The Thiocarbonyl Ligand; Molecular Structure of *trans*-Bis(triphenylphosphine)thiocarbonylchlororhodium(I)

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BAIRD and WILKINSON[1] recently reported the existence of a number of complexes of rhodium and ruthenium containing a thiocarbonyl ligand. We have determined the structure of the first of these to be prepared.

trans-Bis(triphenylphosphine)thiocarbonylchlororhodium(I) [$Rh(CS)Cl(PPh_3)_2$] crystallises as deep orange crystals which are monoclinic. The unit-cell dimensions are $a = 12{\cdot}134$, $b = 24{\cdot}213$, $c = 13{\cdot}156$ Å; $\beta = 123{\cdot}03°$; $U = 3242$ Å^3; $D_{obs} = 1{\cdot}45$ g.

cm.$^{-3}$, $Z = D_{\text{calc}} = 1{\cdot}45$ g. cm.$^{-3}$. The space group was uniquely determined as $P2_1/c$.

The intensity data were collected on a Nonius automatic diffractometer at Groningen using Mo-K_α radiation, and the structure has been determined by standard Patterson and Fourier methods. Least-squares refinement based on 2997 independent reflections has now reached $R = 0{\cdot}062$. For this all atoms were given anisotropic temperature-factors, except the hydrogens which were also fixed in their calculated positions.

As shown in the Figure, the rhodium atom has the expected square-planar co-ordination, although there is slight distortion: the relevant angles are given in the Table. All the bond lengths are comparable to previously determined values. The two triphenylphosphine groups are nearly eclipsed, giving the molecule an approximate non-crystallographic mirror plane.

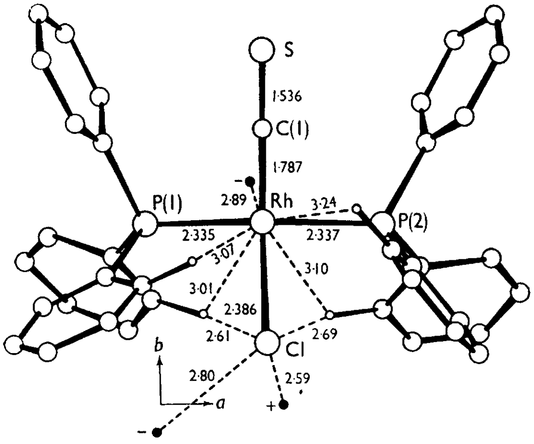

FIGURE: *The molecule viewed perpendicular to the least-squares plane through* Rh, P(1), P(2), Cl, C(1) and S. *Hydrogen atoms from adjoining molecules are represented by* ●; + *indicates above the plane and* — *indicates below it.* (*The standard deviations in the bond distances are* Rh–Cl, 0·003; Rh–P, 0·002; Rh–C(1), 0·010; C–S, 0·010 Å).

TABLE

Angle		Standard deviation
Rh–C(1)–S	177·2°	1·3°
P(1)–Rh–Cl	89·4	0·1
P(2)–Rh–Cl	87·3	0·1
P(1)–Rh–C(1)	91·6	0·2
P(2)–Rh–C(1)	92·0	0·2
Cl–Rh–C(1)	174·5	0·6
P(1)–Rh–P(2)	175·6	0·1

The thiocarbonyl ligand is very nearly linear. The carbon–sulphur distance (**1·536 Å**) appears to be slightly shorter than that in carbon disulphide (1·554 Å)[2] as is also the rhodium–carbon distance (1·787 Å)* compared to that in RhH(CO)(PPh$_3$)$_3$, (1·81 Å).[3] This is in agreement with the mode of bonding postulated by Baird and Wilkinson.

The five nearest rhodium–hydrogen distances, based on calculated hydrogen positions, are shown in the Figure. The shortest of these is an intermolecular contact, and this distance of 2·8$_9$ Å at least is comparable to some recently reported metal–hydrogen interactions.[4] The chlorine atom also has some close hydrogen neighbours. Thus there are two intramolecular distances of 2·6$_1$ and 2·6$_9$ Å and two intermolecular distances of 2·5$_9$ and 2·8$_0$ Å. These are shorter than the sum of the van der Waals radii, suggesting a possible interaction.

(*Received, September* 12*th*, 1966; *Com.* 683.)

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* *Note added in proof:* In a Paper soon to be submitted to *Inorg. Chem.*, by S. F. Watkins, J. Obi, and L. F. Dahl, the length of the Rh–C bond in Rh(CO)Cl(PPh$_3$)$_2$ is reported to be 1·86Å. We are grateful for permission to mention this result.

[1] M. C. Baird and G. Wilkinson, *Chem. Comm.*, **1966**, **267**. We are grateful to Dr. Baird and Prof. Wilkinson for providing the specimen.

[2] A. H. Guenther, *J. Chem. Phys.*, 1959, **31**, 1095.

[3] J. A. Ibers, *J. Amer. Chem. Soc.*, 1963, **85**, 3501.

[4] N. A. Bailey, J. M. Jenkins, R. Mason, and B. L. Shaw, *Chem. Comm.*, 1965, 237; M. Bonamico, G. Dessy, A. Mugnoli, A. Vaciago, and L. Zambonelli, *Acta Cryst.*, 1965, **19**, 886; L. Capacchi, M. Nardelli, and A. Villa, *Chem. Comm.*, 1966, 441; J. A. Ibers, *Abstr. Amer. Cryst. Assoc.*, 1965, B10.