vergence of the isotropic refinement according to the method by Walker and Stuart.[27] Hydrogen atoms in the aromatic rings were placed in calculated positions (C–H = 1.08 Å) and allowed to ride with respect to their carrier atoms; those in the acetone molecule were omitted. The hydrogen atoms in the methyl groups and in the olefin were picked out from a difference Fourier map and refined with the constraint of fixed C–H distances within 0.01 Å from their average value; the final average value turned out to be 0.9 Å. All the hydrogen atoms were assigned the fixed isotropic temperature factor 0.1 Å^2. The final difference-Fourier map showed peaks of residual density lower than 0.3 e Å^{-3}. Unit cell parameters obtained from least-squares treatment of the orienting reflections along with data collection parameters and numerical details of the structure determination are listed in Table VIII.

Acknowledgment. We thank the Consiglio Nazionale delle Richerche and the Ministero della Pubblica Istruzione for financial support and the Centro Interdipartimentale di Metodologie Chimico-fisiche, Università di Napoli, for the use of the Varian XL-200 and Bruker AC-270 NMR spectrometers.

Registry No. 1, 115259-09-1; **1a**, 115287-90-6; **1b**, 115259-10-4; **1b** (diastereomer), 125639-35-2; **1c**, 125594-24-3; **1d**, 125594-25-4; **1e**, 125594-26-5; **1f**, 125594-27-6; **1g**, 115287-91-7; **1h**, 125594-28-7; **1i**, 125594-29-8; **1j**, 125594-30-1; **1j**·$(CH_3)_2CO$, 125760-56-7; **1k**$^+$, 125610-36-8; **2a**, 125594-31-2; **2h**, 125594-32-3; **3**, 125594-33-4; **3a**, 125594-34-5; **3i**, 125594-35-6; **3i** (diastereomer), 125760-56-7; **4**, 125594-36-7; **4a′**, 125594-37-8; **4a″**, 125639-37-4; **5**, 125594-38-9; $[PdClMe(Me_2S)]_2$, 101308-24-1; 6-Mepy-2-CH=NC_6H_4OMe, 26825-36-5.

Supplementary Material Available: Tables of fractional atomic coordinates for the hydrogen atoms, anisotropic thermal parameters, and analytical data (3 pages); a table of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

---

(27) Walker, N.; Stuart, D. *Acta Crystallogr. Sect. A: Found. Crystallogr.* **1983**, *A39*, 158.

Fluoroorganometallic Chemistry: Decarbonylation of Cyclic Perfluoroacyl Complexes

Karin J. Karel,* Thomas H. Tulip,[†] and Steven D. Ittel

Central Research and Development Department,[‡] E. I. du Pont de Nemours and Company, Wilmington, Delaware 19880-0262

Received March 10, 1989

The tetracarbonylferrate dianion reacts with perfluorodiacyl chlorides to yield perfluorometallacycloalkanediones. For instance, perfluorosuccinyl and perfluoroglutaryl chlorides yield $\overline{\mathrm{Fe(CO)_4(COCF_2CF_2CO}}\mathrm{)}$ and $\overline{\mathrm{Fe(CO)_4(COCF_2CF_2CF_2CO}}\mathrm{)}$, respectively. Extrusion of one CO from the six-membered ring of $\overline{\mathrm{Fe(CO)_4(COCF_2CF_2CF_2CO}}\mathrm{)}$ yields the perfluoro-1-metallacyclopentan-2-one $\overline{\mathrm{Fe(CO)_4(CF_2CF_2CF_2CO}}\mathrm{)}$, and extrusion of the second CO yields the perfluorometallacyclobutane $\overline{\mathrm{Fe(CO)_4(CF_2CF_2CF_2}}\mathrm{)}$. In the perfluorosuccinyl chloride derived system, the four-membered monoacyl is not observed, because the second extrusion of CO proceeds quickly to give a three-membered ring. There has been no evidence of the reverse reaction, insertion of CO into a metal–fluoroalkyl bond, including that of $\overline{\mathrm{Fe(CO)_4(CF_2CF_2CF_2CF_2}}\mathrm{)}$. Four of the fluorometallacycle complexes in this series have been characterized crystallographically. $\overline{\mathrm{Fe(CO)_4(COCF_2CF_2CO}}\mathrm{)}$ crystallizes in the space group *C*2/*c* with cell dimensions *a* = 10.957 (2) Å, *b* = 8.652 (1) Å, *c* = 12.335 (2) Å, and *β* = 118.68 (1)°. $\overline{\mathrm{Fe(CO)_4(COCF_2CF_2CF_2CO}}\mathrm{)}$ crystallizes in the space group *P*2$_1$/*c* with cell dimensions *a* = 11.433 (1) Å, *b* = 9.372 (1) Å, *c* = 12.817 (1) Å, and *β* = 116.11 (1)°. $\overline{\mathrm{Fe(CO)_4(CF_2CF_2CF_2CO}}\mathrm{)}$ crystallizes in the space group *P*2$_1$/*c* with cell dimensions *a* = 7.079 (1) Å, *b* = 13.084 (2) Å, *c* = 11.887 (1) Å, and *β* = 101.34 (1)°. $\overline{\mathrm{Fe(CO)_4(CF_2CF_2CF_2}}\mathrm{)}$ crystallizes in the space group *Pnma* with cell dimensions *a* = 15.161 (2) Å, *b* = 9.222 (1) Å, and *c* = 7.229 (1) Å.

Introduction

As part of our ongoing investigation[1] of the role of organometallic chemistry in the synthesis of organofluorine compounds, we have investigated the carbonylation and decarbonylation reactions of metal–fluoroalkyl bonds. Early work in fluoroorganometallic chemistry concerned the oxidative coupling of tetrafluoroethylene by low-valent transition-metal complexes to form perfluorometallacyclopentane compounds.[2,3] The clean formation of a $-C_4F_8-$ fragment from relatively inexpensive starting ma-

---

[†] Current address: Medical Products Department, E. I. du Pont de Nemours and Co., Barley Mill Plaza, Wilmington, De 19880.

[‡] Contribution No. 4813.

(1) (a) Burch, R. R.; Calabrese, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 5359–60. (b) Burch, R. R.; Harlow, R. L.; Ittel, S. D. *Organometallics* **1987**, *6*, 982–7.

(2) (a) Watterson, K. F.; Wilkinson, G. *Chem. Ind.* (*London*) **1959**, 991. (b) *Ibid.* **1960**, 1358. (c) Hoehn, H. H.; Pratt, L.; Watterson, K. F.; Wilkinson, G. *J. Chem. Soc.* **1961**, 2738. (d) Manuel, T. A.; Stafford, S. L.; Stone, F. G. A. *J. Am. Chem. Soc.* **1961**, *83*, 249. (e) Fields, R.; Germain, M. M.; Haszeldine, R. N.; Wiggans, P. W. *J. Chem. Soc. A* **1970**, 1964. (f) Fields, R.; Germain, M. M.; Haszeldine, R. N.; Wiggans, P. W. *Chem. Commun.* **1967**, 243. (g) Manuel, T. A.; Stafford, S. L.; Stone, F. G. A. *J. Am. Chem. Soc.* **1961**, *83*, 249. (h) Manuel, T. A. *Inorg. Chem.* **1963**, *2*, 854.

