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Cyclopentadienylcobalt and -rhodium Complexes Containing Monocyclic and Bicyclic Valence Isomers of Octafluorocyclooctatetraene: Crystal and Molecular Structures of the Exo and Endo Isomers of (η-Cyclopentadienyl)(2–5-η-octafluorobicyclo[4.2.0]octa-2,4,7-triene)rhodium(I)

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Thermal reaction of $[Rh(C_5H_5)(C_2H_4)_2]$ with OFCOT, **1**, initially affords $[Rh(C_5H_5)(C_2H_4)(\eta^2\text{-}C_8F_8)]$, **2**, which loses ethylene to give $[Rh(C_5H_5)(1,2,5,6\text{-}\eta\text{-}C_8F_8)]$, **3**. Reaction of the indenyl derivative $[Rh(\eta^5\text{-}C_9H_7)(C_2H_4)_2]$ with OFCOT yields only $[Rh(\eta^5\text{-}C_9H_7)(1,2,5,6\text{-}\eta\text{-}C_8F_8)]$, **4**. OFCOT reacts with $[Co(C_5H_5)(CO)_2]$ to give low yields of $[Co(C_5H_5)(1,2,5,6\text{-}\eta\text{-}C_8F_8)]$, **5**. In contrast OFCOT reacts with $[Rh(C_8H_{14})_2Cl]_2$ at room temperature to displace both cyclooctene ligands and yield a product, $[Rh(C_8F_8)Cl]_n$, which in turn reacts with $Tl(C_5H_5)$ to give a 3:2 mixture of the mononuclear derivatives **7** and **8**. Displacement of cyclooctene by OFCOT at higher temperatures, followed by reaction with $Tl(C_5H_5)$, affords only **8**. Both **7** and **8** contain the octafluorobicyclo[4.2.0]octatriene valence isomer of OFCOT, as demonstrated by single-crystal X-ray diffraction studies on both compounds. Crystal data for **7**: space group $P2_1/c$ (No. 9), $a = 7.044$ (1) Å, $b = 15.180$ (1) Å, $c = 12.305$ (1) Å; $\beta = 109.10°$; $V = 1243.4$ Å^3; $Z = 4$; $R = 0.022$, $R_w = 0.033$. Crystal data for **8**: space group $P2_1/c$ (No. 9), $a = 7.226$ (3) Å, $b = 11.406$ (3) Å, $c = 15.745$ (4) Å; $\beta = 104.43°$; $V = 1256.7$ Å^3; $Z = 4$; $R = 0.030$, $R_w = 0.031$.

Introduction

The organometallic chemistry of cyclooctatetraene (COT) has been thoroughly studied and has resulted in the synthesis of molecules which have provided considerable stimuli to an understanding of bonding and dynamic behavior of coordinated hydrocarbons.[3] We have embarked on a study of the transition-metal chemistry of the corresponding fluorocarbon octafluorocyclooctatetraene (OFCOT), **1**,[4,5] and have reported significant differences in reactivity in comparison to COT. OFCOT undergoes oxidative addition reactions to low-valent metal centers to afford 1,2,3,6-η-bonded compounds with retention of the monocyclic ring,[6–8] oxidative addition with ring closure to yield the octafluorobicyclo[3.3.0]octadienediyl ligand,[7,8] and metalation reactions to produce mono- and disubstituted cyclooctatetraene rings.[9,10] In this paper we describe the characterization of some simple 1,2,5,6-η-OFCOT complexes containing cyclopentadienylrhodium and -cobalt moieties, an unprecedented ring-closure reaction of OFCOT in the coordination sphere of Rh(I) to afford complexes containing the new ligand octafluorobicyclo[4.2.0]octatriene and the crystallographic characterization of two of the latter derivatives.

Results

The reaction of OFCOT with $[Rh(C_5H_5)(C_2H_4)_2]$ in hexane at room temperature was slow and resulted in only partial conversion to a species whose ^{1}H and ^{19}F NMR spectra were consistent with the 1,2-η-OFCOT complex **2**. Heating resulted in displacement of the second ethylene ligand and formation of the 1,2,5,6-η complex **3**, which exhibited a characteristic ^{19}F NMR spectrum containing only two fluorine resonances: one at δ 116.4 due to the four fluorine atoms on the uncoordinated double bonds and one at δ 163.8 corresponding to the four fluorine atoms on the coordinated olefins. In the corresponding reaction of the indenylrhodium complex $[Rh(\eta^5\text{-}C_9H_7)(C_2H_4)_2]$ with OFCOT, only the 1,2,5,6-η OFCOT complex **4** could be observed, even at ambient temperature. Reaction of $[Co(C_5H_5)(CO)_2]$ with OFCOT required elevated temperatures in octane solution and resulted in formation of low yields of the 1,2,5,6-η complex **5**. The formation and characterization of traces of a ring-closed (octafluorobicyclo[3.3.0]dienediyl)cobalt complex **6** in the thermal, solvent-free reaction of these same reagents in a sealed tube has been described in a previous communication.[7]

