

## Thallium(I) Selectively Abstracts Fluoride from a Tertiary Carbon–Fluorine Bond under Conditions Where Silver(I) Selectively Abstracts Iodide from Rhodium

Russell P. Hughes,\* Trang Le Husebo, and Susan M. Maddock

Department of Chemistry, 6128 Burke Laboratory  
Dartmouth College, Hanover, New Hampshire 03755

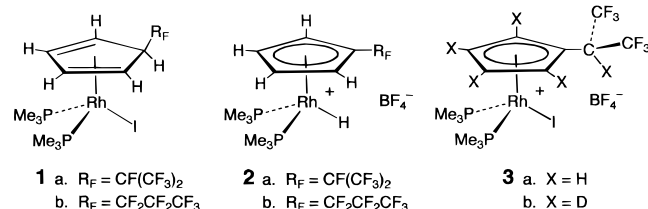
Arnold L. Rheingold and Ilia A. Guzei

Department of Chemistry, University of Delaware  
Newark, Delaware 19716

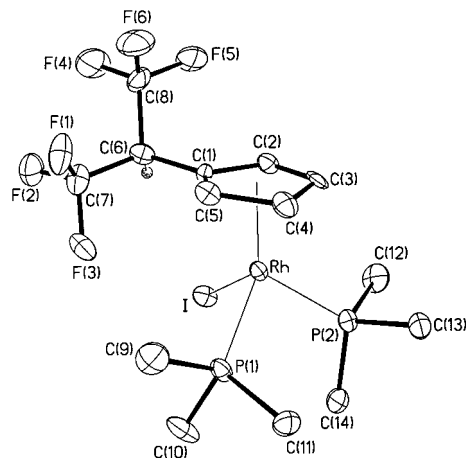
Received July 17, 1997

The metal-promoted activation of the normally inert carbon–fluorine bond in saturated fluorocarbons usually involves strongly reducing conditions with conversion of fluorine to a metal fluoride salt providing much of the driving force for reaction.<sup>1</sup> The Achilles heel of many saturated fluorocarbons, such as perfluorodecalin,<sup>1,2</sup> is the tertiary C–F bond, which upon reduction and initial loss of fluoride affords a stabilized tertiary fluorinated carbanion, which then reacts by further elimination of fluoride. Fluorocarbons lacking tertiary C–F bonds are much more difficult to activate.<sup>3</sup>  $\beta$ -Fluoride elimination reactions of fluoroalkyl organometallics of lithium<sup>4</sup> and magnesium<sup>5</sup> to give fluoroolefins and high lattice energy metal fluorides are (often dangerously) facile; potentially concerted pathways for such fluoride eliminations avoid relatively high-energy fluorocarocation intermediates. In inorganic and organometallic metathesis reactions, silver(I) and thallium(I) salts are often used interchangeably as halide abstraction reagents. Here we report an unusual reaction system in which thallium(I) reacts very differently from silver(I), abstracting fluoride from a tertiary C–F bond; the putative high-energy carbocation intermediate appears to be stabilized by a 1,2-hydride migration from an adjacent carbon atom.

We have previously reported the syntheses of *exo*-fluoroalkylated cyclopentadiene complexes **1** and their reactions with AgBF<sub>4</sub> which proceed, as expected, by abstraction of I<sup>−</sup> from rhodium with migration of the *endo*-H to the metal to afford the hydrido cations **2**.<sup>6</sup> In contrast, when 1 equiv of TIBF<sub>4</sub> or



TIPF<sub>6</sub> is added to a dichloromethane solution of the perfluor-



**Figure 1.** Molecular structure of the cation of **3a**. Selected bond distances (Å) and angles (deg): Rh–I, 2.6576(9); Rh–P(1), 2.309(3); Rh–P(2), 2.278(3); Rh–C(1), 2.267(11); Rh–C(2), 2.256(10); Rh–C(3), 2.230(9); Rh–C(4), 2.189(11); Rh–C(5), 2.310(13); Rh–CENT, 1.889(11); C(1)–C(6), 1.553(14); P(1)–Rh–P(2), 92.65(11); P(1)–Rh–I, 95.15(7); P(2)–Rh–I, 88.38(8).

oisopropyl complex **1a**, a new complex (**3a**) is isolated in 90% yield, along with a precipitate.<sup>7</sup> A single-crystal X-ray structural determination of **3a** clearly establishes its structure as shown;<sup>8</sup> an ORTEP diagram is shown in Figure 1 along with selected bond lengths and angles. The tertiary C–F bond in the starting complex has been replaced by H, and the original  $\eta^4$ -cyclopentadiene has been converted to a  $\eta^5$ -cyclopentadienyl ligand. Although the material is analytically pure, the counterion in the crystal on which the structural analysis was performed was 95% BF<sub>4</sub><sup>−</sup>, with the remaining 5% being iodide occupying the same position in the structure as the B of BF<sub>4</sub><sup>−</sup>. Even though the isolated yield of **3a** is 90%, some decomposition during the synthesis provides small amounts of I<sup>−</sup>. Investigation of the precipitate formed in the reaction, using X-ray microanalysis,<sup>9</sup> indicates that it contains mostly Tl and F, with small amounts of I. Solution NMR spectroscopic data are fully consistent with the structure of **3a**.<sup>7</sup>

