Triphenylphosphoniodithiocarboxylato-*SS'*-carbonylbis(triphenylphosphine)-iridium(I) Tetrafluoroborate: *X*-Ray Structure of an Apparent η-CS_2 Complex of Iridium

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Summary The cation of composition $[Ir(CS_2)(CO)(PPh_3)_3]^+$, previously considered a η-CS_2 complex of the $[Pt(CS_2)(PPh_3)_2]$ type, is shown by an *X*-ray crystal structure determination of the tetrafluoroborate salt to be a 5 co-ordinate complex of iridium(I) containing the bidentate, sulphur-bound, triphenylphosphine–carbon disulphide zwitterion, $Ph_3P^+–CS_2^-$, as ligand.

Reaction of $[IrCl(CO)(PPh_3)_2]$ with CS_2 and an excess of PPh_3 in MeOH leads to a violet solution from which can be isolated, after addition of $NaBPh_4$, violet crystals of a compound of composition $[Ir(CS_2)(CO)(PPh_3)_3]BPh_4$ (I).[1] This and other obviously related cationic complexes of iridium and rhodium have been suggested[1] to be CS_2 complexes of the type $[Pt(CS_2)(PPh_3)_2]$.[2] Several properties of (I) point against this formulation: (i) ν(CO) for (I) at 1980 cm^{-1} is lower than that for the parent cation $[Ir(CO)(PPh_3)_3]^+$ which is at 1995 cm^{-1};[3] (ii) we have found that the violet species is not formed from $[Ir(CO)(PPh_3)_3]BF_4$[3] and CS_2 unless an excess of PPh_3 is also present; and (iii) the violet species does not undergo alkylation reactions at either one or both sulphur atoms as do the CS_2 complexes of ruthenium and osmium,[4] which are clearly of the $[Pt(CS_2)(PPh_3)_2]$ type. For these reasons we have carried out an *X*-ray structure determination of a compound of composition $[Ir(CS_2)(CO)(PPh_3)_3]BF_4$ which was formed from $[Ir(CO)(MeCN)(PPh_3)_2]BF_4$,[3] CS_2, and an excess of PPh_3; purple crystals were grown from CH_2Cl_2–EtOH. The compound crystallizes in the monoclinic space group $P2_1/c$, with a = 10·5876(9), b = 31·581(10), c = 16·2164(5) Å, β = 92·521(1)°, and $Z = 4$. Intensity data were collected on a Hilger and Watts automatic diffractometer with Mo-K_α radiation, three different crystals being required as the count-rates declined steadily with time of irradiation. The structure was solved using Patterson and Fourier syntheses and is being refined by least-squares methods. Thus far the iridium, sulphur, and phosphorus atoms have been assigned anisotropic thermal parameters and the conventional *R* factor is 0·11 for 4648 reflections with $I > 3\sigma(I)$. Absorp-

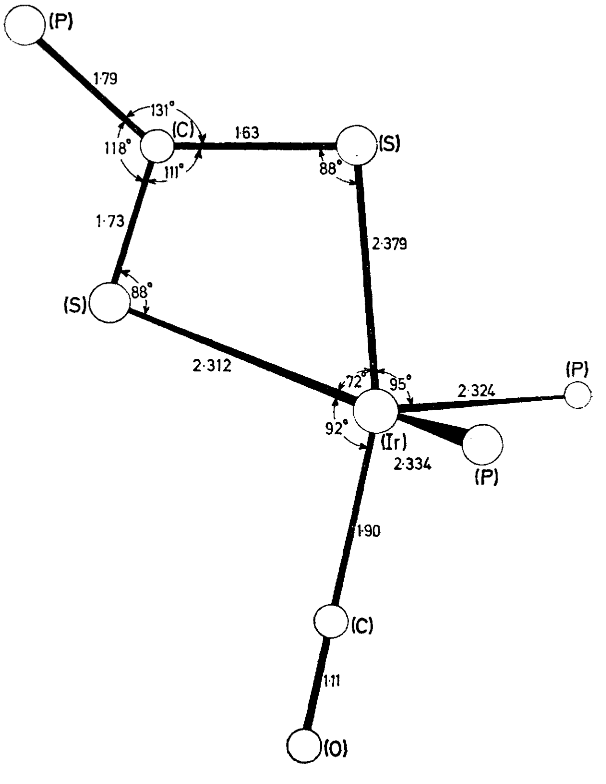

Figure. The iridium co-ordination geometry in $[Ir(S_2CPPh_3)(CO)(PPh_3)_2]^+$.

tion corrections have yet to be applied. The co-ordination about the iridium atom is distorted trigonal bipyramidal. Two PPh_3 ligands are equatorial, the $Ph_3P^+{-}CS_2^-$ group spans the remaining equatorial and one of the axial sites; the CO group fills the last axial position. This overall geometry is illustrated in the Figure. The geometry of the $Ph_3P^+{-}CS_2^-$ ligand can be compared with that found for the unco-ordinated $Et_3P^+{-}CS_2^-$ molecule.[5] The P–C distances are 1·79 and 1·78 Å respectively, the C–S values are 1·63, 1·73, and 1·68, 1·71 Å respectively. In the iridium complex the difference in the two C–S bonds is probably significant (4σ) but this would be expected since one sulphur atom is axial while the other is equatorial. The Ir–S distances reflect this also, Ir–S axial (2·379 Å) being longer than Ir–S equatorial (2·312 Å) (difference = 10σ).

It seems probable that the other cationic iridium and rhodium complexes described in ref. 1 and also the violet ruthenium complex of composition $[RuCl_2(CS_2)(PPh_3)_3]$[6] should now be reformulated as containing $Ph_3P^+{-}CS_2^-$ ligands.

(*Received, 5th April* 1976; *Com.* 355.)

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