In contrast to the reaction of the 18-electron complex $[Rh(C_5H_5)(C_2H_4)_2]$ with OFCOT, reaction of the labile, 16-electron bis(cyclooctene)rhodium complex $[Rh(C_8H_{14})_2Cl]_2$ with OFCOT in benzene solution at room temperature, followed by removal of the volatiles under vacuum, resulted in complete displacement of the hydrocarbon ligands and isolation of a brown, amorphous material, which was only sparingly soluble in organic solvents and which analyzed as $[Rh(C_8F_8)Cl]_n$. This material exhibited a medium-intensity IR band at 1769 cm^{-1}. Treatment of this material with $(C_5H_5)Tl$ in acetonitrile resulted in precipitation of TlCl and formation of a volatile, yellow crystalline substance, whose microanalysis and mass spectrum clearly indicated the formulation $[Rh(C_5$-

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(2) Alfred P. Sloan Research Fellow, 1980–1984.

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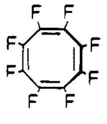

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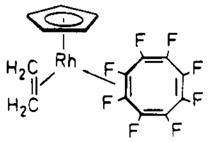

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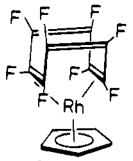

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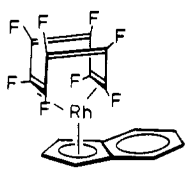

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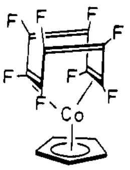

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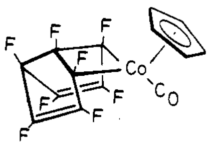
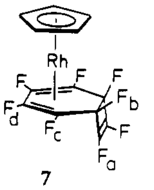


6

H$_5$)(C$_8$F$_8$)] and which retained the fluoroolefin stretch in the IR spectrum at 1771 cm^{-1}. Examination of the ^{19}F NMR spectrum of this material, however, demonstrated the presence of two isomers in a ratio of 3:2, each containing four ^{19}F resonances of equal intensity. This ratio remained unchanged after prolonged reflux in xylene solution. While the components could not be separated by column chromatography, careful fractional sublimation of the mixture allowed separation of small amounts of the major isomer, which was characterized as having structure 7 by a single-crystal X-ray diffraction study.



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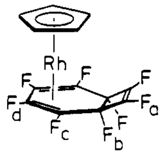

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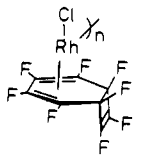

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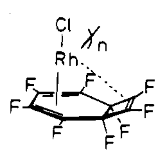

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If the reaction of OFCOT with [Rh(C$_8$H$_{14}$)$_2$Cl]$_2$ was carried out in refluxing benzene or if the room temperature reaction was worked up by solvent evaporation using a rotary evaporator with a heating bath, subsequent treatment of the brown residue with (C$_5$H$_5$)Tl afforded only one isomer of [Rh(C$_5$H$_5$)(C$_8$F$_8$)], whose ^{19}F NMR spectrum was identical with that of the minor isomer of the room temperature reaction and which was characterized by X-ray diffraction as having structure 8.

Compounds 7 and 8 did not interconvert after refluxing for several hours in xylenes nor did they isomerize to 3. Similarly compounds 3–5 were resistant to isomerization under these conditions.

Details of the crystallographic determinations are presented in Table I. ORTEP drawings of 7 and 8 are shown in Figure 1 and 2, and selected bond distances and angles are contained in Table II. More complete information is provided as supplementary material.[11]

Discussion

Thermal displacement by OFCOT of ethylene from the 18-electron cobalt and rhodium complexes M(η-C$_5$H$_5$)L$_2$ (M = Rh, L = C$_2$H$_4$; M = Co, L = CO) to give complexes 3 and 5 is not unexpected, although the yields are disappointing in the case of 5. The stepwise nature of this reaction is evidenced by spectroscopic observation of an intermediate, 2, containing an apparently η^2-OFCOT ligand. Complex 2 is similar to the known compound Rh(C$_5$H$_5$)(C$_2$H$_4$)(C$_2$F$_4$),[12] in that it contains a hydrocarbon and a fluorocarbon olefin bound to the same metal center. Notably the OFCOT ligand in 2 is nonfluxional with respective to ring whizzing on the NMR time scale, as demonstrated by the observation of four sharp ^{19}F resonances. This is compatible with similar NMR observations on η^2-OFCOT complexes Fe(η^2-OFCOT)(CO)$_4$,[6] Pt(η^2-OFCOT)L$_2$,[6] and M(η-C$_5$Me$_5$)(η^2-OFCOT)(*t*-BuNC) (M = Co, Rh)[8] and also with hydrocarbon analogues Mn(η-C$_5$H$_5$)(η^2-COT)(CO)$_2$[13a] and [Fe(η-C$_5$H$_5$)(η^2-COT)(CO)$_2$]$^+$.[13b] Also not surprising is the more facile thermal displacement of ethylene from the indenyl derivative Rh(η^5-C$_9$H$_7$)(C$_2$H$_4$)$_2$ to give 4; possibly slippage of the indenyl ligand to η^3-coordination facilitates this reaction.

