

Lawrence Berkeley National Laboratory

Recent Work

Title

REACTION OF (ME₅C₅)₂YB WITH FLUOROCARBONS: FORMATION OF (ME₅C₅)₄YB₂ (MU-F) BY INTRAMOLECOLAR C-F ACTIVATION

Permalink

<https://escholarship.org/uc/item/69t1q42w>

Authors

Burns, C.J.

Andersen, R.A.

Publication Date

1988-09-01

c.2



Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

Materials & Chemical Sciences Division

LAWRENCE
BERKELEY LABORATORY

DEC 6 1988

Submitted to Chemical Communications

LIBRARY AND
DOCUMENTS SECTION

Reaction of $(\text{Me}_5\text{C}_5)_2\text{Yb}$ with Fluorocarbons: Formation of $(\text{Me}_5\text{C}_5)_4\text{Yb}_2(\mu\text{-F})$ by Intramolecular C-F Activation

C.J. Burns and R.A. Andersen

September 1988

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy
which may be borrowed for two weeks.*



LBL-26006
c.2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

Reaction of $(\text{Me}_5\text{C}_5)_2\text{Yb}$ with Fluorocarbons:
Formation of $(\text{Me}_5\text{C}_5)_4\text{Yb}_2(\mu\text{-F})$
by Intramolecular C-F Activation

Carol J. Burns and Richard A. Andersen*

Chemistry Department and Material and Chemical Sciences Division
of Lawrence Berkeley Laboratory, University of California
Berkeley, California 94720, USA

Addition of C_6F_6 and other fluoroaromatics and fluoroolefins, though not C_2F_6 or $1,1,1\text{-CF}_3\text{CH}_3$, to $(\text{Me}_5\text{C}_5)_2\text{Yb}$ gives the mixed-valence complex $(\text{Me}_5\text{C}_5)_4\text{Yb}_2(\mu\text{-F})$ with a linear, asymmetric Yb(II)-F-Yb(III) bond.

* Address correspondence to Richard A. Andersen at Chemistry Department,
University of California, Berkeley California 94720, USA

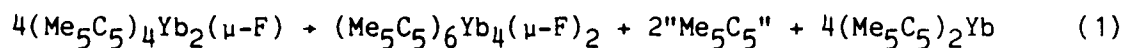
The unusual tetranuclear compound, $(\text{Me}_5\text{C}_5)_6\text{Yb}_4(\mu\text{-F})_4$, is a class I (trapped-valence) mixed-valence Yb(II,III) complex.¹ The compound was prepared by reaction of silver fluoride with $(\text{Me}_5\text{C}_5)_2\text{Yb}$ in toluene; the synthesis initially gave a brown, toluene insoluble precipitate which gave red crystals of $(\text{Me}_5\text{C}_5)_6\text{Yb}_4(\mu\text{-F})_4$ on crystallization from hot toluene. We now show that the brown substance is the dinuclear, mixed-valence compound, $(\text{Me}_5\text{C}_5)_4\text{Yb}_2(\mu\text{-F})$ and that these metal fluorides can be prepared from reaction of $(\text{Me}_5\text{C}_5)_2\text{Yb}$ and fluorocarbons, i.e., an unusual example of intermolecular C-F activation.

A solution of $(\text{Me}_5\text{C}_5)_2\text{Yb}$ (0.57 g) reacts instantaneously with one molar equivalent 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 (dec), by slow cooling of a warm toluene solution to 20°C which were contaminated with red $(\text{Me}_5\text{C}_5)_6\text{Yb}_4(\mu\text{-F})_4$ and orange $(\text{Me}_5\text{C}_5)_2\text{Yb}$. The brown crystals were shown to be $(\text{Me}_5\text{C}_5)_4\text{Yb}_2(\mu\text{-F})$, by X-ray crystallography[‡] (Figure). The angle formed by intersection of the planes formed by Yb(1) and its ring centroids with that of

[‡] Crystal data: $\text{C}_{40}\text{H}_{60}\text{FYb}_2$, M = 906.00, Monoclinic, space group C2/c, a = 16.319(2), b = 14.314(1), c = 16.760(2) Å, $\beta = 104.39(1)^\circ$, V = 3792(2) Å³, D_c = 1.60 g cm⁻³, Mo-K_α radiation, $\lambda = 0.71073$ Å, $\mu(\text{Mo-K}_\alpha) = 49.2$ cm⁻¹. T = 25°C. The structure was solved by a combination of Patterson and Fourier methods and refined using 2256 unique reflections [$F_o^2 > 3_\sigma(F_o^2)$] measured on a CAD4 diffractometer (2θ 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 coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

Yb(2) with its ring centroids is 90°. Since the molecule lies on a crystallographic 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) are also consistent with this deduction.

