanate is shown by the isolation of the complex  $\text{Pt}(\text{S}_2\text{C}:\text{NPh})(\text{PhNC})\text{L}$  (V) (4%); a red oil, possibly an oligomer of phenyl isocyanide, is also obtained.

Phenyl isothiocyanate undergoes sulphur abstraction reactions with  $\text{Fe}(\text{CO})_5$  and  $\text{Mo}(\text{CO})_6$  but the only characterised products from these reactions are  $\text{Fe}(\text{CO})_4\text{PhNC}$  and  $\text{Mo}(\text{CO})_3\text{PhNC}$ .<sup>2</sup>

Reaction of phenyl isothiocyanate with (Ia) in a 1:1 ratio at room temperature gives (III) as the main product.

The formulae proposed† for complexes (IV) and (V) are supported by i.r. [IVa,  $\nu(\text{C}=\text{N})$  1560,  $\nu(\text{C}-\text{S})$  930; IVb  $\nu(\text{C}=\text{N})$  1585,  $\nu(\text{C}-\text{S})$  903; V,  $\nu(\text{NC})$  2180,  $\nu(\text{C}=\text{N})$  1576,  $\nu(\text{C}-$

S) 918  $\text{cm}^{-1}$ ] and  $^1\text{H}$  n.m.r. data [IVb,  $\tau$  ( $\text{CDCl}_3$ ) 6.89 (s, 3H,  $\text{CH}_3$ ), 2.70 (complex, 30H, phenyl)], and by the results of protonation and deprotonation reactions. Protonation of (IVa) and (IVb) with trifluoroacetic acid in benzene affords white crystalline complexes† formulated as  $[\text{Pt}(\text{S}_2\text{C}:\text{NHR})\text{L}_2]^+[\text{CF}_3\text{CO}_2]^-$ , (VIa,  $\text{R}=\text{Ph}$ ; VIb,  $\text{R}=\text{Me}$ ) [VIa,  $\nu(\text{NH}^+)$  2500 br,  $\nu(\text{CO}_2^-)$  1671,  $\nu(\text{C}=\text{N})$  1558,  $\nu(\text{C}-\text{S})$  970; VIb,  $\nu(\text{NH}^+)$  2600 br,  $\nu(\text{CO}_2^-)$  1686,  $\nu(\text{C}=\text{N})$  1574,  $\nu(\text{C}-\text{S})$  950  $\text{cm}^{-1}$ ] which are 1:1 electrolytes in nitromethane. The  $^1\text{H}$  n.m.r. spectrum of (VIa) shows a broad peak centred on  $\tau$  ( $\text{CDCl}_3$  solution) 0.81 (1 H,  $\text{NH}^+$ ) which vanishes on addition of  $\text{D}_2\text{O}$  to the solution. Treatment of (VIa) with base regenerates (IVa). The possibility that the 2180  $\text{cm}^{-1}$  band in the i.r. spectrum of (V) is due to a co-ordinated nitrile was excluded on the grounds that no replacement of the phosphine ligands in (IVa) could be achieved even with a large excess of benzonitrile under forcing conditions.

The formation of the sulphur-rich complexes (IVa, IVb) probably involves the formation of (III) from (Ia), (Ib), or (II) either *via*  $\text{PtL}_2$  as an intermediate or by direct ligand displacement. Co-ordination of an additional molecule of  $\text{RNCS}$  to (III) could then give  $\text{Pt}(\text{RNCS})_2\text{L}_2$ , which collapses to the dithiocarbonimidato complex *via* extrusion of  $\text{RNC}$ . A rhodium compound  $\text{RhCl}(\text{PhNCS})_2\text{L}_2$  has been reported as the major product of the reaction between  $\text{RhClL}_3$  ( $\text{L}=\text{Ph}_3\text{P}$ ) and  $\text{PhNCS}$ .<sup>3</sup>

(Received, 9th May 1974; Com. 529.)

† Complexes (IVa), (IVb), and (V) had correct molecular weights and, like complexes (VIa) and (VIb), gave satisfactory elemental analysis.

<sup>1</sup> F. A. Cotton and J. A. McCleverty, *Inorg. Chem.*, 1967, **6**, 229.

<sup>2</sup> T. A. Manuel, *Inorg. Chem.*, 1964, **3**, 1703.

<sup>3</sup> M. C. Baird and G. Wilkinson, *J. Chem. Soc. (A)*, 1967, 865.