finement of a fully anisotropic model resulted in a site occupancy ratio of 0.631 (5)/0.369 (5). Though the elongated thermal ellipsoids of C(1) and C(8) are suggestive of disorder in these atoms also, no model in which these atoms were treated with partial occupancy was refined successfully.

Acknowledgment. R.P.H. is grateful to the Air Force Office of Scientific Research (Grant AFOSR-86-0075), the National Science Foundation, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for generous research support. R.E.D. gratefully acknowledges the support of the Robert A. Welch Foundation (Grant F-233).

Supplementary Material Available: Listings of bond lengths and angles, fractional atomic coordinates and isotropic (or equivalent isotropic) thermal parameters for hydrogen and non-hydrogen atoms, anisotropic thermal parameters for non-hydrogen atoms, and torsion angles for **17**, **24**, **22**, and **13** (37 pages); tables of observed and calculated structure factors (87 pages). Ordering information is given on any current masthead page.

Synthesis, Structures, and Conformational Dynamics of Dicobalt Complexes Containing the Hexafluorodidehydrocyclooctatetraene (Hexafluorocycloocta-3,5,7-trien-1-yne) Ligand. Crystal and Molecular Structures of $[(Co(L)(CO)_2)_2(\mu_2\text{-}(1\eta,2\eta)\text{-}C_8F_6)]$ (L = CO, PPh_3, $PPhMe_2$, PMe_3)

Russell P. Hughes,*[,1a] Stephen J. Doig,[1a] Richard C. Hemond,[1a] Wayne L. Smith,[1a,2]
Raymond E. Davis,*[,1b] Steven M. Gadol,[1b] and Katherine D. Holland[1b]

Chemistry Departments, Dartmouth College, Hanover, New Hampshire 03755,
and University of Texas at Austin, Austin, Texas 78712

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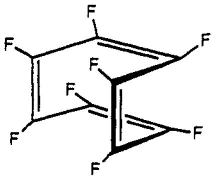
The reactions of the cobalt anions $[Co(CO)_3L]^-$ or the neutral dimers $[Co_2(CO)_6L_2]$ (L = CO, PPh_3, $PPhMe_2$, PPh_2Me, PMe_3, $P(p\text{-tolyl})_3$) with octafluorocyclooctatetraene (OFCOT; **1**) afford the dinuclear μ-hexafluorocyclooctatrienyne complexes **4**, together with mononuclear η^1-heptafluorocyclooctatetraenyl complexes **7**, which are in equilibrium with their heptafluorobicyclo[4.2.0]octatrienyl valence isomers **8**. The conformation of the μ-hexafluorocyclooctatrienyne rings in the four complexes **4** (**a**, L = CO; **b**, L = PPh_3; **c**, L = $PPhMe_2$; **d**, L = PMe_3) has been shown by X-ray crystallographic studies to vary from puckered to planar as the steric bulk of the ligands on the adjacent cobalt atoms increases. Evidence of a weak attractive interaction between the bridging fluorinated ligand and phenyl rings of PPh_3 and $PPhMe_2$ is also presented. Solution NMR studies show that both the steric and electronic interactions are weak. A discussion of the relative barriers to ring inversion in μ-hexafluorocyclooctatrienyne and η^1-heptafluorocyclooctatetraenyl ligands is presented. X-ray data were collected on a Syntex $P2_1$ autodiffractometer at −110 °C, and structures were refined by the full-matrix least-squares method. Crystal data for **4a**: a = 26.808 (6) Å, b = 6.953 (1) Å, c = 17.081 (3) Å, β = 98.10 (1)°, monoclinic $C2/c$, Z = 8, R = 0.026, R_w = 0.030 for 3145 reflections with $F_o \geq 4\sigma(F_o)$. Crystal data for **4b**: a = 20.670 (4) Å, b = 10.038 (2) Å, c = 21.556 (4) Å, β = 108.14 (2)°, monoclinic, $C2/c$, Z = 4, R = 0.055, R_w = 0.053 for 3270 reflections with $F_o \geq 4\sigma(F_o)$. Crystal data for **4c**: a = 10.475 (4) Å, b = 16.604 (5) Å, c = 8.637 (2) Å, α = 99.16 (3)°, β = 91.16 (2)°, γ = 85.74 (2)°, triclinic, $P\bar{1}$, Z = 2, R = 0.034, R_w = 0.036 for 6053 reflections with $F_o \geq 4\sigma(F_o)$. Crystal data for **4d**: a = 7.799 (2) Å, b = 28.071 (7) Å, c = 10.856 (2) Å, β = 98.40 (2)°, monoclinic, $P2_1/c$, Z = 4, R = 0.048, R_w = 0.038 for 4482 reflections with $F_o \geq 4\sigma(F_o)$.

Introduction

Nonplanar ground-state structures for cyclooctatetraene and most of its derivatives are well established.[3] Crystallographic studies of the perfluorinated analogue octafluorocyclooctatetraene (OFCOT; **1**) have shown that fluorination does not result in significant alteration of the skeletal structure.[4] The question of whether the corresponding dehydro[8]annulenes (cycloocta-3,5,7-trien-1-ynes) should be planar or puckered has aroused considerable experimental and theoretical interest. Experimental evidence has been presented for the existence of di-



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(1) (a) Dartmouth College. (b) University of Texas at Austin.

(2) ACS-PRF Summer Faculty Fellow on Sabbatical leave from the Chemistry Department, Colby College, Waterville, ME 04901.

(3) For reviews of the organic and organometallic chemistry of cyclooctatetraene see: (a) Fray, G. I.; Saxton, R. G. *The Chemistry of Cyclooctatetraene and Its Derivatives*; Cambridge University Press: Cambridge, England, 1978. (b) Deganello, G. *Transition Metal Complexes of Cyclic Polyolefins*; Academic Press: New York, 1979.

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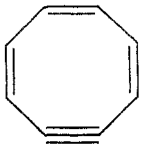
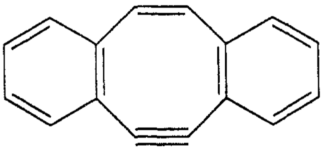
dehydrocyclooctatetraene (**2**) as a reaction intermediate,[5]



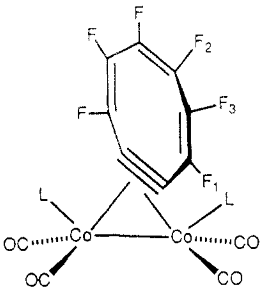
2

and several derivatives with fused benzene rings have been isolated.[6] Theoretical calculations of the structure of the parent compound **2**, and its valence isomers, have been carried out at the MNDO level, resulting in the prediction of a highly strained, planar structure.[7] In agreement, the crystallographically determined structure of 5,6-didehydrodibenzo[*a*,*e*]cyclooctene (**3**) has shown that it possesses a planar eight-membered ring.[8]



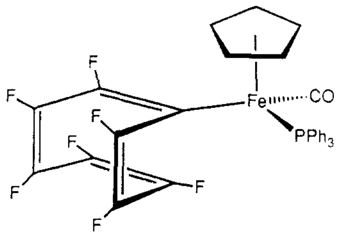
3

We have previously reported on the synthesis and crystal structures of two dinuclear cobalt complexes (**4a**,**b**) containing the μ_2-(1η,2η)-hexafluorocycloocta-3,5,7-trien-1-yne ligand.[9] In complex **4a** the fluorinated ring was severely puckered in the solid state, while in its bis(triphenylphosphine)-substituted analogue **4b** the ring was shown to be planar, sandwiched between the phenyl rings of triphenylphosphine ligands on the adjacent cobalt atoms. These observations indicate that the hexafluorocycloocta-3,5,7-trien-1-yne ring in these compounds can easily be deformed between puckered and planar conformations, although it was unclear whether the planarity of the ring in **4b** was imposed as a result of steric effects of the adjacent phenyl rings or whether some attractive electronic interaction existed between the phenyl groups and the fluorinated ring system.



