Carbon Disulphide Complexes of some Transition-metal Ions

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As part of a general investigation into the properties of carbon disulphide as a ligand, we have earlier shown[1] that tris(triphenylphosphine)platinum(0) forms the stable adduct, $Pt(CS_2)(PPh_3)_2$. The structure of, and bonding in, this complex can now be discussed from the results of a single crystal *X*-ray analysis.

$Pt(CS_2)(PPh_3)_2$ crystallises in the space group $P2_1/n$ with a unit cell, $a = 11{\cdot}50$ Å, $b = 19{\cdot}43$ Å, $c = 14{\cdot}22$ Å, $\beta = 91{\cdot}1°$; $Z = 4$. The intensities of 1360 non-equivalent reflexions have been measured on a "Pailred" automatic diffractometer, the molecular structure, shown in Figure 1, being determined by the usual combination of Patterson and Fourier methods. Block-diagonal least squares refinement of atomic co-ordinates, anisotropic

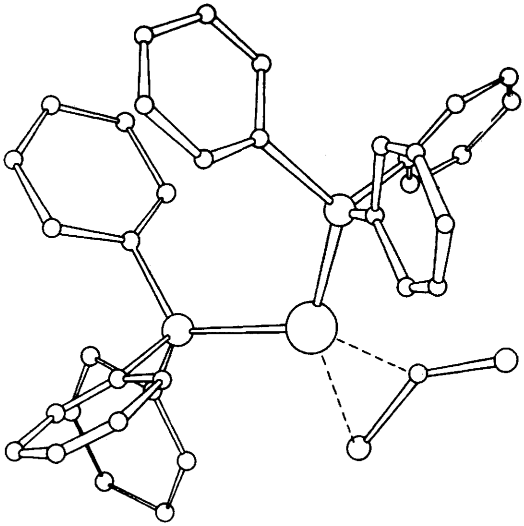


FIGURE 1

thermal parameters of the platinum, phosphorus and sulphur atoms and isotropic thermal factors for all the carbon atoms has reduced the reliability index to a present value of 0·088.

The geometry of the metal co-ordination is shown in detail in Figure 2. The two tristriphenylphosphine ligands are related by an approximate C_2 axis passing through the platinum atom. Average standard deviations in the bond lengths are 0·01 Å (Pt–P), 0·01 Å (Pt–S), 0·04 Å (Pt–C), and 0·05 Å (C–S). The average e.s.d. of the bond angles is 1·5°.

The two planes containing, respectively, Pt, P-1, and P-2 and Pt, C-1, and S-2 intersect on an axis which bisects the angle P-1–Pt–P-2; the dihedral angle between these planes is only 6° so that the CS_2 ligand is essentially co-planar with the platinum and phosphorus atoms.

The two independent platinum–phosphorus bond lengths differ by 0·11 Å (10σ), the longer bond being *trans* to the formally σ-bonded carbon of the CS_2 ligand. Details of the nature of the bonding of the carbon disulphide to the metal are given elsewhere[2] but it is worth pointing out here that

(i) the observed bond angle S–C–S of 136° is identical, within experimental error, with that found, by spectroscopic methods, for the first excited state of CS_2, and

(ii) the C–S bond length of CS_2 in its ground state is 1·554 Å[3] and 1·64 Å in the excited state.[4] The two independent C–S bond lengths of 1·54 Å and 1·72 Å found in the platinum complex are in close agreement with these values.

The bonding of carbon disulphide to platinum can therefore be thought of as involving a one-electron transfer, *via* the intermediacy of the platinum, from the highest lying π-molecular orbital of the ligand to its lowest antibonding molecular orbital.