The ^{1}H and ^{19}F NMR spectra of 3, 4, and 5 clearly indicate the presence of only a single 1,2,5,6-η isomer in solution. Each of the three compounds exhibits two ^{19}F NMR signals, one around 119 ppm (upfield of CFCl$_3$) and one with a higher field chemical shift which varies significantly with the metal and ancillary ligands. Accordingly the higher field resonance in each case has been assigned to the fluorine atoms attached to the coordinated olefinic groups. Observation of a single isomer for 5 contrasts with reports on the hydrocarbon analogue in which an equilibrium mixture of isomers Co(η-C$_5$H$_5$)(1,2,5,6-η-COT) and Co(η-C$_5$H$_5$)(1-4-η-COT) is observed in solution.[14] The behavior of 3 and 5 also differs from their pentamethylcyclopentadienyl analogues in which intramolecular redox equilibrium between 1,2,5,6-η and 1,2,3,6-η coordination of the OFCOT ring is observed.[7,8] Compounds 3, 4, and 5 are all air-stable and have resisted all attempts to induce further hapticity changes or ring closure reactions.

In light of these results, it is most interesting that reaction of OFCOT with the dimeric 16-electron Rh(I) complex [Rh(cyclooctene)$_2$Cl]$_2$, followed by treatment of the crude product with Tl(C$_5$H$_5$), does not afford any traces of 3 but instead affords a 3:2 mixture of 7 and 8. While the immediate precursor to these compounds could not be characterized by ^{19}F NMR spectroscopy due to solubility problems, the presence of an absorption at 1769 cm^{-1}, characteristic of a strained fluorinated olefin,[15] in the IR spectra both of this material and of 7 and 8 suggests that the ring closure of OFCOT to its bicyclo[4.2.0]octatriene valence isomer has occurred prior to introduction of the cyclopentadienyl ring. Therefore the precursors to 7 and

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[11] See note at end of text regarding supplementary material.

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[15] The corresponding value for the cyclobutene olefin stretch in the free fluorocarbon perfluorobicyclo[4.2.0]octa-2,4,7-triene is 1773 cm^{-1}.[16]

Table I. Crystallographic Summary

	isomer 7	isomer 8
A. Crystal Data (−110 °C)[a]		
crystallizatn	sublimatn	hexane
a, Å	7.044 (1)	7.226 (3)
b, Å	15.180 (1)	11.406 (3)
c, Å	12.305 (1)	15.745 (4)
β, deg	109.10 (1)	104.43 (3)
V, Å^3	1243.4	1256.7
d_{calcd}, g cm^{-3} (−110 °C)	2.223	2.200
empirical formula	$C_{13}F_8H_5Rh$	$C_{13}F_8H_5Rh$
fw	416.0	416.0
cryst system	monoclinic	monoclinic
space group	$P2_1/c$ (no. 9)	$P2_1/c$ (no. 9)
Z	4	4
$F(000)$, electrons	800	800
B. Data Collection (−110 °C)[b]		
radiation λ, Å	Mo Kα, 0.710 69	Mo Kα, 0.710 69
mode	ω scan	ω scan
scan range	symmetrically over 1.0° about $K\alpha_{1,2}$ maximum	
background	offset 1.0 and −1.0° in ω from $K\alpha_{1,2}$ maximum	
scan rate, deg min^{-1}	2.0–5.0	2.0–5.0
exposure time, h	31.3	44.8
stability analysis		
computed s	−0.000 01 (2)	−0.000 26 (7)
t	0.000 000 (1)	0.000 001 (2)
correctn range (on *I*)	not applied	1.000–1.012
2θ range, deg	4.0–60.0	4.0–60.0
total reflctns measd	2847	3653
data cryst volume, mm^3	0.0364	0.0143
data cryst faces	$0\bar{2}\bar{1}$, 021, {001}	$0\bar{1}1$, $01\bar{1}$, {011}
data cryst faces	$01\bar{1}$, $0\bar{1}1$, {100}	{010}, 110, $\bar{1}\bar{1}0$, fragment
abs coeff μ(Mo Kα), cm^{-1}	14.26	14.26
transmissn factor range	0.652–0.751	0.717–0.794
C. Structure Refinement[c]		
ignorance factor p	0.02	0.02
reflections used, $F > n(\sigma_F)$	2695, 4.0	3071, 4.0
no. of variables	220	205
R, wR	0.022, 0.033	0.030, 0.031
R for all data	0.030	0.040
max shift/esd	0.19	0.23
max peak in diff map, e Å^{-3}	0.56	1.20

[a] Unit-cell parameters were obtained by least-squares refinement of the setting angles of reflections with $18.0 < 2\theta < 22.0°$; 45 such reflections were used for isomer A and 30 for isomer B. [b] Syntex $P2_1$ autodiffractometer with a graphite monochromator and a Syntex LT-1 inert-gas (N_2) low-temperature delivery system. Data reduction was carried out as described in; Riley, P. E.; Davis, R. E. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1976**, *B32*, 381. Crystal and instrument stability were monitored by remeasurement of four check reflections after every 96 reflections. These data were analyzed as detailed in: Henslee, W. H.; Davis, R. E. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1975**, *B31*, 1511. [c] Relevant expressions are as follows, where *F* represents the structure factor amplitude. Function minimized was $\Sigma w(F_o - F_c)^2$, where $w = (\sigma_F)^{-2}$. $R = \Sigma \text{abs}(F_o - F_c)/\Sigma F_o$. $wR = [\Sigma w(F_o - F_c)^2/\Sigma w F_o^2]^{1/2}$.

