Preliminary communication

Fluoroalkylation of cobalt complexes: selective reactions at the metal or the cyclopentadienyl ring

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Abstract

Reaction of $[Co(\eta^5-C_5H_5)(CO)_2]$ with perfluoro-n-propyl iodide proceeds by selective fluoroalkylation at the metal center to give $[Co(\eta^5-C_5H_5)(CO)(R_F)I]$ (3; $R_F = CF_2CF_2CF_3$). Treatment of 3 with excess PMe_3 affords cationic fluoroalkyl complex $[Co(\eta^5-C_5H_5)(PMe_3)_2(R_F)]^+ I^-$ (4; $R_F = CF_2CF_2CF_3$), which does not react further. The molecular structure of 4 has been determined by single-crystal X-ray diffraction studies. Complex 4 co-crystallizes with two water molecules in the space group $P\bar{1}$, $Z = 2$, $a = 7.9001(5)$ Å, $b = 10.348(1)$ Å, $c = 14.758$ Å, $\alpha = 85.48(1)°$, $\beta = 83.630(10)°$, $\gamma = 77.02(7)°$ at $T = 298$ K. In contrast, reaction of $[Co(\eta^5-C_5H_5)(PMe_3)_2]$ with perfluoro-n-propyl iodide proceeds with completely different selectivity to afford the ring-exo-fluoroalkylated complex $[Co(\eta^4-C_5H_5R_F)(PMe_3)_2I]$ (5; $R_F = CF_2CF_2CF_3$). Possible mechanisms for these reactions are discussed. © 1997 Elsevier Science S.A.

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Transition metal complexes with ligands bearing fluoroalkyl substituents are of considerable interest and potential utility. When the fluoroalkyl groups are of sufficiently long chain length, the resultant complexes show significant solubility in saturated fluorocarbons [1–5], and in supercritical CO_2 [6], two reaction media of recent interest. Recently, we devised a method for introduction of fluoroalkyl substituents on to cyclopentadienes, and used the resultant cyclopentadienyl anions as ligands for a variety of transition metals [2]. However, cyclopentadienyl anions bearing fluorine atoms on the α-carbon of the substituent group are prone to fluoride elimination [2,7,8], and are consequently difficult to use as reagents. As one way of circumventing this problem, we have begun to investigate the possibility of direct fluoroalkylation of coordinated cyclopentadienyl ligands.

There have been extensive studies on the mechanism of the oxidative addition of carbon–iodine bonds to low valent transition metal centers because it is an important method for the synthesis of metal–carbon bonds [9].

Depending on the metal and the alkyl halide, two-electron and a variety of one-electron mechanisms have been shown to operate [9]. [1] Reactions of primary alkyl iodides with $[M(\eta^5-C_5H_5)(CO)_2]$ (M = Co, Rh, Ir) result in apparent nucleophilic attack by the metal atom on the $\delta+$ carbon of the alkyl iodide to produce a metal–carbon bond, which may be followed by alkyl migration to an adjacent CO ligand [10]. The more nucleophilic metal centers in $[M(\eta^5-C_5H_5)(PMe_3)_2]$ (M = Co, Rh) react with primary alkyl iodides to give cations of 1, but with bulkier alkyl groups, such as ^iPr or ^tBu, alkylated cyclopentadienyl complexes 2 are observed [11].
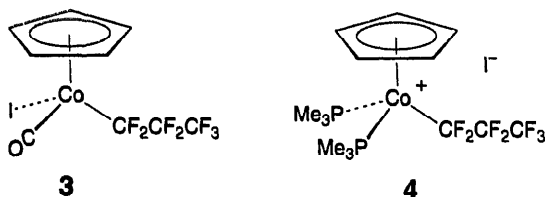

1 M = Co, Rh   2 M = Co, Rh

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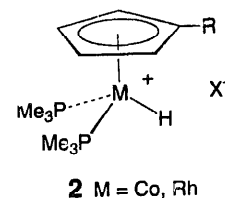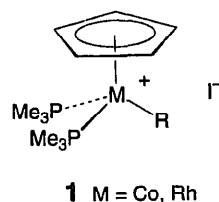
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[1] Ref. [9] provides an overview of this area.

Two mechanisms were considered to account for these observations: a two-electron process involving nucleophilic attack of the metal at the alkyl group, or an initial electron transfer reaction followed by radical coupling [11]. Not unexpectedly, the former is favored for the primary alkyl systems, but the greater stability of the secondary or tertiary alkyl radical, together with steric effects on nucleophilic displacement at carbon, are expected to favor the one-electron pathway. No intermediates en route to the ring alkylated products were observed, but initial alkylation at the metal center, followed by migration of the bulky secondary or tertiary alkyl group to the cyclopentadienyl ring and intermolecular abstraction of the resultant exo-H were proposed [11]. While oxidative additions of fluoroalkyl iodides (R_F–I) to low valent metal centers were reported early on in the development of organometallic chemistry [12,13], they have not been subjected to mechanistic scrutiny. Owing to the powerful electron withdrawing effect of fluorine, the carbon–iodine bond in R_F–I is polarized in the opposite sense to hydrocarbon analogues [14], and nucleophilic attack by the metal at carbon is clearly an unlikely initial event in such reactions. Here we report reactions of fluoroalkyl iodides in which reaction site selectivity is controlled simply by changing ligands on Co(I) from CO to PMe_3, and suggest that an outer sphere electron transfer pathway provides a plausible and consistent mechanism. Some reactions of rhodium analogues have already been reported [15].

