New Entries to and New Reactions of Fluorocarbon Ligands

Dejian Huang and Kenneth G. Caulton*

Department of Chemistry, Indiana University Bloomington, Indiana 47405-4001

Received November 12, 1996

While the subject of CF₂ as a ligand on the later transition metals is a mature one, 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 Me₃SiCF₃ to make a transition metal/carbon bond.²

The reagent Me₃SiCF₃³ represents a new and very effective way to introduce a fluorocarbon ligand. Crucial to success is the synthesis of RuHF(CO)L₂ (L = $P^{t}Bu_{2}Me$) from RuHCl-(CO)L₂ 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 Me₃SiF (identified by ¹H and ¹⁹F NMR) and a six-coordinate product where α-F migration has occurred from the proposed intermediate RuH(CF₃)(CO)L₂.⁶ The hydride signal (C₆D₆, at

$$OC \xrightarrow{Ru} F + Me_3SiCF_3 \longrightarrow OC \xrightarrow{Ru} F + Me_3SiF \quad (1)$$

25 °C) is a triplet of triplets of doublets at −3 ppm due to coupling to ${}^{31}P$ (${}^{2}J_{HP} = 23$ Hz), to equivalent F in $\overline{CF_2}$ (${}^{3}J_{HF} =$ 51 Hz), and to Ru-F (${}^2J_{HF} = 7.5 \text{ Hz}$). The ${}^{31}P\{{}^{1}H\}$ NMR spectrum is a doublet of triplets, and the ¹⁹F NMR spectrum shows a broad line for the CF₂ group at 25 °C which decoalesces below -60 °C into an AMX pattern (X = H on Ru; coupling to the Ru-F is unresolved). The Ru-F bond thus lies in the plane of the CF2 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 ¹⁹F NMR spectrum shows that the CF₂ group rotates at 25 °C. The ¹³C{¹H} NMR spectrum at 25 °C shows the carbonyl carbon as a doublet (${}^{2}J_{CRuF} = 70 \text{ Hz}$) of triplets and the CF₂ carbon as an apparent triplet (${}^{1}J_{CF} = 498 \text{ Hz}$). The CO stretching frequency is quite high (1937 cm⁻¹, to be compared to 1892 cm⁻¹ in RuH(F)(CO)L₂) which can be interpreted either that CF_2 is a very strong π acid (e.g., stronger than CO) or that this is a Ru(IV) complex of dianonic CF₂²⁻; 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 RuH(CF₃)(CO)L₂, 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, this CF₂ ligand is readily transformed to CO (and 2 HF) by water. Fluoride abstraction, using Me₃SiOTf (OTf = O₃SCF₃) (5 min, toluene, 25 °C) leads to a remarkable rearrangement in which coordinated hydride migrates to the carbene ligand to form CF₂H (eq 2). This

$$RuHF(CF_2)(CO)L_2 + Me_3SiOTf \longrightarrow OC \underbrace{- CF_2H}_{L} OTf + Me_3SiF$$
 (2)

product has a higher (1944 cm⁻¹) CO stretching frequency than its precursor, indicating that OTf (as well as CF₂H) is a very weak donor. Proton and ¹³C NMR spectroscopy are most persuasive that a CF₂H group has been formed: the hydrogen shows a triplet (${}^{2}J_{HF} = 60 \text{ Hz}$) of triplets (${}^{3}J_{PH} = 3 \text{ Hz}$) at 7.7 ppm, and the CF₂H carbon also shows a triplet of triplets (${}^2J_{CF}$ = 309 Hz and ${}^{2}J_{CP}$ = 7 Hz) in the ${}^{13}C\{{}^{1}H\}$ NMR spectrum. This complex is not stable at room temperature in solid state or in solution. It decomposes in toluene within hours to form [HP^t-Bu₂Me][OTf] and other unidentified species. This indicates that the hydrogen in CF₂H is acidic. However, attempts to deprotonate this complex using NEt3 or LiN(SiMe3)2.OEt2 failed to give the anticipated four-coordinate complex Ru(CF₂)(CO)L₂.^{9,10}

RuHF(CF₂)(CO)L₂ is long-lived in benzene (>48 h) at 25 °C. However, in THF at 25 °C, it rearranges within 5 h to RuF(CF₂H)(CO)L₂ (eq 3).¹¹ The migrated H shows a large (59 Hz) ${}^2J_{\rm HF}$ value. The $\nu_{\rm CO}$ value is now low (1917 cm⁻¹),

consistent with good π donation from fluoride trans to a carbonyl. The CHF2 ligand is thus at the apical position in a square pyramid. The ¹⁹F NMR spectrum shows a doublet of triplets of doublets (${}^{2}J_{HF} = 59 \text{ Hz}$; ${}^{3}J_{PF} = 17 \text{ Hz}$; ${}^{3}J_{FF} = 6.3$ Hz) for CF₂H at −52 ppm and a broad triplet at −236 ppm $(^2J_{PF} = 20 \text{ Hz})$ for F on Ru. Why is this RuH(CF₂) \rightarrow Ru-(CHF₂) 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 CF₂ 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).