The source of H in the CH(CF<sub>3</sub>)<sub>2</sub> group of **3a** has been identified as the *endo*-H from the original cyclopentadiene ligand as follows. [Rh(C<sub>5</sub>D<sub>5</sub>)(PMe<sub>3</sub>)<sub>2</sub>] was prepared from Tl(C<sub>5</sub>D<sub>5</sub>)<sup>10</sup> according to the method of Werner,<sup>11</sup> its reaction<sup>6</sup> with ICF(CF<sub>3</sub>)<sub>2</sub> affords **1a-d<sub>5</sub>**. Reaction of **1a-d<sub>5</sub>** with TIBF<sub>4</sub> affords as the kinetic product only **3b** containing a CD(CF<sub>3</sub>)<sub>2</sub> group. The D in the (CF<sub>3</sub>)<sub>2</sub>C–D group is quite acidic, and the deuterium exchanges with protons of adventitious H<sub>2</sub>O over a period of hours; likewise the (CF<sub>3</sub>)<sub>2</sub>C–H group in **3a** undergoes complete conversion to (CF<sub>3</sub>)<sub>2</sub>C–D when stirred with D<sub>2</sub>O over several hours. Strong Lewis acids have been shown to be capable of C–F activation in fluorocarbons<sup>12</sup> and transition-metal-coordi-

(1) For leading recent references, see: Kiplinger, J. L.; Richmond, T. G.; Osterberg, C. E. *Chem. Rev.* **1994**, *94*, 373. Burdeniuc, J.; Chupka, W.; Crabtree, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 2525. Burdeniuc, J.; Jedlicka, B.; Crabtree, R. H. *Chem. Ber./Recueil* **1997**, *130*, 145. Saunders, G. C. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2615.

(2) MacNicol, D. D.; Robertson, C. D. *Nature* **1988**, *332*, 59.

(3) A recent report of reductive activation of secondary C–F bonds has appeared: Kiplinger, J. L.; Richmond, T. G. *J. Am. Chem. Soc.* **1996**, *118*, 1805.

(4) Wardell, J. L. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Abel, E., Stone, F. G. A., Eds.; Pergamon: Oxford, 1983; Vol. 1, Chapter 2.

(5) Lindsell, W. E. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Abel, E., Stone, F. G. A., Eds.; Pergamon: Oxford, 1983; Vol. 1, Chapter 4.

(6) Hughes, R. P.; Husebo, T. L.; Rheingold, A. L.; Liable-Sands, L. M.; Yap, G. P. A. *Organometallics* **1997**, *16*, 5.

(7) For **3a**: 90%; <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>)  $\delta$  6.26 (t, *J*<sub>HH</sub> = 1.9 Hz, 2H, C<sub>5</sub>H<sub>4</sub>), 6.12 (br s, 2H, C<sub>5</sub>H<sub>4</sub>), 5.14 (septet of triplets, *J*<sub>HF</sub> = 7.8 Hz, *J*<sub>HP</sub> = 1.5 Hz, 1H, CH), 2.10 (m, 18H, PMe<sub>3</sub>); <sup>19</sup>F NMR (acetone-*d*<sub>6</sub>)  $\delta$  −62.8 (d, *J*<sub>FH</sub> = 7.9 Hz, 6F, BF<sub>4</sub>), −150.2 (s, 4F, BF<sub>4</sub>); <sup>31</sup>P NMR (acetone-*d*<sub>6</sub>)  $\delta$  8.1 (d, *J*<sub>RhP</sub> = 126.7 Hz). Anal. Calcd for C<sub>14</sub>H<sub>23</sub>F<sub>10</sub>IP<sub>2</sub>Rh: C, 24.59; H, 3.39. Found: C, 24.75; H, 3.41.

(8) Crystallographic data for **3a**: monoclinic, *P*2<sub>1</sub>/*n*, *Z* = 4, *a* = 11.5048(5) Å, *b* = 12.1670(5) Å, *c* = 16.9892(7) Å,  $\beta$  = 104.603(2)°, *V* = 2301.3(2) Å<sup>3</sup>, *D*<sub>calcd</sub> = 1.974 g/cm<sup>3</sup>; Mo K $\alpha$  radiation ( $\lambda$  = 0.710 73 Å); 4582 independent reflections with 1.93° <  $\theta$  < 28.28° collected; *R* = 0.0594, *R*<sub>w</sub> = 0.1665, GOF = 0.998.

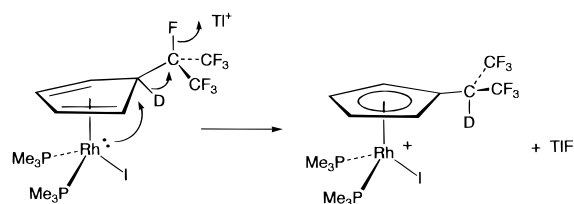
(9) Obtained using an EDS system on an SCM Electron Microscope.

