

Thiocarbonyl Complexes of Transition Metals

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ALTHOUGH carbon monoxide, or carbonyl complexes of transition metals are well known, no corresponding thiocarbonyl complexes containing MCS bonds have, to our knowledge, been prepared.

We have shown that the compound tris(triphenylphosphine)chlororhodium(I) abstracts the CO group from aldehydes¹ to give the well known complex *trans*-bis(triphenylphosphine)carbonyl chlororhodium(I). Similarly, on refluxing the trisphosphine complex with carbon disulphide for fifteen minutes the CS group is abstracted to give the thiocarbonyl analogue of the carbonyl complex, *i.e.*, *trans*-(PPh₃)₂Rh(CS)Cl, in *ca.* 50% yield. It

give the bright orange rhodium(III) complex, RhCl₃(CS)(PPh₃)₂. The infrared spectra of corresponding CO and CS compounds are given in the Table. Assuming a value of 1.8 for the ratio of the CO to CS force constants, it has been shown² that the ratio $\nu_{\text{CO}}/\nu_{\text{CS}}$ should be *ca.* 1.5, although for ketones and thioketones, coupling interactions caused the ratio to vary between 1.14 and 1.61. The observed ratios in the metal complexes suggest that there is considerable back-bonding between the metal and thiocarbonyl groups as, *e.g.*, in (I). Such resonance structures would result in a lowering of the non-bonding electron

TABLE

Comparison of infrared spectra of carbonyl and thiocarbonyl complexes

Compound	$\nu_{\text{CO}}(\text{cm.}^{-1})^{\text{a}}$	Compound	$\nu_{\text{CS}}(\text{cm.}^{-1})^{\text{a}}$	$\nu_{\text{CO}}/\nu_{\text{CS}}$
RhCl(CO)(PPh ₃) ₂	1975	RhCl(CS)(PPh ₃) ₂	1299	1.52
RhCl ₃ (CO)(PPh ₃) ₂	2100	RhCl ₃ (CS)(PPh ₃) ₂	1362	1.54
RhBr(CO)(PPh ₃) ₂	1975	RhBr(CS)(PPh ₃) ₂	1298	1.52
RhBr ₃ (CO)(PPh ₃) ₂ ^b	2096	RhBr ₃ (CS)(PPh ₃) ₂ ^b	1355	1.54

^a In benzene solution using a Grubb-Parsons grating "Spectromaster."

^b X-Ray powder patterns indicate that these compounds are isomorphous.

analyses correctly, has the correct molecular weight and forms bright orange crystals, m.p. 250—252°; it is stable in air.

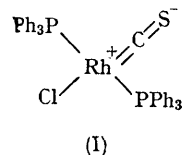
On treatment with chlorine in ice-cold dichloromethane, the complex is additively oxidised to

density on the metal atom compared to that in the analogous carbonyl complex and would explain the failure of the square thiocarbonyl to add hydrogen chloride, although the carbonyl does so react. It is also impossible to replace CS by CO

by interaction at 1 atm. and 25°C. The negative charge delocalised on to the sulphur atom will make this a reactive site and reagents such as methyl iodide and mercuric chloride cause decomposition of the complex.

Thiocarbonyl complexes have also been obtained from the interaction of $\text{RuX}_2(\text{PPh}_3)_3$, $\text{X} = \text{Cl, Br}$, with CS_2 , and attempts to prepare thiocarbonyls of other types, *e.g.*, $\text{Ni}(\text{CS})_4$, which now, in principle, should be capable of existence, are in progress using CS_2 , CSCl_2 , $\text{C}_6\text{H}_5\text{CSCl}$, *etc.*, as sources of CS.

A three-dimensional X-ray study of $\text{RhCl}(\text{CS})(\text{PPh}_3)_2$ is also in progress.³



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¹ M. C. Baird, D. N. Lawson, J. T. Mague, J. A. Osborn, and G. Wilkinson, *Chem. Comm.*, 1966, 129.

² R. Mecke, R. Mecke, and A. Lüttringhaus, *Z. Naturforsch.*, 1955, 10b, 367.

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