Reactions of (MeC$_5$H$_4$)$_3$U(*t*-Bu): Intermolecular Fluorine Atom Abstraction from Fluorocarbons Including Saturated Perfluorocarbons

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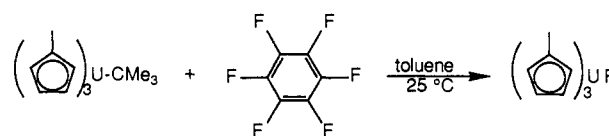*Lawrence Berkeley Laboratory*
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Only a few examples of intermolecular C–F bond activation have been reported.[1] The pronounced inertness of perfluorocarbons is undoubtedly caused by the high C–F bond dissociation energies[2] and by the weakness of metal–fluorocarbon interactions.[3] Thus both thermodynamic and kinetic factors generally disfavor C–F bond activation. Here we report the reactions of (MeC$_5$H$_4$)$_3$-U(*t*-Bu)[4] with fluorocarbons, resulting in efficient fluorine abstraction under mild conditions in the presence of hydrocarbon solvents. To our knowledge, this is the first example of intermolecular C–F activation of a saturated fluorocarbon by a neutral d- or f-transition-metal complex and, in contrast to the results in ref 1i, are not limited to tertiary C–F bonds.
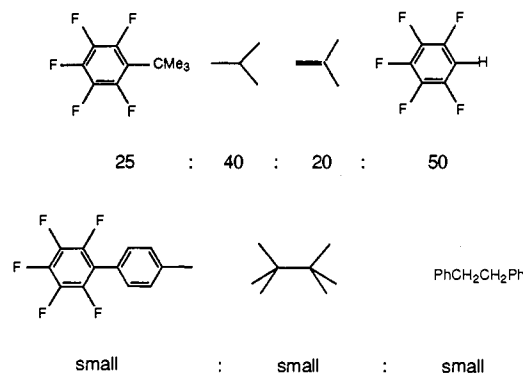
Stirring (MeC$_5$H$_4$)$_3$U(*t*-Bu) with 2 equiv of hexafluorobenzene[5] in toluene solution at room temperature for 24 h gives the uranium-(IV) fluoride (MeC$_5$H$_4$)$_3$UF[6] in quantitative yield (^{1}H NMR spectroscopy). The organic products of this reaction, identified and quantified by ^{1}H and ^{19}F NMR spectroscopy, GC, and GC-MS, were C$_6$F$_5$H,[7] C$_6$F$_5$(*t*-Bu), isobutane, and isobutene in 50, 25, 40, and 20% yields, respectively, based upon uranium. Small amounts of hexamethylethane, bibenzyl, and 2,3,4,5,6-pentafluoro-4'-methyl-biphenyl[8] also were detected (Scheme I). The C$_6$F$_5$-(*t*-Bu) was synthesized independently from *t*-BuLi and C$_6$F$_6$,[9] and the identity of the other products was confirmed by comparison with commercial samples.

Using a known concentration of (MeC$_5$H$_4$)$_3$U(*t*-Bu), the organic product distribution is determined to be temperature dependent. The amount of C$_6$F$_5$(*t*-Bu) formed relative to C$_6$F$_5$H decreases with increasing reaction temperature, and the isobutane:

(1) (a) Ashby, E. C.; Yu, S. H.; Beach, R. G. *J. Am. Chem. Soc.* **1970**, *92*, 433–435. (b) Fahey, D. R.; Mahan, J. E. *J. Am. Chem. Soc.* **1977**, *99*, 2501–2508. (c) Jones, W. T.; McDonald, R. N. *Organometallics* **1988**, *7*, 1221–1223. (d) Burns, C. J.; Andersen, R. A. *J. Chem. Soc., Chem. Commun.* **1989**, 136–137. (e) Watson, P. L.; Tulip, T. H.; Williams, I. *Organometallics* **1990**, *9*, 1999–2009. (f) Blum, O.; Frolow, F.; Milstein, D. *J. Chem. Soc., Chem. Commun.* **1991**, 258–259. (g) Jones, W. D.; Partridge, M. G.; Perutz, R. N. *J. Chem. Soc., Chem. Commun.* **1991**, 264–266. (h) Hofmann, P.; Unfried, G. *Chem. Ber.* **1992**, *125*, 659–661. (i) Harrison, R. G.; Richmond, T. G. *J. Am. Chem. Soc.* **1993**, *115*, 5303–5304, and references therein to related reactions of fluorocarbons with nucleophiles.

(2) Smart, B. E. In *The Chemistry of Functional Groups*, Suppl. D; Patai, S., Rapoport, Z., Eds.; John Wiley: New York, 1983, Chapter 14.

