Organometallics **2002,** *21,* 243−246

Reactions of Perfluoroisopropyl Iodide with Cyclopentadienyl−Rhodium Complexes in Methanol. An Unexpected Route to a Rhodium−Fulvalene Complex

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Received July 9, 2001

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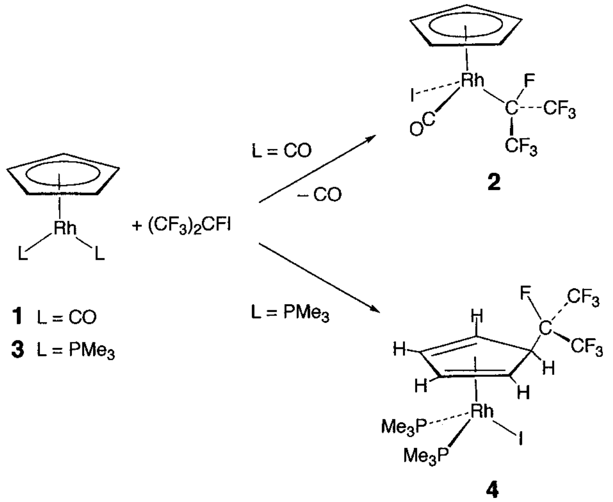
Published on December 6, 2001 on http://pubs.acs.org | doi: 10.1021/om010611f

Summary: Reaction of perfluoroisopropyl iodide with $Rh(C_5H_5)(PMe_3)_2$ *generates a perfluorocarbanion intermediate along with* $[Rh(C_5H_5)(PMe_3)_2I]^+$*, which react to give fluoroalkylation of the cyclopentadienyl ring. When the intermediate fluorocarbanion is trapped by* CH_3OD *to give* $(CF_3)_2CFD$*, the resultant methoxide anion reacts with* $[Rh(C_5H_5)(PMe_3)_2I]^+$ *to give a dinuclear fulvalene complex that has been characterized crystallographically.*

Introduction

Perfluoroalkyl iodides (R_FI) react with $Rh(C_5H_5)(CO)_2$ (**1**)[1] and its cobalt analogue[2] to give a formal oxidative addition reaction, with exclusive formation of fluoroalkyl−metal complexes **2**, as exemplified by the example shown in Scheme 1. However, when the ancillary ligands are changed from CO to PMe_3, the course of the reaction changes, and complex **3** affords product **4**, resulting from fluoroalkylation at the cyclopentadienyl ring instead of at the metal.[1,2] Variation in the site of fluoroalkylation has also been observed in reactions of $M(C_5H_5)_2(C_2H_4)$ (M = Mo, W) with R_FI, in which fluoroalkylation can occur at the metal, at the cyclopentadienyl ring, or at the ethylene ligand, depending on the nature of the R_F group.[3] To distinguish between the possibility of fluoroalkyl radicals and fluoroalkyl anions as intermediates in these group 6 reactions, we used a method previously described[4] and carried them out in the presence of CH_3OD as a trap; an $R_F^{\bullet}$ radical would be trapped as R_FH, and carbanionic R_F^- as R_FD,[5] products easily distinguished using ^{19}F NMR spectroscopy.[6] In the case of primary fluoroalkyl substrates, we were unable to trap any fluoroalkyl intermediates, but in the case of secondary substrates, significant formation of R_FD was observed, providing evidence for the presence of fluoroalkyl carbanions as intermediates in ring fluoroalkylation.[3] The mechanism for reaction with perfluoroisopropyl iodide was proposed to be that shown in Scheme 2, with nucleophilic attack of the metal at the $\delta+$ charged iodine with formation of intermediate **5** and R_F^-; the carbanion attacks the Cp ring to give **6** or is trapped by CH_3OD to give R_FD. The methoxide anion resulting from trapping of R_F^- was shown to appear in product **7**, presumably resulting from attack of CH_3O^- on the ethylene ligand of **5**.[3]

Scheme 1



We have now applied the same trapping procedure to the cyclopentadienyl rhodium system shown in Scheme 1 and have found an unexpected byproduct.

