

New Entries to and New Reactions of Fluorocarbon Ligands

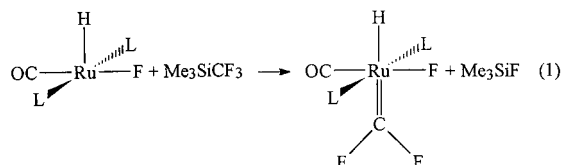
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While the subject of CF_2 as a ligand on the later transition metals is a mature one,¹ we report here new observations which expand current understanding and demonstrate new reactivity. In particular, we demonstrate rapid cleavage and reformation of C–F bonds and the first use of Me_3SiCF_3 to make a transition metal/carbon bond.²

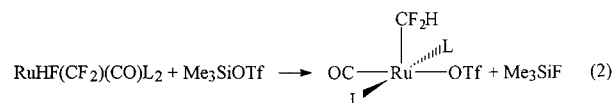
The reagent Me_3SiCF_3 ³ represents a new and very effective way to introduce a fluorocarbon ligand. Crucial to success is the synthesis of $\text{RuHF}(\text{CO})\text{L}_2$ ($\text{L} = \text{P}^t\text{Bu}_2\text{Me}$) from $\text{RuHCl}(\text{CO})\text{L}_2$ and anhydrous CsF in acetone (25 °C, 12 h).⁴ Fluoride abstraction (eq 1)⁵ occurs at 1:1 reactant stoichiometry rapidly and cleanly (25 °C, 0.5 h, THF) to give a quantitative yield of Me_3SiF (identified by ^1H and ^{19}F NMR) and a six-coordinate product where α -F migration has occurred from the proposed intermediate $\text{RuH}(\text{CF}_2)(\text{CO})\text{L}_2$.⁶ The hydride signal (C_6D_6 , at



25 °C) is a triplet of triplets of doublets at -3 ppm due to coupling to ^{31}P ($^2J_{\text{HP}} = 23$ Hz), to equivalent F in CF_2 ($^3J_{\text{HF}} = 51$ Hz), and to $\text{Ru}-\text{F}$ ($^2J_{\text{HF}} = 7.5$ Hz). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum is a doublet of triplets, and the ^{19}F NMR spectrum shows a broad line for the CF_2 group at 25 °C which decoalesces below -60 °C into an AMX pattern ($\text{X} = \text{H}$ on Ru; coupling to the $\text{Ru}-\text{F}$ is unresolved). The $\text{Ru}-\text{F}$ bond thus lies in the plane of the CF_2 group in the ground state structure, which avoids competition with CO for back bonding and also gets maximum π donation (lowest energy d_{π} orbital). Nevertheless, the ^{19}F NMR spectrum shows that the CF_2 group rotates at 25 °C. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum at 25 °C shows the carbonyl carbon as a doublet ($^2J_{\text{CRuF}} = 70$ Hz) of triplets and the CF_2 carbon as an apparent triplet ($^1J_{\text{CF}} = 498$ Hz). The CO stretching frequency is quite high (1937 cm^{-1} , to be compared to 1892 cm^{-1} in $\text{RuH}(\text{F})(\text{CO})\text{L}_2$) which can be interpreted either that CF_2 is a very strong π acid (e.g., stronger than CO) or that this is a $\text{Ru}(\text{IV})$ complex of dianionic CF_2^{2-} ; both are closely similar in underlying meaning (e.g., low electron density on Ru). In either case, it is clear that eq 1 transforms an (operationally) unsaturated species into an 18-electron molecule via C–F cleavage. One implication is that the unsaturation

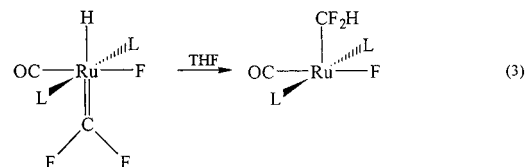
which would exist in $\text{RuH}(\text{CF}_2)(\text{CO})\text{L}_2$, which is devoid of π donor ligands, is unfavorable, and α -F migration occurs.⁷ This is the first dihalocarbene complex synthesis in which a full accounting of reaction stoichiometry is established.⁸ It is also the simplest example (one step) and occurs under the mildest conditions yet observed.