0276-7333/90/2309-1276$02.50/0 © 1990 American Chemical Society

Table I. Infrared Data (ν_{CO}, cm^{-1}) for the Compounds

compd	$Fe—C(=O)—R_f$	Fe—CO
$Fe(CO)_4(COCF_2CF_2CF_2CO)$	1692	2140, 2093, 2083, 2072
$Fe(CO)_4(CF_2CF_2CF_2CO)$	1734	2142, 2093, 2078
$Fe(CO)_4(CF_2CF_2CF_2)$		2143, 2087, 2082, 2061
$Fe(CO)_4(COCF_2CF_2CO)$	1724	2134, 2086, 2077, 2063
$Fe(CO)_4(CF_2CF_2CF_2CF_2)$		2150, 2092, 2072, 2056[a]
$Fe(CO)_4(COCF_2CF_2CF_3)_2$	1696	2139, 2088, 2077, 2068[b]
$Fe(CO)_4(CF_2CF_2CF_3)_2$		2157, 2100, 2098, 2082[b]

[a] Reference 2e. [b] Reference 15.

Table II. NMR Spectroscopic Data (ppm)

compd	$-C(=O)CF_2-$	$FeC_\alpha F_2-$	$-C_\beta F_2-$
$Fe(CO)_4(COCF_2CF_2CF_2CO)$	-122.1 t		-134.1 q
$Fe(CO)_4(CF_2CF_2CF_2CO)$	-130.9 tt	-73.6 m	-141.2 m
$Fe(CO)_4(CF_2CF_2CF_2)$		-83.6 s	-123.9 s
$Fe(CO)_4(COCF_2CF_2CO)$	-135.9 s		
$Fe(CO)_4(CF_2CF_2)$		-108.8 s	
$Fe(CO)_4(CF_2CF_2CF_2CF_2)$		-72.7	-137.7
$Fe(CO)_4(COCF_2CF_2CF_3)_2$	-111.3 q		
$Fe(CO)_4(CF_2CF_2CF_3)_2$		-68.1 m	-116.0 q

terials presents an appealing starting point for further elaboration.

The high strength of the C–F bond[4] imparts to many fluoroorganometallic compounds the high oxidative stability generally associated with saturated fluorocarbons.[5] Similarly, the increased strength of the metal–carbon bond in fluoroorganometallics is reflected in the enhanced thermal stability of such compounds relative to that of their hydrocarbon counterparts. For example, $CF_3Co(CO)_4$ can be distilled at about 90 °C,[6] while $CH_3Co(CO)_4$ decomposes above 35 °C.[7] A theoretical understanding of this enhanced stability of the $M–R_F$ bond is beginning to emerge.[8] When initial attempts to carbonylate $M–R_F$ bonds met with failure, we began to investigate this reaction in more detail. The results of that investigation are reported here.[9]

Experimental Section

All experiments were performed in a nitrogen-filled drybox equipped with a built-in freezer, on a standard Schlenk line with an argon source or on a vacuum line. Infrared spectra were recorded as Nujol mulls on a Perkin-Elmer 983 spectrophotometer; values for well-characterized compounds are presented in Table I. ^{19}F NMR spectra (188 or 282 MHz) are reported relative to $CFCl_3$; values for well-characterized compounds are presented in Table II. Ether and pentane were distilled from sodium benzophenone ketyl, and CH_2Cl_2 and CD_2Cl_2 were distilled from P_2O_5. CO was used as received from Matheson. The starting material $Fe(CO)_4(CF_2)_4$ was prepared by the literature procedure.[2e]

Caution! C_2F_4 is potentially explosive and should be handled in well-shielded equipment with rigorous exclusion of oxygen. Heating uninhibited C_2F_4 should be avoided.

Attempted Carbonylation of $Fe(CO)_4(CF_2CF_2CF_2CF_2)$. A THF solution of $Fe(CO)_4(CF_2CF_2CF_2CF_2)$ was pressurized to 45 psi of CO in a Fisher–Porter bottle. There was no evidence by infrared spectroscopy of carbonylation to a fluoroacyl derivative. The reaction was repeated at 2000 psi in a stainless steel autoclave with the same results. There is presumably no insertion, but there is the remote possibility that if the insertion occurred, it reverses rapidly when the CO pressure is released to take a sample.

Preparation of $Fe(CO)_4(COCF_2CF_2CO)$. In a typical reaction, $ClCO(CF_2)_2COCl$ (1.6 g, 7.1 mmol) that had been freshly distilled was vacuum-transferred into a slurry of 2.3 g (6.65 mmol) of $Na_2Fe(CO)_4{\cdot}1.5diox$ (diox = dioxane) in approximately 70 mL of THF that had been cooled to -78 °C. The resulting red solution was kept at -78 °C overnight and then gradually warmed to -10 °C as the THF was removed under vacuum. The solid residue was then extracted with CH_2Cl_2, which was evaporated, yielding a crude product. The product was washed with pentane and then extracted with toluene and CH_2Cl_2. The combined extracts were evaporated to dryness. The solid residue was then transferred to a sublimator, where the major portion was sublimed at 60 °C under the vacuum of a mechanical pump. Several of the crystals obtained from the sublimation were suitable for X-ray diffraction studies; yield 20–30%. Spectroscopic parameters are presented in Tables I and II. Anal. Calcd for $FeC_8O_6F_4$: C, 29.66; F, 23.46; Fe, 17.2. Found: C, 29.75; F, 23.5; Fe, 17.4.

Preparation of $Fe(CO)_4(COCF_2CF_2CF_2CO)$. $ClCO(CF_2)_3COCl$ (2.0 g, 7.22 mmol) that had been freshly distilled was vacuum-transferred into a slurry of 2.3 g (6.65 mmol) of $Na_2Fe(CO)_4{\cdot}1.5diox$ in approximately 70 mL of THF that had been cooled to -78 °C. The resulting red solution was kept at -78 °C overnight and then gradually warmed to -10 °C as the THF was removed under vacuum. The solid residue was then extracted with CH_2Cl_2, which was evaporated, yielding a crude product. The product was washed with pentane and toluene and then recrystallized from THF; yield 10%. Anal. Calcd for $FeC_9O_6F_6$: C, 28.91; F, 30.48; Fe, 14.9. Found: C, 28.66; F, 31.0; Fe, 14.7. (It is believed that the complex had undergone some decarbonylation in transit to or during the analysis.)

