Five-coordinate Rhodium(III) Complexes Containing the Novel TeF_3 Ligand

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Tellurium tetrafluoride reacts at 195 K in CD_2Cl_2 with $Rh(CO)X(PEt_3)_2$ [X = Cl, Br, NCS, NCO] to give the novel complexes $[Rh(CO)X(PEt_3)_2(TeF_3)^+][TeF_5^-]$, which have been characterised by ^{19}F, ^{31}P and ^{13}C NMR spectroscopy; for X = Cl, Br and NCS the complexes are stable at ambient temperature but for X = NCO decomposition occurs at 215 K.

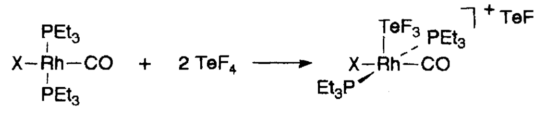
Until recently the only well established examples of transition metal complexes containing fluorinated ligands were those involving carbon (*e.g.* CF_3,[1] C_2F_4[2]), phosphorus (*e.g.* PF_2,[3] PF_3,[4] PF_4[5]) and nitrogen {$[ReF_5(NF)]$[6]}. However, since 1986 Ebsworth *et al.* have produced complexes containing NF_2,[7] SF_3,[8] SF_2^+, SOF,[8] SeF_3, AsF_2[9] and COF[10] ligands.

In this paper we present spectroscopic evidence that clearly shows that TeF_4 undergoes an unusual oxidative addition reaction with $Rh(CO)X(PEt_3)_2$ to form unusual pentacoordinate monocationic complexes containing the terminal TeF_3 ligand, eqn. (1), in pronounced contrast to the equivalent reactions of SF_4 and SeF_4.

The reaction between *trans*-$Rh(CO)Cl(PEt_3)_2$ and TeF_4 in a 1:1 ratio occurred rapidly in CD_2Cl_2 at 195 K to produce a deep-red solution. The $^{31}P\{^1H\}$† NMR spectrum showed two resonances of approximately equal intensity, a doublet at δ 24.3 arising from unreacted starting material **A**, and a doublet of triplets of doublets at δ 27.4 arising from **B**. The latter resonance was in the region of the spectrum associated with PEt_3 complexes of Rh^{III}[9] and showed a narrow doublet coupling (3 Hz) which we assign to $^3J_{PF}$, a larger triplet coupling (16 Hz) which we assign to a second $^3J_{PF}$ and a large doublet coupling (92 Hz) which we assign to $^1J_{PRh}$. This value of $^1J_{PRh}$ is not consistent with PEt_3 coupling to either six-coordinate Rh^{III} or square planar Rh^I. It is, however, indicative of Rh–PR_3 coupling in square pyramidal Rh complexes.[11] The $^{19}F\{^1H\}$ NMR spectrum showed only four resonances, F_1, F_2, F_3 and F_4, each of which showed coupling to ^{125}Te and whose ratios were approximately 2:1:4:1 (see Fig. 1). The resonances F_2 and F_3 were identified as the quintet and doublet of the pentafluorotellurate(IV) anion.[12] Of the remaining two resonances F_1 lay at δ −9.6 and was comprised of a doublet (23 Hz) assigned as $^2J_{FF}$, a doublet (18 Hz) assigned as $^2J_{FRh}$ and a triplet (16 Hz) assigned as $^3J_{FP}$ and F_4 comprised a triplet (23 Hz) assigned as $^2J_{FF}$ of doublets (7 Hz) assigned as $^2J_{FRh}$ at δ −68.4. A sample of $Rh(^{13}CO)Cl(PEt_3)_2$ was prepared and allowed to react with TeF_4. The ^{13}C NMR spectrum of this solution showed a doublet [(71 Hz) assigned as $^1J_{CRh}$] of triplets [(9 Hz) assigned as $^2J_{CP}$] of doublets [(8 Hz) assigned as $^3J_{CF_4}$]. There are two possible ways of viewing the structure. The first would be to assume bonding involving a TeF_3^+ cation bonded to a Rh^I centre, the second involves TeF_3^- attached to a Rh^{III} centre. We believe that the evidence for the second structure is overwhelming on the following grounds. First, the magnitude of $^1J_{PRh}$ unmistakenly characterises the complex as having square pyramidal geometry at Rh. All known rhodium complexes with this geometry are Rh^{III} species (see for example ref. 11). Rhodium(I) complexes would have trigonal bipyramidal geometries and two possible isomers with respect to the locations of the phosphines. In the case where the phosphines were axial we would expect $^1J_{PRh}$ to be lower and where they were equatorial higher than our observed couplings. Secondly, the colour is suggestive of Rh^{III} as Rh^I complexes are generally light in colour. Finally, the assigned product is consistent with results observed in analogous SF_4 and SeF_4 reactions. In the reaction of $M(CO)X(PEt_3)_2$ [M = Ir, Rh; X = Cl, Br, I, NCS, NCO] with SF_4[8,9] various isomers of the M^{III} complex $M(CO)XF(PEt_3)_2(SF_3)$ were observed, the products of oxidative addition reactions. Similarly, complexes $M(CO)XF(PEt_3)_2SeF_3$[9] were observed on reaction of SeF_4 with $M(CO)X(PEt_3)_2$, however, in several cases intermolecular exchange of Rh–F with SeF_5^- was observed, indicating a weak Rh–F bond. It is logical to assume that in this reported work we are observing the continuation of this trend where oxidative addition of TeF_3 and F occurs, followed by removal of F^- by a second molecule of TeF_4, producing a Rh^{III} complex. We have thus formulated the product of this reaction as $[Rh(CO)Cl(PEt_3)_2(TeF_3)]^+$. For X = Br and NCS, similar ^{19}F and ^{31}P NMR spectra were obtained, indicating that similar complexes are obtained, the only differences were in the positions of F_1 and F_4. Both of these complexes were stable at ambient temperature. In the reaction where X = NCO we also observed NMR spectra similar to those seen for $Rh(CO)X(PEt_3)_2$ + TeF_4, where X was Cl, Br or NCS, indicating formation of $[Rh(CO)NCO(PEt_3)_2(TeF_3)^+]$. However, this complex was observed to decompose at 220 K.

