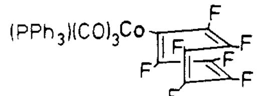
$H_5)(CO)_2]^-$ afforded the 1,5-disubstituted cyclooctatetraene compound **5**.[11]



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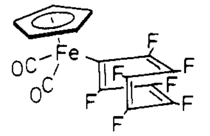

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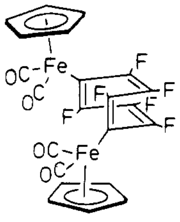

5

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.

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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, *C*2/*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, *C*2/*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 *C*2/*c* have indicated, by the unreasonable geometry in *Cc*, that *C*2/*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

William J. Sartain and John P. Selegue*

Department of Chemistry, University of Kentucky
Lexington, Kentucky 40506-0055

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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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$(NEt_2)_2(NHEt_2)]_2$ (I) in 69% yield. Product I was characterized spectroscopically and by an X-ray diffraction study (R = 5.9%). The molecule is dimeric in the solid state, held together by two $[Mo(\mu\text{-}CO)_2(CO)(Cp)]$ bridges. Each zirconium atom coordinates to three "isocarbonyl" oxygens, two diethylamides, and a diethylamine. NMR spectra suggest that I dissociates into symmetric monomers in benzene solution. Lewis bases, such as ethers, cleave the Zr–O bonds to give $[Mo(CO)_3(Cp)]^-$ anions. Different mole ratios of $[MoH(CO)_3(Cp)]$ and $[Zr(NEt_2)_4]$ yield other mixed-metal products.

Organometallic compounds containing both early and late transition metals act as models for mixed-metal catalysts used in CO hydrogenation systems and other applications.[1,2] We are interested in preparing heterometallic complexes, or clusters, containing both high-valent early transition metals surrounded by "hard", π-donor ligands such as alkoxide, amido, or oxo and low-valent later transition metals surrounded by "soft", π-acceptor ligands. Over 10 years ago, Lappert and co-workers reported that reactions of $[MH(CO)_3(Cp)]$ (M = Cr, Mo, W) with $[Ti(NMe_2)(OCHMe_2)_3]$ or $[Ti(NMe_3)(Cp)_2]_2$ produced mixed-metal products by elimination of dimethylamine.[3] Direct metal–metal bonds were inferred to be present in the products, without full characterization.[4] We are investigating the applicability of amine elimination to the preparation of complexes with early to late transition-metal bonds. We present here the first unambiguous characterization of a dinuclear amine elimination product.

$[Zr(NEt_2)_4]$[5a] reacts smoothly with 2 equiv of $[MoH(CO)_3(Cp)]$[5b] in toluene solution to give $[Zr\{Mo(CO)_3(Cp)\}_2(NEt_2)_2(NHEt_2)]_2$ (I) as yellow crystals in good yield.[6] The compound is very sensitive to air, water, chlorinated solvents, and strong light, both in the solid state and in solution.

Single crystals of I suitable for X-ray diffraction were obtained by slow recrystallization from toluene/pentane at −40 °C.[7] Important bond distances and angles are summarized in Table I, and an ORTEP[8] diagram of the structure is presented in Figure 1. Coordination about the zirconium atom is distorted octahedral, with three isocarbonyl oxygem atoms (O2, O4, and O5), two diethylamido ligands (N1 and N2), and one diethylamine (N3) in a meridional arrangement. The molecule is dimeric in the solid state, held together by bridging $[Mo(\mu\text{-}CO)_2(CO)(Cp)]$ groups with two isocarbonyls (C4–O4 and C5–O5) linking molybdenum (Mo2) and zirconium atoms. The two halves of the dimer are related by a crystallographic inversion center.

Table I. Selected Bond Distances (Å) and Angles (deg) for $[Zr\{Mo(CO)_3(Cp)\}_2\{NEt_2\}_2\{NHEt_2\}]_2$

Bond Distances

Mo1-C1	1.97 (2)	Zr-O5	2.146 (8)
Mo1-C2	1.83 (1)	Zr-N1	2.03 (1)
Mo1-C3	1.94 (2)	Zr-N2	2.017 (9)
Mo1-Cp[a]	2.07 (2)	Zr-N3	2.52 (1)
Mo2-C4	1.90 (1)	C1-O1	1.14 (2)
Mo2-C5	1.86 (2)	C2-O2	1.23 (1)
Mo2-C6	1.97 (2)	C3-O3	1.15 (2)
Mo2-Cp[a]	2.06 (2)	C4-O4	1.15 (1)
Zr-O2	2.099 (8)	C5-O5	1.22 (1)
Zr-O4	2.330 (8)	C6-O6	1.15 (2)

Bond Angles

O2-Zr-O4	83.6 (3)	O5-Zr-N3	81.3 (3)
O2-Zr-O5	162.5 (3)	N1-Zr-N2	99.5 (4)
O2-Zr-N1	92.0 (4)	N1-Zr-N3	166.4 (3)
O2-Zr-N2	101.2 (4)	N2-Zr-N3	93.9 (4)
O2-Zr-N3	85.6 (3)	Zr-O2-C2	174.6 (9)
O4-Zr-O5	82.7 (3)	Zr-O4-C4	158.0 (9)
O4-Zr-N1	87.3 (4)	Zr-O5-C5	163.1 (9)
O4-Zr-N2	171.3 (4)	Mo1-C2-O2	179 (1)
O4-Zr-N3	79.1 (4)	Mo2-C4-O4	177 (1)
O5-Zr-N1	96.1 (4)	Mo2-C5-O5	176 (1)
O5-Zr-N2	91.1 (4)		

[a] Cp is the centroid of the attached cyclopentadienyl ring.