Results and Discussion

Carrying out the reactions of perfluoroisopropyl iodide with cyclopentadienyl−rhodium complexes in the presence of CH_3OD affords results analogous to those observed in the group 6 systems.[3] Whenever fluoroalkylation at the metal is observed, as in the reaction of **1**, no intermediates are trapped and the product **2** is formed exclusively with no observable $(CF_3)_2CFD$ or $(CF_3)_2CFH$. Presumably trapping of an $R_F^{\bullet}$ or R_F^- intermediate at the metal is fast compared to trapping by an external reagent. However, when perfluoroisopropyl iodide reacts with **3** in the presence of CH_3OD, significant formation of $(CF_3)_2CFD$ is observed, along with previously characterized product **4**[1] and an additional organometallic product, identified as the dinuclear fulvalene complex **8** by a single-crystal X-ray

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10.1021/om010611f CCC: $22.00 © 2002 American Chemical Society
Publication on Web 12/06/2001

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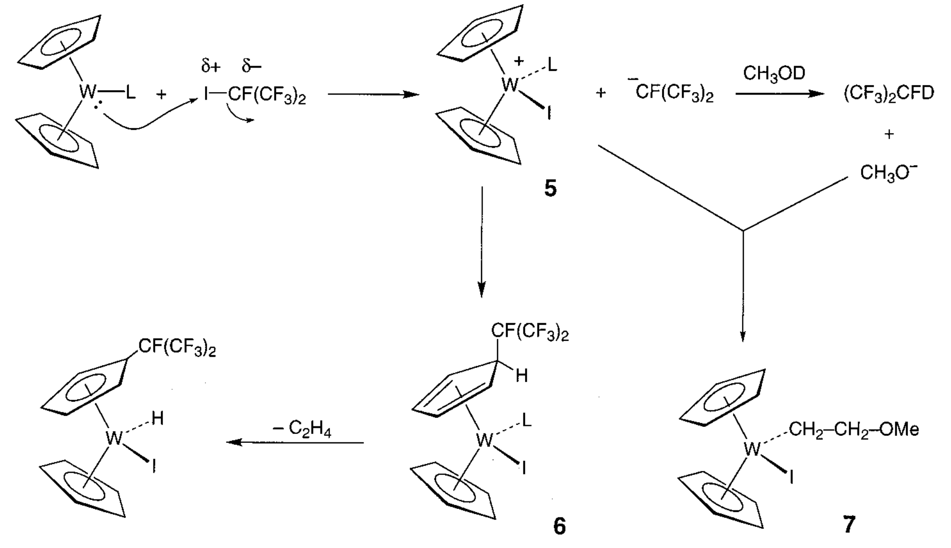
Scheme 2



Scheme 2 (L = C_2H_4)

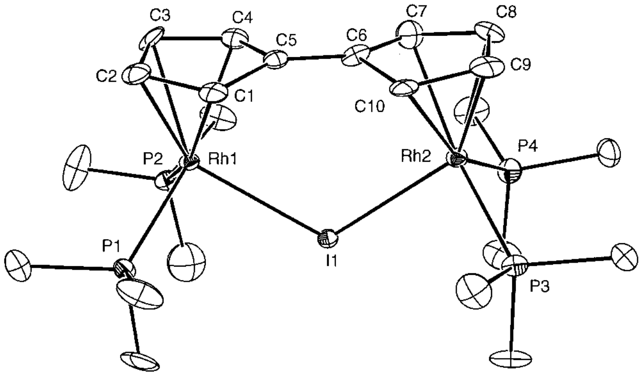


Figure 1. ORTEP diagram of the non-hydrogen atoms of **8**, showing the atom labeling scheme. Thermal ellipsoids are shown at the 30% level.

diffraction study. An ORTEP diagram of the dinuclear monocationic portion is shown in Figure 1. Details of the crystallographic determination are provided in Table 1, and selected bond lengths and angles are in Table 2.

The cationic portion of the molecule contains a single bridging iodo ligand, with the second anionic iodide in two half-occupancy positions in the lattice; one of these is on an inversion center, but the other is in a general position. Consequently, the structure is of reduced quality due to iodide ion disorder. However, the bond distances are sufficiently different for some general conclusions to be drawn. The fulvalene ligand exhibits metal−carbon distances more consistent with an η^4:η^4 than an η^5:η^5 structure. Carbon atoms C(1)−C(4) are significantly closer to Rh(1) [average 2.26(2) Å], and C(7)−C(10) to Rh(2) [average 2.26(2) Å], compared to the Rh(1)−C(5) and Rh(2)−C(6) distances of 2.551(14) and 2.563(12) Å, respectively. In addition, the C(5)−C(6) distance of 1.38(2) Å is significantly shorter than the average C−C distance in the C(1)−C(5) ring [average 1.46(2) Å] and the C(6)−C(10) ring [average 1.44(2) Å]. Consequently, the structural parameters are more consistent with the η^4:η^4-Rh(I)−Rh(I) form **8**, rather than an η^5:η^5-Rh(II)−Rh(II) structure **10**; the latter structural type is far more common in other dinuclear fulvalene complexes of rhodium[7−9] and other metals.[10−32]

