Organometallics **1991,** *10,* 1229–1236

Articles

$Cp_3M_3(CO)_3$ Clusters: Electrocatalytic Isomerization and Effect of Changes in Metal and CO Bonding Mode on Electron-Transfer Properties[†]

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Received June 11, 1990

The electrochemical reduction of three trinuclear complexes of general formula $Cp_3M_3(CO)_3$ (Cp = η^5-cyclopentadienyl, M = Co or Rh) was studied in nonaqueous solutions. The cobalt complex $Cp_3Co_3(CO)_3$ (3) is reduced by one electron to a short-lived anion ($t_{1/2}$ = 2.6 s at 298 K), E^0 = −1.03 V vs SCE, which decomposes to the dinuclear anion $[Cp_2Co_2(\mu\text{-}CO)_2]^-$. Two analogous Rh complexes give more persistent anions. C_{3v}-$Cp_3Rh_3(CO)_3$ (2) forms a stable monoanion, E^0 = −1.01 V, and a dianion which is stable on the cyclic voltammetry time scale, E^0 = −1.75 V. The C_s trirhodium isomer C_s-$Cp_3Rh_3(CO)_3$ (1) is reduced in a first step to an anion somewhat less stable than that of 2, E^0 = −1.22 V, and in a second step to an unstable dianion, E_p = −1.73 V. The more positive E^0 for $2^{0/-}$ compared to $1^{0/-}$ is consistent with the higher electron-withdrawing ability of bridging as opposed to terminal CO groups. The enhanced kinetic stability of the cluster core when M = Rh rather than Co probably arises from the greater M–M bond strength of the second row metal. When the rest potential for voltammetric scans of 1 is more positive than about +0.2 V, the peaks are those of 2 rather than 1. This is shown to be due to anodic electrocatalysis of the C_s to C_{3v} isomerization. The minimum enhancement of the isomerization rate of the $47e^-$ C_s monocation over that of the $48e^-$ neutral complex is about 10^5.

Introduction

Trinuclear clusters with fixed capping groups (especially those with heteroatomic caps) often give rise to reversible electron-transfer reactions.[1-3] The caps or bridges can be thought of as holding together the metal framework as electrons are added to or extracted from orbitals which are antibonding or bonding, respectively, with respect to the M_3 fragment.[2,4,5] In the absence of stabilizing caps or bridges, reduction leads to more highly reactive anions and a greater tendency toward scission of a metal–metal bond.[2] Examples include the reductions of $Fe_3(CO)_{12}$[5-8] and $Ru_3(CO)_{12}$.[9] Carbonyl ligands are quite mobile in many clusters,[11,12] i.e., they may move easily between terminal and various bridging modes. However, the role of carbonyl flexibility in the redox chemistry of clusters has yet to be explored.[13,14]

Several specific questions are of interest. One concerns the effect of bridging carbonyls on the reactivity and structural integrity of a paramagnetic cluster anion or cation. Another relates to the importance of metal–metal bond strength in stabilization of electron-rich or electron-poor carbonyl clusters of second- or third-row transition metals. A third concerns the reputed superior electron-withdrawing ability of bridging CO's compared to terminal CO's,[15,16] a property which can in principle be probed by electrochemical studies of appropriate model systems.

We are attempting to address some of these questions in studies of the trinuclear cobalt-group complexes $Cp_3M_3(CO)_3$, Cp = η^5-cyclopentadienyl and M = Co, Rh, Ir. In a broad sense, these complexes are particularly relevant[17] to the cluster/surface analogy[17-19] in which the carbonyl ligand is viewed as a model for CO chemisorbed

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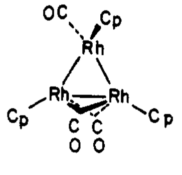
to a metal surface. The attractiveness of this series stems from the variety of members which differ in their modes of carbonyl bonding. The carbonyl isomeric preferences are known to depend on the identity of the metal, the substituents on the cyclopentadienyl ring, and on the sample matrix.[20-28]

This paper reports results on three complexes of this type, namely $Cp_3Co_3(CO)_3$, C_s-$Cp_3Rh_3(CO)_3$, and C_{3v}-$Cp_3Rh_3(CO)_3$. Together they exhibit the three most common isomers reported for this series. The thermodynamically stable form of the rhodium complex is the all edge bridging isomer 2 (C_{3v} symmetry). It and the Rh isomer 1 of C_s symmetry have been characterized by X-ray methods.[20-22] Complex 1, which has two edge-bridging CO's and one terminal CO, is best prepared by photolysis of 2[29,30] and slowly reverts to 2 in boiling benzene.[29] However, ^{13}C NMR studies by Shapley and Lawson[29] showed that the two isomers do not interconvert at room temperature, even though each is a fluxional molecule. The promise of isomeric stability under electrochemical conditions encouraged us to investigate differences in redox behavior between the two isomers.