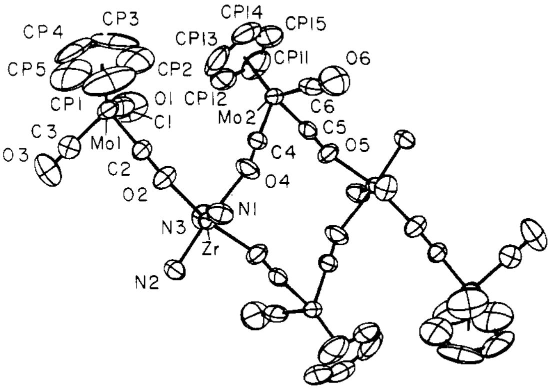

Figure 1. An ORTEP[8] plot of $[Zr\{Mo(CO)_3(Cp)\}_2(NEt_2)_2(NHEt_2)_2]_2$ with 50% probability ellipsoids. Ethyl carbons are omitted for clarity. Unlabeled atoms are related to labeled atoms by an inversion center.

The isocarbonyl ligands in I are quite different from one another. Of the three, carbonyl C2–O2 has the shortest Mo–C bond, the longest C–O bond, the shortest O–Zr bond, and a nearly linear C–O–Zr angle. It thus resembles a "zirconoxycarbyne" complex of molybdenum. The

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(6) $[MoH(CO)_3(Cp)]$ (0.73 g, 3.0 mmol) in 25 mL of toluene was added dropwise to a solution of $[Zr(NEt_2)_4]$ (0.57 g, 1.5 mmol) in 25 mL of toluene. After 15 h, the yellow-orange solution was evaporated in vacuo, and the orange residue was crystallized twice from toluene/pentane at −40 °C. Yellow crystals (0.83 g) of I were obtained in 69% yield: mp 98 °C dec; IR (ν(CO), Nujol) 1950 (s), 1917 (s), 1865 (s), 1830 (s), 1730 (w), and 1580 (w, br) cm^{-1}, (C_6H_6) 1932 (s), 1853 (s), 1810 (sh), 1720 (m), and 1613 (s) cm^{-1}; ^1H NMR (90 MHz, C_6D_6) δ 5.30 (s, 5 H, Cp), 3.38 (q, 4 H, NCH_2), 2.78 (br, 2 H, $HNCH_2$), 1.01 (overlapping t, 9 H, NCH_2CH_3); $^{13}C\{^1H\}$ NMR (50.3 MHz, C_6D_6) δ_C 236.9 (br, CO), 90.3 (s, Cp), 43.3 (s, $HNCH_2$), 42.9 (s, NCH_2), 14.8 (s, NCH_2CH_3), 13.6 (s, $NHCH_2CH_3$).

(7) Crystal data for I: a single crystal approximately 0.5 mm × 0.5 mm × 0.2 mm was mounted in a 0.5 mm glass capillary in a Vacuum Atmospheres drybox, sealed temporarily with silicone grease, removed, and immediately flame sealed. Data were collected on an Enraf-Nonius CAD4 diffractometer using Mo K$\bar{\alpha}$ radiation: space group $P\bar{1}$, Z = 2, a = 12.448 (1) Å, b = 13.871 (3) Å, c = 10.724 (2) Å, α = 104.79 (2)°, β = 100.36 (1)°, γ = 76.40 (1)°, V = 1726.3 $Å^3$, ρ_{calcd} = 1.54 $g\cdot cm^{-3}$, ν = 10.34 cm^{-1}. A total 6075 reflections were collected, and of these 4741 with $(F_o)^2 \geq 3\sigma(F_o)^2$ were used. The structure was solved by using Patterson methods to locate the metal atoms and difference Fourier methods to locate remaining atoms. All atoms were refined anisotropically. Full-matrix least-squares refinement led to R = 5.9% and R_w = 11.4%.