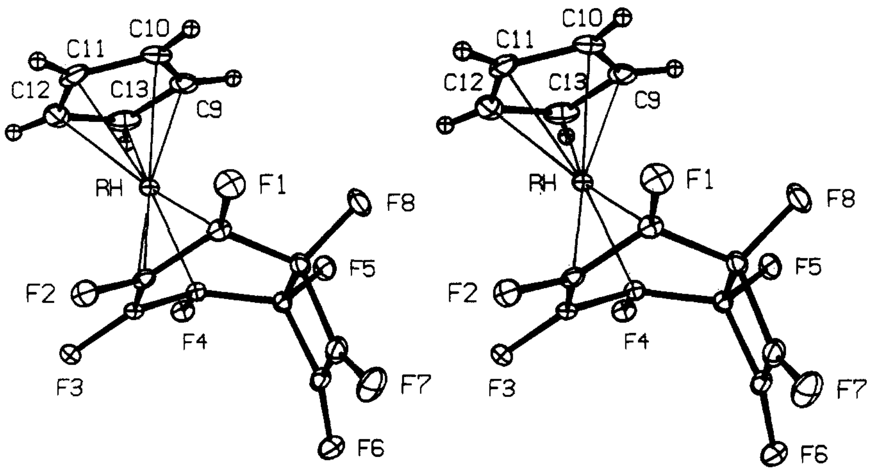

Figure 1. ORTEP stereoview of complex **7**, with 30% probability ellipsoids for non-hydrogen atoms.

8 appear to be the chloride-bridged (possibly polymeric) species **9** and **10**. Notably carrying out the reaction at higher temperatures affords only **8**, indicating that its precursor **10** may be thermodynamically preferred and that

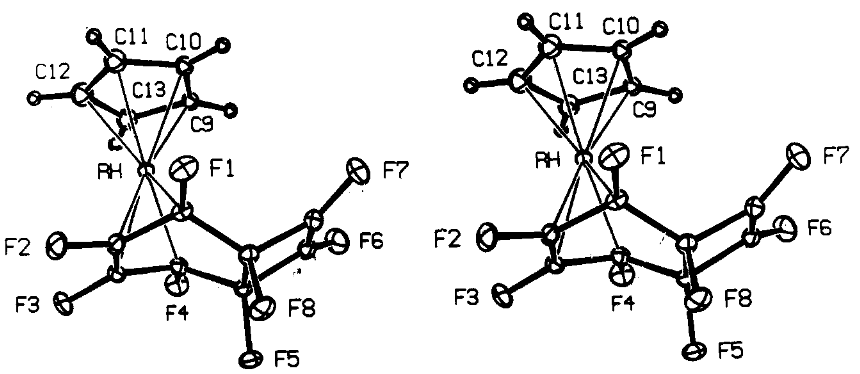

Figure 2. ORTEP stereoview of complex 8, with 30% probability ellipsoids for non-hydrogen atoms.

Table II. Selected Bond Distances (Å) for Complexes 7 and 8

bond	7	8
Rh–C(1)	2.086 (2)	2.085 (3)
Rh–C(2)	2.103 (2)	2.104 (3)
Rh–C(3)	2.102 (2)	2.103 (3)
Rh–C(4)	2.099 (2)	2.083 (3)
C(1)–C(2)	1.426 (3)	1.433 (4)
C(1)–C(8)	1.510 (4)	1.494 (3)
C(2)–C(3)	1.404 (3)	1.408 (4)
C(3)–C(4)	1.433 (4)	1.437 (4)
C(4)–C(5)	1.516 (3)	1.504 (3)
C(5)–C(6)	1.511 (3)	1.491 (4)
C(5)–C(8)	1.562 (3)	1.576 (4)
C(6)–C(7)	1.323 (4)	1.328 (4)
C(7)–C(8)	1.499 (4)	1.491 (4)
C(1)–F(1)	1.365 (3)	1.374 (4)
C(2)–F(2)	1.350 (3)	1.341 (3)
C(3)–F(3)	1.339 (2)	1.336 (3)
C(4)–F(4)	1.366 (3)	1.374 (4)
C(5)–F(5)	1.384 (3)	1.381 (3)
C(6)–F(6)	1.319 (3)	1.325 (4)
C(7)–F(7)	1.321 (3)	1.326 (4)
C(8)–F(8)	1.384 (3)	1.392 (3)

