Fragmentation of Co-ordinated CS_2 *via* Metal Attack at the Carbon Atom: Formation of the Dinuclear Thiocarbonyl Complex $(Ph_2P[CH_2]_2PPh_2)\overline{Pt(\mu\text{-}S)Pt}(PPh_3)CS$

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Attack at the carbon atom of co-ordinated η^2-CS_2 in the complex $Pt(CS_2)(Ph_2P[CH_2]_2PPh_2)$ by $Pt(\eta^2$-$C_2H_4)(PPh_3)_2$ in acetone causes fragmentation of CS_2 and yields the novel sulphido-bridged dinuclear thiocarbonyl complex $(Ph_2P[CH_2]_2PPh_2)\overline{Pt(\mu\text{-}S)Pt}(PPh_3)CS$.

It has been well documented recently[1] that cleavage of the C–S bond in η^2-CS_2 complexes is much more difficult than in analogous η^2-COS complexes of transition metals. Vigorous conditions are often needed to effect such cleavage[2] and usually sulphur accepting agents such as phosphine,[2] activated alkynes,[3] or even CS_2[4] are required. In contrast we describe here a facile cleavage of CS_2 in a monomeric η^2-CS_2 complex involving nucleophilic addition to the carbon atom by a low oxidation state metal complex. It would seem likely that this approach will offer a more general and facile method for the fragmentation of co-ordinated CS_2, a topic of significant current interest, than has previously been possible.

The reaction of $Pt(\eta^2$-$C_2H_4)(PPh_3)_2$ with $Pt(\eta^2$-$CS_2)(Ph_2P$-$[CH_2]_2PPh_2)$[†] in equimolar amounts in acetone results in the

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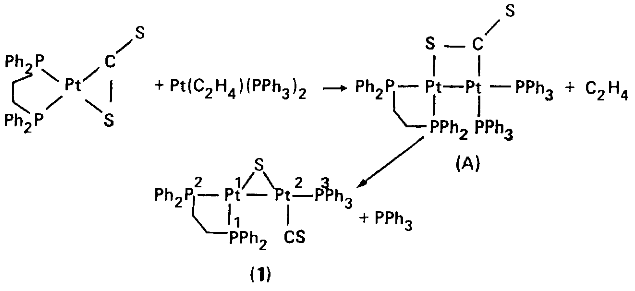
[†] Obtained in our laboratories by phosphine exchange in the complex $Pt(\eta^2$-$CS_2)(PPh_3)_2$ in CS_2. $\nu(CS_2)$ 1141 and 650 cm^{-1}.

rapid formation of a yellow microcrystalline solid (65% yield) which has been characterized‡ by analysis (C, H, S) and infrared and ^{31}P n.m.r. spectroscopy as $(Ph_2P[CH_2]_2PPh_2)Pt(\mu\text{-}S)Pt(PPh_3)CS$ (**1**) in which the thiocarbonyl fragment has been transferred to the other platinum atom. This product can be rationalized in terms of nucleophilic attack at the carbon atom of the co-ordinated CS_2 molecule by $Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2$ as shown in Scheme 1. Nucleophilic attack by zerovalent phosphine complexes of platinum at the carbon atom of other molecules such as carbenes,[5] carbynes,[6] and thiocarbonyls[7] to yield dinuclear metal complexes has been reported recently. The infrared spectrum of complex (**1**) exhibits a very intense band at 1302 cm^{-1} which is in a characteristic region[2] for terminally bound thiocarbonyl groups. The complex is air stable and is only sparingly soluble in nonhalogen containing solvents. It is readily soluble in $CHCl_3$ and CH_2Cl_2 but slow decomposition occurs, in a matter of hours in $CHCl_3$ but over several days in CH_2Cl_2, to yield dark solutions.



Scheme 1

Although the (μ-CS_2) intermediate (A) cannot be isolated in this reaction, an analogous complex is the insoluble product formed from the reaction of $Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2$ with $Pt(\eta^2\text{-}CS_2)(PPh_3)_2$ in acetone. The yellow product $(Ph_3P)_2Pt(\mu\text{-}CS_2)Pt(PPh_3)_2$ has been identified by analysis (C, H, S) and infrared spectroscopy, where $\nu(CS_2)$ 930 cm^{-1} (m, br.) compares well with that reported recently[8] for the related complex $Pt_2Cl_2(\mu\text{-}CS_2)(\mu\text{-}Ph_2PCH_2PPh_2)_2$, the structure of which has been determined by *X*-ray crystallography. The product while perfectly stable in the solid state immediately decomposes to a mixture of complexes when dissolved in a solvent such as tetrahydrofuran and thus n.m.r. data are precluded.

Further studies on the fragmentation of co-ordinated CS_2 by low oxidation state metal complexes are in progress and it now appears likely that the fragmentation may be reversible in some cases as addition of $Ph_2P[CH_2]_2PPh_2$ to a suspension of (**1**) in acetone yields a complex analogous to intermediate (A) but containing two 'diphos' molecules $(Ph_2P[CH_2]_2PPh_2)Pt(\mu\text{-}CS_2)Pt(Ph_2P[CH_2]_2PPh_2)$. This highly insoluble complex also exhibits $\nu(CS_2)$ 929 cm^{-1} (m, br.) and gives a satisfactory analysis (C, H, S).

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‡ ν(CS) 1302 cm^{-1} (vs); M_r in $CHCl_3$ 1060 (1127 calculated); $^{31}P\{^1H\}$ n.m.r. (CH_2Cl_2) δ 32.09 [dd, P^3, ^3J (P^3, P^2) 152.6 Hz, ^3J (P^3, P^1) 26.7 Hz], 52.69 (d, P^1), and 63.54 p.p.m. (d, P^2); ^{195}Pt satellites: ^1J (P^3, Pt^2) 2485.3 Hz, ^2J (P^3, Pt^1) 110.6 Hz, ^1J (P^1, Pt^1) 3308.1 Hz, ^2J (P^1, Pt^2) 91.6 Hz, ^1J (P^2, Pt^1) 3353.1 Hz, and ^2J (P^2, Pt^2) 346.7 Hz. All ^{31}P n.m.r. spectra are with reference to external 85% H_3PO_4. Satisfactory analyses have been obtained for all complexes.