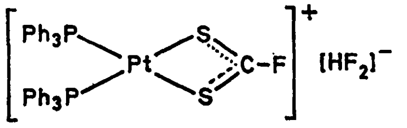
Insertion of Carbon Disulphide into a Metal–Fluorine Bond: Crystal Structure of $[Pt(S_2CF)(PPh_3)_2][HF_2]$

By J. A. EVANS, M. J. HACKER, R. D. W. KEMMITT, D. R. RUSSELL,* and J. STOCKS

(*Department of Chemistry, University of Leicester, Leicester* LE1 7RH)

Summary The reaction of CS_2 with $[PtF(PPh_3)_3][HF_2]$ gives a bisphosphine platinum dithiofluoroformate complex $[Pt(S_2CF)(PPh_3)_2][HF_2]$, the result of insertion of CS_2 into the Pt–F bond.

DURING investigation of the chemistry of the fluorine-containing cationic species[1] $[PtF(PPh_3)_3]^+$, reaction of its bifluoride salt with carbon disulphide in ethanol solution gave yellow crystals of an adduct, which proved by chemical analysis to have the formulation $[PtF(CS_2)(PPh_3)_2][HF_2]$. A crystal structure determination of this compound has now been completed, and shows the adduct to be a cationic platinum complex (**1**) of fluorodithioformic acid, resulting from insertion of CS_2 into the Pt–F bond.



(**1**)

Crystal data: $C_{37}H_{31}F_3P_2PtS_2$, $M = 853{\cdot}9$, triclinic, $a = 13{\cdot}56$, $b = 11{\cdot}01$, $c = 16{\cdot}76$ Å, $\alpha = 125{\cdot}5$, $\beta = 81{\cdot}01$, $\gamma = 115{\cdot}3°$, $U = 1825$ Å^3, $Z = 2$, $D_c = 1{\cdot}55$, $D_m = 1{\cdot}53$. Space group $P\bar{1}$. 3796 reflections measured by Stoe-Weissenberg diffractometer, Mo-K_α radiation, $R = 0{\cdot}059$ by block diagonal least-squares refinement.

Detailed geometry of both cation and anion is shown in the Figure. An unexpected feature of the cation geometry is the large departure from ideal C_{2v} geometry in the immediate Pt co-ordination sphere. This is particularly noticeable in the two C–S bond lengths, which differ by 0·15 Å (e.s.d. 0·03 Å); this difference approaches that of 0·18 Å found between the co-ordinated and unco-ordinated C–S bond lengths in $PtCS_2(PPh_3)_2$.[2] One is forced to conclude that there is a marked difference in bond order in the two C–S bonds. This asymmetry is further reflected in the two S–C–F bond angles (the F atom is apparently repelled by the shorter C–S bond), in different Pt–S bond lengths, and in different Pt–P bond lengths (the longer Pt–P bond is *trans* to the shorter Pt–S). The source of the asymmetric influence could be steric, involving different arrangements of phenyl groups in the two PPh_3 ligands (there are some short S–C contacts from 3·2—3·5 Å, *cf* the Van der Waals radii sum of 3·55 Å)[3] or crystal packing effects involving the $(HF_2)^-$ anion although these must be second order as there are no important (*i.e.* non-phenyl group) cation-anion contacts less than 4 Å. There is no major departure from planarity in the P_2PtS_2 unit, the C–F bond is bent by 10·5° away from this plane.

The F......F distance in the HF_2^- anion is unusually long (*cf.* 2·28 Å in KHF_2)[4]; at this distance it is unlikely that the hydrogen atom lies midway between the fluorine atoms. It has proved difficult to observe a band in the i.r. spectrum attributable to the anion; a very broad absorption at ν 1770 cm^{-1}, $\Delta\nu_{\frac{1}{2}}$ 120 cm^{-1}, which varies in intensity with different samples may be due to the anion. A similar band is sometimes observed in the i.r. spectrum of $[PtF(PPh_3)_3]$-$[HF_2]$.

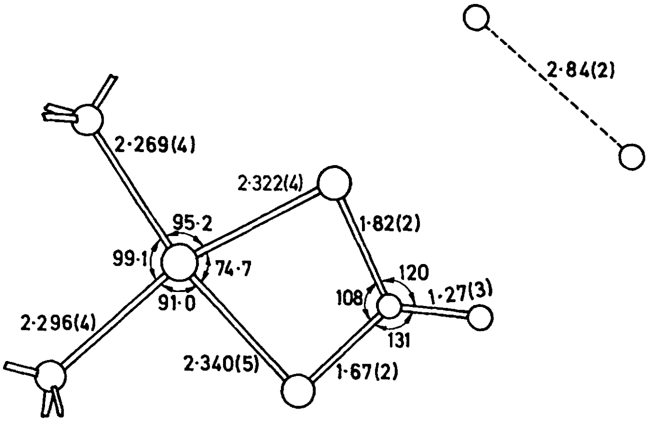


FIGURE. *The molecular geometry of* $[Pt(S_2CF)(PPh_3)_2][HF_2]$. *E.s.d.'s of bond lengths* (Å) *are in parentheses, e.s.d.'s of angles are* 0·2° *around* Pt, 1·5° *about the* S_2CF *group. Phenyl groups are omitted for clarity.*

The fluoro-dithioformate ligand is hydrolytically unstable. Thus if the reaction between $[PtF(PPh_3)_3][HF_2]$ and CS_2 is carried out in damp acetone or methanol, a yellow colouration is initially produced which rapidly fades and white crystals of dithiocarbonatobis(triphenylphosphine)platinum-

(II), $Pt(S_2CO)(PPh_3)_2$ separate, identified by analysis and i.r. spectrum.[5]

Recently, insertion reactions of CS_2 into the Pt–H bond have been studied.[6] The reported product, $PtCl(S_2CH)(PPh_3)_2$, could well have an analogous ionic structure to (**1**), which is also related to the structure found for $Re(S_2CH)(CO)_2(PPh_3)_2$.[7]

We thank the S.R.C. for financial support, and Johnson Matthey and Co. Ltd. for a loan of platinum.

(*Received, October* **13*th*,** 1971; *Com.* 1777.)

[1] R. D. W. Kemmitt, R. D. Peacock, and J. Stocks, *J. Chem. Soc.* (*A*), 1971, 846.
[2] R. Mason and A. I. M. Rae, *J. Chem. Soc.* (*A*), 1970, 1767.
[3] L. Pauling, "The Nature of the Chemical Bond", 3rd Ed., Cornell University Press, Ithaca, New York, 1960.
[4] J. A. Ibers, *J. Chem. Phys.*, 1964, **40**, 402.
[5] J. P. Fackler and W. C. Seidel, *Inorg. Chem.*, 1969, **8**, 1631.
[6] A. Palazzi, L. Busetto and M. Graziani, *J. Organometallic. Chem.*, 1971, **30**, 273.
[7] V. G. Albano, P. L. Bellon and G. Ciani, *J. Organometallic Chem.*, 1971, **31**, 75.