4a L = CO
4b L = PPh_3
4c L = PMe_2Ph
4d L = PMe_3
4e L = $PMePh_2$

The previous paper in this issue focused on the synthesis, structural characterization, and dynamic properties of transition-metal complexes containing the η^1-heptafluorocyclooctatetraenyl ligand, derived from formal nucleophilic displacement of fluoride from **1** by metal carbonyl anions.[10] Analysis of the kinetic parameters for the isodynamic ring inversion (RI) and bond shift isomerization (BS) processes indicated that both the RI and BS processes in the iron complex **5** had significantly larger activation energies than those in its hydrocarbon analogue **6**,[11] an effect that can only be attributed to the presence of fluorines on the ring. In contrast to the apparent ease of conformational deformation of the fluorinated ring in complexes **4**, the barrier to ring inversion in complex **5** and its relatives is sufficiently high so as to allow room-temperature separation of the (*RR*,*SS*) and (*RS*,*SR*) pairs of diastereoisomers.[10]



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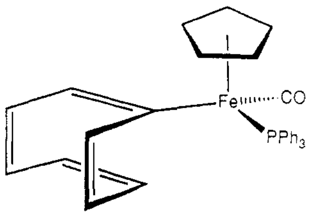

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In order to probe further the conformational dynamics of the hexafluorocycloocta-3,5,7-trien-1-yne ligand, it was decided to prepare a larger series of derivatives via the reactions of cobalt carbonylate anions and neutral dinuclear cobalt carbonyl complexes with OFCOT. Here we report fully on the synthesis and structural characterization of **4a**,**b** as well as the two analogues **4c**,**d** containing phosphines with differing steric and electronic effects.

Results and Discussion

The room-temperature reaction of $Na^+[Co(CO)_4]^-$ with OFCOT afforded no monosubstitution product analogous to **5** after 5 days in THF. However, a red solid was isolated in low yield after extraction of the residue with dichloromethane and purification by column chromatography on Florisil. This complex was characterized as having structure **4a** by single-crystal X-ray crystallography (Table I), and a thermal ellipsoid plot of the structure, which exhibits a severely puckered fluorinated ring, is shown in Figure 1a. The ^{19}F NMR spectrum of **4a** exhibited three resonances of equal intensity (Table II: assignments of ^{19}F NMR resonances were made by $^{19}F\{^{19}F\}$ decoupling).

In contrast, the reaction of a THF solution of $[Co(PPh_3)(CO)_3]^-$ with **1** for 24 h afforded the heptafluorocyclooctatetraenyl complex **7b**, resulting from displacement of one fluoride from OFCOT. As observed for other η^1-heptafluorocyclooctatetraenyl analogues,[10] complex **7a**

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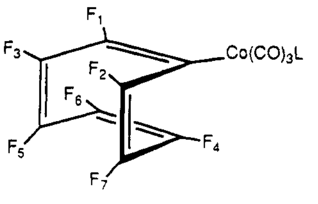
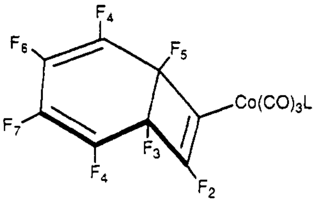
(11) Radcliffe, M. D.; Jones, W. M. *Organometallics* **1983**, *2*, 1053.

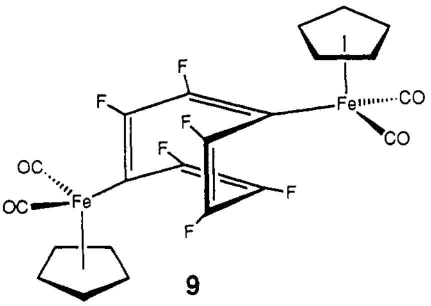


7a L = PPh_3
7b L = PMe_2Ph
7c L = PMe_3
7d L = P(p-tolyl)$_3$
7e L = $PMePh_2$

is in equilibrium in solution with its bicyclic valence isomer **8a**. While details of the synthesis of **7a** are provided in the Experimental Section of this paper, information concerning its ^{19}F NMR spectrum and that of **8a** (and those of other cobalt analogues) have been included in the previous paper in this issue, in order to facilitate comparison with data for other complexes of these two structural types. In addition to **7a**, this reaction also afforded the dinuclear complex **4b**. Reaction of a second equivalent of $[Co(PPh_3)(CO)_3]^-$ with **7a** afforded only recovered **7a** (>90%), demonstrating that the 1,2-disubstituted complex **4b** is not produced by a consecutive displacement reaction in contrast to the formation of the 1,5-disubstituted complex **9** from the reaction of 2 equiv of $[Fe(\eta^5\text{-}C_5H_5)(CO)_2]^-$ with **1**.[10] The solid-state structure of **4b** was determined crystallographically (Table I). A plot of the structure is shown in Figure 1b, illustrating the planarity of the fluorinated ring.



8a L = PPh_3
8b L = PMe_2Ph
8c L = PMe_3
8d L = P(p-tolyl)$_3$
8e L = $PMePh_2$



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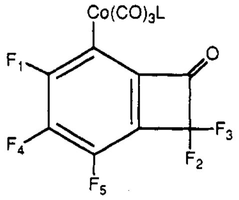
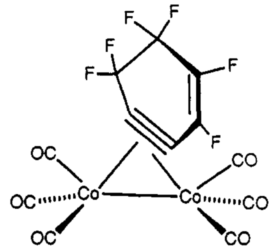
Similarly, the room-temperature reaction of $[Co(PMe_2Ph)(CO)_3]^-$ with **1** afforded the fluorinated products **7b** (in equilibrium with **8b**), and **4c**, in the crude product mixture.[10] Column chromatography on Florisil allowed separation of the mononuclear and dinuclear complexes and also resulted in partial conversion of the **7b**/**8b** mixture to the bicyclic ketone complex **10a**, as has previously been observed for other η^1-heptafluorocyclooctatetraenyl analogues.[10] The mechanism of this conversion is currently unclear. A drawing of the crystallographically determined (Table I) structure of **4c** is shown in Figure 1c. The fluorinated ring in this complex is also puckered in the solid state, but the observation of only a single "virtual triplet" ^1H NMR resonance at δ 1.70 for the methyl protons on the phosphine ligands is consistent either with a planar cyclooctatrienyne ring in solution or, more likely, with a low energy barrier for inversion of the fluorinated ring. The ^{31}P NMR resonances for **4b** and **4c** were very broad, presumably due to the cobalt quadrupolar nuclei, and were not useful in detecting the presence or absence of dynamic ring inversion.



10a L = PMe_2Ph
10b L = $PMePh_2$

Likewise the reaction of $[Co(CO)_3(PPh_2Me)]^-$ with **1** afforded a mixture of **7e**/**8e** and **4e**. Chromatography resulted in partial conversion of **7e**/**8e** to the bicyclic ketone complex **10b**.

The literature report that the reaction of $[Co_2(CO)_8]$ with octafluoro-1,3-cyclohexadiene afforded the dinuclear complex **11**[12] suggested that complexes of general structure **4** might be produced by an analogous reaction of **1** with the appropriate dinuclear cobalt presursors. Indeed the dinuclear complexes **4b** and **4e** were the sole products of the reactions of $[Co(PPh_3)(CO)_3]_2$ or $[Co(PPh_2Me)(CO)_3]_2$ with **1** in refluxing benzene. In contrast, reaction of $[Co(PMe_2Ph)(CO)_3]_2$ with **1** in refluxing benzene afforded both the mononuclear (**7b**/**8b**) and dinuclear (**4c**) complexes. Similarly the reaction of $[Co(PMe_3)(CO)_3]_2$ with **1** in refluxing benzene afforded both the monosubstituted (**7c**/**8c**) and disubstituted (**4d**) derivatives. A plot of the crystallographically determined (Table I) structure of **4d** is shown in Figure 1d. As observed for **4c**, the fluorinated ring in **4d** is puckered in the solid state, but the ^1H NMR spectrum displayed only a single "virtual triplet" for the phosphorus methyl groups, as previously noted for the PMe_2Ph analogue **4c** (vide supra).