9 is the kinetic product of ring closure. The 18-electron complexes 7 and 8 are thermally stable at temperatures in excess of those required to isomerize 9 to 10, and no sign of isomerization to 3 is observed; 3 also exhibits no proclivity for thermal conversion to 7 and/or 8. The free valence isomer of OFCOT, perfluorobicyclo[4.2.0]octa-2,4,7-triene, has recently been characterized.[16] It exhibits an IR band at 1773 cm^{-1} (argon matrix) due to the cyclobutene ring C═C stretch and ^{19}F NMR resonances at δ 118.3 (F$_a$), 159.1 (F$_b$), 154.5 (F$_c$), and 150.4 (F$_d$). In complexes 7 and 8 therefore, the cyclobutene olefinic fluorine resonance is relatively unperturbed (7, δ 123.5 (F$_a$); 8, δ 124.9 (F$_a$)), whereas the coordinated diene fluorines undergo a significant (ca. 25–30 ppm) upfield shift (7, δ 184.3 (F$_c$), 179.1 (F$_d$); δ 180.0 (Fc), 177.7 (F$_d$)) relative to the free fluorocarbon. Interestingly, the bridgehead fluorines in isomer 7 (δ 175.2 (F$_b$)) also undergo a substantial upfield shift, presumably because they occupy endo positions with respect to the metal, but the corresponding exo fluorines in 8 (δ 158.0 (F$_b$)) remain unperturbed. The upfield shift on coordination has been observed for the diene fluorines in Fe(CO)$_3$ complexes of perfluorocyclohexa-1,3-diene[17] and perfluorocyclohepta-1,3-diene,[18] in Fe(CO)$_4$ complexes of cyclic fluoroolefins,[19] and in various complexes of monocyclic OFCOT[6,7] (also vide infra). In contrast, both exo and endo fluorines on saturated carbons α to coordinated fluoroolefins or dienes have been reported to undergo downfield shifts relative to free fluorocarbon.[17-19]

Compounds 9 and 10 can arise a priori either by selective trapping of traces of the bicyclo[4.2.0]octatriene isomer by a 16-electron Rh(I) center in solution or by a metal-promoted ring closure of OFCOT within the coordination sphere. While OFCOT undergoes Diels–Alder chemistry via this valence isomer the equilibrium lies far to the side of monocyclic OFCOT at ambient temperatures, and the half-life of the bicyclic valence isomer is only 14 min. at 0 °C.[16] It seems unlikely that the bicyclic isomer should be selectively trapped by the metal, especially since 18-electron Rh(I) precursors fail to do so. Moreover conversion of precursor 9 to 10 under conditions of thermodynamic control would require complete dissociation of the bicyclic ligand, following by addition of the metal center to the more hindered face of the fluorodiene, all in the absence of any trapping of monocyclic OFCOT. Accordingly, while the evidence is circumstantial, we feel that it points to Rh(I)-promoted disrotatory electrocyclic ring closure of OFCOT in a 16-electron intermediate, a reaction which does not occur in the corresponding 18-electron system. However it has been shown that 18-electron complexes Fe(1–4-η-COT)(CO)$_3$ (COT = substituted cyclooctatetraene) will isomerize to their *exo*-bicyclo[4.2.0]octatriene valence isomers in refluxing octane.[20] We can only speculate as to whether the initial ring-closure reaction requires η^6-coordination of OFCOT to rhodium, but it seems clear that in order for exo–endo isomerization to occur *more than two coordination sites must be available on the metal*, presumably requiring an η^6-OFCOT intermediate. This is not possible in 7 or 8 without an energetically costly η^5 to η^3 slippage of the cyclopentadienyl ring. We had envisaged that isomerization of the indenyl complex 4 to its bicyclo[4.2.0]octatriene isomer might be facilitated by a similar indenyl ligand slippage, thus creating a vacant coordination site, but this reaction was unsuccessful in refluxing octane.

These conclusions are at variance with that reached by Pettit in his study of the exo and endo isomers 11 and 12, which were inert to interconversion or isomerization to Fe(1–4-η-COT)(CO)$_3$ in refluxing hexane.[21] The conclusion that disrotary electrocyclic opening of the cyclohexadiene ring in 11 or 12 is forbidden because it would lead to an energetically unfavorable, 16-electron η^2-COT intermediate is also valid for an energetically unfavorable, 20-electron η^6-COT intermediate.

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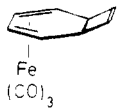
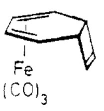
While we do not understand the apparent kinetic preference for formation of **9**, it is possible that the thermodynamic preference for isomer **10**, the precursor to **8**, arises from interaction of the Rh center with the remote cyclobutene double bond to give an 18-electron species as shown, which is subsequently trapped in this configuration as its cyclopentadienyl derivative, with concomitant release of this interaction. Further experiments to test these mechanistic conclusions are in progress.