Preparation of $Fe(CO)_4(COCF_2CF_2CF_2CF_2CO)$. The reaction was carried out in the same manner as the reactions above. $FCO(CF_2)_4COF$ (1.0 g, 3.40 mmol) was combined with 1.2 g (3.47 mmol) of $Na_2Fe(CO)_4{\cdot}1.5diox$ in approximately 70 mL of THF. Workup of the product was the same as before, but no solid products were obtained. The infrared spectrum of the oil contained bands at 2150, 2100, 2085, 2040, and 1700 cm^{-1} attributable to the desired product (compare Table I), but there were also bands at 2130, 1995, 1880, 1785, and 1670 cm^{-1}. The ^{19}F NMR spectrum had two equal-intensity peaks at -118.7 and -122.9 ppm.

Decarbonylation of $Fe(CO)_4(COCF_2CF_2CF_2CO)$. A toluene solution of $Fe(CO)_4(COCF_2CF_2CF_2CO)$ was heated on an oil bath at 75 °C. Decarbonylation to $Fe(CO)_4(CF_2CF_2CF_2CO)$ was quantitative within 24 h. The decarbonylation was also carried out under 35 psig of CO in a Fisher–Porter bottle and at 100 °C under 2000 psig of CO with the same results. $Fe(CO)_4(CF_2CF_2CF_2CO)$ was isolated as a colorless crystalline compound by evaporation of the toluene solution.

Decarbonylation of $Fe(CO)_4(CF_2CF_2CF_2CO)$. A $CF_3C_6H_5$ solution of $Fe(CO)_4(COCF_2CF_2CF_2)$ was heated on an oil bath at 110 °C for 3 days. Decarbonylation to $Fe(CO)_4(CF_2CF_2CF_2)$

---

(3) (a) Cundy, C. S.; Green, M.; Stone, F. G. A. *J. Chem. Soc. A* **1970**, 1647–53. (b) Browning, J.; Empsall, H. D.; Green, M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1973**, 381–7. (c) Maples, P. K.; Green, M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1973**, 388–92. (d) Tolman, C. A.; Seidel, W. C. *J. Am. Chem. Soc.* **1974**, *96*, 2774–80. (e) Tolman, C. A. *J. Am. Chem. Soc.* **1974**, *96*, 2780–9.

(4) Carbon–fluorine bond dissociation energies range from 109 to 130 kcal/mol and are substantially stronger than analogous C–H bonds.[1b]

(5) (a) Chambers, R. D. *Fluorine in Organic Chemistry*; Wiley: New York, 1973. (b) Smart, B. E. In *The Chemistry of Functional Groups*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1983; Supplement D, Chapter 14.

(6) Heck, R. F. In *Advances in Organometallic Chemistry*; Stone, F. G. A., West, R., Eds.; Academic Press: New York, 1966, Vol. 4, p 243.

(7) Breslow, D. S.; Heck, R. F. *Chem. Ind. (London)* **1960**, 467.

(8) (a) King, R. B.; Bisnette, M. B. *J. Organomet. Chem.* **1964**, *2*, 15. (b) Clark, H. C.; Tsai, J. H. *J. Organomet. Chem.* **1967**, *7*, 515. (c) Bennett, M. A.; Chee, H.; Robertson, G. B. *Inorg. Chem.* **1979**, *18*, 1061, 1071. (d) Cotton, F. A.; Wing, R. M. *J. Organomet. Chem.* **1967**, *9*, 511. (e) Graham, W. A. G. *Inorg. Chem.* **1968**, *7*, 315–21. (f) Hall, M. B.; Fenske, R. F. *Inorg. Chem.* **1972**, *11*, 768. (g) Lichtenberger, D. L.; Fenske, R. F. *Inorg. Chem.* **1974**, *13*, 486.

(9) This work was presented at the 185th meeting of the American Chemical Society, Seattle, WA, 1983 (K. J. Karel and T. H. Tulip, Inorganic Division, Abstract INOR 33) and at the Trilateral Japan, China, U.S. Meeting on Catalysis and Organometallic Chemistry (Tsukuba, Japan, 1986).

Table III. Crystal Structure Data for Compounds 1–4

	1	2	3	4
formula	$FeC_8F_4O_6$	$FeC_9F_6O_6$	$FeC_8F_6O_5$	$FeC_7F_6O_4$
fw	323.93	373.93	345.92	317.91
space group	$C2/c$	$P2_1/c$	$P2_1/c$	$Pnma$
a, Å	10.957 (2)	11.433 (1)	7.079 (1)	15.161 (2)
b, Å	8.652 (1)	9.372 (1)	13.084 (2)	9.222 (1)
c, Å	12.335 (2)	12.817 (1)	11.887 (1)	7.229 (1)
β, deg	118.68 (1)	116.11 (1)	101.34 (1)	90
V, Å^3	1025.9 (6)	1233.2 (4)	1059.5 (4)	1010.7 (4)
Z	4	4	4	4
D(calcd), g cm^{-3}	2.10	2.01	2.17	2.089
cryst dimens, mm	0.12 × 0.24 × 0.28	0.20 × 0.28 × 0.29	0.20 × 0.25 × 0.40	0.20 × 0.23 × 0.29
temp, °C	−100	−60	−90	−100
radiation	Mo Kα (graphite monochromated, λ = 0.71069 Å)			
μ, cm^{-1}	16.01	13.73	15.80	16.38
2θ limits, deg	4–55			
scan width (ω), deg	1.0			
scan speed, deg min^{-1}	4.0–10.0			
no. of data, $I_o \geq 3\sigma(I_o)$	1061	2150	1973	990
anomalous terms	Fe	Fe	Fe	Fe
final no. of variables	87	199	181	103
R	0.026	0.028	0.025	0.038
R_w	0.035	0.029	0.029	0.053

was evident by NMR spectroscopy. The solvent was removed under vacuum, taking care not to lose the volatile product. $Fe(CO)_4(CF_2CF_2CF_2)$ was isolated as a colorless crystalline compound by sublimation at 0.5 atm to a cold finger at −50 °C. The crystals obtained were not suitable for X-ray crystallography, and neither were those obtained from pentane solution. Fortuitously, a sample contained in a vial placed on the floor of the drybox sublimed to the top of the vial, presumably as a result of the heat from the pumps below the box. This gives a good indication of the volatility of this complex. The crystals were used for a crystallographic determination.

Decarbonylation of $Fe(CO)_4(COCF_2CF_2CO)$. A $CF_3C_6H_5$ solution of $Fe(CO)_4(COCF_2CF_2CO)$ was heated in a sealed NMR tube in an oil bath at 100 °C. After 56 h, the ^{19}F NMR spectrum displayed two new peaks at −108.8 and −133.0 ppm, which accounted for about 55 and 5% of the integrated intensities, respectively. The peak at −108.8 ppm was attributed to $Fe(CO)_4(CF_2CF_2)$ in accord with literature references and an authentic sample. The peak at −133.0 ppm could be attributed to the $FeCOCF_2$ resonance of the expected intermediate species $Fe(CO)_4(CF_2CF_2CO)$, but a companion peak of equal intensity around −80 to −90 ppm would have been expected.