11

It has been demonstrated thus far that those dinuclear complexes that have puckered rings in the solid state exhibit ^1H NMR spectra consistent with either a conformationally static, planar cyclooctatrienyne ring in solution or a ground-state structure with a puckered ring that undergoes a facile inversion process on the NMR time scale. While these data do not allow a distinction to be made between these two possibilities, it is clear that the activation energy for deformation of the puckered hexafluorocyclooctatrienyne must be considerably lower than that observed for the η^1-heptafluorocyclooctatetraenyl analogues.

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[12] Hunt, R. C.; Wilkinson, G. *Inorg. Chem.* **1965**, *4*, 1270. Bailey, N. A.; Churchill, M. R.; Hunt, R. L.; Mason, R.; Wilkinson, G. *Proc. Chem. Soc., London* **1964**, 401.

Table I. Crystallographic Summary for 4a, 4b, 4c, and 4d

	4a	**4b**	**4c**	**4d**
	A. Crystal Data (−110 °C)[a]			
a, Å	26.808 (6)	20.670 (4)	10.475 (3)	7.799 (2)
b, Å	6.953 (1)	10.038 (2)	16.604 (5)	28.071 (7)
c, Å	17.081 (3)	21.556 (4)	8.637 (2)	10.856 (2)
α, deg	90	90	99.16 (3)	90
β, deg	98.10 (1)	108.14 (2)	91.16 (2)	98.40 (2)
γ, deg	90	90	85.74 (2)	90
V, Å^3	3152.0 (1)	4250.6 (15)	1479.1 (7)	2351.1 (9)
no. of reflns for cell data	45	45	45	60
2θ range for cell data, deg	25.0–28.0	19.8–24.0	23.0–31.1	20.9–25.0
d_{calcd}, g cm^{-3} (−110 °C)	2.091	1.508	1.609	1.674
d_{measd}, g cm^{-3} (21 °C)		1.497	1.589	
chem formula	$C_{14}O_6F_6Co_2$	$C_{48}H_{30}O_4F_6P_2Co_2$	$C_{28}H_{22}O_4F_6P_2Co_2$	$C_{18}H_{18}O_4F_6P_2Co_2$
fw	496.01	964.57	716.29	592.14
cryst syst	monoclinic	monoclinic	triclinic	monoclinic
space group, *Z*	*C*2/*c* (No. 15), 8	*C*2/*c* (No. 15), 4	$P\bar{1}$ (No. 2), 2	$P2_1/c$ (No. 14), 4
F(000), electrons	1920	1952	720	1184
	B. Data Collection (−110 °C)[b]			
radiation, λ, Å	Mo Kα, 0.71069			
mode	ω scan			
scan range	symmetrically over 1.0° about K$\alpha_{1,2}$ max			
bkgd	offset 1.0 and −1.0° in ω from K$\alpha_{1,2}$ max			
scan rate, deg min^{-1}	2.0–5.0	3.0–6.0	3.0–6.0	3.0–6.0
2θ range, deg	4.0–55.0	4.0–55.0	4.0–57.0	4.0–60.0
exposure time, h	75.9	80.8	94.7	78.7
stability analysis				
computed *s*, *t*	−0.00052, 0.000007	0.000393, −0.000005	0.000179, −0.000001	−0.000014, −0.000001
correction range (on *I*)	1.00–1.01	0.99–1.01	0.99–1.00	1.00–1.01
total no. of reflns measd	3605	4869	7498	6854
data cryst vol, mm^3	0.0321	0.0114	0.0318	0.0143
data cryst faces	{001}, 111, 111, 101, 111, 311, 311, fragment	{101}, {103}, {110}	{230}, {110}, 223, 010, 011, 113, 110, fragment	{011}, {100}
abs coeff. μ(Mo Kα), cm^{-1}	22.26	9.22	13.45	16.76
transmissn factor range	0.469–0.645	0.806–0.886	0.665–0.723	0.652–0.849
	C. Structure Refinement[c]			
ignorance factor, *p*	0.02	0.02	0.02	0.02
no. of reflns used, $F_o \geq 4\sigma(F_o)$	3145	3270	6053	4482
no. of variables	253	244	359	362
R, R_w	0.026, 0.030	0.055, 0.053	0.034, 0.036	0.048, 0.038
R, R_w for all data	0.033, 0.031	0.094, 0.056	0.047, 0.037	0.091, 0.041
goodness of fit, *S*	1.72	1.89	1.67	1.41
max shift/esd	0.05	0.40	0.27	0.34
max peak in diff map, e Å^{-3}	0.40	0.51	0.57	0.51

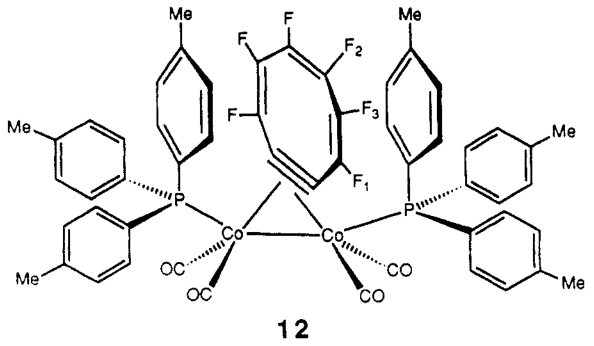
[a] Unit cell parameters were obtained by least-squares refinement vs the number of reflections shown, in the 2θ range given. Crystal densities for **4b** and **4c** were measured by flotation in an aqueous $ZnCl_2$ solution. Densities of the other two crystals were not measured because no suitably dense solution was readily available. [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* **1976**, *32*, 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* **1975**, *31*, 1511. [c] Relevant expressions are as follows: function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = (\sigma|F|)^{-2}$; $R = \sum|(|F_o| - |F_c|)|/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $S = [\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$.

Table II. ^{19}F NMR Data for μ-Hexafluorocyclooctatrienyne Complexes[a] ($[(Co(L)(CO)_2)_2(C_8F_6)]$)

complex	[L]	F_1	F_2	F_3
4a	CO	105.4	124.9	136.3
4b	PPh_3	104.0	138.3	142.7
4c[b]	PMe_2Ph	103.5	127.5	139.7
4d	PMe_3	99.8	131.2	144.7
4e	$PMePh_2$	104.0	135.8	143.5
12	$P(p\text{-}MeC_6H_4)_3$	104.9	130.9	141.1

[a] Chemical shifts quoted in ppm upfield of internal $CFCl_3$. [b] Summary of the ^{19}F NMR coupling constant data (Hz) for **4c**: $J_{1,2} = 6$; $J_{1,3} = 25$; $J_{2,3} = 10$.

It was also intriguing to contemplate whether the crystallographically observed planarity of the fluorinated ring in complex **4b** was the result of steric factors or whether an attractive electronic interaction existed between the phenyl rings of the phosphine ligands and the fluorinated ligand. Crystallographic evidence pertaining to this question is discussed below. In order to probe the magnitude of any such interactions in solution, a dinuclear complex was required that contained an NMR "handle" to allow more ready differentiation of individual aryl rings. Accordingly the reaction of the cobalt anion $[Co(P(p\text{-}MeC_6H_4)_3)(CO)_3]^-$ with **1** was carried out, to afford a mixture of mononuclear (**7d**/**8d**) and dinuclear (**12**) com-