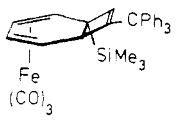
Finally, some comments should be made concerning the structural features of coordinated octafluorobicyclo[4.2.0]octa-2,4,7-triene in **7** and **8** (see Figures 1 and 2). Although the free ligand has recently been isolated,[16] its structural dimensions are unavailable for comparison. Only a single complex, **13**, containing a hydrocarbon bicyclo[4.2.0]octatriene analogue has been structurally characterized,[20] although both exo and endo $Fe(CO)_3$ complexes **11** and **12** of the parent hydrocarbon have been prepared by an indirect method.[21] The internal bond distances in the C_8F_8 ligands of **7** and **8** are very similar, as are the rhodium distances to the coordinated diene carbon atoms (see Table II). The uncoordinated olefins in **7** and **8** are the same length as those in OFCOT itself [1.323 Å (av)][5] and are also identical in length with the cyclobutene olefin in **13** [1.330 (6) Å].[20] The C–F bonds of the uncoordinated olefins are significantly shorter than those in OFCOT [1.346 Å (av)],[5] presumably reflecting somewhat higher carbon s character associated with exocyclic bonds in a strained ring. In contrast, the C–F bond lengths associated with the other formally sp^2 carbons [C(1)–C(4)] in both isomers are longer than those in OFCOT, presumably reflecting some coordination-induced rehybridization toward sp^3; the C(1)–F(1) and C(4)–F(4) distances notably are longer than the C(2)–F(2) and C(3)–F(3) lengths. The overall geometries of the bicyclo[4.2.0]octatriene ligands can be described in terms of three intersecting least-squares planes comprising C(1)–C(2)–C(3)–C(4) [plane 1], C(1)–C(4)–C(5)–C(8) [plane 2], and C(5)–C(6)–C(7)–C(8) [plane 3]. The dihedral angles between planes 1 and 2 are 137.38 (14)° for **7** and 134.36 (16)° for **8**; these compare reasonably well with the corresponding angle of 142° (no esd given) for **13**.[20] The dihedral angles between planes 2 and 3 are 124.21 (14)° for **7** and 121.03 (15)° for **8**, in comparison with a value of 117° (no esd given) for **13**.[20] Perhaps the most significant differences between compounds **7** and **8**, and their hydrocarbon analogue **13** involve the carbon–carbon and metal–carbon bond lengths within the coordinated diene fragments. In **7** and **8** the three carbon–carbon bonds of the 1,3-diene adopt a "long–short–long" sequence, whereas the corresponding three distances in **13** are clearly "short–long–short" as expected for a 1,3-diene.[20] In **7** and **8** the metal–carbon distances to C(1) and C(4) are significantly shorter than those to C(2) and C(3); the reverse is found for **13**.[20] These observations cannot be attributed to different bonding properties of the $Rh(C_5H_5)$ and $Fe(CO)_3$ fragments, since the molecular structure of an $Fe(CO)_3$ complex of perfluorocyclohexa-1,3-diene also exhibits "long–short–long" distances within the 1,3-diene framework and shorter bonds from iron to the terminal diene carbons than to the internal carbons.[22] They can be rationalized if the fluorinated 1,3-diene is a better π-acceptor than its hydrocarbon analogue, with correspondingly greater back-bonding from the metal to the the diene ψ_3 orbital in the former case.



11



12



13

Experimental Section

General Procedures. Reactions were carried out under an atmosphere of dinitrogen which was deoxygenated over BASF catalyst and dried over P_4O_{10}. Hydrocarbon and ethereal solvents were dried by distillation from sodium or potassium benzophenone ketyl. Acetonitrile and methylene chloride were distilled from P_4O_{10}. All solvents were stored and transferred under purified dinitrogen.

^{19}F and ^1H NMR spectra were obtained on a Varian XL-300 or a JEOL FX-60Q spectrometer; ^{19}F chemical shifts are reported in parts per million upfield from internal $CFCl_3$ and ^1H shifts in parts per million downfield from internal tetramethylsilane. Infrared spectra were recorded on a Perkin-Elmer 599 spectrometer and calibrated against the 1601-cm^{-1} peak of polystyrene. Electron-impact (70-eV) mass spectra were run on a Finnegan 4023 spectrometer. Microanalyses were performed by Spang, Eagle Harbor, MI.

$Tl(C_5H_5)$ was purchased from Aldrich and freshly sublimed before use. $Co(C_5H_5)(CO)_2$ was purchased from Pressure Chemical Co. and used as received. OFCOT,[4] $[Rh(C_8H_{14})_2Cl]_2$,[23] $Rh(C_5H_5)(C_2H_4)_2$,[24] and $Rh(\eta^5\text{-}C_9H_7)(C_2H_4)_2$,[25] were prepared by literature procedures.

Reaction of $Rh(C_5H_5)(C_2H_4)_2$ with OFCOT. At Room Temperature. A solution of $Rh(C_5H_5)(C_2H_4)_2$ (0.52 g, 2.3 mmol) and OFCOT (0.62 g, 2.5 mmol) in hexane (10 mL) was stirred for 1 week. The volatiles were removed in vacuo, and the yellow-brown residue was extracted with hexane (4 × 20 mL) until the extract was colorless. The extract was evaporated to dryness to afford a yellow crystalline solid (0.50 g) which comprised $Rh(C_5H_5)(C_2H_4)_2$ (90%) and $Rh(C_5H_5)(C_2H_4)(\eta^2\text{-}C_8F_8)$, **2** (10%), as judged by integration of Cp resonances in the ^1H NMR spectrum. **2** ^{19}F NMR (C_6D_6) δ 91.6 (m, 2 F), 134.4 (m, 2 F), 139.3 (m, 2 F), 156.7 (m, 2 F); ^1H NMR (C_6D_6) δ 5.00 (s, C_5H_5), C_2H_4 resonances obscured by those of $Rh(C_5H_5)(C_2H_4)_2$.