X-ray Structure Determinations. Details of the crystal structure determinations are given in Table III. The procedures employed are standard for the Du Pont laboratories. Data were collected on a Syntex P3 diffractometer using the ω-scan method. In each data collection, four standards were collected every 200 reflections; there were no significant variations in any of the data collections. An absorption correction was applied to the data for $Fe(CO)_4(COCF_2CF_2CO)$ with use of the ψ-scan technique; transmission coefficients varied from 92.3 to 99.9%. Lorentz and polarization corrections were applied to all four data sets. The structures were solved by Patterson techniques; in the case of $Fe(CO)_4(CF_2CF_2CF_2CO)$, the iron atom alone did not adequately phase the data and brute-force techniques were required. Refinements were carried out by full-matrix least squares on F with use of scattering factors from ref 10 and included anomalous terms for the atoms indicated in Table III. The weighting scheme was proportional to $[\sigma^2(I) + (0.02I)^2]^{-0.5}$. All atoms (there were no hydrogen atoms in any of the structures) were refined anisotropically. The only exceptions were three atoms in the structure of $Fe(CO)_4(CF_2CF_2CF_2)$ that were involved in a ring-flip disorder. The minor fractions of these three atoms were refined isotropically, and their occupancy factors were refined to 35%. In $Fe(CO)_4(COCF_2CF_2CO)$, the five largest residual densities (maximum 0.58 e/Å^3) were found near the C_2 axis. In $Fe(CO)_4(COCF_2CF_2CF_2CO)$, the largest residual density of 0.31 e/Å^3 was found near the iron atom and all of the residual peaks appeared to be of bonding density. In $Fe(CO)_4(CF_2CF_2CF_2CO)$, the largest residual

Table IV. Fractional Coordinates and Isotropic Thermal Parameters for $Fe(CO)_4(COCF_2CF_2CO)$

atom	x	y	z	B_{iso},[a] Å^2
Fe	0.500	0.59253 (5)	0.250	1.276 (7)
F(1)	0.6274 (1)	0.2490 (2)	0.4040 (1)	2.77 (3)
F(2)	0.4208 (1)	0.1442 (2)	0.3159 (1)	3.11 (3)
O(1)	0.3710 (2)	0.4283 (2)	0.3749 (1)	2.60 (3)
O(2)	0.7787 (2)	0.5745 (2)	0.4713 (1)	2.26 (3)
O(3)	0.3981 (2)	0.8186 (2)	0.3719 (2)	2.75 (4)
C(1)	0.4397 (2)	0.4228 (3)	0.3230 (2)	1.58 (4)
C(2)	0.4960 (2)	0.2636 (3)	0.3096 (2)	1.91 (5)
C(3)	0.6727 (2)	0.5798 (3)	0.3870 (2)	1.62 (4)
C(4)	0.4374 (2)	0.7358 (3)	0.3258 (2)	1.90 (5)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table V. Fractional Coordinates and Isotropic Thermal Parameters for $Fe(CO)_4(COCF_2CF_2CF_2CO)$

atom	x	y	z	B_{iso},[a] Å^2
Fe	0.21052 (3)	0.18805 (3)	0.27164 (2)	1.956 (5)
F(1)	0.4153 (1)	0.4711 (2)	0.1494 (1)	4.52 (3)
F(2)	0.4902 (1)	0.3784 (2)	0.3215 (1)	3.33 (3)
F(3)	0.2069 (1)	0.5760 (2)	0.1662 (1)	4.22 (4)
F(4)	0.3955 (1)	0.6503 (2)	0.2994 (1)	4.29 (4)
F(5)	0.3725 (1)	0.4650 (2)	0.4553 (1)	3.54 (3)
F(6)	0.2174 (1)	0.6211 (2)	0.3766 (1)	4.84 (4)
O(1)	0.2796 (1)	0.2423 (2)	0.0864 (1)	3.27 (3)
O(2)	0.0673 (1)	0.4033 (2)	0.3252 (1)	3.17 (4)
O(3)	0.4701 (1)	0.1617 (2)	0.4737 (1)	3.31 (4)
O(4)	0.2458 (2)	−0.0899 (2)	0.1741 (2)	4.79 (5)
O(5)	0.0807 (2)	0.0606 (2)	0.4076 (1)	4.05 (4)
O(6)	−0.0309 (2)	0.2378 (2)	0.0556 (1)	3.87 (4)
C(1)	0.2922 (2)	0.2828 (2)	0.1799 (2)	2.18 (4)
C(2)	0.3792 (2)	0.4175 (3)	0.2282 (2)	2.69 (5)
C(3)	0.3139 (2)	0.5373 (2)	0.2637 (2)	2.90 (5)
C(4)	0.2686 (2)	0.5013 (2)	0.3555 (2)	2.69 (5)
C(5)	0.1679 (2)	0.3767 (2)	0.3209 (2)	2.13 (4)
C(6)	0.3718 (2)	0.1770 (2)	0.3988 (2)	2.34 (4)
C(7)	0.2347 (2)	0.0135 (3)	0.2130 (2)	3.06 (5)
C(8)	0.1293 (2)	0.1068 (2)	0.3555 (2)	2.73 (5)
C(9)	0.0583 (2)	0.2172 (2)	0.1387 (2)	2.51 (4)

[a] See footnote *a* of Table IV.

---

(10) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

Table VI. Fractional Coordinates and Isotropic Thermal Parameters for $Fe(CO)_4(CF_2CF_2CF_2CO)$

atom	x	y	z	B_{iso},[a] Å^2
Fe	0.31646 (3)	0.00146 (2)	0.22723 (2)	1.430 (4)
F(1)	0.0951 (2)	−0.22086 (9)	0.1226 (1)	2.54 (2)
F(2)	−0.1563 (2)	−0.1889 (1)	0.1985 (1)	2.86 (3)
F(3)	0.1649 (2)	−0.27835 (9)	0.3490 (1)	3.08 (3)
F(4)	0.0664 (2)	−0.1302 (1)	0.3991 (1)	2.81 (2)
F(5)	0.4602 (2)	−0.20122 (9)	0.2814 (1)	2.86 (2)
F(6)	0.4359 (2)	−0.1161 (1)	0.4371 (1)	3.03 (3)
O(1)	−0.0875 (2)	−0.0044 (1)	0.1128 (1)	2.23 (3)
O(2)	0.4356 (2)	−0.1117 (1)	0.0339 (1)	2.63 (3)
O(3)	0.7248 (2)	0.0527 (1)	0.3337 (2)	3.49 (4)
O(4)	0.2242 (2)	0.1864 (1)	0.0782 (1)	2.40 (3)
O(5)	0.1657 (2)	0.0967 (1)	0.4208 (1)	2.75 (3)
C(1)	0.0491 (3)	−0.0481 (2)	0.1675 (2)	1.61 (3)
C(2)	0.0280 (3)	−0.1614 (2)	0.2014 (2)	1.98 (4)
C(3)	0.1531 (3)	−0.1787 (2)	0.3206 (2)	2.15 (4)
C(4)	0.3488 (3)	−0.1291 (2)	0.3220 (2)	1.94 (3)
C(5)	0.3880 (3)	−0.0690 (2)	0.1065 (2)	1.86 (3)
C(6)	0.5711 (3)	0.0350 (2)	0.2924 (2)	2.17 (4)
C(7)	0.2615 (3)	0.1176 (2)	0.1347 (2)	1.74 (3)
C(8)	0.2225 (3)	0.0606 (2)	0.3475 (2)	1.90 (3)

[a] See footnote *a* of Table IV.