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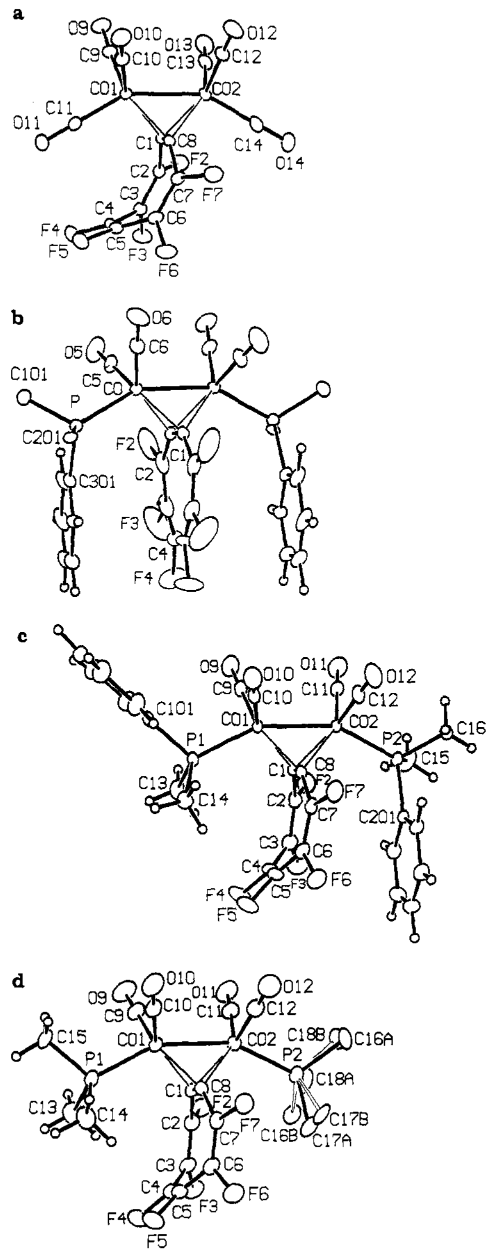

Figure 1. Thermal ellipsoid plots and atomic numbering schemes: (a) complex **4a**; (b) complex **4b**; (c) complex **4c**; (d) complex **4d**.

plexes. The ground-state structure of **12** was assumed to be the same as that of its triphenylphosphine analogue **4b**, with a planar μ-C$_8$F$_6$ ligand sandwiched between two *p*-tolyl rings. If this structure were maintained in solution, it was expected that two different methyl signals in a ratio of 1:2 would be observed, corresponding to the *p*-tolyl groups that form part of the sandwich and those that do not. The room-temperature ^{1}H NMR spectrum of **12** exhibited, in addition to the phenyl ring signals, a singlet at δ 2.32 ppm due to the methyl groups in the para positions of the aryl rings. This methyl singlet was temperature-invariant down to −55 °C, indicating facile rotation about the Co–P bond with exchange of *p*-tolyl groups between sandwiching and nonsandwiching sites. Clearly any electronic π-system interaction or steric impediment between aryl and C$_8$F$_6$ rings is very weak in solution.

The thermal ellipsoid plots shown in Figure 1 depict the structures determined in this work (**4c** and **4d**) as well as those reported previously (**4a** and **4b**).[9] Figure 2 shows the bond lengths and angles for the μ-C$_8$F$_6$ rings in all four complexes. Selected average geometric features of the fluorinated rings in these four structures, compared with those of the uncomplexed fluorocarbon octafluorocyclooctatetraene (OFCOT; **1**),[4] appear in Table III. Fractional atomic coordinates, full listings of bond lengths and angles, anisotropic thermal parameters, and structure factor tables for all four complexes are included as supplementary material.

Table III. Comparison of Average Structural Parameters for OFCOT (1), 4a, 4d, 4c, and 4b

	OFCOT (1)	4a	4d	4c	4b
-C≡C—C, deg		131.9	135.7	136.4	139.8
-C=C—C, deg	126.7	127.5	129.5	130.2	133.3
-C=C—F, deg	119.1	118.2	117.1	116.9	114.6
-C—C—F, deg	114.0	114.0	113.1	113.5	112.0
(-C=C—F)-(-C—C—F), deg	5.1	4.2	4.0	3.4	2.6
C≡C, Å		1.371	1.351	1.362	1.348
C=C, Å	1.322	1.332	1.326	1.328	1.348
C—C, Å	1.447	1.446	1.441	1.439	1.419
C—F, Å	1.346	1.350	1.359	1.364	1.359
F···F across C=C, Å	2.63	2.56	2.57	2.56	2.45
F···F across C—C, Å	2.76	2.73	2.65	2.60	2.39
α_1, deg[a]	41.4	33.0	20.5	20.4	0.9
α_2, deg[a]	41.4	42.4	38.4	33.6	1.8

[a] See text for definition of α_1 and α_2.

The bonding of the cyclooctatrienyne ligand to the dicobalt framework is identical in all four compounds, with the eight-membered ring bound via its formal triple bond. The perpendicular geometry between the C–C triple bond and the Co–Co bond is consistent with alkyne–dicobalt geometry as described in previous literature and as predicted by theory.[13] The Co–Co bond lengths are significantly shorter than the Co–Co bond length of 2.52 Å in [Co$_2$(CO)$_8$][14] but are similar to Co–Co lengths found in related μ-alkyne complexes, e.g. 2.47 Å in (μ_2-(1η,2η)-diphenylacetylene)hexacarbonyldicobalt,[15] 2.463 (1) Å in (μ_2-(1η,2η)-di-*tert*-butylacetylene)hexacarbonyldicobalt,[16] and 2.471 Å in the fluorocarbon complex **11**.[12]

In **4b** the molecule is located on a crystallographic 2-fold rotation axis. In this structure the atoms of the C$_8$F$_6$ ring are coplanar to within 0.04 Å, but the quite high thermal ellipsoids cast considerable doubt on details of its bond lengths. These ellipsoids could represent disorder of two slightly nonplanar conformers; however, the distances of C(4) and C(5) (1.20 and 1.32 Å) and F(4) and F(5) (2.31 and 2.38 Å) from the plane [C1,C2,C7,C8] in **4c** indicate that the planar structure in **4b** cannot represent disorder of two conformations even nearly as tub-shaped as that in **4c** (the least tublike of the other three structures).

The ring adopts a tub-shaped conformation in structures **4a**, **4c**, and **4d** and is planar in **4b**. This nonplanarity is quantified in Table III by the dihedral angles α_1 and α_2, where α_1 is the angle between planes [C(1),C(2),C(7),C(8)] and [C(2),C(3),C(6),C(7)] and α_2 is the angle between planes [C(2),C(3),C(6),C(7)] and [C(3),C(4),C(5),C(6)].[17] The ring becomes systematically flattened with increasing steric bulk of the ligand trans to Co–Co (i.e., the ligand closest to the C$_8$ ring). Thus, in the series **4a** → **4d** → **4c** → **4b**, α_1 ranges 33.0 (3)° → 20.3 (3)° → 20.2 (2)° → 0.9

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(17) Due to the location of the molecule of **4b** at a crystallographic 2-fold axis, atom C(1′) in **4b** corresponds to C(8) in the other structures, C(2′) to C(7), C(3′) to C(6), and C(4′) to C(5).

