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The simple formation of the donor–acceptor Fe–Hg adducts, such as **5**, may open a new method for the stabilization of other electron-rich, 18-electron metal complexes.

Supplementary Material Available: Tables of crystallographic data, interatomic distances and angles, final positional and thermal parameters, and structure factor amplitudes (19 pages). Ordering information is given on any current masthead page.

Cobalt Complexes of Hexafluorodehydrocyclooctatetraene: Synthesis and Crystal and Molecular Structures of $[Co(CO)_3]_2(C_8F_6)$ and $[Co(CO)_2(PPh_3)]_2(C_8F_6)$

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Summary: While octafluorocyclooctatetraene (OFCOT) reacts with $[Co(CO)_4]^-$ to afford low yields of a dinuclear complex **1**, shown by X-ray diffraction studies to contain a severely puckered hexafluorodehydrocyclooctatetraene ring, reaction with $[Co(CO)_3(PPh_3)]^-$ yields a dinuclear analogue **2**, shown by X-ray diffraction to contain an almost planar C_8F_8 ring sandwiched between phenyl rings of adjacent triphenylphosphine ligands and a mononuclear complex **3**. Dinuclear **2** is shown not to arise by fluoride displacement from mononuclear **3**, but OFCOT reacts with $[Fe(C_5H_5)(CO)_2]^-$ by a consecutive displacement mechanism to afford initially the mononuclear complex **4** and subsequently the dinuclear complex **5**, which contains a 1,5-disubstituted cyclooctatetraene ring.

The nonplanar ground-state structure of cyclooctatetraene and its derivatives is well established,[4] and the molecular structure of octafluorocyclooctatetraene (OFCOT) has been shown to resemble closely that of its hydrocarbon analogue.[5] There has been considerable interest in whether the corresponding dehydro[8]annulenes (cyclooctatrienynes) are planar or puckered;[6] low-temperature X-ray diffraction studies of the highly reactive 5,6-didehydrodibenzo[*a*,*e*]cyclooctene show it to have a planar eight-membered ring.[7] In a previous communication[8] we reported the serendipitous synthesis of a compound $[Co(CO)_3]_2(C_8F_6)$, **1**, whose spectroscopic properties suggested the presence of a metal-stabilized hexafluorodehydrocyclooctatetraene ring. Here we report details of an X-ray crystallographic study of **1** which shows that the C_8F_6 ring is severely puckered, and the synthesis and X-ray diffraction study of a bis(triphenylphosphine) derivative, **2**, in which the C_8F_6 ring is almost planar.

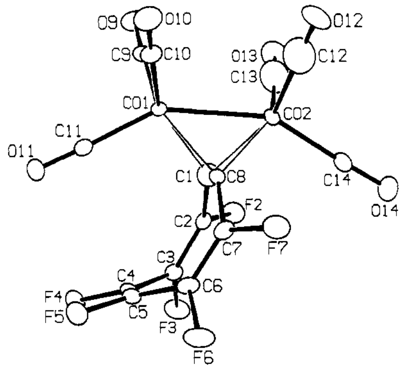


Figure 1. ORTEP drawing of the structure of **1**, showing 30% equiprobability ellipsoids.

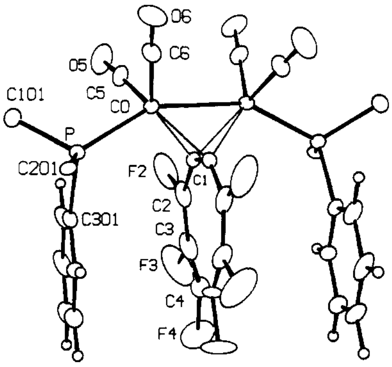
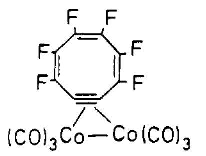
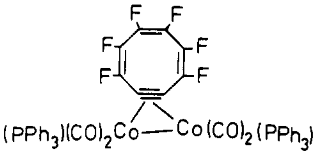


Figure 2. ORTEP drawing of the structure of **2**, showing 30% equiprobability ellipsoids for non-hydrogen atoms. Phenyl carbons are numbered C101–C106, C201–C206, and C301–C306. The phenyl rings that sandwich the C_8F_6 ring are shown; for the other phenyl rings, only the C atoms bonded to P are shown.



