

Bis(triphenylphosphine)(carbon disulphide)platinum

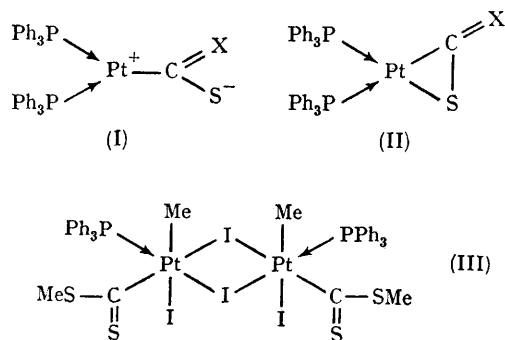
By M. C. BAIRD and G. WILKINSON

(Department of Chemistry, Imperial College, London, S.W.7.)

DURING studies of potential synthetic methods for thiocarbonyl (CS) complexes of transition metals,¹ we have found that tris(triphenylphosphine)platinum(0)² undergoes a rapid and essentially quantitative reaction with carbon disulphide at room temperature producing the novel complex of stoichiometry $(\text{Ph}_3\text{P})_2\text{PtCS}_2$; the only previous report of a carbon disulphide complex is $\text{Co}_4(\text{CO})_{10}\text{CS}_2$ which is alleged to be formed in low yield by the interaction of cobalt carbonyl and carbon disulphide.³ The monomeric platinum complex forms beautiful orange needles, m.p., 165–172°, which analyse correctly. The infrared spectrum (i.r.) has a strong band at 1147 cm^{-1} which may be assigned as a C–S frequency. A less stable pink complex, $(\text{Ph}_3\text{P})_2\text{PtCOS}$, obtained similarly using carbonyl sulphide, has a C–O stretching frequency at 1727 cm^{-1} . The action of carbon dioxide on $(\text{Ph}_3\text{P})_3\text{Pt}$ gives an unstable solid which could not be obtained pure but which had i.r. bands at 1580 and 1680 cm^{-1} .

Two structures appear possible for $(\text{Ph}_3\text{P})_2\text{PtCSX}$, (X = O, S), (I) being similar to that⁴ of $\text{Et}_3\text{P}^+\text{CS}_2^-$, while (II) is similar to that proposed⁵ for complexes of the formula $(\text{Ph}_3\text{P})_2\text{Pt}$ (acetylene); an X-ray structure determination is in progress.⁶ It would seem that (II) is more likely, and it is of interest that the CS_2 complex can be obtained by a displacement reaction from the phenylacetylene complex⁵ $(\text{Ph}_3\text{P})_2\text{Pt}(\text{PhC}_2\text{H})$ in CS_2 solution.

The interaction of $(\text{Ph}_3\text{P})_2\text{PtCS}_2$ with methyl iodide yields $(\text{Ph}_3\text{PMe})\text{I}$ and a bright yellow, sparingly soluble complex $[\text{PtMeI}_2(\text{CS}_2\text{Me})(\text{PPh}_3)]_2$. This complex is a non-electrolyte in nitrobenzene, and the i.r. spectrum shows bands at 1410 and 1394 cm^{-1} and at 932 and 845 cm^{-1} due to methyl deformation and rocking modes, respectively, and at 989 cm^{-1} due to ν_{CS} . The most reasonable structure is (III) which involves a carbon bonded dithiomethyl ester group and iodide bridges.



The carbonyl sulphide adduct on refluxing in chloroform yields a bright yellow complex, which analyses as $\text{Pt}_2\text{S}(\text{CO})_2(\text{PPh}_3)_3$ and clearly has terminal carbon monoxide groups since the i.r.

spectrum shows strong bands at 1989 and 1960 (sh) cm^{-1} .

It now seems likely that carbon disulphide complexes are more common than has previously been recognised and also that complexes of the type (II) may be intermediates in reactions leading to thiocarbonyl complexes. Thus from the interaction of $\text{RhCl}(\text{PPh}_3)_3$ with refluxing CS_2 , a red CS_2

adduct, which, at higher temperatures, gives the thiocarbonyl, has been isolated, while $\text{IrCl}(\text{CO})_2(\text{PPh}_3)_2$ in refluxing CS_2 yields a deep green adduct ($\nu_{\text{CO}} = 2013 \text{ cm}^{-1}$, $\nu_{\text{CS}} = 1154, 1161 \text{ cm}^{-1}$), the latter being another example of the well known addition of neutral molecules to this square complex.⁷

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⁴ T. N. Margulis and D. H. Templeton, *J. Amer. Chem. Soc.*, 1961, **83**, 995.

⁵ J. Chatt, G. A. Rowe, and A. A. Williams, *Proc. Chem. Soc.*, 1957, 208; A. D. Allen and C. D. Cook, *Canad. J. Chem.*, 1964, **42**, 1063.

⁶ By Prof. R. Mason, Sheffield University.

⁷ cf. L. Vaska, *Science*, 1966, **150**, 769; 1963, **140**, 809.