Table VII. Fractional Coordinates and Isotropic Thermal Parameters for $Fe(CO)_4(CF_2CF_2CF_2)$

atom	x	y	z	B_{iso},[a] Å^2
Fe	0.1206 (3)	0.2500	0.3830 (7)	1.42 (1)
F(1)	0.0894 (1)	0.4546 (2)	0.6813 (3)	4.1 (1)
F(2)	0.2203 (1)	0.4713 (2)	0.5778 (3)	4.1 (1)
F(3)	0.1727 (6)	0.2500	0.8919 (13)	4.7 (2)
F(3′)[b]	0.2119 (14)	0.2500	0.8657 (30)	5.3 (6)
F(4)	0.2827 (2)	0.2500	0.7031 (6)	3.5 (1)
F(4′)[b]	0.0710 (6)	0.2500	0.8400 (10)	3.1 (2)
O(1)	0.3103 (2)	0.2500	0.2845 (5)	2.9 (1)
O(2)	0.0833 (1)	0.4997 (2)	0.1340 (3)	2.9 (1)
O(3)	−0.0615 (2)	0.2500	0.5294 (4)	3.2 (1)
C(1)	0.1536 (2)	0.3761 (3)	0.5990 (4)	1.9 (1)
C(2)	0.1933 (5)	0.2500	0.7115 (8)	2.4 (2)
C(2′)[b]	0.1463 (11)	0.2500	0.7437 (22)	2.5 (4)
C(3)	0.2381 (2)	0.2500	0.3179 (5)	1.8 (1)
C(4)	0.0972 (2)	0.4038 (3)	0.2241 (4)	1.9 (1)
C(5)	0.0069 (2)	0.2500	0.4734 (5)	2.0 (1)

[a] See footnote *a* of Table IV. [b] Alternate disordered positions that refined to 35% occupancy.

density of 0.32 e/Å^3 was found near the Fe atom. In $Fe(CO)_4(CF_2CF_2CF_2)$, the largest residual density of 0.8 e/Å^3 was found near the disordered atoms. Fractional coordinates and isotropic thermal parameters are presented in Tables IV–VII for the complexes $Fe(CO)_4(COCF_2CF_2CO)$, $Fe(CO)_4(COCF_2CF_2CF_2CO)$, $Fe(CO)_4(CF_2CF_2CF_2CO)$, and $Fe(CO)_4(CF_2CF_2CF_2)$, respectively. Listings of anisotropic thermal parameters and structure factor data and detailed listings of bond distances and angles are given in the supplementary material. A summary of the most important bond distances and angles for all four structures is given in Table VIII.

Results and Discussion

The perfluorometallacyclopentane complex $Fe(CO)_4(CF_2CF_2CF_2CF_2)$ was prepared by the standard literature technique[2e] through oxidative cyclization of two tetrafluoroethylene molecules on a zerovalent metal center.

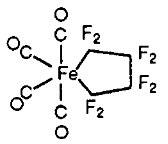


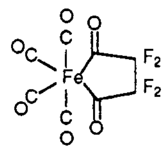
Table VIII. Important Bond Distances (Å) and Angles (deg) for Compounds 1–4

	1[a]	2	3	4[a,b]
Fe—C(O)	1.994 (2)	2.002 (2)	1.992 (1)	
	1.994 (2)	2.008 (2)		
Fe—$C_\alpha F_2$			2.023 (2)	2.009 (2)
				2.009 (2)
Fe—CO_{eq}	1.870 (2)	1.871 (2)	1.866 (2)	1.855 (2)
	1.870 (2)	1.864 (2)	1.860 (2)	1.855 (2)
Fe—CO_{ax}	1.838 (2)	1.850 (2)	1.836 (2)	1.841 (3)
	1.838 (2)	1.843 (2)	1.838 (2)	1.851 (3)
C═O	1.201 (2)	1.204 (2)	1.195 (2)	
	1.201 (2)	1.202 (2)		
CO—CF_2	1.551 (2)	1.558 (2)	1.549 (2)	
	1.551 (2)	1.561 (3)		
CF_2—CF_2	1.514 (3)	1.524 (3)	1.512 (2)	
		1.519 (3)		
$C_\alpha F_2$—CF_2			1.527 (2)	1.540 (4)
				1.540 (4)
C-Fe-C (cycle)	85.13 (9)	91.99 (7)	85.06 (6)	70.9 (1)
C-Fe-C (CO_{eq})	97.0 (1)	94.21 (9)	96.86 (7)	99.6 (1)
C-Fe-C (CO_{ax})	173.1 (1)	172.95 (8)	173.23 (6)	173.8 (1)
Fe-CO-C	111.8 (1)	120.5 (1)	110.8 (1)	
	111.8 (1)	119.9 (1)		
Fe-C-O	129.8 (1)	124.2 (1)	130.1 (1)	
	129.8 (1)	124.5 (1)		
Fe-C_α-C			110.4 (1)	93.9 (2)
				93.9 (2)
CO-C-C	108.4 (1)	113.9 (2)	108.0 (1)	
		114.0 (2)		
C-C-C		116.6 (2)	108.2 (1)	98.3 (3)

[a] Some numbers repeated due to symmetry operations. [b] Atomic positions from the 35% disorder are not included.

Attempted carbonylation of this compound under moderate and high pressures of CO gave no evidence for expansion of the ring. The starting materials were recovered unchanged. The carbonylation was also attempted under Lewis-acidic conditions, again to no avail. It was not clear whether the failed reaction was a result of a high kinetic barrier or unfavorable thermodynamics. Preparation of the acyl complexes by an alternative route would allow the reverse of the desired reaction to be explored. Addition of perfluoroacyl halides to metal carbonyl anions is a well-established reaction,[11-14] and if we started with Collman's reagent, two oxidative additions could be carried out in the same step.

Synthesis of the Diacyls. Slow addition by vacuum transfer of perfluorosuccinyl chloride to a THF solution of $Fe(CO)_4^{2-}$ at −78 °C yields $Fe(CO)_4(COCF_2CF_2CO)$ (1), which is isolated as a colorless compound by sublimation.



1

Elemental analyses, infrared spectroscopy (Table I), NMR spectroscopy (Table II), and an X-ray structure determination (Tables III–V) define the compound as the diacyl metallacyclopentanedione. The most dramatic spectro-

---

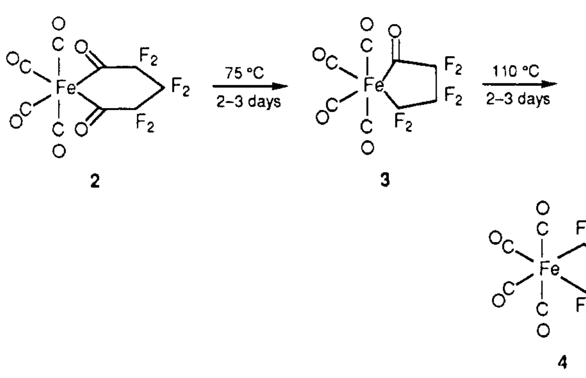
(11) Kaesz, H. D.; King, R. B.; Stone, F. G. A. *Z. Naturforsch.* **1960**, *15B*, 763.