⁽³⁾ Krishnamurti, R.; Bellew, D. R.; Prakash, G. K. S. J. Org. Chem. **1991**, 56, 984.

⁽⁴⁾ Poulton, J. T.; Sigalas, M. P.; Folting, K.; Streib, W. E.; Eisenstein,

⁽⁵⁾ For other examples of group (X) transfers to M-F from Me₃SiX, 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.

⁽⁶⁾ THF is crucial to this reaction. If a nonpolar solvent such as benzene is used, the reaction proceeds much slower and cannot be completed before side reactions take place; thus, the product is not isolable.

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

⁽⁸⁾ Lewis acids will however both abstract and replace X in MCX3 groups: Reger, D. L.; Dukes, M. D. J. Organomet. Chem. 1978, 153, 67. Richmond, T. G.; Crespi, A. M.; Shriver, D. F. Organometallics 1984, 3, 314 and references therein.

⁽⁹⁾ For the literature of the four-coordinate Ru(0) 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⁾ CF₂ 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 [RhHCl(CF₂)(PPh₃)₂]⁺ has been proposed, but not observed, by Roper *et al.* to account for the preparation of RhCl₂(CF₂H)-(PPh₃)₂ from RhHCl₂(PPh₃)₃ and Hg(CF₃)₂. See: Burrell, A. K.; Clark, G. R.; Jeffrey, J. G.; Rickard, C. E. F.; Roper, W. R. J. Organomet. Chem. 1990, 388, 391.

The dissociating ligand could be CO or $P'Bu_2Me$ or F^- , and THF could then act by lightly stabilizing RuHF(CF₂)L₂, RuHF-(CF₂)(CO)L or RuH(CF₂)(CO)L₂⁺, respectively. To test for rate suppression in a CO dissociation mechanism, we have stirred RuHF(CF₂)(CO)L₂ in THF at 25 °C with 95% ¹³CO and find immediate *adduct* formation, but with combination of F and CF₂ into a CF₃ ligand (I). While this new reaction is *consistent*

with a fluoride dissociation mechanism, where "naked" F-attacks an electrophilic CF₂ carbon in a cationic intermediate RuH(CF₂)(CO)₂L₂⁺, the slow rearrangement reaction in benzene is not accelerated by added hydrogen bond donor indole (0.2 equiv), ¹² and thus, fluoride dissociation seems less likely. On the other hand, in the presence of equimolar-added P'Bu₂Me in THF, the rearrangement in eq 3 is completely halted (over 24 h), which supports P'Bu₂Me as the dissociating ligand. The implied intermediate is thus RuHF(CF₂)(CO)L.

The surprising observation that CO reacts with RuHF(CF₂)-(CO)L₂ within time of mixing in benzene led us to suspect there is an equilibrium between RuHF(CF₂)(CO)L₂ and RuH(CF₃)-(CO)L₂. Evidence crucial to this was established with a search for spin saturation transfer (SST) from the CF₂ group to the RuF group of RuHF(CF₂)(CO)L₂. Indeed, at 75 °C in toluene-d₈, ¹⁹F NMR experiments show that preirradiation (saturation) of the CF₂ group causes loss of intensity of the fluoride bound directly to Ru (Figure 1). At room temperature, no spin saturation transfer effect is observed. Since ¹³C NMR of the product **I** reveals production of only the isotopomer with ¹³CO *trans* to the hydride, this is consistent with the geometry of the

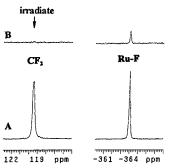


Figure 1. 19 F NMR of RuHF(CF₂)(CO)L₂ (toluene- d_8 , 75 °C, 378 MHz): A, irradiation off; B, irradiation on.

five-coordinate intermediate being a square-based pyramid with hydride at the apical site. The SST is thus explained by eq 4, where product stereochemistry (F *trans* to CO) is influenced by CO acting as a directing ligand: the π donor ligand F is favored *trans* to CO.

Taking advantage of the strong Si-F bond energy (142 kcal mol⁻¹), reaction of Me₃SiCF₃ with a transition metal fluoride complex can be a simple method to generate CF₂ or CF₃ complexes, which otherwise may be difficult to synthesize. The thermodynamic preferences and kinetic lability of Ru-F and C-F bonds is both remarkable and worth exploiting.

Acknowledgment. This work was supported by NSF. We are especially grateful to Dr. M. Pagel for enthusiastic help on the spin saturation transfer experiment.

Supporting Information Available: Synthetic and spectroscopic details of all new compounds cited (4 pages). See any current masthead page for ordering and Internet access instructions.

JA963903U

⁽¹²⁾ Wessel, J.; Lee, J. C., Jr.; Peris, E.; Yap, G. P. A.; Fortin, J. B.; Ricci, J. S.; Sini, G.; Albinati, A.; Koetzle, T. F.; Eisenstein, O.; Rheingold, A. L.; Crabtree, R. H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2507.