(3) Nayak, S. K.; Burkey, T. J. *Organometallics* **1991**, *10*, 3745–3750.

(4) Obtained from (MeC$_5$H$_4$)$_3$UCl and *t*-BuLi, mp 224–228 °C dec ^{1}H NMR (C$_6$D$_6$, 30 °C): δ = 9.96 (s, 6H), –6.25 (s, 6H), –8.98 (s, 9H), –18.96 (s, 9H). IR (Nujol, CsI): 1260 (w), 1086 (w), 1040 (m), 845 (m), 814 (m), 773 (s), 720 (m), 400 (w), 330 (w) cm^{-1}. Anal. Calcd for C$_{22}$H$_{30}$U: C, 49.6; H, 5.68. Found: C, 49.9; H, 5.29.

(5) Heated at reflux over sodium and distilled from sodium prior to use.

(6) Brennan, J. G.; Stults, S. D.; Andersen, R. A.; Zalkin, A. *Organometallics* **1988**, *7*, 1329–1334.

(7) The C$_6$F$_6$ starting material was determined by GC to be free of C$_6$F$_5$H, implying that the C$_6$F$_5$H that was found in the reaction results from the solvent, C$_7$H$_8$.
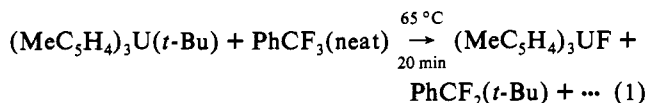
(8) (a) Brune, H. A.; Hess, R.; Schmidtberg, G. *Z. Naturforsch.* **1984**, *39B*, 1772–1780. (b) Bolton, R.; Sandall, J. P. B. *J. Fluorine Chem.* **1978**, *12*, 463–470. (c) Birchall, J. M.; Hazard, R. N.; Haszeldine, W. W. *J. Chem. Soc. C* **1967**, 47–50.

(9) ^{1}H NMR (C$_6$D$_6$, 30 °C): δ = 1.22 (t, $^5J_{H-F}$ = 2.3 Hz). ^{19}F NMR (C$_6$D$_6$, 30 °C): δ = –139.04 (m, 2F), –159.32 (m, 1F), –163.75 (m, 2F). HRMS: M$^+$ = 224.0627 amu; calcd for C$_{10}$H$_9$F$_5$, 224.0624 amu.

Scheme I

Organic Products: Percent yields at 25 °C, based upon uranium

25 : 40 : 20 : 50

small : small : small

Scheme II Proposed Mechanism for the Reaction of (MeC$_5$H$_4$)$_3$U(*t*-Bu) with Hexafluorobenzene
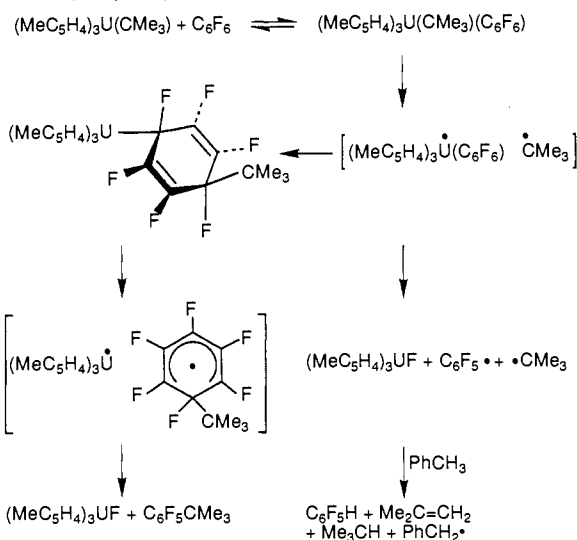
isobutene ratio also approaches 1:1. At a given temperature and concentration of (MeC$_5$H$_4$)$_3$U(*t*-Bu), the rate of reaction qualitatively increases with increasing concentration of C$_6$F$_6$. The complexity of the organic product distribution, its temperature dependence, and the observation of small amounts of radical recombination products are consistent with a radical cage mechanism, as proposed in Scheme II. Initial attack for C$_6$F$_6$ on (MeC$_5$H$_4$)$_3$U(*t*-Bu) leads to a caged radical pair and accounts for the observed rate dependence on C$_6$F$_6$ concentration. A *tert*-butyl radical can then escape from the cage, leading to C$_6$F$_5$H and products arising from free *tert*-butyl radical,[10] or the *tert*-butyl radical can recombine in the cage with the pentafluorophenyl radical to give C$_6$F$_5$(*t*-Bu). Such a "branching point" would account for the observed temperature dependence of the product distribution.