Table 1. Crystal Data and Summary of X-ray Data Collection for 6

complex	**6**
formula	$C_{35}H_{27}F_7P_2Pt$
fw	837.60
space group	$P2_1/c$
a, Å	10.192(3)
b, Å	18.106(8)
c, Å	17.018(3)
α, deg	90
β, deg	91.008(17)
γ, deg	90
V, Å3	3140.0(17)
Z	4
D(calcd), g/cm^3	1.772
abs coeff, mm^{-1}	4.637
temp, K	293(2)
diffractometer	Siemens P4
radiation	Mo Kα, 0.71073 Å
R(*F*), %[a]	3.95
R(*wF*^{2}), %[a]	10.03

[a] Quantity minimized = $R(wF^2) = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[(wF_o^2)^2]^{1/2}$; $R = \Sigma\Delta/\Sigma(F_o)$, $\Delta = |(F_o - F_c)|$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 6

bond lengths (Å)		bond angles (deg)	
Pt(1)−C(19)	2.072(7)	C(19)−Pt(1)−C(33)	177.1(3)
Pt(1)−C(33)	2.186(8)	C(19)−Pt(1)−P(2)	81.67(19)
Pt(1)−P(2)	2.2770(18)	C(33)−Pt(1)−P(2)	97.96(16)
Pt(1)−P(1)	2.2818(18)	C(19)−Pt(1)−P(1)	81.35(19)
C(33)−C(34)	1.376(12)	C(33)−Pt(1)−P(1)	98.89(16)
C(34)−C(35)	1.547(13)	P(2)−Pt(1)−P(1)	162.89(8)
F(1)−C(33)	1.374(8)	C(34)−C(33)−Pt(1)	120.2(5)
F(2)−C(33)	1.370(7)	F(2)−C(33)−F(1)	104.2(6)
F(3)−C(34)	1.412(9)	F(4)−C(34)−F(3)	104.8(6)
F(4)−C(34)	1.388(9)	C(33)−C(34)−C(35)	120.7(7)
F(5)−C(35)	1.274(11)	F(5)−C(35)−F(7)	110.5(10)
F(6)−C(35)	1.351(11)	F(5)−C(35)−F(6)	108.9(9)
F(7)−C(35)	1.340(11)	F(7)−C(35)−F(6)	106.3(8)

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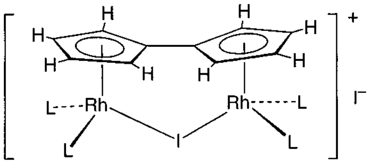

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The solution spectra of **8** are also consistent with this conclusion. The two sets of fulvalene protons appear as multiplets at δ 5.59 and 2.52 ppm in the ^{1}H NMR spectrum of **8**; the high field chemical shift is inconsistent with η^5:η^5-fulvalene complexes of rhodium, in which the fulvalene protons all resonate in the δ 4−6 ppm region.[7,8] The chemical shifts of the fulvalene protons in **8** are more consistent with those of η^4 conjugated diene complexes of rhodium.[33]

How is **8** formed in this reaction? It appears clear from our trapping experiment that the initial step in the fluoroalkylation mechanism is analogous to that proposed for group 6 systems (vide supra)[3] and that reaction of **3** with perfluoroisopropyl iodide affords the intermediate cation **9** and the $(CF_3)_2CF^-$ anion, as shown in Scheme 3. Subsequent attack of the anion on the Cp ring of **9** affords **4**. However, when $(CF_3)_2CF^-$ is trapped with methanol, methoxide is produced, and **8** is formed. Control experiments verify that neither starting complex **3** nor product **4** react with methanol. The cation **9**, prepared independently, does react with methoxide to afford **8**, as predicted. While the mechanism of this transformation is unclear, and radical pathways cannot be excluded for this part of the reaction sequence, a possible pathway thats fits the experimental observations is shown in Scheme 4.

