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# The Formation of a Polymeric Platinum(II) Complex Containing a Metallodithiocarboxylato–Metal Linkage

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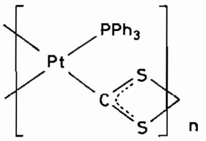
There have been several recent reports of the nucleophilic character of zerovalent phosphine complexes of platinum towards the carbon atom of metal–carbenes [1, 2] and thiocarbonyls [3]. These reactions result in the formation of platinum–metal bonds and either carbene transfer or bridging thiocarbonyl formation.

It now seems clear that the complex $(Ph_3P)_2\overline{Pt(\mu\text{-}S)Pt}(Ph_3P)CO$ isolated some years ago [4, 5] by refluxing $Pt(\eta^2\text{-}COS)(Ph_3P)_2$ in chloroform is formed by a similar process. The coordinated carbonyl sulphide molecule is very labile and is easily replaced by phosphine even in hexane suspension to yield $Pt(Ph_3P)_4$ [6]. Thus attack by $Pt(Ph_3P)_2$, formed *in situ* in solution, upon the carbon atom of the $(\eta^2\text{-}COS)$ ligand of the original molecule would lead to an intermediate which could then easily lead to the observed product.

Our attempt to prepare the analogous thiocarbonyl complex $(Ph_3P)_2\overline{Pt(\mu\text{-}S)Pt}(Ph_3P)CS$ by a similar route involving the thermal decomposition of the complex $Pt(\eta^2\text{-}CS_2)(Ph_3P)_2$ met with failure. Although we have now synthesized molecules of this type by a different route, details of which will be shortly published elsewhere, the above decomposition reaction does not lead to a thiocarbonyl product.

We have observed that refluxing solutions of $Pt(\eta^2\text{-}CS_2)(Ph_3P)_2$ in benzene under nitrogen leads to decomposition by loss of a phosphine molecule rather than carbon disulphide. We found, for example, that if excess triphenylphosphine is added to such solutions no decomposition is observed at all even after 12 hours of refluxing. In the absence of excess phosphine however, a highly insoluble reddish–brown powder is deposited (52% by weight) after 15 hours of reflux. This product has been characterized by elemental analysis (Found: C, 42.78; H, 2.85; S, 11.92; Reqd.: C, 42.77; H, 2.83; S, 12.02%; M.P. 163 °C), infrared spectroscopy, its chemical reactivity and its method of synthesis as a polymeric platinum(II) complex containing a metallodithiocarboxylato–metal linkage and it is suggested that it has the structure:



The infrared spectrum contains a very strong broad band at 925 $cm^{-1}$ and a medium intensity band at 863 $cm^{-1}$. Dinuclear platinum(II) complexes containing the metallodithiocarboxylato–metal linkage have been recently well established both by X-ray structural determination [7] and by infrared studies [8] where they have all been shown to have a very characteristic and constant band pattern of *ca.* 930s, 870m $[\nu_{asy}, \nu_{sy}(CS_2)]$ $cm^{-1}$.

The complex is virtually insoluble in all common organic solvents thus precluding any NMR studies but its chemical reactivity supports the above formulation. Thus no reaction is observed upon prolonged heating of a benzene suspension of the complex with excess triphenylphosphine, as well might be expected for such a polymer, but after prolonged reflux in methyl iodide (24 hours) a yellow crystalline product was isolated from solution in 31% yield. This product was identified by its very characteristic $CS_2$ intensity pattern in the infrared spectrum (990 $cm^{-1}$ (s); 933 $cm^{-1}$ (s); 845 $cm^{-1}$ (m)) and its melting point (252 °C) as the neutral carbene $PtI_2(Ph_3P)\{C(SMe)_2\}$ which we have reported earlier [9]. This would be the expected product upon alkylation of the sulphur atoms and breakage of the metallodithiocarboxylato–metal linkage.

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