Ancillary Ligand-Controlled Selectivity for Metal or Cyclopentadienyl Ring Fluoroalkylation in Reactions of Fluoroalkyl Iodides with Cyclopentadienylrhodium Complexes

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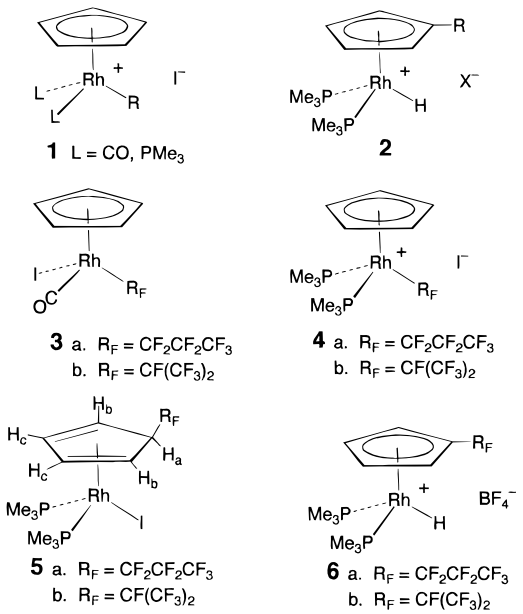
Received October 3, 1996[⊗]

Summary: Reactions of $[Rh(\eta^5\text{-}C_5H_5)(CO)_2]$ *with isomeric primary and secondary fluoroalkyl iodides proceed by selective fluoroalkylation at the metal center to give* $[Rh(\eta^5\text{-}C_5H_5)(CO)(R_F)I]$*, and treatment of these compounds with excess* PMe_3 *affords cationic fluoroalkyl complexes* $[Rh(\eta^5\text{-}C_5H_5)(PMe_3)_2(R_F)]^+I^-$*. In contrast, reactions of* $[Rh(\eta^5\text{-}C_5H_5)(PMe_3)_2]$ *with the same fluoroalkyl iodides proceed with completely different selectivity to afford ring-exo-fluoroalkylated products* $[Rh(\eta^4\text{-}C_5H_5R_F)(PMe_3)_2I]$*, which, in turn, react with* $Ag^+BF_4^-$ *to give the cationic hydrido complexes* $[Rh(\eta^5\text{-}C_5H_4R_F)(PMe_3)_2H]^+[BF_4]^-$.

Oxidative addition of carbon−iodine bonds to low-valent transition metal centers is an important method for synthesis of metal−carbon bonds, and reactions of hydrocarbon alkyl iodides have been extensively studied. Depending on the metal and the alkyl halide, two-electron and a variety of one-electron mechanisms have been shown to operate.[1] Reactions of primary alkyl iodides with $[M(\eta^5\text{-}C_5H_5)(CO)_2]$ (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 and afford an ionic species **1** (L = CO) (Chart 1), which can undergo CO ligand loss or alkyl migration to CO, each with incorporation of iodide.[2] The more nucleophilic metal centers in $[M(\eta^5\text{-}C_5H_5)(PMe_3)_2]$ (M = Co, Rh) react with primary alkyl iodides to give analogous cations **1** (L = PMe_3), but with bulkier alkyl groups such as ^{i}Pr or ^{t}Bu, alkylated cyclopentadienyl complexes **2** are observed.[3] No intermediates en route to the ring-alkylated products were observed, but 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.[3] The former is favored for the primary alkyl systems, but the greater stability of the secondary or tertiary alkyl radical, coupled with steric effects on nucleophilic displacement at carbon, would favor the one-electron pathway. In both cases, initial alkylation at the metal center was proposed, with subsequent migration of the bulky secondary or tertiary alkyl group to the cyclopentadienyl ring and intermolecular abstraction of the resultant *exo*-H to give the observed product.[3] While oxidative additions of fluoroalkyl iodides (R_F−I) to low-valent metal centers were reported early on in the development of organometallic chemistry,[4] the mechanisms of these reactions have not been studied. However, since the carbon−iodine bond in R_F−I is polarized in the opposite sense to hydrocarbon analogues,[5] nucleophilic attack by the metal at carbon is clearly an unlikely initial event in such reactions. Here we report complete changes in reaction site selectivity in reactions of fluoroalkyl iodides that are not a function of whether the alkyl group is primary or secondary. The reaction selectivity is controlled simply and cleanly by changing ligands on Rh(I) from CO to PMe_3 and affords the first apparent examples of *exo*-fluoroalkylation of an organic ligand rather than the metal center.

Chart 1



[⊗] Abstract published in *Advance ACS Abstracts,* December 15, 1996.