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Mo1–C2 bond is about as short as the Mo–C double bond in $[Mo\{C{=}C(CN)_2\}Cl\{P(OMe)_3\}_2(Cp)]$ (1.833 (6) Å)[9] but not as short as the Mo–C triple bond in $[Mo(CCH_2CMe_3)\{P(OMe)_3\}_2(Cp)]$ (1.798 (2) Å).[10] Carbonyl C4–O4 has a much longer Mo–C bond, a C–O bond indistinguishable from the three terminal carbonyls in the structure, a long Zr–O bond, and a bent C–O–Zr linkage. This suggests that O4 is simply acting as a relatively weak, ketone-like σ-donor to the electron-deficient zirconium. The third isocarbonyl, C5–O5, is intermediate in all lengths and angles; its interaction with zirconium is strong, but it is less like a "carbyne" than C2–O2.

The two zirconium amide bonds (to N1 and N2) are the shortest Zr–N bonds that have been reported, comparable to those in $[Zr_2(\mu\text{-}NCMe_3)_2(NMe_2)_4]$ which range from 2.057 to 2.071 Å,[11] suggesting that N to Zr π-donation is important in alleviating the electron deficiency of zirconium. The zirconium–amine (N3) bond (in which π-donation is not possible) is considerably longer, comparable to Zr–N bonds in other zirconium amine complexes (2.43–2.54 Å).[12–14] The bonds from Zr to O4 and N3 are the longest in the structure, suggesting a structural trans influence due to effective π-donation from amides N1 and N2.[15] The major distortions of the zirconium coordination sphere from octahedral symmetry are toward these two weakly bonded ligands.

The 12-membered ring in I resembles that in $[(Cp)_2TiMo(CO)_3(C_5H_4Me)]_2$ (II), recently prepared from $[Mo_2(CO)_4(C_5H_4Me)_2]$ and $[Ti(CO)_2(Cp)_2]$ by Merola and co-workers.[16] One major difference between I and Merola's compound is the absence of cyclopentadienyl ligands on zirconium. The severe electron deficiency of zirconium in I may explain why the isocarbonyls in I are more "carbyne"-like than those in II, with slightly shorter Mo–C distances and more linear M–O–C angles by about 20°. A similar 12-membered $(Al–O–C–W–C–O)_2$ ring has been observed in $[AlMe_2\{W(CO)_3(Cp)\}]_2$, prepared from $[WH(CO)_3(Cp)]$ and Me_2AlX (X = H, Me) by Smith and coworkers.[17] In this case, one independent Al–O–C angle is bent (149°) and the second is nearly linear (176°). The origins of structural variation in Lewis acid adducts of metal carbonyls warrant further study.

Infrared spectra of I[6] show weak, low-frequency absorptions at ca. 1725 and 1600 cm^{-1}, characteristic of Lewis acid addition to the oxygen of a metal carbonyl.[18] Proton and carbon NMR spectra[6] suggest that I dissociates into monomers in benzene solution, since only one cyclopentadienyl resonance is observed, whereas there are two distinct environments in the solid state. (Rapid exchange between bridging and terminal sites cannot be ruled out.) Cleavage probably occurs at the weak Zr–O4 bond. Since diethylamine and diethylamido ligands retain distinct magnetic environments in solution, the amine proton does not pass rapidly from site to site. Presumably, the NH resonance itself is too broad to directly observe in the NMR spectrum.[19]

$[Zr\{Mo(CO)_3(Cp)\}_2(NEt_2)_2(NHEt_2)]_2$ reacts with Lewis bases. For example, dissolution in 1,2-dimethoxyethane rapidly causes I to dissociate into ions, as evidenced by the resulting IR spectrum of the $[Mo(CO)_3(Cp)]^-$ anion: $\nu(CO) = 1897$ (s), 1780 (s) cm^{-1}. Dissolution in tetrahydrofuran produced similar spectral changes, which are partially reversed when the product is redissolved in benzene.

$[Zr(NEt_2)_4]$ and $[MoH(CO)_3(Cp)]$ also react in molar ratios other than 1:2. Reaction in a 1:1 ratio produces only I and unreacted $[Zr(NEt_2)_4]$. Reaction in a 1:3 ratio in pentane gives a precipitate of I, whereas the same reaction in toluene leads to $[Zr\{Mo(CO)_3(Cp)\}_3(NEt_2)(NHEt_2)_2]$. The product of the 1:4 reaction is a red solid containing no ethyl groups (by NMR). Full characterization of these products is in progress.

Several important conclusions can be drawn from this work: (1) Dinuclear amine elimination is a useful method for preparing mixed-metal complexes under mild conditions, without competing oxidation–reduction reactions. (2) Multiple amine eliminations can be used to build polynuclear species. (3) Isocarbonyl bridges, rather than direct metal–metal bonds as earlier assumed, may be present in the products. (4) Eliminated amines may be *retained* as ligands.

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Supplementary Material Available: Listings of positional and thermal atomic parameters (Tables II and III) and experimental and calculated structure factors (Table IV) (34 pages). Ordering information is given on any current masthead page.

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Synthesis and Structural Characterization of a Cationic Rhenium Selenoformaldehyde Complex

Fred B. McCormick

3M Central Research Laboratories
St. Paul, Minnesota 55144

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Summary: The first cationic selenoformaldehyde complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}CH_2{=}Se)]^+$ (3) has been pre-