(10) Anderson, G. K.; Cross, R. J.; Phillips, I. G. *J. Chem. Soc., Chem. Commun.* **1978**, 709.

(11) Werner, H.; Feser, R.; Harder, V.; Hofmann, W. *Inorg. Synth.* **1990**, *28*, 280.

(12) Kopaevich, Yu. L.; Belen'kii, G. G.; Mysov, E. I.; German, L. S.; Knunyants, I. L. *Zh. Vses. Khim. Ova* **1972**, *17*, 236. Olah, G. A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 767.

## Scheme 1



nated trifluoromethyl groups.<sup>10</sup> However, while conversion of **1a** to **3a** occurs cleanly on treatment with  $\text{BF}_3$ , clearly indicating that fluoride abstraction is indeed a key step, it is also clear that traces of  $\text{BF}_3$  are not the important Lewis acid component in the  $\text{TlBF}_4$  reaction. Thallium(I) tetrakis{3,5-bis(trifluoromethyl)phenyl}borate,<sup>14</sup> containing an anion incapable of generating a Lewis acid under these conditions, also reacts cleanly with **1a** to afford the corresponding salt of cation **3a**, indicating that thallium(I) is indeed the fluoride acceptor. That the tertiary C–F center is essential is demonstrated by the reaction of **1b** with thallium(I) salts; no activation of the secondary C–F bond occurs and only iodide abstraction with formation of **2b** is observed.

We propose the mechanism shown in Scheme 1. Simple abstraction of fluoride from the  $\text{FC}(\text{CF}_3)_2$  group in **1a** seems unlikely since the resultant carbocation bearing two  $\text{CF}_3$  groups would be strongly destabilized.<sup>15</sup> Consequently, it seems likely that, as fluoride leaves, the evolving carbocation site is stabilized by a concomitant 1,2-migration of the *endo*-H(D); that this

(13) Brothers, P. J.; Roper, W. R. *Chem. Rev.* **1988**, *88*, 1293. Richmond, T. G.; Crespi, A. M.; Shriver, D. F. *Organometallics* **1984**, *3*, 314. Reger, D. L.; Dukes, M. D. *J. Organomet. Chem.* **1978**, *153*, 67. Koola, J. D.; Roddick, D. M. *Organometallics* **1981**, *10*, 591.

(14) Hughes, R. P.; Lindner, D. C.; Rheingold, A. L.; Yap, G. A. P. *Inorg. Chem.* **1997**, *36*, 1726.

(15) Smart, B. E. In *The Chemistry of Functional Groups, Supplement D*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: New York, 1983; Chapter 14.

results in aromatization of the cyclopentadienyl ligand undoubtedly provides additional impetus.

While theoretical studies indicate that the tertiary C–F bonds in perfluorocarbons are weaker than both secondary and primary C–F bonds,<sup>16</sup> the X-ray crystal structure of **1a**<sup>6</sup> does not reveal a tertiary C–F bond significantly longer than those in the trifluoromethyl groups. Furthermore the reason for the remarkable difference between the reaction of silver(I) and thallium(I) salts with **1a** is not immediately clear. Lattice energy considerations are often invoked to explain the driving force for metal fluoride eliminations, but our results indicate that such arguments should perhaps be used with caution. Although the lattice energy of  $\text{TlF}$  (845 kJ/mol) is indeed higher than that of  $\text{TlI}$  (709 kJ/mol), the lattice energy of  $\text{AgF}$  (967 kJ/mol) is also higher than that of  $\text{AgI}$  (889 kJ/mol).<sup>17</sup> Nevertheless, in reactions with **1a**, silver(I) chooses  $\text{I}^-$  and thallium(I) chooses  $\text{F}^-$ , perhaps implying a more fundamental difference in reaction mechanism between  $\text{Ag(I)}$  and  $\text{Tl(I)}$  reactions than has previously been contemplated.

**Acknowledgment.** R.P.H. acknowledges support of this research by the National Science Foundation and the Petroleum Research Fund, administered by the American Chemical Society. The assistance of Charles P. Daghljan in obtaining X-ray microanalyses at the Rippel Electron Microscope Facility at Dartmouth College is also acknowledged.

**Supporting Information Available:** Details of the X-ray structure determination, tables of atomic coordinates and anisotropic thermal parameters, bond lengths and bond angles, anisotropic displacement parameters, and hydrogen atom coordinates for **3a** (7 pages). See any current masthead page for ordering information and Internet access instructions.

JA972398D

(16) Cooper, D. L.; Allan, N. L.; Powell, R. L. *J. Fluorine Chem.* **1990**, *49*, 421.

(17) *CRC Handbook of Chemistry and Physics*; Lide, D. R., Ed.; CRC Press, Inc.: Boca Raton, FL, 1996.