The molecule can be viewed as being a donor-acceptor complex, the $(Me_5C_5)_2Yb(1)$ is the Lewis acid and the lone pair of electrons on the fluoride of $(Me_5C_5)_2YbF$ 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 Me_5C_5 ligands on Yb(1) and Yb(2) is only 3.6 to 3.7 Å and the closest contact distance of the methyl groups on the Me_5C_5 ligand on Yb(2), C(19)···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 Eq. (1), since



the tetranuclear compound has two ytterbium atoms with a single Me_5C_5 ring attached rather than two as in the binuclear compound.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 behavior 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, $\mu_{\text{eff}} = 4.11$ B.M., per Yb(III), and $\theta = 0$ K from 7-35 K, and $\mu_{\text{eff}} = 4.69$ B.M. 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 $\text{Me}_5\text{C}_5\text{H}$ and $\text{C}_6\text{F}_5\text{H}$ by ^1H and ^{19}F NMR spectroscopy. The ^1H NMR spectrum of the purple solid in C_6D_6 (30°C) contains Me_5C_5 resonances at 52.1 ($\nu_{1/2} = 90$ Hz), 35.5 ($\nu_{1/2} = 87$ Hz), and 25.9 ($\nu_{1/2} = 16$ 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 $\delta 11.1$ ($\nu_{1/2} = 115$ Hz) is always present in the ^1H NMR spectrum though its intensity varies from sample to sample between ca. 2 and 3 times that of $\delta 25.9$ resonance. The identity of this chemical species is $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{C}_6\text{F}_5)$, which was prepared by reaction of $(\text{Me}_5\text{C}_5)_2\text{Yb}$ and $\text{Hg}(\text{C}_6\text{F}_5)_2$ in pentane followed by crystallization as purple crystals, ** m.p. 129-132°, from toluene (-70°C), since the ^1H NMR spectrum (C_6D_6 , 30°C) has a resonance at $\delta 12.0$ ($\nu_{1/2} = 335$ Hz).

Reaction of $(\text{Me}_5\text{C}_5)_2\text{Yb}$ and CFHCH_2 , 1,1- 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 $(\text{Me}_5\text{C}_5)_4\text{Yb}_2(\mu\text{-F})$ by m.p., IR, and X-ray powder photographs. The binuclear

** Satisfactory elemental analysis for C and H and a molecular ion in the mass spectrum were obtained. The ^{19}F NMR spectrum consists of resonances at $\delta 47.0$ ($\nu_{1/2} = 1400$ Hz, 2F), 1.79 ($\nu_{1/2} = 29$ Hz, 1F), and -7.30 ($\nu_{1/2}$, 2F), relative to CFCl_3 at $\delta = 0$.

compound is also isolated in reaction of $(\text{Me}_5\text{C}_5)_2\text{Yb}$ and PhCF_3 (67% yield in 14 h) or PhF (20% yield in 2 weeks). Neither C_2F_6 nor $1,1,1\text{-CF}_3\text{CH}_3$ give an observable amount of $(\text{Me}_5\text{C}_5)_4\text{Yb}_2(\mu\text{-F})$ after 3 days. The rate of reaction between $(\text{Me}_5\text{C}_5)_2\text{Yb}$ and C_2F_4 is faster in hexane than in toluene and very slow in diethyl ether.

The reaction of fluorocarbons with $(\text{Me}_5\text{C}_5)_2\text{Yb}$ is obviously complex though it doubtless involves the activation and cleavage of C-F bonds, perhaps by processes related to those described for $(\text{Me}_5\text{C}_5)_2\text{M}(\text{OEt}_2)$, $\text{M} = \text{Yb}, \text{Eu}, \text{Sm}$, and R-X where $\text{X} = \text{Cl}, \text{Br}, \text{I}$.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 ($D = 154 \text{ kcal mol}^{-1}$)⁴ is activated whereas C_2F_6 ($D = 127 \text{ kcal mol}^{-1}$)⁴ is not. The functional group and solvent dependence suggests that a polarizable functional group on the fluorocarbon and a vacant coordination site on the metal is necessary for efficient activation forming perhaps a weak complex similar to the isolated molecule, $(\text{Me}_5\text{C}_5)_2\text{Yb}(\eta^2\text{-MeC}\equiv\text{CMe})$.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 intermolecular⁶ and intramolecular⁷ C-F activation processes.