Conclusions

Reaction of perfluoroisopropyl iodide with RhCp$(PMe_3)_2$ (**3**) generates a perfluorocarbanion intermediate along with $[RhCp(PMe_3)_2I]^+$ (**9**), which react to give **4** by fluoroalkylation of the cyclopentadienyl ring. When the intermediate fluorocarbanion is trapped by CH_3OD to give $(CF_3)_2CFD$, the resultant methoxide anion reacts with **9** to give fulvalene complex **8**.

Experimental Section

General Considerations. Unless otherwise noted, all reactions were performed in oven-dried glassware, using standard Schlenk techniques, under an atmosphere of nitrogen, which had been deoxygenated over BASF catalyst and dried using Aquasorb, or using drybox techniques. THF, diethyl ether, hexanes, and CH_2Cl_2 were dried and degassed over alumina columns under N_2. ^{1}H (300 MHz), ^{31}P (121 MHz), and ^{19}F (282 MHz) NMR were recorded on a Varian UNITY plus 300 System in the solvent indicated. ^{1}H NMR chemical shifts were referenced to TMS using the protio impurity in the solvent peak, ^{19}F chemical shifts to internal $CFCl_3$, and ^{31}P chemical shifts to external H_3PO_4. Microanalysis were performed by Schwarzkopf Microanalytical Laboratory (Woodside, NY).

RhCp$(CO)_2$,[34] RhCp$(PMe_3)_2$,[35] and $[RhCp(PMe_3)_2I]^+I^-$ [36] were prepared by literature routes. $(CF_3)_2CFI$ (Aldrich) was purified by washing with a solution of sodium thiosulfate to remove iodine, followed by washing with water and then drying over magnesium sulfate and deoxygenation by several cycles of freeze−evacuate−thaw. CH_3OD (Aldrich) was used as received.

Control Experiments. Samples of complexes RhCp$(CO)_2$, RhCp$(PMe_3)_2$, **4**, and $[RhCp(PMe_3)_2I]^+I^-$ were shown not to undergo any reaction with CH_3OD. Photolysis of $(CF_3)_2CFI$, to give the $(CF_3)_2CF^\bullet$ radical, in CH_3OD afforded only $(CF_3)_2CFH$, identified by its ^{19}F NMR spectrum,[6] by abstraction from the weaker CH bond.[5]

Trapping Experiments. A sample of RhCp$(CO)_2$ (0.047 g, 0.210 mmol) in C_6D_6 (0.6 mL) was treated with CH_3OD (14 μL, 0.420 mmol), and then $(CF_3)_2CFI$ (75 μL, 0.252 mmol) was added. NMR monitoring of the reaction indicated that the only product formed was RhCp$[(CF_3)_2CF](CO)I$, as previously reported.[1]

A sample of RhCp$(PMe_3)_2$ (0.010 g, 0.0312 mmol) in C_6D_6 (0.6 mL) was treated with CH_3OD (1 μL, 0.0312 mmol), and then $(CF_3)_2CFI$ (4.4 μL, 0.0312 mmol) was added. The solution rapidly turned red, and NMR monitoring of the reaction indicated approximately 50% conversion to complex **4**, with formation of complex **8**, identified as described below, and $(CF_3)_2CFD$, identified by its ^{19}F NMR spectrum.[6] No formation of $(CF_3)_2CFH$ was observed.

Synthesis of 8. $[RhCp(PMe_3)_2I]I$ (0.150 g, 0.261 mmol) was suspended in methanol (20 mL) and NaOMe (0.100 g, 1.922 mmol) was added. The solution was stirred for 2 days during which time the solid dissolved and the solution became dark red. The methanol was removed and the residue was extracted

