to a new type of bridge-assisted, addition reaction for cluster synthesis.[17] Because of the possible variation of metal acetylide[2b] (and hydride) reagents, this approach might also afford heterodinuclear clusters. In addition, complex **2** (and related hydrides) might add to other types of unsaturated bonds to give di- and polynuclear clusters or to other types of unsaturated bonds to give di- and polynuclear clusters having different types of bridging groups. The investigations of these possibilities as well as the reaction chemistry of complex **3** are being pursued.[18]

Acknowledgment. C.M.L. thanks the National Science Foundation (Grant CHE-8106140), the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the University Research Council of Vanderbilt University for support of this research. P.G.L. acknowledges support from NIH BRSG (Grant RR 07089-13). D.A. thanks Dr. Thomas M. Harris for assistance in acquiring NMR spectra.

Supplementary Material Available: A complete listing of final positional and thermal parameters, final observed and calculated structure factors, selected interatomic distances and angles, and selected least-squares planes data, and a brief description of the details of the solution and refinement (33 pages). Ordering information is given on any current masthead page.

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[18] In separate but analogous reactions, complex 2 reacts with acetylide complexes of Ni(II), Pd(II), Ir(I), and $(\eta\text{-}C_5H_5)(OC)_2Fe(C{\equiv}CPh)$ to give distinctive color changes like that observed for eq 1. Preliminary spectroscopic data are consistent with the formation of heterodinuclear complexes that are analogous to 3.

Structural Rearrangements in the Two-Electron Oxidations of Dimetal Cyclooctatetraene Compounds. Structure of the 34-Electron "Triple-Decker" Dication[†]

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A study of the two-electron oxidation[2] of the pseudo-triple-decker dicobalt compound $(CpCo)_2(cot)$ (Cp = η^5-C_5H_5; cot = η^8-cyclooctatetraene) (**1**) suggested that the dication might have a flattened cyclooctatetraene ring since this would give a delocalized 34-electron[3] triple-decker structure. $\mathbf{1}^{2+}$ was too unstable to be structurally characterized, but we now report the isolation of analogous dications in which the central C_8H_8 ring has two planar four-carbon fragments connected by a minor twist and the metal atoms are slipped to the sides of the C_8 ligand. Voltammetry experiments suggest that electron-transfer-induced movement of the two metal atoms over the C_8 ligand is much more facile for cobalt than for rhodium.

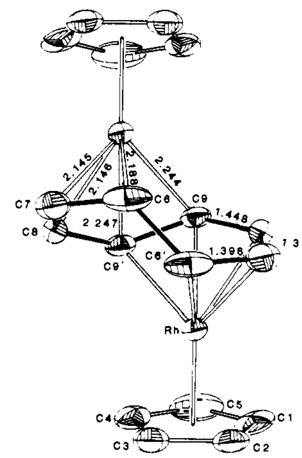
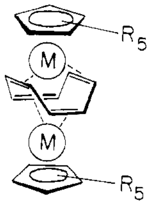


Figure 1. Thermal ellipsoid (40% probability) diagram and label scheme for $[CpRh(cot)RhCp](PF_6)_2$. A crystallographic 2-fold axis is perpendicular to the drawing and passes through the midpoints of the C6–C6′ and C9–C9′ bonds. Important bond distances not given on the figure are C6–C6′ 1.501, C9–C9′ 1.500, Rh–centroid (Cp) 1.823 Å. Estimated standard deviations on Rh–C bonds, 0.006; on C–C bonds, 0.01.

Cyclic voltammetric (CV) and controlled potential coulometric experiments on **2**[4] and the dirhodium complex[5] **3** show that both



2, M = Co; R = CH_3
3, M = Rh; R = H

undergo chemically reversible two-electron oxidations in which the electron transfer is either quasi-reversible (for **2**) or irreversible (for **3**). The $(\eta^5\text{-}C_5Me_5)Co_2$ complex **2** undergoes oxidation at a $E°$ potential (-0.24 V vs. SCE) 140 mV lower than **1**. Unlike **1**, for which a nearly Nernstian CV peak separation (ΔE_p) as low as 32 mV was obtained,[2] the smallest peak separation found for **2** in dichloromethane was 61 mV (v = 16 mV/s). Moreover, the peak potentials are scan-rate and temperature dependent, giving a ΔE_p of ca. 380 mV (v = 160 mV/s) at -40 °C.