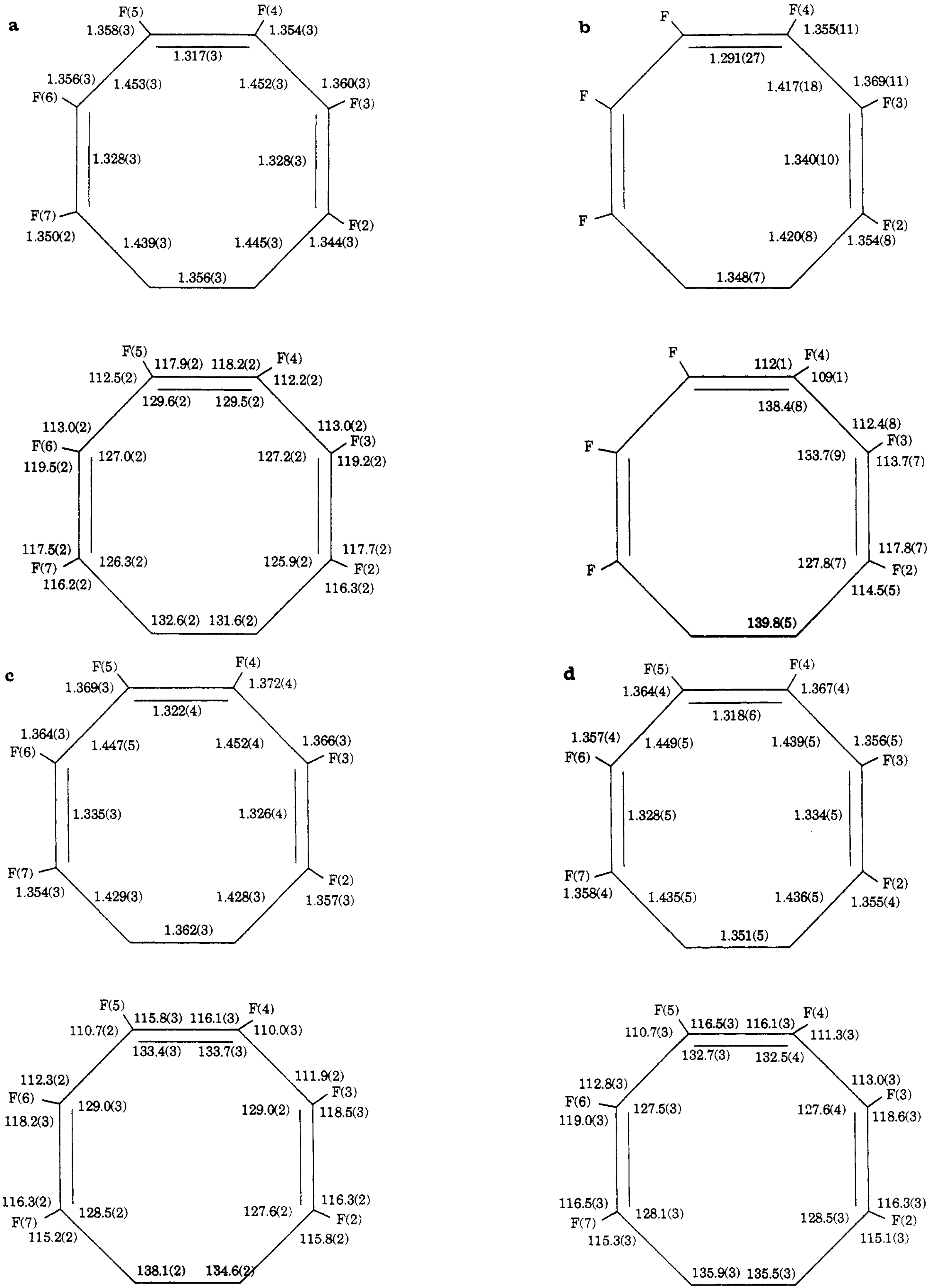

Figure 2. Bond lengths (Å) and angles (deg) for the fluorinated rings in complexes 4: (a) complex **4a**; (b) complex **4b**; (c) complex **4c**; (d) complex **4d**. Values for C–C lengths and C–C–C angles appear inside the ring. Values for C–F lengths and C–C–F angles appear outside the ring.

(3)°, while α_2 ranges 42.4 (3)° → 38.4 (3)° → 33.6 (2)° → 1.8 (3)°. The corresponding dihedral angle in OFCOT (1) is 41.4 (2)°.[4] Therefore, it is clear that steric interactions with the ancillary ligands bound to cobalt play a major role in determining the conformation of the hexafluorocyclooctatrienyne ring.

In complex **4b** the distance between C(1) on the C_8F_6 ligand and C(301) on the phenyl ring is 3.34 Å, which is less than the sum (3.40 Å) of their van der Waals radii.[18] This type of structure could be indicative of a favorable orbital overlap between the orbitals on the phenyl rings and those of the C_8F_6 ligand, or this short distance may simply be imposed on the rings by the steric requirements of the phosphine ligands and the fluorinated ring. However, in complex **4c** the observation that the C_8F_6 ring and the phenyl ring on only one phosphine ligand are in the "eclipsed" arrangement implies that both steric and electronic factors may play a role in determining the optimum conformation of the perfluorinated ligand. If steric factors alone were dominant, then the preferred structure of **4c** should be that in which both phenyl groups were directed away from the eight-membered ring. In such a structure the values of α_1 and α_2 should be approximately equal to those found in the trimethylphosphine complex **4d**. The values of α_1 for complexes **4c** and **4d** are indeed equal, but the value of α_2 is significantly smaller in **4c** (33.6°) than in **4d** (38.4°). This is surprising, since the steric effect of the eclipsing phenyl ring in **4c** should be larger than that of the corresponding methyl group in **4d** and may indicate the presence of a weak attractive interaction between the fluorinated ring and this phenyl group in the former compound. Such weak complexation between benzene and hexafluorobenzene is well-known.[31] However, any such attractive interactions present in **4b** and **4c** are clearly insufficient to prevent rapid inversion of the fluorinated ring or rapid rotation about the Co–P bonds in solution (vide supra).

Concluding Remarks

The theoretically predicted and experimentally observed structures of cyclooctatrienynes are planar (see Introduction). However, it is clear that the most favorable conformation for the μ-hexafluorocyclooctatrienyne ligand in complexes **4** is a severely puckered one, in the absence of steric, and possible electronic, effects associated with ancillary ligands on the metals. In addition, both solution NMR and crystallographic studies indicate that the energy required to invert or otherwise distort the fluorinated ring toward a more planar structure is significantly lower than that for a η^1-heptafluorocyclooctatetraenyl ligand, such as that in complex **5**. We suggest that while the fluorinated ligand in complexes **4** would be considered formally to be a cyclooctatrienyne were it not coordinated to the dicobalt framework, use of the acetylenic π-electrons to bind to the bimetallic subunit leaves the coordinated molecule resembling a cyclooctatriene rather than a cyclooctatrienyne. In contrast to the case for cyclooctatrienynes, the structure of cycloocta-1,3,5-triene[19] is known to be puckered, with a barrier to ring inversion $\Delta G^{*}(-145\ °C) = 6.2\ (\pm 0.5)$ kcal/mol.[20] This inversion barrier is much lower than that observed for derivatives of cyclooctatetraene (e.g. for ethoxycyclooctatetraene ring inversion $\Delta G^{*}(0\ °C) = 12.47$ ($\pm$0.03) kcal/mol),[21] presumably because a planar cyclooctatriene intermediate does not have the antiaromatic character of its planar cyclooctatetraene analogue. Recognition that the fluorinated ring in complexes **4** may be closer in character to a cyclooctatriene than a cyclooctatetraene also provides a rationale for the relative barriers to ring inversion observed in complexes **4** and **5**.

Experimental Section

General Considerations. Infrared spectra were recorded on a Bio-Rad Digilab FTS-40 Fourier transform infrared spectrophotometer. ^{1}H (300 MHz), ^{31}P{^{1}H} (121 MHz), and ^{13}C{^{1}H} (75 MHz) NMR spectra were recorded on a Varian Associates XL-300 spectrometer at 25 °C unless otherwise noted. ^{19}F NMR spectra were recorded on a JEOL FX60Q spectrometer (56 MHz) or on a Varian Associates XL-300 spectrometer (282 MHz) at 25 °C unless otherwise noted. All ^{19}F NMR shifts were recorded as ppm upfield from the internal standard $CFCl_3$. All ^{1}H and ^{13}C{^{1}H} shifts were recorded as ppm downfield from tetramethylsilane. Chemical shifts for ^{31}P{^{1}H} spectra were referenced to the deuterium resonance of the solvent by using the internal frequency lock of the spectrometer so that the resonance from a 5-mm NMR tube of 85% H_3PO_4 appeared at 0.0 ppm at 20 °C.[22] All variable-temperature NMR spectra were recorded on a Varian Associates XL-300 spectrometer. The probe was calibrated at various temperatures by using samples of methanol (low temperature)[23] and ethylene glycol (high temperature).[24] Melting points were determined with an Electrothermal capillary melting point apparatus and are uncorrected. Positive ion fast atom bombardment (FAB) mass spectra were recorded at the Johns Hopkins School of Medicine Middle Atlantic Mass Spectrometry Laboratory. Microanalyses were done at Atlantic Microlab, Inc., Atlanta, GA, or Spang Microanalytical Laboratory, Eagle Harbor, MI.