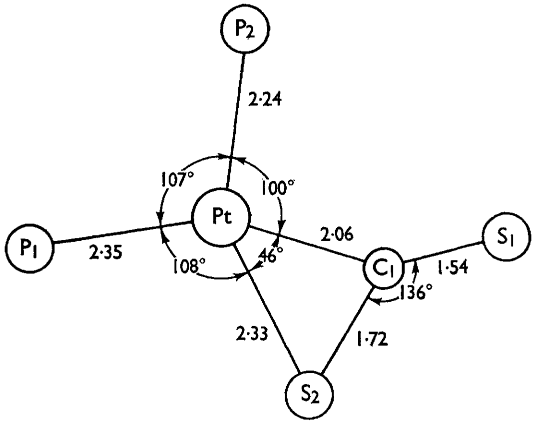
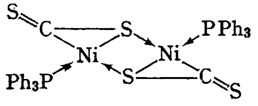
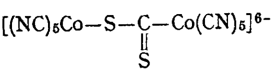


FIGURE 2

The orange isostructural palladium compound, $Pd(CS_2)(PPh_3)_2$ (ν_{C-S} = 1193 cm.$^{-1}$), can be prepared in a like manner, that is by treating tetrakis(triphenylphosphine)palladium[5] with carbon disulphide: refluxing $Ni(CO)_2(PPh_3)_2$[6] in CS_2 for several hours gives the very dark red $Ni(CS_2)(PPh_3)_2$, which has a much simpler X-ray powder diffraction pattern than the palladium and platinum compounds. The nickel complex (I) is

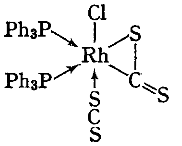


(I)

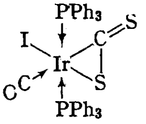


$$[(NC)_5Co-S-\underset{\underset{S}{\|}}{C}-Co(CN)_5]^{6-}$$

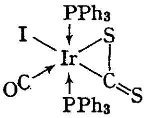
(II)



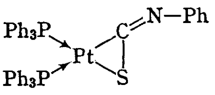
(III)



(IV)



(V)



(VI)

only very slightly soluble in organic solvents and is probably dimeric or polymeric with CS_2 bridges ($\nu_{C-S} = 1122$ cm.$^{-1}$).

The yellow cobalt complex, $K_6[(NC)_5Co{\cdot}S{\cdot}CS{\cdot}Co(CN)]_5$, prepared by treating an aqueous solution of $K_2[(Co(CN)_5]$[7] with CS_2, undoubtedly contains a bridging CS_2 ligand (II). The complex has ν_{C-S} at 983 cm.$^{-1}$ and 840 cm.$^{-1}$ and is probably similar to the complexes $Me_3\,Sn{\cdot}S{\cdot}CS{\cdot}NMe_2$[8] and $Bu_3Sn{\cdot}S{\cdot}CS{\cdot}OMe$,[9] obtained by the insertion of CS_2 into Me_3SnNMe_2 and $Bu_3Sn{\cdot}OMe$, respectively.

Treatment of $RhCl(PPh_3)_3$[10] and $IrICO(PPh_3)_2$[11] with CS_2 gives the deep-red $RhCl(CS_2)_2(PPh_3)_2$ and the yellow–brown $IrICO(PPh_3)_2(CS_2)$, respectively. The former appears to contain both a "π-bonded" CS_2 ($\nu_{C-S} = 1028$ cm.$^{-1}$) and an S-bonded CS_2 group ($\nu_{C-S} = 1510$ cm.$^{-1}$) and is formally a six-co-ordinate complex of rhodium(III) (III). The iridium compound has two C–S stretching bands in the infrared spectrum centred at 1188 cm.$^{-1}$ and 1165 cm.$^{-1}$ and may be a mixture of isomers differing in the orientation of the CS_2 ligand (IV and V); both complexes are sensitive to air.

Structurally related compounds of methyl and phenyl isothiocyanate have been obtained. The complexes $Pt(RNCS)(PPh_3)_2$ (R = Me, Ph) appear, on the basis of their infrared spectra, to contain the organic groups "π-bonded" to the metal atoms *via* the C–S bonds (VI) while the complex $RhCl(PhNCS)_2(PPh_3)_2$ appears to contain both "π-bonded" and S-bonded PhNCS groups. Further preparative and structural work is continuing with these and similar complexes of metals with unsaturated organic ligands.

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