Even larger CV peak separations are observed for the dirhodium complex **3** (E_{pa} = +0.47, E_{pc} = -0.17 V at v = 200 mV/s in 1:1 acetone/dichloromethane and E_{pa} = +0.55, E_{pc} = -0.14 V in dichloromethane). Bulk electrolysis of **3** in dichloromethane at +0.9 V caused the precipitation of the dicationic complex. $\mathbf{3}^{2+}$ was also obtained by chemical oxidation of **3** with 2 mol equiv of $AgPF_6$ in CH_2Cl_2. The product precipitated as dark red crystals and was separated from silver by dissolution in nitromethane, filtration, and crystallization by addition of benzene. The structure $\mathbf{3}^{2+}(PF_6)_2$ was determined by single-crystal X-ray diffraction studies. The key feature of the structure (Figure 1) is that the metal atoms are slipped to the side of the C_8 ring, which has two nearly planar C_4 fragments twisted by 34.8°. Each Rh is formally bonded to five carbons, requiring two carbons (C9 and C9′) to be bridging between the metals to give a 34-electron structure. The ^1H NMR spectrum of $\mathbf{3}^{2+}$ at reduced temperatures suggests that it retains this structure in solution (four sets of resonances from the C_8 ring).[7]

[†] Structural Consequences of Electron-Transfer Reactions 9. Part 8: J. Am. Chem. Soc. 1983, 105, 1772.

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[6] $[(CpRh)_2(cot)](PF_6)_2$ crystallizes in the orthorhombic, noncentrosymmetric group $P2_12_12$: a = 14.073 (3) Å, b = 11.353 (2) Å, c = 6.748 (1) Å, V = 1078.1 (4) Å^3, d(calcd) = 2.25 g cm^{-3}, Z = 2 (asymmetric unit consists of one Cp ring, one Rh atom, and one half of a cot ring). Refinement converged at R_F = 0.0299, R_{wF} = 0.0346, and GOF = 1.305.

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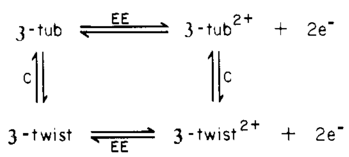
Scheme I



The dicationic species of the dicobalt complex **2** is also obtained in quantitative yields by chemical oxidation of **2** with $AgPF_6$ in diethyl ether. Despite numerous attempts we were unable to grow crystals of **2**$^{2+}$ suitable for X-ray structure determination. However, the low-temperature ^{1}H NMR spectrum of this complex in CD_3NO_2 shows four signal groups,[7] with the same chemical shift and splitting patterns, corresponding to four nonequivalent protons of cot, as for the dirhodium complex **3**$^{2+}$. It seems reasonable therefore to suggest a structure for the dicobalt species similar to that in Figure 1.

The electrochemistry of **2**$^{2+}$ and **3**$^{2+}$ is complementary to that of the neutral complexes. The dicobalt complex shows the same quasi-reversible wave observed for the electrochemical oxidation product of **2**. The dirhodium dication, which is virtually insoluble in CH_2Cl_2, is reduced in nitromethane irreversibly at −0.30 V, with a coupled irreversible oxidation at +0.35 V.

An intriguing question involves the difference in *apparent* electron-transfer rates of **2**$^{0/2+}$ and **3**$^{0/2+}$, the heterogenous standard electron-transfer rate of **2** (ca. 6×10^{-3} cm/s by digital simulation of CV curves) being about 5 orders of magnitude larger than that predicted from the very large CV peak separations of **3**. The voltammetry can be best explained if the structural rearrangements involving **3** and **3**$^{2+}$ occur subsequent to (not concerted with) the electron-transfer steps. Thus, the oxidation/reduction peaks of $(CpRh)_2$(cot) do not form a quasi-reversible couple; rather each peak represents an electron-transfer reaction followed by a chemical reaction (the structural rearrangement). For example, reduction of the cot-twisted dication, **3**-twist^{2+}, involves initial formation of a *neutral* cot-twisted complex (the bottom line of Scheme I) followed by rearrangement to the neutral cot-tub form **3**-tub. In this regard, the structural rearrangements are viewed as isomerizations coupled to the electron transfer (EEC mechanism, Scheme I).[8]

This interpretation suggests that it should be possible to find experimental conditions in which the tub form of **3**$^{2+}$ or the twisted form of **3** can be observed prior to rearrangement. Indeed rapid CV scans of **3**-twist^{2+} in acetone give a reversible reduction at $E° = -0.11$ V, suggesting that the neutral twisted form **3**-twist has a finite lifetime in this solvent.

