Reaction of $(C_5Me_5)_2Yb$ with Fluorocarbons: Formation of $(C_5Me_5)_4Yb_2(\mu\text{-}F)$ by Intermolecular C–F Activation

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Addition of C_6F_6 and other fluoroaromatics and fluoroalkenes, though not C_2F_6 or CF_3CH_3, to $(C_5Me_5)_2Yb$ gives the mixed-valence complex $(C_5Me_5)_4Yb_2(\mu\text{-}F)$ with a linear, asymmetric Yb^{II}–F–Yb^{III} bond.

The unusual tetranuclear compound, $(C_5Me_5)_6Yb_4(\mu\text{-}F)_4$, is a class I (trapped-valence) mixed-valence $Yb^{II,III}$ complex.[1] The compound was prepared by reaction of silver fluoride with $(C_5Me_5)_2Yb$ in toluene; the synthesis initially gave a brown, toluene-insoluble precipitate which gave red crystals of $(C_5Me_5)_6Yb_4(\mu\text{-}F)_4$ on crystallization from hot toluene. We now show that the brown substance is the binuclear, mixed-valence compound, $(C_5Me_5)_4Yb_2(\mu\text{-}F)$ and that these metal fluorides can be prepared from the reaction of $(C_5Me_5)_2Yb$ and fluorocarbons, *i.e.*, an unusual example of intermolecular C–F activation.

A solution of $(C_5Me_5)_2Yb$ (0.57 g) reacts instantaneously with 1 mol. equiv. of C_6F_6 in hexane at 20 °C to give a brown precipitate (0.26 g) and a purple solution from which a purple powder (0.10 g) may be isolated on cooling. The brown precipitate gives brown crystals, m.p. 290 °C (decomp), by slow cooling of a warm toluene solution to 20 °C which were contaminated with red $(C_5Me_5)_6Yb_4(\mu\text{-}F)_4$ and orange $(C_5Me_5)_2Yb$. The brown crystals were shown to be $(C_5Me_5)_4Yb_2(\mu\text{-}F)$, by *X*-ray crystallography[†] (Figure 1). The angle formed by intersection of the planes formed by Yb(1)

[†] *Crystal data*: $C_{40}H_{60}FYb_2$, M = 906.00, monoclinic, space group $C2/c$, a = 16.319(2), b = 14.314(1), c = 16.760(2) Å, β = 104.39(1)°, U = 3792(2) Å^3, D_c = 1.60 g cm^{-3}, (Mo-K_α) radiation, λ = 0.71073 Å, μ(Mo-K_α) = 49.2 cm^{-1}, T = 25 °C. The structure was solved by a combination of Patterson and Fourier methods and refined using 2256 unique reflections $[F_0^2 > 3\sigma(F_0^2)]$ measured on a CAD4 diffractometer ($2\theta_{max.}$ 45°). An analytical absorption correction was applied to the data, all non-hydrogen atoms were refined anisotropically, the hydrogen atoms on the methyl groups were located in a difference map, placed in idealized positions and given isotropic thermal parameters 1.20 times those of the carbons to which they are attached, and included in the structure factor calculation but not refined. The final residuals for 197 variables refined against 2256 data were R = 0.017, R_W = 0.025 and GOF = 1.75. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors Issue No. 1.

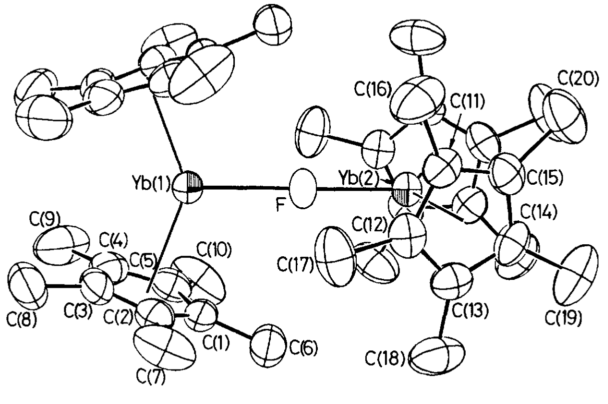

Figure 1. An ORTEP diagram of $(C_5Me_5)_4Yb_2(\mu\text{-F})$. The average Yb(1)–C distance is 2.69(2) Å, the average Yb(2)–C distance is 2.58(2) Å, the Yb(1) ring-centroid distance is 2.41 Å, the Yb(2) ring-centroid distance is 2.29 Å, the ring centroid–Yb(1)–ring centroid angle is 140°, and the ring centroid–Yb(2)–ring centroid angle is 139°.

and its ring centroids with that of Yb(2) with its ring centroids is 90°. Since the molecule lies on a crystallography two-fold axis of symmetry the angle at F is constrained to be linear. The cyclopentadienyl rings on each metal atom are nearly eclipsed with torsion angles of 16 and 17°. If the Yb–F distances were equal then the molecule would have ideal S_4 symmetry. The bridging fluoride is asymmetric, Yb(1)–F = 2.317(2) Å and Yb(2)–F = 2.084(2) Å, consistent with Yb(1) being bivalent and Yb(2) being trivalent since Shannon has shown that the radius of Yb^{II} is at least 0.15 Å larger than Yb^{III}.[2] The Yb–C bond lengths (Figure 1) are also consistent with this deduction.