1



2

Compound **1** was prepared in low yield by the reaction of OFCOT with $[Co(CO)_4]^-$ as described previously.[8] The bis(triphenylphosphine) derivative **2**[9] was prepared in higher yield by the reaction of OFCOT with the $[Co(CO)_3(PPh_3)]^-$ anion in THF at 20 °C; a second product of this reaction was the mononuclear complex **3**.[10] Compound **2** was also obtained by direct reaction of OFCOT with dinuclear $[Co(CO)_3(PPh_3)]_2$ in refluxing benzene; no **3** was detected in this reaction and no reaction occurred between these substrates at room temperature. Notably, reaction of pure **3** with a further equivalent of $[Co(CO)_3(PPh_3)]^-$ yielded no trace of **2**. In contrast, treatment of the mononuclear iron complex **4**[8] with excess [Fe(C_5-

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(1) Dartmouth College.
(2) Alfred P. Sloan Research Fellow 1980–1984.
(3) University of Texas.
(4) Fray, G. I.; Saxton, R. G. "*The Chemistry of Cyclooctatetraene and Its Derivatives*"; Cambridge University Press: Cambridge, 1978.
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(6) Huang, N. Z.; Sondheimer, F. *Acc. Chem. Res.* **1982,** *15,* 96–102.
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(8) Doig, S. J.; Hughes, R. P.; Patt, S. L.; Samkoff, D. E.; Smith, W. L. *J. Organomet. Chem.* **1983,** *250,* C1–C4.
(9) Compound **2**: 25% mp 182–185 °C; IR (CH_2Cl_2) ν_{CO} 2046 (s), 2002 (m), 1995 (m) cm^{-1}; mass spectrum, *m/e* 964 (P^+); ^{19}F NMR ($CDCl_3$, shifts in ppm upfield from internal $CFCl_3$) 104.0 (m, 2 F), 138.3 (m, 2 F), 142.7 (m, 2 F). Satisfactory microanalysis results have been obtained for all compounds reported here.
(10) Compound **3**: 14%; mp 119–122 °C dec; IR (hexanes) ν_{CO} 2062 (m), 1990 (vs) cm^{-1}; ^{19}F NMR ($CDCl_3$, shifts in ppm upfield from internal $CFCl_3$) 73.4, 94.5, 120.2, 125.0, 128.7, 130.9, 142.2 (all multiplets, each having relative intensity = 1 F). See ref 8 for NMR data for analogues of **3**.

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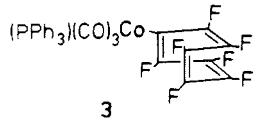
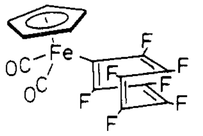
$H_5)(CO)_2]^-$ afforded the 1,5-disubstituted cyclooctatetraene compound **5**.[11]



3



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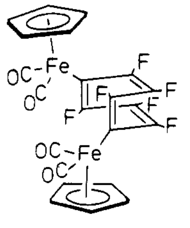

5

The structures of **1** and **2** were determined by single-crystal X-ray diffraction at -110 °C.[12] Complex **1** is well determined, having well-behaved thermal parameters and displaying geometry as shown in Figure 1.[12] The hexafluorodehydrocyclooctatetraene is bound via its triple bond to the hexacarbonyldicobalt fragment in the manner already well established for (alkyne)dicobalt compounds.[13] The nonplanarity of the tub-shaped ring is indicated by the interplanar angles of 33.0 (3)° between planes C1,C2,C7,C8 and C2,C3,C6,C7 and 42.4 (3)° between planes C2,C3,C6,C7 and C3,C4,C5,C6. The corresponding interplanar angle in OFCOT is 41.4 (2)°.[5] In the crystal of **2**,[12] the molecule occupies a crystallographic twofold rotation axis. The C_8F_6 ring in **2** is coplanar to within 0.04 Å, but the quite high thermal ellipsoids cast considerable doubt on its bond lengths. These ellipsoids could represent disorder of two slightly nonplanar conformers; however, the distances of C4 and C5 (1.80 and 1.83 Å) and F4 and F5 (2.96 and 3.01 Å) from the plane C1,C2,C7,C8 in **1** indicate that the planar structure in **2** cannot represent disorder of two conformations as tub-shaped as those in **1**. The C_8F_6 ring of **2** is sandwiched between phenyl rings of the two phosphine ligands, 3.2 Å from each ring. It is unclear what roles steric repulsion, favorable orbital interaction between the π-systems of the three rings, and the different donor/acceptor properties of CO and PPh_3 play in determining the conformation of the fluorinated ring. Future structure determinations on bis(dimethylphenylphosphine) and bis(trimethylphosphine) derivatives should answer these questions.

Since **3** is not a precursor of **2**, it seems clear that dinuclear complexes **1** and **2** do not arise by consecutive displacement of two adjacent fluorines by 2 equiv of cobalt carbonyl anion. Indeed, an example of consecutive displacement is provided by the reaction of OFCOT with Fp^- to give initially **4**[8] and subsequently **5**; notably consecutive displacement results in a 1,5- rather than a 1,2-disubstituted ring. Furthermore, the observation that **2** can be formed directly from the dinuclear $[Co(CO)_3(PPh_3)]_2$ and OFCOT only at elevated temperatures, but from $[Co(CO)_3(PPh_3)]^-$ and OFCOT at ambient temperatures, suggests that **2** may lie at the convergence of two mechanistic pathways. Details of either path are unclear at present, but thermal defluorination of perfluorocyclohexa-1,3-diene by $[Co_2(CO)_8]$ to give an (alkyne)dicobalt complex has precedent.[14]

Further chemical, structural, and electrochemical studies on organometallic compounds derived from OFCOT are in progress.