The quasi-reversibility of **2**$^{0/2+}$ implies that interconversion of the dicobalt tub and twisted forms occurs rapidly during the electron-transfer process:

$$\mathbf{2}\text{-tub} \rightleftharpoons \mathbf{2}\text{-twist}^{2+} + 2e^-$$

A final point is that both **2**$^{2+}$ and **3**$^{2+}$ are fluxional at elevated temperatures. At 80 °C the four cot resonances of **2**$^{2+}$ and **3**$^{2+}$ merge into a broad singlet at 4.8 and 5.8 ppm, respectively. These compounds have promise as models with which to probe the redox-induced mobility of two or more metals bonded to polyolefinic hydrocarbons.

Acknowledgment. This work was generously supported by the National Science Foundation (CHE-8004242 and 8303974), which also provided funds to the University of Delaware for the purchase of the diffractometer. We gratefully acknowledge loan of rhodium salts from the Matthey Bishop Co. and a sample of **3** from Dr. A. Salzer.

Supplementary Material Available: Details of electrochemical measurements, complete listings of atomic coordinates, anisotropic thermal parameters, bond lengths and angles, hydrogen atom coordinates, and structure factor tables (14 pages). Ordering information is given on any current masthead page.

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[7] ^{1}H NMR data: **2**$^{2+}$ in $CD_3NO_2/(CD_3)_2CO$ (2:1) at 213 K, δ 7.8 (t, 2 H, H8), 6.3 (t, 2 H, H7), 5.4 (d, 2 H, H6), 4.9 (d, 2 H, H9), 1.5 (s, 30 H, Me Cp); **3**$^{2+}$ in CD_3NO_2 at 243 K, δ 7.37 (t, 2 H, H8), 5.31 (t, 2 H, H7), 3.56 (d, 2 H, H6), 3.05 (d, 2 H, H9), 6.05 (s, 10 H, H Cp) ppm.

[8] This analysis is made more complicated by the fact that these are overall two-electron processes, and the structural rearrangement might possibly come after the first electron transfer in an ECE-type process.

Direct Determination of Fe–C Bond Lengths in Iron(II) and Iron(III) Cyanide Solutions Using EXAFS Spectroelectrochemistry

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Received January 30, 1984

We describe the development and implementation of EXAFS spectroelectrochemistry (extended X-ray absorption fine structure spectroelectrochemistry), a new technique that permits determination of local structure in species that are electrochemically generated and maintained. The ability to determine the oxidation-state dependence of metal–ligand bond lengths in solution species is desirable for the evaluation and further development of electron-transfer theories.[1-3] In addition, this methodology can be used to structurally characterize biological materials that normally are unstable to reduction or oxidation in an X-ray beam.[4] We report here experiments with the ferricyanide/ferrocyanide couple leading to the first direct, solution determination of the Fe^{III}–C and Fe^{II}–C bond distances.

The electrochemical cell used must allow X-rays to pass through the sample while having the capability for rapid and exhaustive electrolysis. A modified version of the optically transparent, thin-layer electrochemical cell[5] works satisfactorily. The electrolysis region measures 38 × 14 × 1 mm and the electrolysis volume is ca. 500 μL. The working electrode consists of three layers of 100 lines per in. gold minigrid (Buckbee-Mears Co.) that lie parallel to the cell windows. Platinum wire auxiliary and Ag/Ag^+ reference electrodes are inserted in the filling ports. All electrochemical procedures were performed with a CV-27 Voltammograph (Bioanalytical Systems, Inc.). Ferricyanide solutions were prepared as 10 mM solutions of $K_3Fe(CN)_6$ in deionized, organic-free water (Sybron/Barnstead). Ferrocyanide solutions were generated by electrochemical reduction of the ferricyanide solutions. Either sodium acetate or lithium acetate was added at a concentration of 1 M as the supporting electrolyte in all experiments. Electrolysis of 10 mM ferricyanide solution was 95% complete in 30 min when the cell potential was maintained at −200 mV for reduction to the ferrocyanide complex or in 20 min at +500 mV for reoxidation to ferricyanide.

X-ray absorption spectra about the iron K edge (6.6 to 8.1 keV) were recorded at the Stanford Synchrotron Radiation Laboratory (SSRL). Data were recorded in the fluorescence mode. Iron K edge spectra were converted to electron volts by a single-point calibration based on the L_{III} edge of $Eu_2(CO_3)_3$ whose spectrum was recorded simultaneously. Changes that occur in the iron K edge region of the absorption spectrum upon reduction of $[Fe(CN)_6]^{3-}$ to $[Fe(CN)_6]^{4-}$ clearly indicate that reduction has taken place. The K edge region of each spectrum is dominated by an intense absorption peak, which can be attributed to an allowed 1s → 4p transition.[6] This transition shifts to lower energy and

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