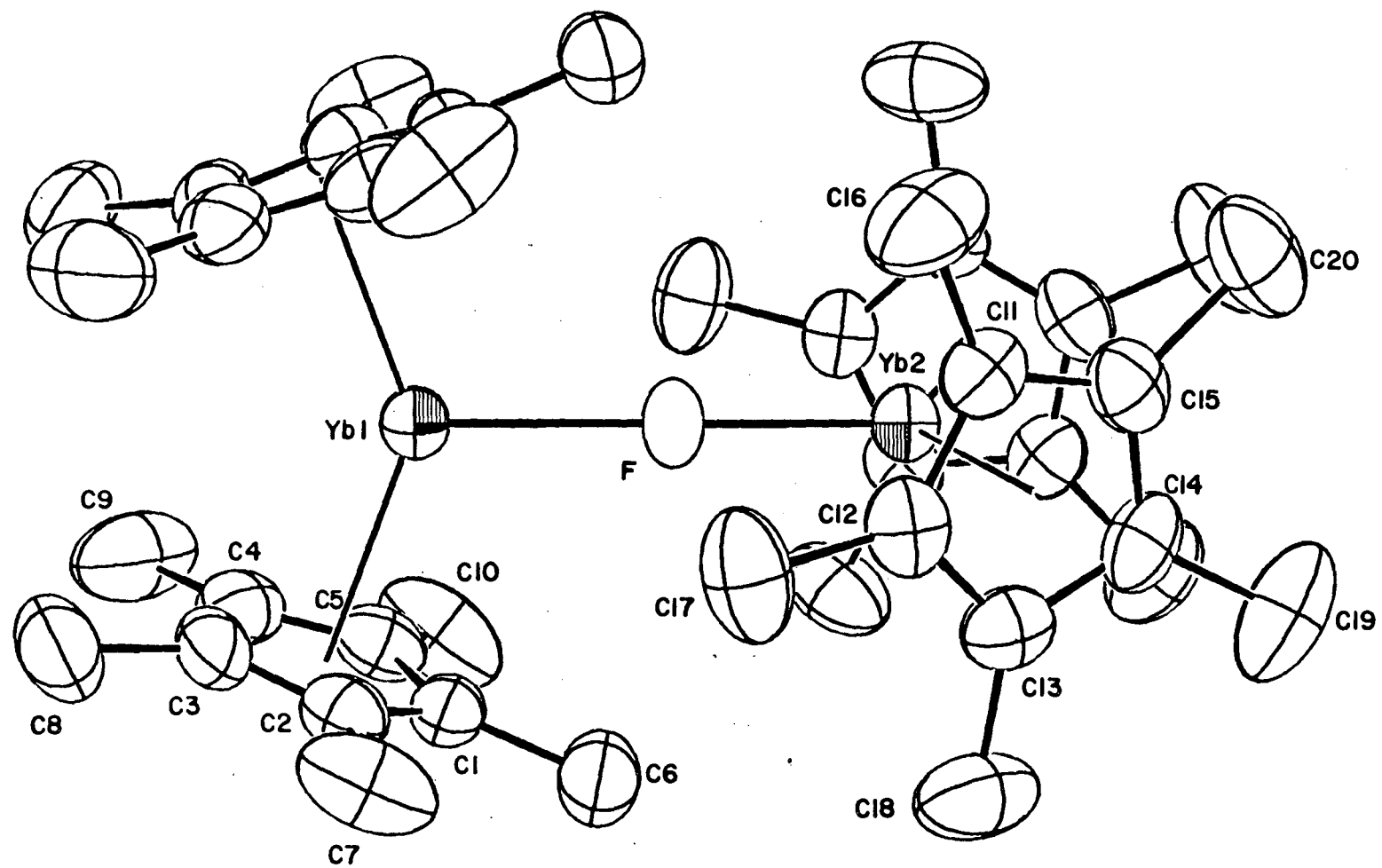
We thank the Fannie and John Hertz Foundation for a fellowship (C.J.B.), Dr. F.J. Hollander, staff crystallographer of the University of California X-ray facility, for his help with the crystallography and Dr. D.J. Berg for the magnetic moment. This work was supported by the director, Office of Energy Research, Office of Basic Energy Science, Chemical Division of the U.S. Department of Energy.

References

1. C.J. Burns, D.J. Berg, and R.A. Andersen, J. Chem. Soc. Chem. Comm. 1987, 272.
2. R.D. Shannon, Acta Cryst. 1976, 32A, 751.
3. R.G. Finke, S.R. Keenan, D.C. Schiraldi, and P.L. Watson, Organometallics 1986, 5, 598 and 1987, 6, 1356.
4. B.E. Smart in "The Chemistry of Functional Groups," Supplement D, edited by S. Patai and Z. Rapoport, 1983. John Wiley, New York, Chapter 14.
5. C.J. Burns and R.A. Andersen, J. Am. Chem. Soc. 1987, 109, 941.
6. E.C. Ashby, S.H. Yu, and R.G. Beach, J. Am. Chem. Soc. 1970, 92, 433.
D.R. Fahey, J.E. Mahan Ibid. 1977, 99, 2501.
7. M.I. Bruce, B.L. Goodall, G.L. Sheppard, and F.G.A. Stone, J. Chem. Soc. Dalton Trans. 1975, 591. T.G. Richmond, C.E. Osterberg, and A.M. Arif, J. Am. Chem. Soc. 1987, 109, 8091.

Figure Caption

An ORTEP diagram of $(\text{Me}_5\text{C}_5)_4\text{Yb}_2(\mu\text{-F})$. The averaged Yb(1)-C distance is 2.69(2) Å, the averaged 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°.



XBL 868-2899

*LAWRENCE BERKELEY LABORATORY
TECHNICAL INFORMATION DEPARTMENT
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720*