(12) King, R. B. *J. Am. Chem. Soc.* **1963**, *85*, 1922.

(13) Hensley, D. W.; Wurster, W. L.; Stewart, R. P. *Inorg. Chem.* **1981**, *20*, 645.

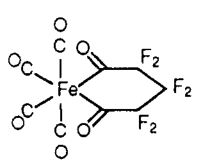
(14) Schulze, W.; Hartl, H.; Seppelt, K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 185.

Scheme I



scopic change upon coordination was observed in the acyl C=O stretches; the C=O stretching frequency drops from 1798 cm^{-1} for perfluorosuccinyl chloride to 1724 cm^{-1} for the metallacycle. The ^{19}F NMR spectrum of both compounds is a sharp singlet.

A similar reaction can be carried out with perfluorosuccinyl chloride, yielding the perfluorometallacyclohexanedione 2. In this case, the C=O bands are observed at 1801 cm^{-1} in the acyl halide and drop to 1692 cm^{-1} in the complex. The ^{19}F–^{19}F coupling between the α- and β-fluorides in the parent acyl is zero due to rotational averaging of the trans and gauche couplings of opposite sign. In the complex, rotational averaging is precluded, so coupling is observed. As a first approximation, the spectrum can be described as an A_4B_2 spin system, but the coupling pattern is more complex than this simple description or even an $A_2A'_2B_2$ description. We have not analyzed the spectrum in detail.



2

Synthesis of the analogous seven-membered ring was attempted with use of perfluoroadipoyl chloride. While there were spectroscopic indications that the desired compound had been formed, it was not possible to isolate it from the reaction mixture. The yield of these three reactions is clearly dependent on the size ring being formed. Formation of the five-membered ring from succinyl chloride proceeded in 20–30% yields; yields of the six-membered ring dropped to 10%, and the seven-membered ring expected from adipoyl chloride was not isolated at all. There appeared to be higher nuclearity products resulting from intermolecular additions of the diacyl compounds in the reaction mixture.

Decarbonylation of the Diacyls. At elevated temperatures in solution, the metallacyclohexanedione complex $\overline{\mathrm{Fe(CO)_4(COCF_2CF_2CF_2CO)}}$ (2) cleanly loses one carbon monoxide as one acyl C=O is extruded to form the metallacyclopentanone $\overline{\mathrm{Fe(CO)_4(CF_2CF_2CF_2CO)}}$ (3). The reaction is virtually quantitative. If the temperature of the reaction is increased to 110 °C, a second C=O is extruded to yield the volatile metallacyclobutane $\overline{\mathrm{Fe(CO)_4(CF_2CF_2CF_2)}}$ (4). This sequence of reactions is illustrated in Scheme I.

Each of the compounds in this series has been isolated and characterized both spectroscopically and structurally (see below). Each of the products has been purified by sublimation, but the volatility of the perfluorometallacyclobutane is rather remarkable. Under only moderate vacuum, the complex quickly sublimes to a cold finger as a microcrystalline mat. When the compound was left in a vial at atmospheric pressure on the floor of the drybox, which was warmed only by pumps and refrigerator compressors below, it sublimed to the top of the vial as crystals suitable for an X-ray determination.

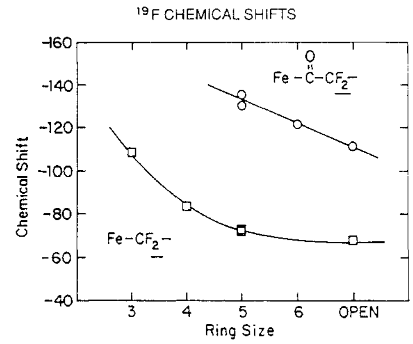
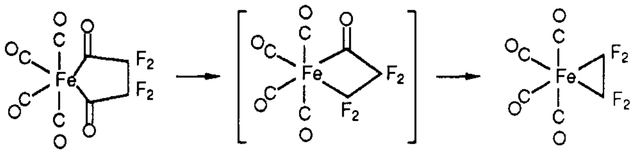


Figure 1. Dependence of ^{19}F chemical shifts of α-CF_2 and $-C(O)CF_2-$ on ring size.

Scheme II



Trends in the infrared spectra of the complexes are not particularly informative. The number of C≡O stretching frequencies of the $Fe(CO)_4$ group is reduced from the expected four to three when the symmetry of the complex is reduced. Thus, one band is lost in going from 2 to 3 but reappears in the spectrum of 4 (see Table I). More information is obtained from the ^{19}F NMR spectra of the complexes (Table II). The ^{19}F NMR spectrum of 2 was described above. The ^{19}F NMR spectrum of 3 consists of three complex multiplets, and the spectrum of 4 consists of two broadened singlets. The ^{19}F chemical shifts of the $M-C_\alpha F_2$ and $CO-CF_2$ groups correlate with ring size in both the acyl and metallacycloalkane series (Figure 1) despite rather significant changes in the nature of the complexes.

The decarbonylation of $\overline{\mathrm{Fe(CO)_4(COCF_2CF_2CO)}}$ is somewhat different from that just described for $\overline{\mathrm{Fe(CO)_4(COCF_2CF_2CF_2CO)}}$. While it takes place under similar conditions, the intermediate monocarbonyl complex is not observed (Scheme II). The second decarbonylation seems to proceed more easily than the first, so the metallacyclopropane $Fe(CO)_4(CF_2CF_2)$ is the only product observed. The metallacyclopropane description is adopted because of the chemical origin of the complex, but this complex is identical with the tetrafluoroethylene π-complex reported earlier.[15] Distinctions between the π-olefin[16] and metallacyclopropane descriptions of the bonding are largely semantic in nature, but it is interesting to note that the ^{19}F chemical shift of the complex falls on the $-C_\alpha F_2-$/ring size correlation noted earlier.

---

(15) Fields, R.; Germain, M. M.; Haszeldine, R. N.; Wiggans, P. W. *J. Chem. Soc. A* **1970**, 1969.

(16) Ittel, S. D.; Ibers, J. A. In *Advances in Organometallic Chemistry*; Stone, F. G. A., West, R., Eds.; Academic Press: New York, 1976; Vol. 14, p 33.