With regard to the principal driving force for the reaction of (MeC$_5$H$_4$)$_3$U(*t*-Bu) with C$_6$F$_6$, a U–C bond and a C–F bond have to be broken. This is offset by the formation of a U–F bond and either a C–C bond (C$_6$F$_5$(*t*-Bu)), a C–H bond (isobutane

(10) Pryor, W. A.; Tang, F. Y.; Tang, R. H.; Church, D. F. *J. Am. Chem. Soc.* **1982**, *104*, 2885–2891.

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Communications to the Editor

and C_6F_5H), or a C–C double bond (isobutene). The U–F bond energy can be estimated at *ca.* 150 kcal/mol based on known thermochemical data for uranium fluorides.[11] Its strength offsets the C–F bond dissociation energy of C_6F_6, which is reported to be 154 kcal/mol.[2] The U–C bond strength can be estimated at *ca.* 80 kcal/mol based on thermochemical measurements on primary actinide alkyl compounds.[12] Because a tertiary alkyl-uranium bond is likely to be significantly weaker than 80 kcal/mol, its dissociation energy is compensated by the formation of C–H bonds in the successive reactions of the organic radical intermediates formed in the reaction.

To expand the range of substrates to compounds with saturated C–F bonds, we first investigated $PhCF_3$. This substrate possesses an aromatic phenyl ring which can potentially coordinate to the metal center and perhaps facilitate C–F bond activation. As expected, $(MeC_5H_4)_3U(t\text{-}Bu)$ reacts with benzotrifluoride[5] to form $(MeC_5H_4)_3UF$ in essentially quantitative yield (eq 1). In

$$(MeC_5H_4)_3U(t\text{-}Bu) + PhCF_3(\text{neat}) \xrightarrow[20\,\text{min}]{65\,°C} (MeC_5H_4)_3UF +$$
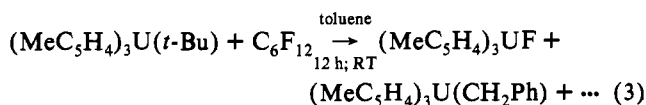$$PhCF_2(t\text{-}Bu) + \cdots \quad (1)$$

neat $PhCF_3$, $PhCF_2(t\text{-}Bu)$ was identified among the volatile reaction products by GC-MS. Since isobutane and isobutene are also present, it seems likely that the radical recombination product, $PhCF_2CF_2Ph$, should be present as well; however, it was not detected. Aromatic solvent such as *p*-xylene-d_{10} can also be used; in this case, $PhCF_2(t\text{-}Bu)$ was not detected.

Extension of the C–F activation process to saturated perfluorocarbons was examined next. The choice of a suitable substrate is more difficult because of the physical and chemical properties of perfluorocarbons.[13] They are poor solvents and are poorly soluble in hydrocarbon solvents. We therefore attempted a heterogeneous reaction between perfluoromethylcyclohexane[5] and $(MeC_5H_4)_3U(t\text{-}Bu)$ (eq 2). Over 4 h at 65 °C, formation of

$$(MeC_5H_4)_3U(t\text{-}Bu) + C_7F_{14}(\text{neat}) \xrightarrow[4\,\text{h}]{65\,°C} (MeC_5H_4)_3UF + \cdots$$
$$(2)$$
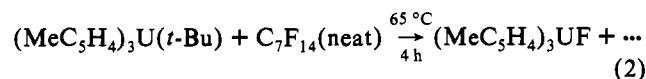
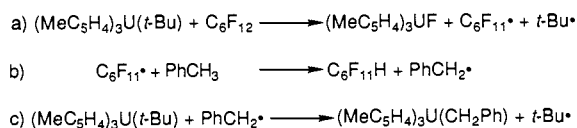$(MeC_5H_4)_3UF$ was observed, although the conversion was not quantitative (*ca.* 70%).

Since the incomplete conversion in the above region might have been a consequence of working with a heterogeneous system, a homogeneous system was needed. Perfluorocyclohexane,[14] in contrast to most other saturated perfluorocarbons, is reasonably soluble in aromatic solvents.[15] When the reaction between $(MeC_5H_4)_3U(t\text{-}Bu)$ and C_6F_{12} was carried out in toluene solution at room temperature for 12 h with a 5-fold excess of C_6F_{12}, a 1:1 mixture of $(MeC_5H_4)_3UF$ and $(MeC_5H_4)_3U(CH_2Ph)$[16] was obtained (eq 3).

$$(MeC_5H_4)_3U(t\text{-}Bu) + C_6F_{12} \xrightarrow[12\,\text{h};\,RT]{\text{toluene}} (MeC_5H_4)_3UF +$$
$$(MeC_5H_4)_3U(CH_2Ph) + \cdots \quad (3)$$

