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Preliminary communication

OCTAFLUOROCYCLOOCTATETRAENE TRANSITION METAL COMPOUNDS: DISPLACEMENT OF FLUORIDE BY METAL CARBONYL ANIONS

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Summary

Octafluorocyclooctatetraene (OFCOT) reacts with some metal carbonyl anions $[ML_n]^-$ to give monosubstitution products $(C_8F_7)ML_n$ [ML_n = $Mn(CO)_5$, $Re(CO)_5$, $Fe(CO)_2(\eta\text{-}C_5H_5)$]. ^{19}F and ^{13}C $\{^{19}F\}$ NMR studies show that the cyclooctatetraene ring in these monosubstitution products does not undergo rapid ring-inversion or bond shifting on the NMR time scale. Reaction of OFCOT with $[Co(CO)_4]^-$ affords the distributed derivative $[(C_8F_6)Co_2(CO)_6]$ as the only product in poor yield.

The organometallic chemistry of cyclooctatetraene (COT) has been thoroughly explored and invariably COT binds to transition metals via the π-bond system of the ring [1,2]. We have been investigating the corresponding chemistry of the recently synthesized [3] and characterized [4] perfluorinated analogue, octafluorocyclooctatetraene (OFCOT), and have uncovered novel bonding modes [5] and transannular ring closure reactions [6] which are quite different from COT chemistry. The known reactions of fluorocarbon olefins, arenes and heterocycles [7] with metal carbonyl anions to afford products arising from net fluoride ion displacement has prompted us to attempt such substitution reactions with OFCOT, with a view to preparing metal derivatives bound to the cyclooctatetraene skeleton via a σ-bond.

Reaction of equimolar amounts of OFCOT and $[Fe(CO)_2(\eta\text{-}C_5H_5)]^-$ Na^+ in dry THF (20°C; 24 h) afforded, after chromatography (Florisil), the yellow,

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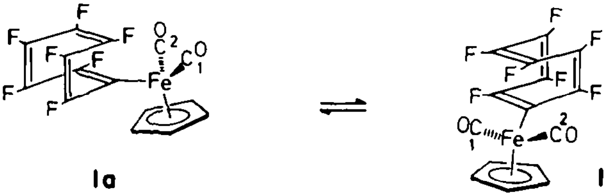
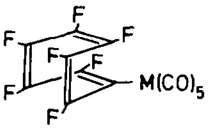
sublimable, crystalline monosubstitution product 1 [40%; m.p. 92°C; IR (hexane) ν(CO) 2041 s, 1997s cm^{-1}; mass spectrum, *m/e* 406 (P^+), 378 ($P^+ - CO$), 350 (P^+ - 2CO); ^{19}F NMR ($CDCl_3$; 20°C; 56 MHz) δ (upfield from internal $CFCl_3$) 74.55, 93.82, 119.03, 124.84, 128.97, 130.83, 140,29 (all multiplets of relative intensity = 1)*; ^{13}C {^{19}F} NMR spectrum** ($CDCl_3$; 20°C; 50 MHz) δ (downfield from internal TMS) 85.51 (d, *J*(C—H) 181 Hz, C_5H_5), 126.07 (=*C*—Fe), 127.60, 136.30, 137.73, 138.84, 140.24, 149.81, 152.87 (all =*C*—F), 212.53 (*C*O), 212.45 ppm (*C*O)***; Analysis: Found: C, 44.50; H, 1.27. $C_{15}H_5F_7FeO_2$ calcd.: C, 44.37; H, 1.24%]. Likewise, reaction of OFCOT with either $[Re(CO)_5]^-$ or $[Mn(CO)_5]^-$ afforded the white, sublimable, crystalline products 2 [60%; m.p. 100°C; IR (hexane) ν(CO) 2142w, 2034s, 2004s cm^{-1}; *m/e* 556 (P^+ using ^{187}Re); ^{19}F NMR δ 65.09, 93.65, 120.46, 125.23, 127.75, 129.66, 142.24 ppm; ^{13}C {^{19}F} NMR spectrum δ 115.95 (=*C*—Re), 128.30, 136.56, 137.49, 138.48, 139.80, 150.64, 152.94 (all =CF), 179.37 (*CO trans*), 179.68 ppm (*CO cis*); Analysis, C, 28.16; H, 0.0. $C_{13}F_7ReO_5$ calcd.: C, 28.11; H, 0.00%], and 3 [60%; m.p. 77°C; IR (hexane) ν(CO) 2127w, 2039s, 2013s cm^{-1}; *m/e* 424 (P^+); ^{19}F NMR, δ 67.10, 93.91, 119.85, 125.67, 127.75, 130.09, 141.29 ppm; Analysis, C, 36.88; H, 0.0 $C_{13}F_7MnO_5$ calcd.: C, 36.82; H, 0.00%], respectively. In contrast, the reaction of OFCOT with the weakly nucleophilic [8] $[Co(CO)_4]^-$ anion was extremely sluggish and yielded no monosubstitution product after 5 days in THF (20°C); however, traces (2%) of a red crystalline compound apparently resulting from net displacement of two adjacent fluorines were obtained under these conditions. On the basis of its physical and spectroscopic properties this compound is formulated as $[Co_2(CO)_6(C_8F_6)$ [m.p. 110°C; IR (hexane)