The molecule can be viewed as being a donor–acceptor complex; the $(C_5Me_5)_2Yb(1)$ is the Lewis acid and the lone pair of electrons on the fluoride of $(C_5Me_5)_2YbF$ is the Lewis base. The molecule is rather sterically crowded; the two ytterbium atoms approach each other close enough so that the closest contact distance between the methyl groups on the C_5Me_5 ligands on Yb(1) and Yb(2) is only 3.6—3.7 Å and the closest contact distance of the methyl groups on the C_5Me_5 ligand on Yb(2), C(19) $\cdots$ C(20′) is 3.42 Å. In addition, C(8,9,19,20) are out of the cyclopentadienyl ring plane by 0.25 Å. It seems reasonable to ascribe the linear Yb–F–Yb unit to intramolecular steric repulsions between rings on adjacent metal atoms rather than to Yb–F π-bonding. Further, relief of steric crowding can be used to rationalize the thermal rearrangement in equation (1), since the tetranuclear compound has two ytterbium atoms with a single C_5Me_5 ring attached, rather than two as in the binuclear compound.[1]

$$4(C_5Me_5)_4Yb_2(\mu\text{-F}) \rightarrow (C_5Me_5)_6Yb_4(\mu\text{-F})_2 + 2\text{`}C_5Me_5\text{'} + 4(C_5Me_5)_2Yb \quad (1)$$

Variable temperature magnetic susceptibility studies on the binuclear complex are consistent with the $Yb^{II,III}$ trapped-valence formulation as suggested by the room temperature *X*-ray crystallographic study. Powdered samples follow Curie–Weiss behaviour and the shape of the plot of χ_m^{-1} *vs.* T is as expected for an isolated Yb^{III} paramagnet. At 5 kG field strength, $\mu_{eff} = 4.11\ \mu_B$, per Yb^{III}, and $\theta = 0$ K from 7—35 K, and $\mu_{eff} = 4.69\ \mu_B$ and $\theta = -25$ K from 100—280 K.

The purple powder is a mixture of paramagnetic compounds. Hydrolysis of a portion of the solid in C_6D_6 shows the presence of C_5HMe_5 and C_6F_5H by ^1H and ^{19}F n.m.r. spectroscopy. The ^1H n.m.r. spectrum of the purple solid in C_6D_6 (30 °C) contains C_5Me_5 resonances at 52.1 ($\nu_{\frac{1}{2}}$ 90 Hz), 35.5 ($\nu_{\frac{1}{2}}$ 87 Hz), and 25.9 ($\nu_{\frac{1}{2}}$ 16 Hz) in area ratio 2 : 2 : 1. These resonances are reproducible from sample to sample though we do not know the chemical species to which these resonances belong. Another resonance at δ 11.1 ($\nu_{\frac{1}{2}}$ 115 Hz) is always present in the ^1H n.m.r. spectrum though its intensity varies from sample to sample between *ca.* 2 and 3 times that of δ 25.9 resonance. The identity of this chemical species is $(C_5Me_5)_2Yb(C_6F_5)$, which was prepared by reaction of $(C_5Me_5)_2Yb$ and $Hg(C_6F_5)_2$ in pentane followed by crystallization as purple crystals,‡ m.p. 129—132 °C, from toluene (−70 °C), since the ^1H n.m.r. spectrum (C_6D_6, 30 °C) has a resonance at δ 12.0 ($\nu_{\frac{1}{2}}$ 335 Hz).

Reaction of $(C_5Me_5)_2Yb$ and $CFHCH_2$, CF_2CH_2, or C_2F_4 in hexane yields a purple solution and a brown precipitate (84% isolated yield in 4 h) which is $(C_5Me_5)_4Yb_2(\mu\text{-F})$ by m.p., i.r., and *X*-ray powder photographs. The binuclear compound is also isolated in reaction of $(C_5Me_5)_2Yb$ and $PhCF_3$ (67% yield in 14 h) or PhF (20% yield in 2 weeks). Neither C_2F_6 nor 1,1,1-CF_3CH_3 give an observable amount of $(C_5Me_5)_4Yb_2(\mu\text{-F})$ after 3 days. The rate of reaction between $(C_5Me_5)_2Yb$ and C_2F_4 is faster in hexane than in toluene and very slow in diethyl ether.

The reaction of fluorocarbons with $(C_5Me_5)_2Yb$ is obviously complex though it doubtless involves the activation and cleavage of C–F bonds, perhaps by processes related to those described for $(C_5Me_5)_2M(OEt_2)$, M = Yb, Eu, Sm, and R–X where X = Cl, Br, I.[3] In a qualitative sense, the C–F activation reaction does not depend only upon the averaged C–F bond dissociation energy since C_6F_6 (*D* 154 kcal mol^{-1}; cal = 4.184 J)[4] is activated whereas C_2F_6 (*D* 127 kcal mol^{-1})[4] is not. The functional group and solvent dependence suggest that a polarizable functional group on the fluorocarbon and a vacant co-ordination site on the metal is necessary for efficient activation forming perhaps a weak complex similar to the isolated molecule, $(C_5Me_5)_2Yb(\eta^2\text{-MeC}{\equiv}\text{CMe})$.[5] In addition, the electron affinity of the fluorocarbon and the strength of the metal to fluorine bond are important. The reaction described in this paper is one of the very few examples of intermolecular[6] and intramolecular[7] C–F activation processes.

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‡ Satisfactory elemental analyses for C and H and a molecular ion in the mass spectrum were obtained. The ^{19}F n.m.r. spectrum consists of resonances at δ 47.0 ($\nu_{\frac{1}{2}}$ 1400 Hz, 2F), 1.79 ($\nu_{\frac{1}{2}}$ 29 Hz, 1F), and −7.30 ($\nu_{\frac{1}{2}}$, 2F), relative to $CFCl_3$ at δ 0.