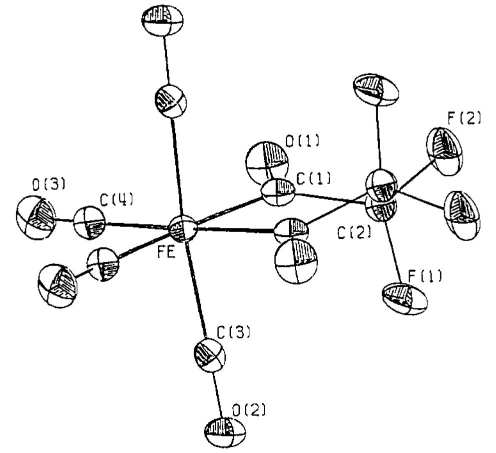


Figure 2. Perspective view of $\overline{\mathrm{Fe(CO)_4(COCF_2CF_2CO)}}$ showing the atom-labeling scheme.

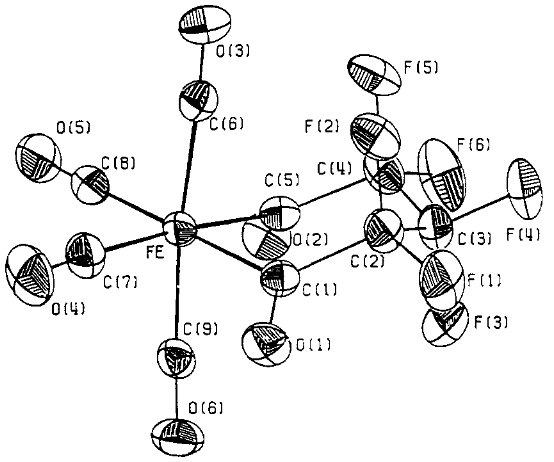


Figure 3. Perspective view of $\overline{\mathrm{Fe(CO)_4(COCF_2CF_2CF_2CO)}}$ showing the atom-labeling scheme.

Results of the Structure Determinations. Crystallographic information for the structure determinations on compounds 1–4 is given in Table III. Fractional coordinates and isotropic thermal parameters for 1–4 are given in Tables IV–VII, respectively. Tables of complete bond distances and angles have been submitted as supplementary material; the most important values for all four compounds have been summarized in Table VIII. Perspective views of the four complexes with atom-labeling schemes are presented in Figures 2–5, respectively.

The structures of the four complexes have several features in common. Coordination about each metal center is pseudooctahedral. In each structure, the axial carbonyl groups are bent toward the fluorocarbon group with a C–Fe–C angle of 173°. In each case, the Fe–C bonds of the axial CO ligands are shorter than those of the equatorial CO ligands. The C–Fe–C angles of the metallacycles reflect the size of the metallacycle ring at 92° for the six-membered ring, 85° for the five-membered rings, and 71° for the four-membered ring. As the metallacycle C–Fe–C angle is reduced over 20° by ring contraction, the angle between the equatorial CO ligands opens slightly (5°) to fill the gap in the coordination sphere.

The complex $\overline{\mathrm{Fe(CO)_4(COCF_2CF_2CO)}}$, shown in Figure 2, has a crystallographically imposed 2-fold symmetry through the equatorial plane. The conformation of the ring is that of a twisted envelope; the twist allows the fluorine substituents on the two sp^3 carbon atoms to adopt a normal staggered conformation. This is easily recognized in the figure; the three torsional angles defined by the symmetry-related atoms are F(1)-C(2)-C(2′)-F(1′) = 168.8°, F(1)-C(2)-C(2′)-F(2′) = 50.3°, and F(2)-C(2)-C(2′)-F(2′) = -68.1°.

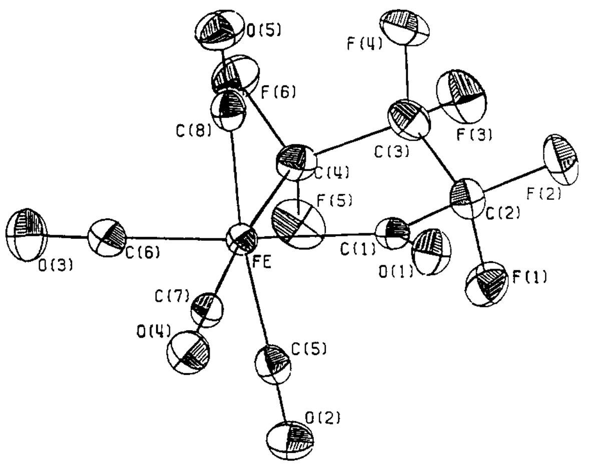


Figure 4. Perspective view of $\overline{\mathrm{Fe(CO)_4(CF_2CF_2CF_2CO)}}$ showing the atom-labeling scheme.

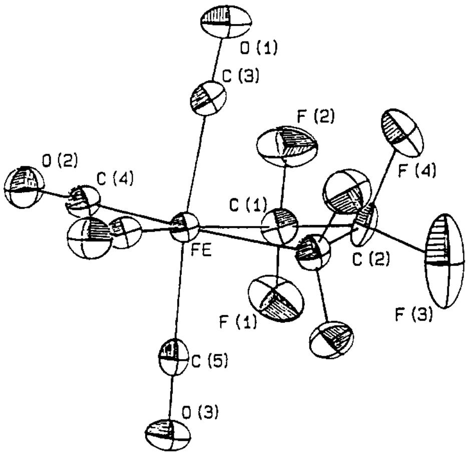


Figure 5. Perspective view of $\overline{\mathrm{Fe(CO)_4(CF_2CF_2CF_2)}}$ showing the atom-labeling scheme.

The metallacyclohexanedione $\overline{\mathrm{Fe(CO)_4(COCF_2CF_2CF_2CO)}}$ is shown in Figure 3. The ring adopts a chair conformation with the fluorine substituents occupying axial and equatorial sites. The acyl oxygen atoms are bent significantly below the equatorial coordination plane and eclipse the equatorial fluorine atoms on the adjacent carbon centers.

The five-membered ring of $\overline{\mathrm{Fe(CO)_4(CF_2CF_2CF_2CO)}}$ adopts an envelope conformation with C(3) out of the plane. Figure 5 demonstrates that the staggered arrangement of fluorine substituents about the ring is maintained. As has been noted in previous structures[17] of complexes bearing metal fluoroalkyl groups, the C_α–F bond lengths are lengthened relative to others on the fluoroalkyl chain; the average C_α–F length is 1.373 (2) Å while the other C–F distances average 1.352 (3) Å. This weakening of the α-C–F bond is also reflected in reduced infrared stretching frequencies.[18] Bond angles around the

---

[17] (a) Mason, R.; Russell, D. R. *J. Chem. Soc., Chem. Commun.* **1965**, 182–3. (b) Churchill, M. R. *Inorg. Chem.* **1965**, *4*, 1734–9. (c) Churchill, M. R. *Inorg. Chem.* **1967**, *6*, 185–90. (d) Churchill, M. R.; Fennessey, J. R. *Inorg. Chem.* **1967**, *6*, 1213–20.