On warming the samples where X = Br and NCS, we observed different temperatures at which the TeF_5^- became fluxional, indicating probable interaction of TeF_5^- with $[Rh(CO)X(PEt_3)_2(TeF_3)^+]$. This was supported by the fact that, on reaction of two equivalents of TeF_4 with $Rh(CO)X(PEt_3)_2$, no unreacted starting material was observed, indicating that the product formulation was $[Rh(CO)X(PEt_3)_2(TeF_3)^+][TeF_5^-]$.

Unfortunately, these complexes are highly reactive with moisture and air and, although we have grown deep-red, single crystals in the form of elongated, rectangular blocks on several occasions, we have been unable so far to obtain a



$$\mathrm{X{-}Rh(PEt_3)_2{-}CO} + 2\,\mathrm{TeF_4} \longrightarrow [\mathrm{X{-}Rh(TeF_3)(PEt_3)_2{-}CO}]^+\,\mathrm{TeF_5^-} \quad (1)$$

A **B**

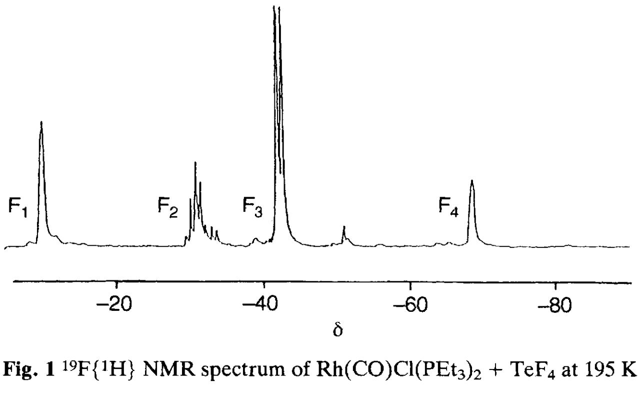


Fig. 1 $^{19}F\{^1H\}$ NMR spectrum of $Rh(CO)Cl(PEt_3)_2$ + TeF_4 at 195 K

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† NMR standards: all NMR shifts are reported as positive to high frequency of 85% H_3PO_4 (for ^{31}P), CCl_3F (for ^{19}F) and Me_4Si (for ^{13}C).

single crystal X-ray diffraction structure, but are continuing to try. The instabilities of these complexes have prevented obtention of satisfactory infrared, FAB mass spectrometric and analytical data.

Preliminary reactions of TeF_4 with the analogous iridium starting materials indicate that similar reactions may by occurring but the products appear to be significantly less stable than their rhodium analogues.

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References

1 E. M. Hyde, J. D. Kennedy, B. L. Shaw and W. McFarlane, *J. Chem. Soc., Dalton Trans.*, 1977, 1571.

2 M. Green and S. H. Taylor, *J. Chem. Soc., Dalton Trans.*, 1975, 1128.

3 E. A. V. Ebsworth, R. O. Gould, N. T. McManus, D. W. H. Rankin, M. D. Walkinshaw and J. D. Whitelock, *J. Organomet. Chem.*, 1983, **249**, 227.

4 T. Kruck and K. Baur, *Chem. Ber.*, 1965, **98**, 3070.

5 E. A. V. Ebsworth, J. H. Holloway, N. J. Pilkington and D. W. H. Rankin, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 630.

6 J. Fawcett and R. D. Peacock, *J. Chem. Soc., Chem. Commun.*, 1982, 958.

7 R. W. Cockman, E. A. V. Ebsworth and J. H. Holloway, *J. Chem. Soc., Chem. Commun.*, 1986, 1622.

8 R. W. Cockman, E. A. V. Ebsworth and J. H. Holloway, *J. Am. Chem. Soc.*, 1987, **109**, 2194.

9 R. W. Cockman, E. A. V. Ebsworth, J. H. Holloway and P. G. Watson, unpublished results.

10 A. J. Blake, R. W. Cockman, E. A. V. Ebsworth and J. H. Holloway, *J. Chem. Soc., Chem. Commun.*, 1988, 529.

11 H. L. Van Gaal, J. M. Verlak and T. Posno, *Inorg. Chim. Acta*, 1977, **23**, 43; C. Masters and B. L. Shaw, *J. Chem. Soc.*, (*A*), 1971, 3679; M. Ghedini, G. Dolcetti, O. Gandolfi and B. Giovannitti, *Inorg. Chem.*, 1976, **15** (**10**), 2385.

12 R. J. Morris and K. C. Moss, *J. Fluorine Chem.*, 1979, **13**, 551.