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S0276-7333(96)00848-5 CCC: $14.00

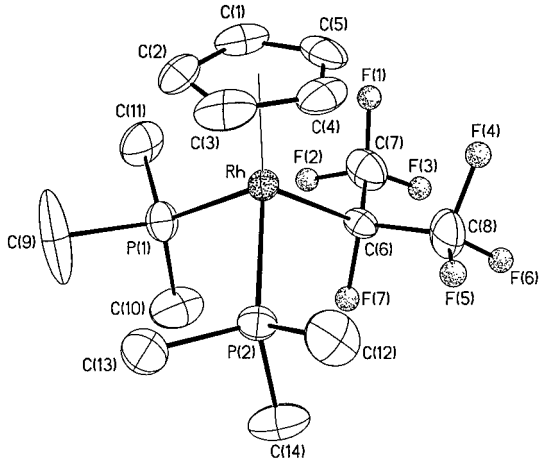

Figure 1. ORTEP diagram with labeling scheme for **4b**. Thermal ellipsoids are drawn at 30% probability. Thermally active fluorine atoms were anisotropically refined but spherically depicted for clarity. The iodide counterion, cocrystallized solvent molecule, and hydrogen atoms are not depicted for clarity. Selected bond distances (Å) and angles (deg): Rh−C(6), 2.153(9); Rh−P(1), 2.322(3); Rh−P(2), 2.319(3); Rh−C(1), 2.239(10); Rh−C(2), 2.222(9); Rh−C(3), 2.214(9); Rh−C(4), 2.229(10); Rh−C(5), 2.222(9); C(6)−F(7), 1.377(9); C(6)−C(7), 1.53(2); C(6)−C(8), 1.53(2): (P(1)−Rh−P(2) 94.46(10); P(1)−Rh−C(6), 93.4(2); P(2)−Rh−C(6), 94.6(2).

In agreement with the pioneering work of Wilkinson[6] we find that [Rh(η^5-C_5H_5)$(CO)_2$] reacts with perfluoro-*n*-propyl iodide in THF at −78 °C to afford the oxidative addition product **3a** with loss of CO and formation of a rhodium−carbon bond; an analogous reaction occurs with the secondary perfluoroisopropyl iodide to give **3b**.[7] Each of these products reacts with excess PMe_3 to afford the cationic complexes **4**.[8] The molecular structure of the perfluoroisopropyl complex **4b** has been determined by X-ray crystallography; an ORTEP is shown in Figure 1, along with representative bond lengths and angles.[9] Complexes **4** are stable at room temperature, and neither shows any aptitude for migration of the fluoroalkyl group to the cyclopentadienyl ring.

In contrast, reactions of the same fluoroalkyl iodides with [Rh(η^5-C_5H_5)$(PMe_3)_2$] under the same conditions of solvent and temperature show no evidence for alkylation at rhodium to give **4** but instead afford exclusive alkylation at the cyclopentadienyl ring to give the cyclopentadiene complexes **5**.[10] The molecular structure of the perfluoroisopropyl derivative **5b** has been determined crystallographically; an ORTEP is shown in Figure 2, along with representative bond lengths and angles.[11] Most significantly, this structure confirms the *exo*-stereochemistry of the fluoroalkyl group. ^{1}H and ^{19}F NMR spectroscopy indicate a correspondence between the solid-state structure of **5b** and its solution structure; in particular a large coupling constant is observed between the vicinally related tertiary ^{1}H and ^{19}F atoms.[10b] Similar coupling is observed in the perfluoro-*n*-propyl analogue **5a**.[10a] While we have no confirming X-ray data, the fluoroalkyl group in **5a** is assumed to be *exo* for the following reasons. Solid-state IR spectroscopy (KBr) of both complexes **5a,b** indicates that the tertiary cyclopentadiene hydrogen is *endo*; in analogous cyclopentadiene complexes *exo*-C−H bonds have unusu-