All solvents were dinitrogen-saturated and distilled over a variety of drying agents. Benzene and tetrahydrofuran were dried over potassium, toluene was dried over sodium, hexane, petroleum ether, and diethyl ether were dried over sodium–potassium alloy, and methylene chloride was dried over P_4O_{10}. All organometallic reactions were run in oven-dried glassware with use of conventional Schlenk techniques, under an atmosphere of dinitrogen that was deoxygenated over BASF catalyst and dried with Aquasorb or in a Vacuum Atmospheres Dry Box equipped with a HE-492 gas purification system. Column chromatography was done under dinitrogen in jacketed columns with dry, N_2-saturated chromatography supports and solvents. All deuterated solvents were dried over P_4O_{10} and degassed prior to use.

Silica gel (Davisil 62, activity III) was obtained from Davison Chemical, Inc. Alumina (activity III) was obtained from ICN Pharmaceuticals, Inc. Florisil was obtained from Fisher Scientific Co. Octacarbonyldicobalt was obtained from Pressure Chemical Co. and stored in a Schlenk tube under dinitrogen at −78 °C. Triphenylphosphine was obtained from Aldrich Chemical Co. and used as supplied. Dimethylphenylphosphine, diphenylmethylphosphine, and tri-*p*-tolylphosphine were obtained from Strem Chemical Co. Trimethylphosphine was prepared by a modification of the method of Schmidbaur.[25] Octafluorocyclooctatetraene (OFCOT; **1**) was prepared according to the method of Lemal.[26] The complexes $[Co(CO)_3L]_2$ (L = PPh_3, PPh_2Me, $PPhMe_2$, PMe_3, $P(p\text{-}MeC_6H_4)_3$) were prepared by literature procedures.[27]

Reaction of $Na^+[Co(CO)_4]^-$ with OFCOT. To a stirred solution of $Na^+[Co(CO)_4]^-$ (3 mmol) in THF (50 mL), prepared in situ from the reaction of a solution of $[Co_2(CO)_8]$ (0.52 g, 1.5 mmol) in THF (50 mL) with Na/Hg, was added OFCOT (0.75 g, 3 mmol). The reaction mixture was stirred for 5 days, during which time the color darkened to a deep yellow/brown. Removal of the solvent under reduced pressure afforded a deep yellow oil. The residue was redissolved in CH_2Cl_2 and filtered through a medium-porosity frit to produce a red/orange filtrate. Chromatography of the filtrate on Florisil afforded an orange band after elution with hexane (total amount of solvent 100 mL). Removal of the solvent under reduced pressure followed by crystallization from CH_2Cl_2/hexane afforded red crystals of **4a** (0.1 g, 6%), mp 109–110 °C. ^{19}F NMR ($CDCl_3$): δ 105.4 (m, F_1), 124.9 (m, F_2), 136.3 (m, F_3); see text for numbering (a complete analysis of the coupling constants for the isostructural complex **4c** appears later in this section, and inspection reveals a similar coupling pattern for **4a**). IR (hexane): ν_{CO} = 2105, 2074, 2054

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cm^{-1}. MS: *m/e* 496 (M$^+$), 468 (M$^+$ - CO), 440 (M$^+$ - 2CO), 412 (M$^+$ - 3CO), 384 (M$^+$ - 4CO), 356 (M$^+$ - 5CO), 328 (M$^+$ - 6CO). Anal. Calcd for $C_{14}Co_2F_6O_6$: C, 33.90. Found: C, 34.06.

Reaction of Na$^+$[Co(CO)$_3$(PPh$_3$)]$^-$ with OFCOT. To a stirred solution of Na$^+$[Co(CO)$_3$(PPh$_3$)]$^-$ (0.50 g, 1.2 mmol) in THF (30 mL) at -78 °C, prepared from the reaction of a solution of [Co(CO)$_3$(PPh$_3$)]$_2$ in THF with Na/Hg, was added a -78 °C solution of OFCOT (0.31 g, 1.2 mmol). The reaction mixture was stirred at -78 °C for 15 min and then warmed to -20 °C, where it was stirred for 2 h and then warmed to room temperature. After 36 h the solvent was removed under reduced pressure to afford a red oil. The oil was subjected to column chromatography on Florisil. Elution with CH$_2$Cl$_2$/hexane (5%/95%; total amount of solvent 400 mL) produced a yellow band. Removal of the solvent under reduced pressure followed by crystallization from CH$_2$Cl$_2$/hexane afforded yellow crystals of **7a** (0.13 g, 17%), mp 119–122 °C dec. ^{19}F NMR (CDCl$_3$): δ 73.4 (m, F$_1$), 94.5 (m, F$_2$), 120.2 (m, F$_3$), 125.0 (m, F$_4$), 128.7 (m, F$_5$), 130.9 (m, F$_6$), 142.2 (m, F$_7$); see text for numbering (a complete analysis of the coupling constants for analogous complexes appears in the previous paper in this issue, and inspection reveals a similar coupling pattern for **7a**. IR (hexane): ν_{CO} = 2062, 1990 cm^{-1}. Anal. Calcd for $C_{29}H_{15}CoF_7O_3P$: C, 54.91; H, 2.38. Found: C, 54.82; H, 2.25. There is an equilibrium in solution between **7a** and its bicyclic valence isomer **8a** (**8a**: ^{19}F NMR (CDCl$_3$) δ 97.4 (m, F$_2$), 146.0 (m, F$_3$), 151.3 (m, F$_4$), 156.2 (m, F$_5$), 158.8 (m, F$_6$), 160.9 (m, F$_7$)). Further elution with CH$_2$Cl$_2$/hexane (30%/70%; total amount of solvent 200 mL) produced a red band. Removal of the solvent under reduced pressure followed by crystallization from CH$_2$Cl$_2$/hexane afforded red crystals of **4b** (0.075 g, 13%), mp 182–185 °C dec. ^{19}F NMR (CDCl$_3$): δ 104.0 (m, F$_1$), 138.3 (m, F$_2$), 142.7 (m, F$_3$) (a complete analysis of the coupling constants for the isostructural complex **4c** appears later in this section, and inspection reveals a similar coupling pattern for **4b**). IR (hexane): ν_{CO} = 2046, 2002, 1995 cm^{-1}. MS: *m/e* 964 (M$^+$). The elemental composition was confirmed by an X-ray diffraction study (see below).

Reaction of [Co(CO)$_3$(PPh$_3$)]$_2$ with OFCOT. To a stirred solution of [Co(CO)$_3$(PPh$_3$)]$_2$ (0.50 g, 0.6 mmol) in benzene (25 mL) was added OFCOT (0.46 g, 1.8 mmol). The reaction mixture was refluxed for 6 h, during which time the solution became a deep red/black. After it was stirred an additional 12 h at room temperature, the solution was filtered to remove unreacted [Co(CO)$_3$(PPh$_3$)]$_2$ (0.40 g, 80%). The reaction solvent was removed under reduced pressure and the resulting red oil subjected to column chromatography on Florisil. Elution with CH$_2$Cl$_2$/hexane (15%/85%; total amount of solvent 200 mL) produced a red band. Evaporation of the solvent afforded pure **4b** (0.03 g, 5%). There was no evidence, as determined by infrared and ^{19}F NMR spectroscopy of the crude reaction mixture, for the formation of the monosubstituted complex **7a**.