Consistent with earlier work,¹ this CF_2 ligand is readily transformed to CO (and 2 HF) by water. Fluoride abstraction, using Me_3SiOTf ($\text{OTf} = \text{O}_3\text{SCF}_3$) (5 min, toluene, 25 °C) leads to a remarkable rearrangement in which coordinated hydride migrates to the carbene ligand to form CF_2H (eq 2). This



product has a higher (1944 cm^{-1}) CO stretching frequency than its precursor, indicating that OTf (as well as CF_2H) is a very weak donor. Proton and ^{13}C NMR spectroscopy are most persuasive that a CF_2H group has been formed: the hydrogen shows a triplet ($^2J_{\text{HF}} = 60$ Hz) of triplets ($^3J_{\text{PH}} = 3$ Hz) at 7.7 ppm, and the CF_2H carbon also shows a triplet of triplets ($^2J_{\text{CF}} = 309$ Hz and $^2J_{\text{CP}} = 7$ Hz) in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum. This complex is not stable at room temperature in solid state or in solution. It decomposes in toluene within hours to form $[\text{HP}^t\text{-Bu}_2\text{Me}][\text{OTf}]$ and other unidentified species. This indicates that the hydrogen in CF_2H is acidic. However, attempts to deprotonate this complex using NEt_3 or $\text{LiN}(\text{SiMe}_3)_2 \cdot \text{OEt}_2$ failed to give the anticipated four-coordinate complex $\text{Ru}(\text{CF}_2)(\text{CO})\text{L}_2$.^{9,10}

$\text{RuHF}(\text{CF}_2)(\text{CO})\text{L}_2$ is long-lived in benzene (>48 h) at 25 °C. However, in THF at 25 °C, it rearranges within 5 h to $\text{RuF}(\text{CF}_2\text{H})(\text{CO})\text{L}_2$ (eq 3).¹¹ The migrated H shows a large (59 Hz) $^2J_{\text{HF}}$ value. The ν_{CO} value is now low (1917 cm^{-1}),



consistent with good π donation from fluoride *trans* to a carbonyl. The CHF_2 ligand is thus at the apical position in a square pyramid. The ^{19}F NMR spectrum shows a doublet of triplets of doublets ($^2J_{\text{HF}} = 59$ Hz; $^3J_{\text{PF}} = 17$ Hz; $^3J_{\text{FF}} = 6.3$ Hz) for CF_2H at -52 ppm and a broad triplet at -236 ppm ($^2J_{\text{PF}} = 20$ Hz) for F on Ru. Why is this $\text{RuH}(\text{CF}_2) \rightarrow \text{Ru}(\text{CHF}_2)$ rearrangement so solvent-dependent? Does its rapid occurrence in eq 2, with the weak triflate ligand, implicate dissociation of anionic ligand from Ru in eq 3? We propose that the reaction is not instantaneous because hydride is *trans* to CF_2 and thus blocked from rapid 1,2-H migration. It is likely that the rearrangement goes by a dissociative mechanism, and hydrogen migration is rapid in the five-coordinate intermediate.

(1) For major reviews, see: (a) Brothers, P. J.; Roper, W. R. *Chem. Rev.* **1988**, *88*, 1293. (b) Morrison, J. A. *Adv. Organomet. Chem.* **1993**, *35*, 211. (c) Doherty, N. M.; Hoffman, N. W. *Chem. Rev.* **1991**, *91*, 553.

(2) For recent reviews of C–F chemistry, see: Kiplinger, J. L.; Richmond, T. G.; Osterberg, C. E. *Chem. Rev.* **1994**, *94*, 373. *Chem. Rev.* **1996**, *96* (5).

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(5) For other examples of group (X) transfers to M–F from Me_3SiX , see: Doherty, N. M.; Chritchlow, S. C. *J. Am. Chem. Soc.* **1987**, *109*, 7906. Hoffman, N. W.; Prokopuk, N.; Robbins, M. J.; Jones, C. M.; Doherty, N. M. *Inorg. Chem.* **1991**, *30*, 4177.

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(7) Caulton, K. G. *New J. Chem.* **1994**, *18*, 25.

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(9) For the literature of the four-coordinate $\text{Ru}(\text{O})$ complexes, see: (a) Ogasawara, M.; Macgregor, S. A.; Streib, W. E.; Folting, K.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1995**, *117*, 8869. (b) Flügel, R.; Windmüller, B.; Gevert, O.; Werner, H. *Chem. Ber.* **1996**, *129*, 1007.

(10) CF_2 is considered as a stronger π -acceptor than CO. See: Brothers, P. J.; Burrell, A. K.; Clark, G. R.; Rickard, C. E. F.; Roper, W. R. *J. Organomet. Chem.* **1990**, *394*, 615.

(11) An intermediate $[\text{RhHCl}(\text{CF}_2)(\text{PPh}_3)_2]^+$ has been proposed, but not observed, by Roper *et al.* to account for the preparation of $\text{RhCl}_2(\text{CF}_2\text{H})(\text{PPh}_3)_2$ from $\text{RhHCl}_2(\text{PPh}_3)_3$ and $\text{Hg}(\text{CF}_3)_2$. See: Burrell, A. K.; Clark, G. R.; Jeffrey, J. G.; Rickard, C. E. F.; Roper, W. R. *J. Organomet. Chem.* **1990**, *388*, 391.