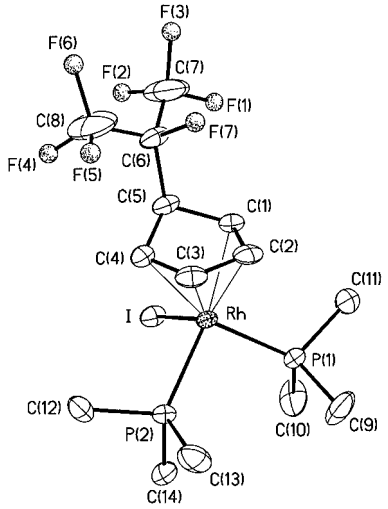

Figure 2. ORTEP diagram with labeling scheme for the cation of **5b**. Thermal ellipsoids are drawn at 30% probability. Thermally active fluorine atoms were anisotropically refined but spherically depicted for clarity. Hydrogen atoms are not depicted for clarity. Selected bond distances (Å) and angles (deg): Rh−I, 2.7621(10); Rh−P(1), 2.300(2); Rh−P(2), 2.294(2); Rh−C(1), 2.210(8); Rh−C(2), 2.127(8); Rh−C(3), 2.116(8); Rh−C(4), 2.214(8); C(1)−C(2), 1.436(11); C(2)−C(3), 1.400(12); C(3)−C(4), 1.419(11); C(4)−C(5), 1.480(12); C(1)−C(5), 1.510(12); C(6)−F(7), 1.362(11); C(5)−C(6), 1.567(11); C(6)−C(7), 1.49(2); C(6)−C(8), 1.445(14): P(1)−Rh−P(2), 95.13(8); P(1)−Rh−I, 97.03(6); P(2)−Rh−I, 92.89(7).

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(7) **3b**: 68%, mp 139−141 °C; IR (THF) ν_{CO} 2087 cm^{-1}; ^{1}H NMR (C_6D_6) δ 4.64 (s, 5H, C_5H_5); ^{19}F NMR (C_6D_6) δ −69.7 (ddq, J_{F-F} = 10 Hz, J_{Rh-F} = 2 Hz, 3F, CF_3), −72.1 (ddq, J_{F-F} = 10 Hz, J_{Rh-F} = 2 Hz, 3F, CF_3), −158.1 (dqq, J_{F-F} = 10 Hz, J_{Rh-F} = 2Hz, 1F, CF). Anal. Calcd for $C_9H_5F_7IORh$ (519.94): C, 21.97; H, 1.02. Found: C, 21.74; H, 1.24.

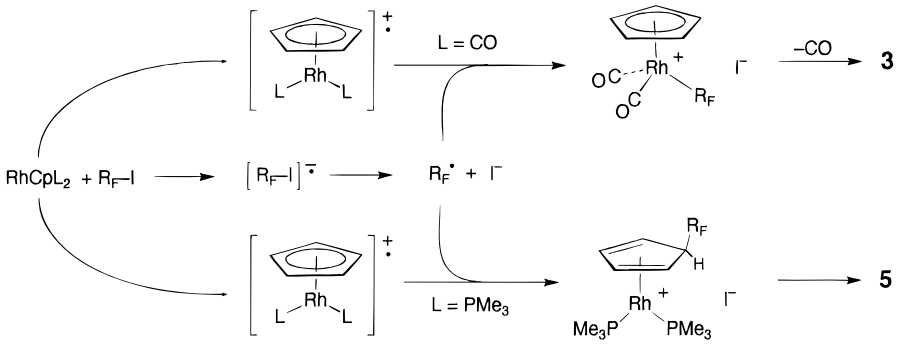
(8) **4a**: 68%, mp 202−205 °C; ^{1}H NMR ($CDCl_3$) δ 5.93 (s, 5H, C_5H_5), 1.89 (mult,[17] $^2J_{P-H}$ = −14.1 Hz, $^4J_{P-H}$ = 3.0 Hz, $^2J_{P-P}$ = −57 Hz, $^3J_{Rh-H}$ = −1.0 Hz, 18H, $P(CH_3)_3$); ^{19}F NMR ($CDCl_3$) δ −66.2 (br,m, 2F, α-CF_2), −82.2 (t, J_{F-F} = 11.5 Hz, 3F, CF_3), −117.1 (br, m, 2F, β-CF_2); ^{31}P {^{1}H} NMR ($CDCl_3$) δ 8.3 (d, J_{Rh-P} = 136 Hz, $P(CH_3)_3$). Anal. Calcd for $C_{14}H_{23}F_7IP_2Rh$ (616.09): C, 27.29; H, 3.76. Found: C, 27.19; H, 3.74. **4b**: 61%, mp 176−179 °C; ^{1}H NMR ($CDCl_3$) δ 5.8 (s, 5H, C_5H_5), 1.79 (mult,[17] $^2J_{P-H}$ = −14.4 Hz, $^4J_{P-H}$ = 2.6 Hz, $^2J_{P-P}$ = −59 Hz, $^3J_{Rh-H}$ = −1.4 Hz, 18H, $P(CH_3)_3$); ^{19}F NMR ($CDCl_3$) δ −70.4 (d, J_{F-F} = 8 Hz, 6F, CF_3), −178.78 (m, 1F, CF); ^{31}P{^{1}H}NMR ($CDCl_3$) δ 4.7 (d, J_{Rh-P} = 133 Hz, $P(CH_3)_3$). Anal. Calcd for $C_{14}H_{23}F_7IP_2Rh$ (616.09): C, 27.29; H, 3.76. Found: C, 27.31; H, 3.66.