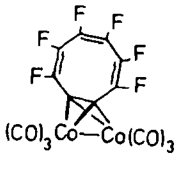
Ia

Ib



2 M = Re

3 M = Mn



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*A detailed analysis of ^{19}F—^{19}F coupling constants in these molecules will be published separately.

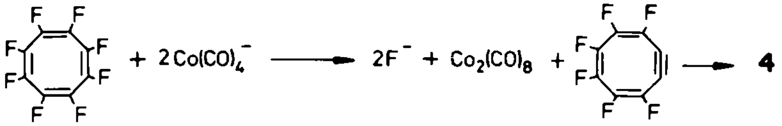
**^{13}C {^{19}F} NMR spectra were run at 50 MHz on a Varian XL-200 instrument modified to decouple ^{19}F rather than ^{1}H.

***In the ^{13}C {^{1}H} NMR spectrum the carbonyl carbons appear as multiplets due to coupling with ^{19}F.

ν(CO) 2105m, 2074s, 2054s cm^{-1}; *m/e* 496 (P^+), 468 (P^+ – CO), 440 (P^+ – 2CO), 412 (P^+ – 3CO), 384 (P^+ – 4CO), 356 (P^+ – 5CO), 328 (P^+ – 6CO); ^{19}F NMR δ 105.4 (m, 2F), 124.9 (m, 2F), 136.3 (m, 2F); Analysis, C, 34.06; H, 0.0. $C_{14}F_6Co_2O_6$ calcd.: C, 33.90; H, 0.00%]. Accordingly we have assigned structure 4 to this compound by analogy to the large number of known (μ-alkyne)hexacarbonyldicobalt species [9]. Final confirmation of the structure awaits an X-ray crystallographic study; a related fluorocarbon compound (μ-C_6F_6)$Co_2(CO)_6$ has been reported [10].

The activation energy barriers for ring inversion of the tub conformation of COT and its derivatives, and of bond-shift isomerism in the corresponding planar intermediate, have been the subject of considerable interest [11]. No such data have been reported for fluorinated derivatives. Observation of seven discrete ^{19}F NMR resonances for compounds 1, 2 and 3 clearly rules out a facile combined ring inversion-bond shift process for these molecules. Observation of eight separate olefinic carbon resonances in the ^{13}C {^{19}F} NMR spectra of 1 and 2 is also compatible with this conclusion. These data do not exclude the possibility of rapid ring inversion without concomitant bond shift isomerism. However the observation that the two carbonyl ligands in 1 are diastereotopic in the ^{13}C {^{19}F} NMR spectrum rules out this option since rapid ring inversion must interconvert CO environments between conformations 1a and 1b as shown. The ^{19}F NMR spectra of 1—3 are unchanged at +60° C.

It is not clear why reaction of the weakly nucleophilic [8] $[Co(CO)_4]^-$ with OFCOT results in net displacement of two fluorines, with no trace of a monosubstitution product analogous to 1—3, whereas the more powerful nucleophiles [8] give only the products of monosubstitution. A possible rationale involves formation of 4 by the reductive route shown below to yield $[Co_2(CO)_8]$ and hexafluorocycloocta-3,5,7-trien-1-yne, followed by trapping of the alkyne by the $[Co_2(CO)_8]$. The chemical product(s) of reduction of



OFCOT are unknown; attempts to generate the OFCOT mono- or dianions electrochemically result in irreversible behavior and decomposition [12]. Alternatively 4 may be formed by interaction of OFCOT with traces of a polynuclear cobalt carbonyl anion. It seems extremely unlikely that two consecutive nucleophilic displacements of F^- occur using $[Co(CO)_4]^-$, which is unreactive towards other fluorocarbons [7].

Experiments designed to gain more information regarding the ring-inversion barriers in 1—3, to understand better the mechanism of formation of 4, and to use 4 as a source of free hexafluorocycloocta-3,5,7-trien-1-yne are currently in progress.

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