As King et al. reported [12], we also find that $[Co(\eta^5\text{-}C_5H_5)(CO)_2]$ reacts with perfluoro-n-propyl iodide in benzene to afford the oxidative addition product 3 with loss of CO and formation of a cobalt–carbon bond. This product reacts with excess PMe_3 to afford the cationic complex 4. [2]
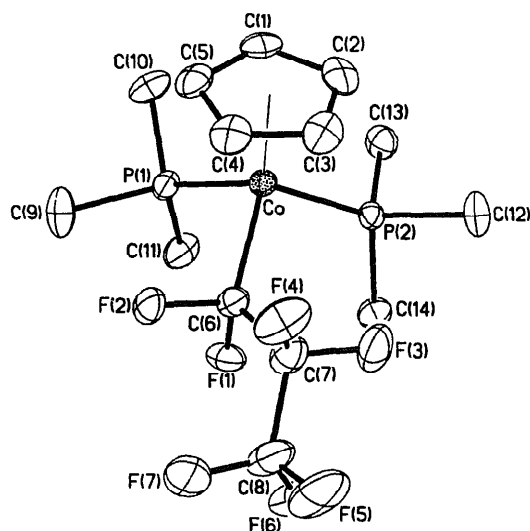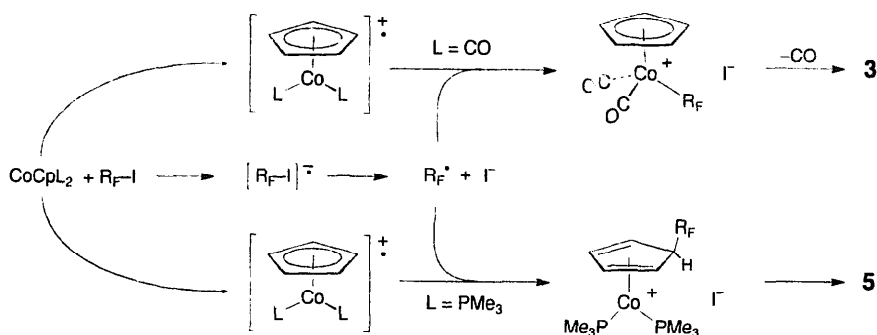

Fig. 1. ORTEP diagram with labeling scheme for 4. Thermal ellipsoids are drawn at 30% probability. Thermally active fluorine atoms were anisotropically refined but spherically depicted for clarity. The iodide counterion, co-crystallized solvent molecule, and hydrogen atoms are not depicted for clarity. Selected bond distances (Å) and angles (deg). Co–C(6), 1.968(6); Co–P(1), 2.237(2); Co–P(2), 2.226(2); Co–C(1), 2.109(6); Co–C(2), 2.111(6); Co–C(3), 2.092(6); Co–C(4), 2.094(6); Co–C(5), 2.089(6); C(6)–F(1), 1.394(6); C(6)–F(2), 1.379(7); C(6)–C(7), 1.529(9). P(1)–Co–P(2), 97.03(6); P(1)–Co–C(6), 91.2(2); P(2)–Co–C(6), 97.4(2).

PMe_3, the major product being the neutral complex $[Co(\eta^5\text{-}C_5H_5)(C_3F_7)I(PMe_3)]$ [16]. We have determined the molecular structure of 4, which crystallizes as a dihydrate, by X-ray crystallography; an ORTEP is shown in Fig. 1, along with representative bond lengths and angles. [3] The closest structure for comparison is that of $[Co(\eta^5\text{-}Indenyl)(C_3F_7)\{P(OMe)_3\}_2][SbF_6]$, which contains trimethylphosphite instead of trimethylphosphine, and an indenyl instead of a cyclopentadienyl ligand [16]. The $Co\text{-}CF_2$ distance in this latter cationic complex, 1.95(1) Å, is not significantly different from the analogous distance in 4, 1.968(6) Å, and is similar to other $Co\text{–}CF_2$ distances found in neutral analogues $[Co(\eta^5\text{-}C_5H_5)(CF_2C_6F_5)I(CO)]$, 1.990(7) Å [17], $[Co(\eta^5\text{-}Indenyl)(n\text{-}C_3F_7)I(Ph_2PNHCH(CH_3)(Ph))]$ 1.962(2) Å [18], $[Co(\eta^5\text{-}Indenyl)(n\text{-}C_3F_7)(PMe_3)(P(O)(OMe)_2)]$ 1.972(4) Å [16], $[Co(\eta^5\text{-}Indenyl)(n\text{-}C_3F_7)(PMe_3)(P(O)Ph(OMe))]$, 1.987(7) Å [16], $[Co(\eta^5\text{-}Indenyl)(n\text{-}C_3F_7)(PMe_2Ph)(P(O)Ph(OMe))]$ 1.979(5) Å [16], and

3   4

This complex has previously been reported as a by-product in the reaction of 3 with one equivalent of

Scheme 1.