(9) Crystallographic data for **4b**·$CHCl_3$: monoclinic, $P2_1/n$, Z = 4, a = 11.512(2) Å, b = 17.621(2) Å, c = 12.865(2) Å, b = 101.43(1)°, V = 2558.0(5) Å^3, D_{calc} = 1.910 g/cm^3; Mo Kα radiation (λ = 0.710 73 Å); 3346 independent reflections with 2.14° < θ < 22.50° collected, 4240 reflections used in refinement with $I > 3\sigma(I)$; R = 0.0470, R_w = 0.0718, GOF = 1.031. A cocrystallized molecule of chloroform solvent was located in the asymmetric unit of structure **4b**.

(10) (a) **5a**: 90%, mp 94 °C; ^{1}H NMR (C_6D_6) δ 5.22 (t, J_{H-F} = 7.8 Hz, 1H, H_a), 4.67 (br s, 2H, H_c), 3.15 (br s, 2H, H_b), 0.87 (mult,[17] $^2J_{P-H}$ = −10.1 Hz, $^4J_{P-H}$ = 1.1 Hz, $^2J_{P-P}$ = −33 Hz, $^3J_{Rh-H}$ = −1.0 Hz, 18H, $P(CH_3)_3$); ^{19}F NMR (C_6D_6) δ −84.41 (t, J_{F-F} = 9.5 Hz, 3F, CF_3), −123.22 (m, J_{H-F} = 7.8 Hz, J_{F-F} = 9.5 Hz, 2H, α-CF_2), −130.02 (br s, 2F, β-CF_2); ^{31}P{^{1}H} NMR (C_6D_6) δ −13.5 (d, J_{Rh-P} = 131 Hz, $P(CH_3)_3$). Anal. Calcd for $C_{14}H_{23}F_7IP_2Rh$ (616.09): C, 27.29; H, 3.76. Found: C, 26.8; H, 3.99. (b) **5b**: 91%, mp 121 °C; ^{1}H NMR (C_6D_6) δ 5.30 (d, J_{H-F} = 23.7 Hz, 1H, H_a), 4.65 (br s, 2H, H_c), 3.23 (br s, 2H, H_b), 0.85 (mult,[17] $^2J_{P-H}$ = −10.6 Hz, $^4J_{P-H}$ = 1.8 Hz, $^2J_{P-P}$ = −39 Hz, $^3J_{Rh-H}$ = −1.0 Hz, 18H, $P(CH_3)_3$); ^{19}F NMR (C_6D_6) δ −76.6 (d, J_{F-F} = 7.6 Hz, 6F, CF_3), −189.94 (d sept, J_{H-F} = 23.7 Hz, J_{F-F} = 7.6 Hz, 1F, CF); ^{31}P{^{1}H} NMR (C_6D_6) δ −14.2 (d, J_{Rh-P} = 136 Hz, $P(CH_3)_3$). Anal. Calcd for $C_{14}H_{23}F_7IP_2Rh$ (616.09): C, 27.29; H, 3.76. Found: C, 26.86; H 3.74.

(11) Crystallographic data for **5b**: monoclinic, $P2_1/n$, Z = 4, a = 8.233(3) Å, b = 12.168(3) Å, c = 21.577(7) Å, b = 96.67(3)°, V = 5630(5) Å^3, D_{calc} = 1.906 g/cm^3; Mo Kα radiation (λ = 0.710 73 Å); 2795 independent reflections with 2.53° < θ < 22.52° collected, 3867 reflections used in refinement with $I > 3\sigma(I)$; R = 0.0473, R_w = 0.0539, GOF = 1.903. Attempts to resolve the disorder in the trifluoromethyl moieties in **5b** were less than satisfactory, and the trifluoromethyl moieties were treated as rigid, idealized tetrahedral groups with an average, refined carbon to fluorine interatomic distance.