In Refluxing Hexane. A solution of $Rh(C_5H_5)(C_2H_4)_2$ (0.22 g, 0.98 mmol) and OFCOT (0.305 g, 1.23 mmol) in hexane (10 mL) was refluxed for 21 h and then cooled. Filtration removed some insoluble brown material, and removal of the volatiles left a yellow solid, which was recrystallized from hexane to afford yellow crystals of **3** (0.25 g, 61%): mp 130–134 °C; IR (hexane) $\nu_{C=C}$ 1729 cm^{-1}; ^1H NMR (C_6D_6) Δ 5.20 (s, C_5H_5); ^{19}F NMR ($CDCl_3$) δ 116.4 (m, 4 F), 163.8 (m, 4 F); mass spectrum, *m/e* 416 (P^+). Anal. Calcd for $C_{13}H_5F_8Rh$: C, 37.52; H, 1.20. Found: C, 37.83; H, 1.27. Complex **3** was unchanged after refluxing in xylene for 12 h.

Reaction of $Rh(\eta^5\text{-}C_9H_7)(C_2H_4)_2$ with OFCOT. A solution of $Rh(\eta^5\text{-}C_9H_4)_2$ (0.500 g, 1.82 mmol) and OFCOT (0.625 g, 2.52 mmol) in hexane (10 mL) was refluxed for 21 h and cooled to room temperature. Removal of the volatiles in vacuo followed by chromatography of the residue (silica gel/hexane; 1 cm × 4 cm) yielded a yellow band. Evaporation of the eluate and recrystallization of the residue from hexane afforded air-stable, yellow crystals of $Rh(\eta^5\text{-}C_9H_7)(1,2,5,6\text{-}\eta\text{-}C_8F_8)$, **4** (0.285 g, 34%): mp 125–127 °C; IR (hexane) ν C=C 1729 cm^{-1}; ^1H NMR (acetone-d_6) δ 6.21 (d, *J* = 3 Hz, 2 H), 6.62 (t, *J* = 3 Hz, 1 H), 7.70 (m, 4 H); ^{19}F NMR ($CDCl_3$) δ 115.9 (m, 4 F), 165.1 (m, 4 F), 165.1 (m, 4 F); mass spectrum, *m/e* 466 (P^+). Anal. Calcd for $C_{17}H_7F_8Rh$: C, 43.80; H, 1.50. Found: C, 43.94; H, 1.55. Complex **4** was unchanged after refluxing in xylene for 12 h.

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Reaction of $Co(C_5H_5)(CO)_2$ with OFCOT. A solution of $Co(C_5H_5)(CO)_2$(1.00 g, 5.6 mmol) and OFCOT (1.99 g, 8.0 mmol) in *n*-octane (15 mL) was refluxed for 48 h and then cooled. Evaporation of the volatiles and chromatography of the residue (silica gel/hexane; 2 cm × 50 cm) yielded first a large diffuse band containing unreacted $Co(C_5H_5)(CO)_2$ (0.08 g) and then a small bright orange band which was evaporated to dryness. Recrystallization of the residue from hexane yielded orange crystals of $Co(C_5H_5)(1,2,5,6\text{-}\eta\text{-}C_8F_8)$, **5** (0.080 g, 4%): mp 173–174 °C; IR (hexane) $\nu_{C=C}$ 1734 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.29 (s, C_5H_5); ^{19}F NMR ($CDCl_3$) δ 114.0 (m, 4 F), 163.9 (m, 4 F); mass spectrum, *m/e* 372 (p^+). Anal. Calcd for $C_{13}H_5F_8Co$: C, 41.93; H, 1.34. Found: C, 50.06; H, 1.38%.

Reactions of $[Rh(C_8H_{14})_2Cl]_2$ with OFCOT. At Room Temperature. A solution of $[Rh(C_8H_{14})_2Cl]_2$ (0.500 g, 0.70 mmol) and OFCOT (0.700 g, 2.8 mmol) in benzene (40 mL) was stirred for 12 h. The resultant dark brown solution was evaporated to dryness to leave a fine insoluble brown solid which could not be crystallized but which was washed with hexane and dried in vacuo (0.53 g): IR (KBr) $\nu_{C=C}$ 1769 cm^{-1}. Anal. Calcd for $[C_8F_8ClRh]_n$: C, 24.84; H, 0.00. Found: C, 25.30; H, 0.00. On the basis of its reaction with $Tl(C_5H_5)$ [see below] this solid was assumed to be a 3:2 mixture of compounds **9** and **10**. This brown solid (0.45 g) was suspended in acetonitrile (100 mL), $Tl(C_5H_5)$ (0.83 g, 3.1 mmol) was added, and the mixture was stirred for 6 h. The mixture was filtered and the filtrate evaporated to dryness. The residue was dissolved in CH_2Cl_2 (20 mL), and an equal volume of hexane was added to precipitate some insoluble brown material whose IR spectrum lacked any bands attributable to C–F bonds. Filtration and evaporation of the filtrate to dryness left a pale yellow solid (0.30 g, 51% based on Rh starting material), shown by its ^{19}F NMR spectrum to contain a 3:2 mixture of complexes **7** and **8**. Careful sublimation of this mixture (25–30 °C; 0.03 mm) afforded a sample of pure **7**, which was recrystallized from heptane to yield pale yellow crystals (0.103 g): IR (hexane) $\nu_{C=C}$ 1771 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.57 (d, J_{Rh-C} = 2 Hz, C_5H_5); ^{19}F NMR ($CDCl_3$) [see drawing for numbering scheme] δ 123.5 (m, F_a), 175.2 (m, F_b), 184.3 (m, F_c), 179.1 (m, F_d); mass spectrum, *m/e* 416 (P^+). A single crystal was subjected to X-ray crystallographic analysis (see below).