[18] (a) Pitcher, E.; Stone, F. G. A. *Spectrochim. Acta* **1962**, *18*, 585–94. (b) King, R. B.; Bisnette, M. B. *J. Organomet. Chem.* **1964**, *2*, 15–37. (c) Graham, W. A. G. *Inorg. Chem.* **1968**, *7*, 315–21. (d) Hall, M. B.; Fenske, R. F. *Inorg. Chem.* **1972**, *11*, 768–75.

acyl carbon atom more closely resemble those of the five-membered ring of $\overline{Fe(CO)_4(COCF_2CF_2CO)}$ than those of $\overline{Fe(CO)_4(COCF_2CF_2CF_2CO)}$, from which this compound came.

The metallacyclobutane complex $\overline{Fe(CO)_4(CF_2CF_2CF_2)}$ has a crystallographically imposed mirror plane passing through the axial CO ligands and the β-CF_2 group. The four-membered ring displays a slight pucker to relieve the eclipsed fluorine interactions indicated by the dihedral angles F(1)–C(1)–C(2)–F(4) = 133.7°, F(1)–C(1)–C(2)–F(3) = 12.9°, F(2)–C(1)–C(2)–F(4) = 19.2°, and F(2)–C(1)–C(2)–F(3) = 101.6°. These eclipsed interactions are reduced by the acute nature of the angles at each of the corners of the ring. The pucker in the ring is indicated by the interplane angle between the planes defined by C(1)–Fe–C(1′) and C(1)–C(2)–C(1′), which is 18.8°. For comparison, this angle is 2° in a 3,3-dimethyltitanacyclobutane complex[19] and 22° in a 3,3-dimethylplatinacyclobutane complex.[20] The F–C distance across the ring is 2.613 (5) Å, too long for a bonding interaction.

Conclusions

The goal of this research program was to develop organometallic-based synthetic methods for fluorocarbon chemistry. The construction of four-carbon fragments on an organometallic center followed by insertion of small molecules was the initial goal. It became clear that insertion of CO into preformed M–R_F bonds was not a viable approach. Our investigation of the reverse reaction indicates, under all circumstances, the preferred reaction is decarbonylation of the fluoroacyl, though the kinetic barriers to decarbonylation can be substantial compared to those for the analogous hydrocarbon analogues.

Acknowledgment. We wish to acknowledge the skilled technical assistance of Donald Soring and Lou Lardear. Drs. Joseph Calabrese and Richard Harlow were particularly helpful in preparing the crystallographic portions of this work for publication.

Supplementary Material Available: Listings of anisotropic thermal parameters and additional bond distances and angles (9 pages); listings of structure factors (36 pages). Ordering information is given on any current masthead page. Inquiries for copies of these materials can also be directed to K.J.K.

---

[19] Lee, J. B.; Gajda, G. J.; Schaefer, W. P.; Howard, T. R.; Ikariya, T.; Straus, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1981**, *103*, 7358.

[20] Tulip, T. H. Unreported structure determination of a 3,3-dimethylplatinacyclobutane complex.

Arene Complexes of Tantalum(III) Prepared by Alkyne Cyclization and Alkoxide-Exchange Reactions. Arene Folding and π Localization upon Coordination

David J. Arney, Pamela A. Wexler, and David E. Wigley*

Carl S. Marvel Laboratories of Chemistry, Department of Chemistry, University of Arizona, Tucson, Arizona 85721

Received October 3, 1989

$Ta(DIPP)Cl_4$ (**1**, DIPP = 2,6-diisopropylphenoxide) has been prepared from the reaction of $TaCl_5$ with 1 equiv of $Me_3SiDIPP$ in CH_2Cl_2 and is shown to be dimeric. While $Ta(DIPP)Cl_4$ reacts with Et_2O to form *trans*-$Ta(DIPP)Cl_4(OEt_2)$ (**2**), $TaCl_5$ and Me_3SiDMP (DMP = 2,6-dimethylphenoxide) react in CH_2Cl_2/Et_2O solution to provide *trans*-$Ta(DMP)Cl_4(OEt_2)$ (**3**). Me_3SiDMP (2 equiv) reacts with $TaCl_5$ in CH_2Cl_2/Et_2O solution to form the bisphenoxide complex $Ta(DMP)_2Cl_3{\cdot}OEt_2$ (**6**). All of these compounds cyclize 3-hexyne upon their two-electron reduction to form $(\eta^6\text{-}C_6Et_6)Ta(OR)_xCl_{3-x}$ (**4**, OR = DIPP, $x = 1$; **5**, OR = DMP, $x = 1$; **7**, OR = DMP, $x = 2$) but do not readily undergo the analogous reaction with 2-butyne. However, $(\eta^6\text{-}C_6Me_6)Ta(DIPP)Cl_2$ (**10**) can be prepared in essentially quantitative yield from the reaction of $(\eta^6\text{-}C_6Me_6)Ta(DIPP)_2Cl$ (**9**) with $Ta(DIPP)_2Cl_3{\cdot}OEt_2$, which also provides $Ta(DIPP)_3Cl_2{\cdot}OEt_2$ as the byproduct. Likewise, $(\eta^6\text{-}C_6Et_6)Ta(DMP)_2Cl$ (**7**) is completely converted to $(\eta^6\text{-}C_6Et_6)Ta(DMP)Cl_2$ (**5**) upon its reaction with $Ta(DMP)_2Cl_3{\cdot}OEt_2$ (**6**). $(\eta^6\text{-}C_6Me_6)Ta(DIPP)Cl_2$ (**10**) crystallizes in the orthorhombic space group *Pnma* (No. 62) with $a = 16.506$ (3) Å, $b = 17.237$ (3) Å, $c = 8.911$ (1) Å, and $V = 2535.3$ Å^3 with $Z = 4$ and $\rho_{calcd} = 1.55$ g cm^{-3}. The arene ligand in **10** is characterized by a folded structure and considerable localization of the π-electron density in a 1,4-diene fashion. The thermolysis of **10** produces free C_6Me_6 as the only identifiable product, while the thermal decomposition of **9** produces free C_6Me_6 along with the "tucked in" complex $(\eta^1\text{-}C_6Me_5CH_2)Ta(DIPP)_2Cl_2$ (**11**). Compound **11** can be prepared in higher yields from **9** by its thermal decomposition in the presence of Me_3SiCl.

Introduction

Although most transition metals form stable complexes with arenes,[1] the only ones that have found significant applications in organic synthesis are those of chromium, particularly $(\eta^6\text{-arene})Cr(CO)_3$.[2,3] Coordination to the electron-withdrawing $Cr(CO)_3$ fragment renders the arene susceptible to nucleophilic attack, deactivates the ring with respect to electrophilic substitution, and results in both the arene and benzylic protons becoming more acidic.[4] We

---

[1] (a) Silverthorn, W. E. *Adv. Organomet. Chem.* **1975**, *13*, 47. (b) Muetterties, E. L.; Bleeke, J. R.; Wucherer, E. J.; Albright, T. A. *Chem. Rev.* **1982**, *82*, 499. (c) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

[2] Davis, R.; Kane-Maguire, L. A. P. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 3, pp 953–1077.

[3] Semmelhack, M. F. *J. Organomet. Chem. Libr.* **1976**, *1*, 361.

0276-7333/90/2309-1282$02.50/0