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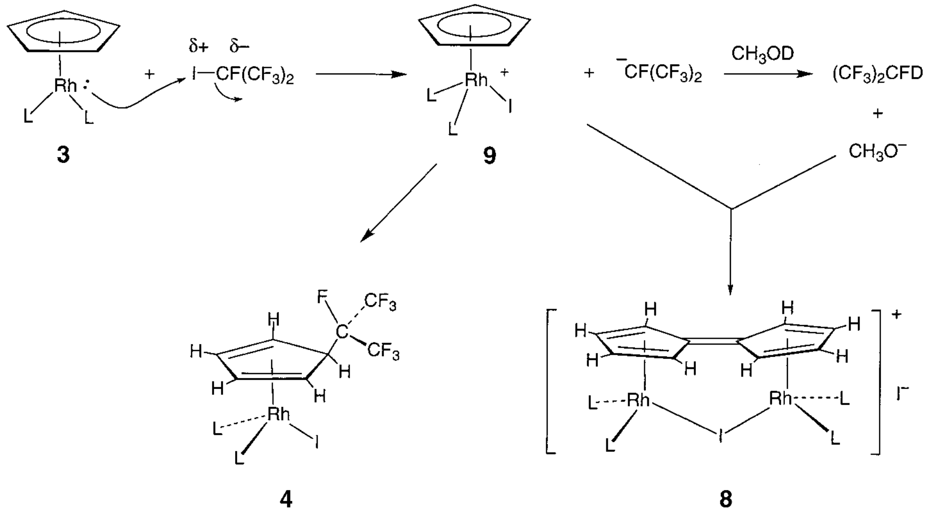
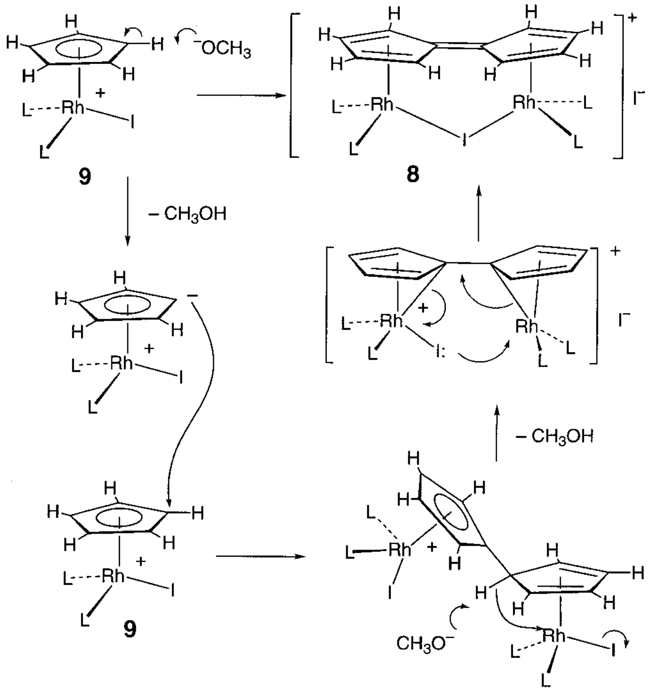
Scheme 3



Scheme 3 (L = PMe_3)

Scheme 4



Scheme 4 (L = PMe_3)

with a dichloromethane/hexane (3:1) mixture (15 mL) and filtered. All solvent was removed and this procedure was repeated. The dark red residue was dissolved in acetone (7 mL) and filtered, and the volume was reduced to 1−2 mL. The flask was placed in a freezer (−20 °C) to crystallize the product (0.025 g, 25%): mp ~220 °C dec; ^{1}H NMR (CD_2Cl_2) δ 5.59 (br s, 4H, $C_{10}H_8$), 2.52 (m, 4H, $C_{10}H_8$), 1.43 (m, 36H, PMe_3); ^{13}C{^{1}H}NMR (CD_2Cl_2) δ 95.3 (dt, J_{CRh} = 3 Hz, $^2J_{CP}$ = 2 Hz, $C_{5,6}$), 82.2 (d, J_{CP} or J_{CRh} = 6 Hz, $C_{10}H_8$), 78.9 (m, $C_{10}H_8$), 33.8 (m, PMe_3). ^{31}P{^{1}H}NMR (CD_2Cl_2) δ ∠1.5 (d, J_{PRh} = 116 Hz, PMe_3). Calcd for $C_{22}H_{44}I_2P_4Rh_2$: C, 29.62; H, 4.97. Found: C, 29.42; H 4.78.

Crystallographic Structural Determination. Crystal, data collection, and refinement parameters are collected in Table 1. The systematic absences in the diffraction data are uniquely consistent for the reported space groups. The structure was solved using direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures. A DIFABS absorption correction was applied. All non-hydrogen atoms were refined with anisotropic displacement coefficients, and hydrogen atoms were treated as idealized contributions. All software and sources of the scattering factors are contained in the SHELXTL (5.10) program library.

Acknowledgment. R.P.H. is grateful to the National Science Foundation and to the Petroleum Research Fund, administered by the American Chemical Society, for generous financial support. Useful discussions with Professor Clark R. Landis are also acknowledged.

Supporting Information Available: Atomic fractional coordinates, bond distances and angles, and anisotropic thermal parameters for complex **8**. This material is available free of charge via the Internet at http/::pubs.acs.org.

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