In Refluxing Benzene. A solution of $[Rh(C_8H_{14})_2Cl]_2$ (0.500 g, 0.70 mmol) and OFCOT (0.700 g, 2.8 mmol) in benzene (40 mL) was refluxed for 12 h. The resultant dark brown solution was filtered to remove traces of insoluble material and then evaporated to dryness to yield a brown solid which could not be crystallized but which was washed with hexane and dried in vacuo (0.57 g): IR (KBr) $\nu_{C=C}$ 1769 cm^{-1}. Anal. Calcd for $[C_8F_8ClRh]_n$: C, 24.84; H, 0.00. Found: C, 25.08; H, 0.00. On the basis of its reaction with $Tl(C_5H_5)$ [see below] this solid was assumed to be compound **10**. This brown solid (0.45 g) was suspended in acetonitrile (100 mL), $Tl(C_5H_5)$ (0.83 g, 3.1 mmol) was added, and the mixture was stirred for 6 h. The mixture was filtered, and the filtrate was evaporated to dryness. The residue was dissolved in CH_2Cl_2 (20 mL), and an equal volume of hexane was added to precipitate some insoluble brown material whose IR spectrum lacked any bands attributable to C–F bonds. Filtration and evaporation of the filtrate to dryness left a pale yellow oil (0.40 g, 68% based on Rh starting material), shown by its ^{19}F NMR spectrum to contain only complex **8**. Crystallization from hexane yielded pale yellow crystals (0.32 g): IR (hexane) $\nu_{C=C}$ 1771 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.53 (d, J_{Rh-C} = 2 Hz, C_5H_5); ^{19}F NMR ($CDCl_3$) [see drawing for numbering scheme] δ 124.9 (m, F_a), 158.0 (m, F_b), 180.0 (m, F_c), 177.7 (m, F_d); mass spectrum, *m/e* 416 (P^+). A single crystal was subjected to X-ray crystallographic analysis (see below).

X-ray Diffraction Studies. Single crystals of **7** were obtained by vacuum gradient sublimation, while those of **8** were formed by recrystallization from hexane. For each substance, a single crystal was mounted and transferred to a Syntex $P2_1$ autodiffractometer, where it was maintained in a cold (−110 °C) stream of dry dinitrogen for the duration of the diffraction experiments. Preliminary diffraction studies allowed determination of crystal symmetry and space group and verification of the suitable quality of the crystals for intensity data collection. A summary of pertinent crystal data and details of the X-ray diffraction data collection and processing is presented in Table I. Preliminary processing of the diffraction data was accomplished as described in detail previously,[26,27] including corrections for absorption based on measured crystal shape.

Each structure was solved by the heavy-atom method, using positions determined from a sharpened Patterson map. Both structures were refined by full-matrix least-squares methods, using the program SHELX. For **7**, all non-hydrogen atoms were refined anisotropically and all hydrogen atoms isotropically; an extinction parameter was also refined to a final value of 0.002 43 (18). In the crystal structure of **8**, the C_5H_5 ring was found to be disordered, occupying two positions tilted with respect to one another by about 5° and rotated by approximately 31°. The occupancies of these two orientations were allowed to refine, converging to 0.527 (8) and 0.473 (8). The C_5H_5 atoms were refined isotropically, with each hydrogen riding on its carbon atom. Additional details of the two refinements appear in Table I.

Listing of observed and calculated structure factor amplitudes, final coordinates and thermal parameters, bond lengths and angles, and selected planes for both crystal structures are available.[11]

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Registry No. 1, 57070-35-6; 2, 96666-28-3; 3, 96666-29-4; 4, 96688-73-2; 5, 83781-43-5; 7, 96666-30-7; 8, 96744-25-1; $Rh(C_5H_5)(C_2H_4)_2$, 12211-95-9; $Rh(\eta^5\text{-}C_9H_7)(C_2H_4)_2$, 63428-46-6; $Co(C_5H_5)(CO)_2$, 12078-25-0; $[Rh(C_8H_{14})_2Cl]_2$, 12279-09-3; $Tl(C_5H_5)$, 34822-90-7.

Supplementary Material Available: Tables of observed and calculated structure factor amplitudes, fractional coordinates and equivalent isotropic thermal parameters, aniostiopic thermal parameters, bond distances and angles, and selected least-squares planes for **7** (Supplementary Tables I–V) and **8** (Supplementary Tables VI–X) (41 pages). Ordering information is given on any current masthead page.

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