$[Co(\eta^5-C_5H_5)(n-C_3F_7)(PMe_3)(P(O)Ph(OMe))]$ 1.968(4) Å [16]. The ^{1}H NMR spectrum of the cis-PMe$_3$ ligands in 4 was simulated as an $X_3AA'X'_3$ spin system. [4] Complex 4 is stable at room temperature, and shows no aptitude for migration of the fluoroalkyl group to the cyclopentadienyl ring.

In contrast, reaction of perfluoro-n-propyl iodide with $[Co(\eta^5-C_5H_5)(PMe_3)_2]$ shows no evidence for alkylation at cobalt to give 4, but instead affords alkylation at the cyclopentadienyl ring to give the cyclopentadiene complex 5. [5]
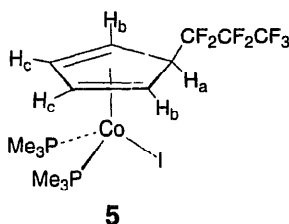
5

^{1}H and ^{19}F NMR spectroscopy confirm the structure of 5; in particular, a large coupling constant is observed between the vicinally related tertiary ^{1}H and ^{19}F atoms of the α-CF$_2$ group. While we have no confirming X-ray crystallographic data, the perfluoropropyl group in 5 is assumed to be exo since a similar coupling pattern is observed in a crystallographically characterized rhodium analogue [15].

As this point we have no direct evidence for intermediates in either of these reactions; monitoring by NMR revealed no CIDNP effects. However, these results, and

those of related rhodium analogues [15], indicate that the reaction pathway is dictated by the metal center, since the fluoroalkyl group is the same in both systems. The inertness of 4 emphasizes that fluoroalkylation at the metal clearly does not precede fluoroalkylation at the ring, as suggested for ring alkylations observed with hydrocarbon alkyl iodides [11]. There is a considerable body of evidence to suggest that oxidative addition reactions of hydrocarbon iodides with transition metal centers proceed via initial electron transfer from the metal to the alkyl iodide [9,11]. Electrochemical studies have shown that fluorocarbon iodides are more easily reduced than their hydrocarbon analogues [19], and they are known to react with a variety of nucleophiles by single electron transfer to give $[R_F-I]^{\cdot-}$, with subsequent rapid collapse to give I^- and $R_F^{\cdot}$ [19,20]. A consistent mechanism would involve electron transfer from cobalt to the fluoroalkyl iodide as the first step, as suggested [15] for the corresponding rhodium system (Scheme 1). Combination of $R_F^{\cdot}$ with the resultant $[Co(C_5H_5)L_2]^{\cdot+}$ radical cation, either at the metal (L = CO) or at the ring (L = PMe$_3$), would then determine the product. However, we cannot discount a mechanism involving a two-electron attack at the iodine, to give the fluorinated carbanion R_F^- [21] and $[Co(C_5H_5)L_2I]^+$; attack of R_F^- at cobalt or at the ring could also be determined by the ancillary ligands present on the metal. Attempts to differentiate between radical and carbanionic mechanisms by experimental and computational means are presently under way.

In summary, we have demonstrated that it is possible to control the site of fluoroalkylation by a primary fluoroalkyl group simply by choice of ligand on cobalt. Eventually, such control of fluoroalkylation sites may be useful in methodology for the synthesis of fluoroalkylated ligands bound to transition metals.

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[4] ^{1}H NMR spectra of the cis-PMe$_3$ ligands were simulated as $X_3AA'X'_3$ spin systems using the computer program gNMR 3.6 (Cherwell Scientific).

[5] 5: 75%; m.p.: 135–139°C; ^{1}H NMR (C$_6$D$_6$): δ 4.92 (br s, 2H, H$_c$), 3.46 (t, J_{H-F} = 14 Hz, 1H, H$_a$), 2.39 (br s, 2H, H$_b$), 0.87 (mult, 18H, P(CH$_3$)$_3$); ^{19}F NMR (C$_6$D$_6$): δ −84.6 (t, J_{F-F} = 10 Hz, 3F, CF$_3$), −125.7 (m, J_{F-F} = 10 Hz, J_{H-F} = 14 Hz, 2H, α-CF$_2$), −130.7 (br s, 2F, β-CF$_2$).

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