Reaction of Na$^+$[Co(CO)$_3$(P(*p*-MeC$_6$H$_4$)$_3$)]$^-$ with OFCOT. To a stirred solution of Na$^+$[Co(CO)$_3$(P(*p*-MeC$_6$H$_4$)$_3$)]$^-$ (3.4 mmol) in THF (25 mL), prepared in situ from the reaction of a solution of [Co(CO)$_3$(P(*p*-MeC$_6$H$_4$)$_3$)]$_2$ in THF (25 mL) with Na/Hg, was added OFCOT (0.34 g, 1.4 mmol). The reaction mixture was stirred for 5 days, during which time it darkened to a deep red/black. Removal of the solvent under reduced pressure afforded a deep red oily solid, which was subjected to column chromatography on Florisil. Elution with CH$_2$Cl$_2$/hexane (5%/95%; total amount of solvent 200 mL) produced a yellow band. Removal of the solvent under reduced pressure followed by crystallization from CH$_2$Cl$_2$/hexane afforded yellow crystals of **7d** (0.04 g, 4%), mp 138–140 °C dec. ^{19}F NMR (CDCl$_3$): δ 73.9 (m, F$_1$), 94.1 (m, F$_2$), 120.2 (m, F$_3$), 125.0 (m, F$_4$), 129.1 (m, F$_5$), 130.1 (m, F$_6$), 142.8 (m, F$_7$). IR (CH$_2$Cl$_2$): ν_{CO} = 2061, 1990 cm^{-1}. There is an equilibrium in solution between **7d** and its bicyclic valence isomer **8d** (**8d**: ^{19}F NMR (CDCl$_3$) δ 98.1 (m, F$_2$), 147.4 (m, F$_3$), 151.8 (m, F$_4$), 155.7 (m, F$_5$), 159.3 (m, F$_6$), 161.4 (m, F$_7$)). Further elution with CH$_2$Cl$_2$ (30%/70%; total amount of solvent 100 mL) afforded a red band. Removal of the solvent under reduced pressure followed by crystallization from CH$_2$Cl$_2$/hexane afforded red crystals of **12** (0.03 g, 4%), mp 197–198 °C dec. ^{19}F NMR (CDCl$_3$): δ 104.9 (m, F$_1$), 130.9 (m, F$_2$), 141.1 (m, F$_3$). ^{1}H NMR (CDCl$_3$): δ 2.32 (s, C*H*$_3$), 7.1–7.5 (m, Ph). IR (CH$_2$Cl$_2$): ν_{CO} = 2042, 1996, 1990 cm^{-1}. MS: *m/e* 992 (M$^+$ - 2CO), 936 (M$^+$ - 4CO). Anal. Calcd for $C_{54}H_{42}Co_2F_6O_4P_2$: C, 61.84; H, 4.04. Found: C, 61.47; H, 4.14.

A solution of **12** (0.02 g, 0.02 mmol) in CDCl$_3$ was subjected to low-temperature ^{1}H NMR spectroscopy studies. Temperature independence of the sharp singlet at δ 2.32, assigned to the methyl groups on the phosphorus ligands, was observed at -30, -40, and -55 °C.

Reaction of Na$^+$[Co(CO)$_3$(PPhMe$_2$)]$^-$ with OFCOT. To a stirred solution of Na$^+$[Co(CO)$_3$(PPhMe$_2$)]$^-$ (1.1 mmol) in THF (25 mL), prepared in situ from the reaction of a solution of [Co(CO)$_3$(PPhMe$_2$)]$_2$ in THF (25 mL) with Na/Hg, was added OFCOT (0.18 g, 0.7 mmol). The reaction mixture was stirred for 5 days, during which time it darkened to a deep red/black. Removal of the solvent under reduced pressure afforded a deep orange/red oil, which was subjected to column chromatography on Florisil. Elution with hexane (total amount of solvent 600 mL) produced a yellow band. Removal of the solvent under reduced pressure afforded a yellow oil identified as **7b** (0.05 g, 9%). ^{19}F NMR (CDCl$_3$): δ 73.9 (m, F$_1$), 94.5 (m, F$_2$), 120.1 (m, F$_3$), 125.1 (m, F$_4$), 129.1 (m, F$_5$), 130.9 (m, F$_6$), 142.2 (m, F$_7$). IR (CH$_2$Cl$_2$): ν_{CO} = 2056, 1990 cm^{-1}. There is an equilibrium in solution between **7b** and its bicyclic valence isomer **8b** (**8b**: ^{19}F NMR (CDCl$_3$) δ 97.7 (m, F$_2$), 146.5 (m, F$_3$), 151.8 (m, F$_4$), 156.0 (m, F$_5$), 159.0 (m, F$_6$), 161.7 (m, F$_7$)). Further elution afforded a second yellow band. Evaporation and crystallization of the residue from Et$_2$O/hexane afforded yellow crystals of complex **10a** (0.01 g, 2%). ^{19}F NMR (CDCl$_3$): δ 94.5 (m, F$_1$), 98.2 (m, F$_2$), 98.2 (m, F$_3$), 142.0 (m, F$_4$), 143.9 (m, F$_5$). IR (hexane): ν_{CO} = 2055, 2000 cm^{-1}; $\nu_{C=O}$ = 1785 cm^{-1}. The structure of this complex has been confirmed by an X-ray crystallographic study.[28] Further elution with CH$_2$Cl$_2$/hexane (15%/85%; total amount of solvent 200 mL) produced an orange band. Removal of the solvent under reduced pressure followed by crystallization from CH$_2$Cl$_2$/hexane afforded red crystals of **4c** (0.03 g, 8%), mp 145–150 °C. ^{19}F NMR (CDCl$_3$): δ 103.5 (m, F$_1$), 127.5 (m, F$_2$), 139.7 (m, F$_3$); $J_{1,2}$ = 6, $J_{1,3}$ = 25, $J_{2,3}$ = 10 Hz. ^{1}H NMR (CDCl$_3$): δ 1.70 (m, C*H*$_3$), 7.35–7.50 (m, Ph). IR (CH$_2$Cl$_2$): ν_{CO} = 2037, 1987 cm^{-1}. The elemental composition was confirmed by an X-ray diffraction study (see below).

Reaction of [Co(CO)$_3$(PPhMe$_2$)]$_2$ with OFCOT. To a stirred solution of [Co(CO)$_3$(PPhMe$_2$)]$_2$ (0.50 g, 0.7 mmol) in benzene (15 mL) was added OFCOT (0.62 g, 2.5 mmol). The reaction mixture was refluxed for 29 h, during which time the solution became a deep red/black. After it was stirred an additional 12 h at room temperature, the solution was filtered and the reaction solvent was removed under reduced pressure. The resulting dark red oily solid was subjected to column chromatography on Florisil at -20 °C. Elution with CH$_2$Cl$_2$/hexane (25%/75%; total amount of solvent 150 mL) produced a red band that contained **4c** and a small amount (intensity ca. 5% of the ^{19}F NMR signals assigned to **4c**) of the monosubstituted complex **7b**, which was unambiguously identified by a comparison of its ^{19}F NMR spectrum with that of a sample prepared by the anion reaction described above. Removal of the solvent under reduced pressure followed by crystallization from CH$_2$Cl$_2$/hexane afforded red crystals of **4c** (0.09 g, 18%).

Reaction of [Co(CO)$_3$(PMe$_3$)]$_2$ with OFCOT. To a stirred solution of [Co(CO)$_3$(PMe$_3$)]$_2$ (0.35 g, 0.8 mmol) in benzene (25 mL) was added OFCOT (0.65 g, 2.6 mmol). The reaction mixture was refluxed for 5 h and stirred at room temperature for 12 h. The reaction solvent was removed under reduced pressure to afford a deep red oil. The ^{19}F NMR spectrum of the crude reaction residue displayed resonances (ca. 1:1 mixture of complexes) assigned to **7c** (^{19}F NMR (CH$_2$Cl$_2$) δ 72.8 (m, F$_1$), 90.0 (m, F$_2$), 116.2 (m, F$_3$), 122.6 (m, F$_4$), 130.4 (m, F$_5$), 131.2 (m, F$_6$), 147.4 (m, F$_7$)) and **4d** (^{19}F NMR (CDCl$_3$) δ 99.8 (m, F$_1$), 131.2 (m, F$_2$), 144.7 (m, F$_3$); ^{1}H NMR (CDCl$_3$) δ 1.71 (m, PC*H*$_3$)). The reaction residue was subjected to column chromatography on Florisil. Elution with CH$_2$Cl$_2$/hexane (25%/75%; total amount of solvent 200 mL) afforded an orange band that contained both **7c** and **4d**, as evidenced by ^{19}F NMR spectroscopy. The solvent was removed under reduced pressure and the residue subjected to column chromatography on silica gel at -50 °C. Elution with toluene/hexane (10%/90%; total amount of solvent 150 mL) again af-

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[28] Davis, R. E. Unpublished results.

forded an orange band that contained both **7c** and **4d**. The solvent was removed under reduced pressure and the residue subjected to column chromatography on alumina at -20 °C. Elution with toluene/hexane (30%/70%; total amount of solvent 100 mL) afforded a light orange band that contained both **7c** and **4d**. Further elution with the same solvent mixture produced an orange band. Removal of the solvent under reduced pressure followed by crystallization from CH_2Cl_2/hexane afforded red crystals of **4d** (0.02 g, 6%), mp 117–118 °C. IR (KBr pellet): ν_{CO} = 2045, 1995, 1974 cm^{-1}. MS: *m/e* 592 (M^+). Anal. Calcd for $C_{18}H_{18}Co_2F_6O_4P_2$: C, 36.51; H, 3.06. Found: C, 36.31; H, 3.08.