Scheme 1



ally distinctive low-frequency stretches at approximately 2800 cm^{-1}.[12] Finally, reactions of **5** with $Ag^+BF_4^-$ afford the cationic hydrido complexes **6**, consistent with iodide abstraction from the metal, followed by expected migration of the *endo*-H from carbon to rhodium.[13]

We have no direct evidence for intermediates in these reactions based on NMR observations of the reacting system. However the results clearly indicate that the reaction pathway is dictated by the metal center and not by relative stabilities of primary and secondary fluoroalkyl radicals[5,14] or carbanions.[15] A consistent mechanism would involve electron transfer from rhodium to the fluoroalkyl iodide as the first step (Scheme 1). Fluoroalkyl iodides are known to react with a variety of nucleophiles by single electron transfer to give $[R_F-I]^{\bullet-}$ with subsequent rapid collapse to give I^- and $R_F^{\bullet}$. Combination of $R_F^{\bullet}$ with the resultant $[Rh(C_5H_5)L_2]^{\bullet+}$ radical cation either at the metal (L = CO) or at the ring (L = PMe_3) would then determine the product. Clearly, we cannot discount a mechanism involving a two electron attack at the iodine, to give the fluorinated carbanion R_F^- [15] and $[Rh(C_5H_5)L_2I]^+$; the site of attack of the fluorinated carbanion at rhodium or at the ring could also be determined by the ancillary ligands present on the metal. However, complexes **4**, with metal−fluoroalkyl bonds, are clearly not intermediates en route to fluoroalkylation at the ring, as suggested for ring alkylations observed with hydrocarbon alkyl iodides.[3]

In summary, we have demonstrated that it is possible to control the site of fluoroalkylation by primary and secondary fluoroalkyl groups, simply by choice of ligand on rhodium. Control of fluoroalkylation site is important in methodology for the synthesis of fluoroalkylated ligands bound to transition metals. Such fluoroalkylated ligands are of potentially significant interest as a means of increasing the solubility of transition metal and main group metal complex reagents and catalysts in saturated fluorocarbon (fluorous) media and in supercritical CO_2.[17] We are presently engaged in attempts to further elucidate the mechanisms of fluoroalkylation in this and other systems, to extend the range of fluoroalkyl groups used, and to differentiate between radical and carbanionic mechanisms, by experimental and computational means.

Acknowledgment. R.P.H. acknowledges support of this research by the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Supporting Information Available: Tables giving details of the X-ray structure determinations, atomic coordinates and isotropic thermal parameters, bond lengths and bond angles, anisotropic displacement parameters, and hydrogen atom coordinates, for **4b**·$CHCl_3$ and **5b** (10 pages). Ordering information is given on any current masthead page.

OM960848P

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(13) **6a**: 35%; ^1H NMR (CD_3COCD_3) δ 6.16 (br m, 2H, C_5H_4), 6.02 (br m, 2H, C_5H_4), 1.89 (mult,[17] $^2J_{P-H} = -14.4$ Hz, $^4J_{P-H} = 2.9$ Hz, $^2J_{P-P} = -55$ Hz, $^3J_{Rh-H} = -1.2$ Hz, 18H, $P(CH_3)_3$), −13.1 (tdd, $J_{P-H} = 29.7$ Hz, $J_{Rh-H} = 23.1$ Hz, $J_{F-H} = 4.4$ Hz); ^{19}F NMR (CD_3COCD_3) δ −84.5 (t, $J_{F-F} = 9.5$ Hz, 3F, CF_3), −106.2 (br m, 2F, α-CF_2), −130.6 (br s, 2F, β-CF_2), −155.4 (s, 4F, BF_4); $^{31}P\{^1H\}$ NMR (CD_3COCD_3) δ 9.9 (d, $J_{Rh-P} = 136$ Hz, $P(CH_3)_3$). Anal. Calcd for $C_{14}H_{23}BF_{11}P_2Rh$: C, 29.19; H, 4.02. Found: C, 29.46; H, 4.19. **6b**: 56%, ^1H NMR (CD_3COCD_3) δ 6.08 (br m, 2H, C_5H_4), 6.01 (br m, 2H, C_5H_4), 1.89 (mult,[17] $^2J_{P-H} = -14.2$ Hz, $^3J_{P-H} = 2.6$ Hz, $^2J_{P-P} = -47$ Hz, $^3J_{Rh-H} = -1.3$ Hz, 18H, $P(CH_3)_3$), −13.0 (tdd, $J_{P-H} = 29.7$ Hz, $J_{Rh-H} = 23.1$ Hz, $J_{F-H} = 4.4$ Hz); ^{19}F NMR (CD_3COCD_3) δ −79.7 (d, $J_{F-F} = 8.8$ Hz, 6F, CF_3), −155.2 (s, 4F, BF_4), −171.2 (sept, $J_{F-F} = 8.3$ Hz, 1F, CF); $^{31}P\{^1H\}$ NMR (CD_3COCD_3) δ 8.7 (d, $J_{Rh-P} = 133$ Hz, $P(CH_3)_3$).

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(16) ^1H 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).

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