Among the organic products, $C_6F_{11}H$, isobutane, and isobutene were detected by GC and GC-MS. Because the thermal decomposition of $(MeC_5H_4)_3U(t\text{-}Bu)$ in toluene in the absence of C_6F_{12} does not lead to formation of $(MeC_5H_4)_3U(CH_2Ph)$,[17]

Scheme III

a) $(MeC_5H_4)_3U(t\text{-}Bu) + C_6F_{12} \longrightarrow (MeC_5H_4)_3UF + C_6F_{11}\text{•} + t\text{-}Bu\text{•}$

b) $\quad C_6F_{11}\text{•} + PhCH_3 \longrightarrow C_6F_{11}H + PhCH_2\text{•}$

c) $(MeC_5H_4)_3U(t\text{-}Bu) + PhCH_2\text{•} \longrightarrow (MeC_5H_4)_3U(CH_2Ph) + t\text{-}Bu\text{•}$

the fluorocarbon must be involved in the formation of the uranium benzyl species. We rationalize these observations by the radical reaction sequence outlined in Scheme III. The reaction of a $C_6F_{11}\text{•}$ radical with toluene to yield $C_6F_{11}H$ and benzyl radical has been documented.[18] The benzyl radical then attacks another molecule of $(MeC_5H_4)_3U(t\text{-}Bu)$ to yield $(MeC_5H_4)_3U(CH_2Ph)$ and a *tert*-butyl radical. The yield of $C_6F_{11}H$ (*ca.* 45% based upon uranium) and the detection of $C_6F_{11}D$ in toluene-d_8 are consistent with this mechanism. To test this hypothesis, the reaction between $(MeC_5H_4)_3U(t\text{-}Bu)$ and C_6F_{12} (5-fold excess) was carried out in toluene in the presence of a 3-fold excess of 9,10-dihydroanthracene, a radical trap. After being stirred for 12 h at room temperature, a 20:1 mixture of $(MeC_5H_4)_3UF$ and $(MeC_5H_4)_3U(CH_2Ph)$ was obtained, and anthracene was detected by GC among the volatile organic products. Given this high trapping efficiency, it seems likely that the dihydroanthracene is trapping primarily the relatively stable benzyl radical rather than the reactive $C_6F_{11}\text{•}$ radical. The conversion in these reactions was essentially quantitative based on uranium. When the reaction between $(MeC_5H_4)_3U(t\text{-}Bu)$ and C_6F_{12} was carried out in *o*-xylene-d_{10} as a solvent, conversion to $(MeC_5H_4)_3UF$ was essentially quantitative. Apparently, the *o*-xylyl radical, presumably formed when the reaction is carried out in *o*-xylene, is too hindered to displace a *tert*-butyl group from the uranium center at an appreciable rate.

(11) Lau, K. H.; Hildenbrand, D. L. *J. Chem. Phys.* **1982**, *33*, 2646–2652.

(12) (a) Bruno, J. W.; Marks, T. J.; Morss, L. R. *J. Am. Chem. Soc.* **1983**, *105*, 6824–6832. (b) Sonnenberger, D. C.; Morss, L. R.; Marks, T. J. *Organometallics* **1985**, *4*, 352–355. (c) Bruno, J. W.; Stecher, H. A.; Morss, L. R.; Sonnenberger, D. C.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 7275–7280.

(13) Banks, R. E. *Fluorocarbons and their Derivatives*, 2nd ed.; MacDonald Technical & Scientific, London, 1970.

(14) Sublimed under nitrogen through a P_2O_5 plug prior to use and shown to be a single substance by GC.

(15) Hudlicky, M. *Chemistry of Organic Fluorine Componds*, 2nd ed., Ellis Horwood: Chichester, West Sussex, 1992; p 544.

(16) $(MeC_5H_4)_3U(CH_2Ph)$ was prepared independently from $(MeC_5H_4)_3$-UCl and KCH_2Ph: mp 95–97 °C. ^1H NMR (C_6D_6, 30 °C): $\delta = 1.40$ (t, 2H), 1.24 (s, 6H), 0.78 (s, 6H), −3.18 (t, 1H), −9.27 (s, 9H), −21.62 (d, 2H), −204.00 (s, 2H). IR (Nujol, KBr): 1590 (m), 1490 (m), 1380 (s), 1210 (m), 1040 (w), 920 (m), 910 (m), 875 (w), 860 (w), 815 (w), 800 (s), 780 (s), 745 (m), 700 (w). Anal. Calcd for $C_{24}H_{34}U$: C, 53.0; H, 4.99. Found: C, 52.7; H, 5.07.

(17) Weydert, M.; Andersen, R. A.; Bergman, R. G., manuscript in preparation.

(18) Barlow, G. B.; Tatlow, J. C. *J. Chem. Soc.* **1952**, 4695–4698.