Reaction of $Na^+[Co(CO)_3(PPh_2Me)]^-$ with OFCOT. To a stirred solution of $Na^+[Co(CO)_3(PPh_2Me)]^-$ (1.5 mmol) in THF (25 mL), prepared in situ from the reaction of a solution of $[Co(CO)_3(PPh_2Me)]_2$ in THF (25 mL) with Na/Hg, was added OFCOT (0.25 g, 1.0 mmol). The reaction mixture was stirred for 24 h, during which time the color darkened to a deep red. Removal of the solvent under reduced pressure afforded a deep red oily solid. The reaction residue was subjected to column chromatography on Florisil. Elution with CH_2Cl_2/hexane (5%/95%; total amount of solvent 200 mL) produced a yellow band. Removal of the solvent under reduced pressure afforded a yellow oil that was spectroscopically identified as **7e** (0.13 g, 16%). ^{19}F NMR ($CDCl_3$): δ 73.8 (m, F_1), 94.6 (m, F_2), 120.2 (m, F_3), 125.2 (m, F_4), 129.1 (m, F_5), 130.0 (m, F_6), 142.5 (m, F_7). IR (CH_2Cl_2): ν_{CO} = 2057, 1985 cm^{-1}. Further elution with CH_2Cl_2/hexane (15%/85%; total amount of solvent 300 mL) afforded a red band. Removal of the solvent under reduced pressure followed by crystallization from CH_2Cl_2/hexane afforded red crystals of **4e** (0.04 g, 2%), mp 170–180 °C. ^{19}F NMR ($CDCl_3$): δ 104.0 (m, F_1), 135.8 (m, F_2), 143.5 (m, F_3). IR (hexane): ν_{CO} = 2041, 2003, 1983 cm^{-1}. MS: *m/e* 840 (M^+). Anal. Calcd for $C_{38}H_{26}Co_2F_6O_4P_2$: C, 54.29; H, 3.10. Found: C, 54.37; H, 3.15. Subsequent elution with CH_2Cl_2/hexane (50%/50%; total amount of solvent 250 mL) afforded a yellow band. Removal of the solvent under reduced pressure followed by crystallization from CH_2Cl_2/hexane afforded yellow crystals of **10b** (0.03 g, 4%), mp 130–140 °C dec. ^{19}F NMR ($CDCl_3$): δ 95.6 (m, F_1), 98.2 (m, F_2), 98.2 (m, F_3), 142.0 (m, F_4), 144.0 (m, F_5). IR (CH_2Cl_2): ν_{CO} = 2057, 1990 cm^{-1}; $\nu_{C=O}$ = 1780 cm^{-1}. MS: *m/e* 550 (M^+). Anal. Calcd for $C_{24}H_{13}CoF_5O_4P$: C, 52.40; H, 2.36. Found: C, 52.65; H, 2.36.

Reaction of $[Co(CO)_3(PPh_2Me)]_2$ with OFCOT. To a stirred solution of $[Co(CO)_3(PPh_2Me)]_2$ (0.25 g, 0.4 mmol) in benzene (25 mL) was added OFCOT (0.18 g, 0.7 mmol). The reaction mixture was refluxed for 48 h, during which time the solution became a deep red/black. After the mixture was stirred an additional 72 h at room temperature, the reaction solvent was removed under reduced pressure and the resulting red oil subjected to column chromatography on Florisil. Elution with CH_2Cl_2/hexane (5%/95%; total amount of solvent 250 mL) produced a red band. Removal of the solvent under reduced pressure followed by crystallization from CH_2Cl_2/hexane afforded red crystals of **4e** (0.07 g, 24%). There was no evidence, as determined by ^{19}F NMR spectroscopy, for the formation of the monosubstituted complex **7e**.

Crystallographic Analysis. For each experiment a single crystal was affixed to a glass fiber attached to a goniometer head and then transferred to a Syntex $P2_1$ autodiffractometer, where it was maintained in a cold stream (-110 °C) of dry nitrogen gas for the duration of the data collection. Preliminary diffraction studies allowed determination of crystal symmetry and verification of the suitability of the crystals for data collection. A summary of the pertinent crystal data and of details of the X-ray diffraction data collection and processing is presented in Table I. The measured intensities were reduced and assigned standard deviations as described elsewhere,[29] including correction for absorption based on crystal shape.

Solution and Refinement of the Structures.[29] Each structure was solved by the heavy-atom method, with use of heavy-atom positions determined from a sharpened Patterson map. All structures were refined by full-matrix least-squares methods, with use of the program SHELX76. Neutral atom scattering factors[30] for H, C, O, F, P, and Co were used, including real and imaginary corrections for anomalous dispersion.

In each structure, all non-H atoms were refined anisotropically and H atoms were treated isotropically. Details of the refinements appear in Table I. Each refinement was continued until the shifts in all parameters were less than 1 esd in the respective parameter.

In **4b**, the molecule resides at the 2-fold axis of space group *C2/c*. The phenyl rings were treated as rigid groups, constrained with C–C = 1.395 Å, C–H = 1.00 Å, and C–C–C = C–C–H = 120°. The isotropic thermal parameter of each H atom was fixed at the final U_{iso} value of the carbon to which it is attached. Parallel refinements with unconstrained isotropic parameters in the two space groups *Cc* and *C2/c* have indicated, by the much more unreasonable geometry and more erratic behavior of thermal parameters in all parts of the molecule in *Cc*, that *C2/c* is the correct space group.

In the refinement of **4c**, the phenyls were treated as rigid groups with the geometrical constraints described above for **4b**, but with U_{iso} for each H atom refined independently. The methyls were treated as rigid groups constrained with C–H = 1.00 Å and H–C–H = 109.5°, with individually refined H U_{iso} values.

In the structure solution of **4d**, difference density maps showed multiple peaks of the methyl groups on one of the trimethylphosphines. Refinement resulted in a site occupancy ratio of 0.56/0.44. Methyls were constrained as rigid groups as described above for **4c**, but U_{iso} values for the methyl hydrogens were fixed at 0.05 Å^2.

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Supplementary Material Available: Listings of bond lengths and angles, fractional atomic coordinates and isotropic (or equivalent isotropic) thermal parameters for hydrogen and non-hydrogen atoms, anisotropic thermal parameters for non-hydrogen atoms, and torsion angles for **4a–d** (27 pages); tables of observed and calculated structure factors (107 pages). Ordering information is given on any current masthead page.

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(29) Riley, P. E.; Davis, R. E. *Acta Crystallogr., Sect. B* **1976**, *B32*, 381. Computer programs used in the data reduction and in the structure refinement and analysis are as detailed in: Gadol, S. M.; Davis, R. E. *Organometallics* **1982**, *1*, 1607. See the note at the end of the paper regarding the availability of supplementary material.

(30) Scattering factors for H, C, O, F, and P atoms were used as programmed in SHELX76. Values for Co atoms were obtained from: *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(31) Laposa, J. D.; McGlinchey, M. J.; Montgomery, C. *Spectrochim. Acta* **1983**, *39A*, 863 and references cited therein. We are grateful to a reviewer for bringing this work to our attention.