Acknowledgment. R.P.H. is grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, to the National Science Foundation, and to the Alfred P. Sloan Foundation, for generous support of this work. R.E.D. acknowledges support by the Robert A. Welch Foundation (Grant F-233) and a grant from the National Science Foundation (Grant GP-37028) for purchase of a Syntex P21 diffractometer.

Supplementary Material Available: Tables of fractional coordinates and thermal parameters, anisotropic thermal parameters, and bond distances and angles for **1** (Tables I-III) and **2** (Tables IV-VII) (8 pages). Ordering information is given on any current masthead page.

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(11) Compound **5**: 25%; mp 158-160 °C dec; IR (CH_2Cl_2) ν_{CO} 2037 (s), 1989 (s) cm^{-1}; mass spectrum, *m/e* 564 (P^+); ^{19}F NMR ($CDCl_3$, shifts in ppm upfield from $CFCl_3$) 76.7 (m, 2 F), 100.6 (m, 2 F), 137.1 (m, 2 F). The structure of **5** has been unambiguously confirmed by an X-ray diffraction study: Davis, R. E., unpublished results.

(12) The structures of **1** and **2** were determined by using intensity data (symmetry-unique sets of reflections with 2θ less than 55°) collected with Mo Kα radiation at -110 °C by the ω scan method on a Syntex $P2_1$ diffractometer. Both data sets were corrected for absorption. Refinement, including the effects of anomalous scattering, was carried out by using the program SHELX76. Scattering factors for H, C, O, F, and P were used as programmed in SHELX76; values for Co were obtained from: "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV. Each reflection was weighted as $(\sigma(F_o))^{-2}$. In this footnote F_o and F_c represent, respectively, the observed and calculated structure factor amplitudes. Crystal and data collection data for **1**: asymmetric unit, $C_{14}O_6F_6Co_2$, fw 496.0; d(calcd) = 2.091 g cm^{-3}; density not measured due to unavailability of suitably dense liquid; reflections collected, 4332; absorption correction range, 1.550-2.130. Crystals of **1** are monoclinic, $C2/c$, with a = 26.808 (6) Å, b = 6.953 (1) Å, c = 17.081 (3) Å, β = 98.10 (1)°, and Z = 8. The structure was solved by heavy-atom methods and refined (253 parameters) by full-matrix least-squares procedures to final agreement factors $R = \sum \mathrm{abs}(F_o - F_c)/F_o = 0.056$ and $R_w = [\sum w(F_o - F_c)^2/\sum F_o^2]^{1/2} = 0.057$, using 3145 reflections with $F_o \geq 4.0\ \sigma(F_o)$. Selected bond lengths (Å): Co1-Co2 = 2.473 (1), Co1-C1 = 1.972 (5), Co1-C8 = 1.958 (5), Co2-C1 = 1.930 (5), Co2-C8 = 1.936 (4), C1-C8 = 1.371 (7), C1-C2 = 1.436 (7), C2-C3 = 1.338 (7), C3-C4 = 1.454 (7), C4-C5 = 1.329 (8), C5-C6 = 1.457 (7), C6-C7 = 1.330 (7), C7-C8 = 1.435 (7). Crystal and data collection data for **2**: asymmetric unit, $C_{24}H_{15}O_2F_3PCo$, fw 482.3; d(calcd) = 1.508 g cm^{-3}; d(measd) (room temp) = 1.497 g cm^{-3}; reflections collected, 5683; absorption correction range, 1.129-1.240. Crystals of **2** are monoclinic, $C2/c$, with a = 20.670 (4) Å, b = 10.038 (2) Å, c = 21.557 (4) Å, β = 108.13 (2)°, and Z = 4. The structure was solved by heavy-atom methods and refined (244 parameters, phenyls as rigid groups, H atom U values fixed to those of carbons) by full-matrix least-squares procedures to final agreement factors R = 0.055 and R_w = 0.046, using 3270 reflections with $F_o \geq 4.0\sigma(F_o)$. Parallel refinements with unconstrained isotropic parameters in the two space groups Cc and $C2/c$ have indicated, by the unreasonable geometry in Cc, that $C2/c$ is the correct space group. The molecule is located at a crystallographic twofold rotation axis. Selected bond lengths (Å): Co-Co′ = 2.467 (1), Co-C1 = 1.940 (4), Co-C1′ = 1.969 (4), C1-C1′ = 1.348 (7), C1-C2 = 1.420 (8), C2-C3 = 1.340 (10), C3-C4 = 1.417 (18), C4-C4′ = 1.291 (27).

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Preparation and Structure of $[Zr\{Mo(CO)_3(C_5H_5)\}_2\{N(C_5H_5)_2\}_2\{NH(C_2H_5)_2\}]_2$ from a Double Amine Elimination Reaction

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Summary: $[MoH(CO)_3(Cp)]$ reacts with $[Zr(NEt_2)_4]$ in a 2:1 ratio at room temperature to give $[Zr\{Mo(CO)_3(Cp)\}_2$-

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