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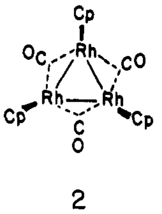

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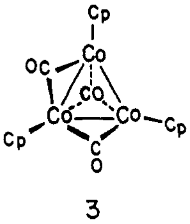

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Table I. Formal Potentials (V vs SCE) for Compounds Studied

compd	solvent	0/1- couple	1-/2-couple
	Reductions		
$Cp_3Co_3(CO)_3$	THF	−1.03	−1.9[a]
$Cp_3Co_3(CO)_3$	DMF[b]	−1.06	−1.9[a]
C_{3v}-$Cp_3Rh_3(CO)_3$ (2)	THF	−1.01	−1.75
C_s-$Cp_3Rh_3(CO)_3$ (1)	THF	−1.22	−1.73[a]
$Cp_2Rh_2(CO)_2(\mu$-CO)	THF	−1.58	−1.92[a]
	Oxidation		
C_{3v}-$Cp_3Rh_3(CO)_3$ (2)	CH_2Cl_2	+0.55[a]	

[a] Chemically irreversible. Peak potential given for v = 0.10 V/s, all other processes are reversible. [b] T = 238 K, all other measurements at 298 ± 2 K.

A different situation is found for the cobalt complex of analogous stoichiometry. In nonpolar solvents such as benzene a structure analogous to 1 is apparently favored.[24,31] However, in more polar solvents such as those employed in electrochemistry, $Cp_3Co_3(CO)_3$ is known to have structure 3, also found in the solid state. X-ray crystallography of this complex revealed two edge-bridging (μ_2) CO's and one face-bridging (μ_3) CO.[24]

This paper reports information on the relative fragmentation tendencies of anions of these clusters differing either in the metal (Co vs Rh) or in the CO arrangement (C_{3v}-Rh vs C_s-Rh). Formal potentials are reported, apparently for the first time, of two clusters differing only in their CO bonding modes. Finally, an enormously enhanced rate of C_s–C_{3v} isomerization is found upon oxidation of 1, in an electrocatalytic process. A preliminary account of some of this work has appeared.[32]

Experimental Section

All preparative procedures were carried out under a dinitrogen atmosphere with dried solvents, consistent with standard Schlenck procedures. Most electrochemical experiments were performed in a Vacuum Atmospheres drybox.

Tris(cyclopentadienylcobalt carbonyl), $Cp_3Co_3(CO)_3$, 3. This complex was prepared by photolysis of $CpCo(CO)_2$ under argon as previously described.[31,33] We found that toluene extracts of the photolysis residues contained significant amounts of the dinuclear complex $Cp_2Co_2(\mu$-$CO)_2$, much of which was removed by sublimation at 10^{-2} mmHg for 3 h. The dark sublimation residues were extracted with pentane until the washings were no longer green. Subsequent extraction with diethyl ether gave brown solutions which when evaporated gave the pure (by elemental analysis) cluster 3. Its IR spectrum in benzene was as reported.[24]

Tris(cyclopentadienylrhodium carbonyl), $Cp_3Rh_3(CO)_3$, C_{3v} Isomer 2 and C_s Isomer 1. The two isomers of $Cp_3Rh_3(CO)_3$ were prepared by using the methods of Shapley and Lawson.[29,30] The necessary precursors [$[Rh(CO)Cl]_2$[34] and $CpRh(CO)_2$[35]] were obtained from known procedures. Problems were experienced obtaining significant amounts of the C_s isomer 1 from photolysis of 2. Typically, 60 mg of 2 afforded pure 1, albeit in quantities of only 5–20 mg.[36]

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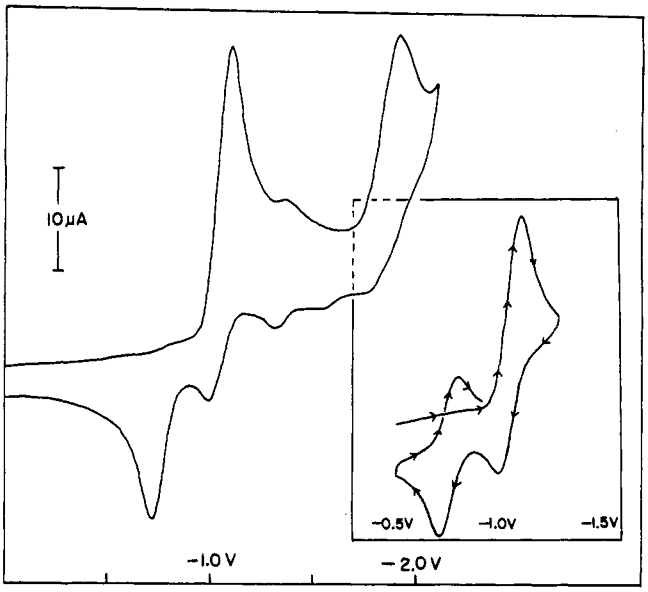

Figure 1. Voltammetry of ca. 2 mM $Cp_3Co_3(CO)_3$ in THF/0.1 M Bu_4NPF_6 at Pt disk electrode, T = ambient. Main figure: Scan from 0 to −2.1 V with v = 0.05 V/s. Inset: Multiple scan from 0 to −1.3 V with scan reversal at −0.5 V on second scan, showing reversible product couple assigned to $[Cp_2Co_2(\mu\text{-}CO)_2]^{0/-}$, v = 0.10 V/s.

Instrumentation and Electrochemistry. Electrochemical experiments were conducted as earlier described.[37] The supporting electrolyte was 0.1 M Bu_4NPF_6 in all cases, and potentials are referenced to the aqueous saturated calomel electrode (SCE), against which the ferrocene/ferrocenium couple had a voltage of + 0.46 V (CH_2Cl_2) or + 0.56 V (THF). Throughout the text, the symbol E^0 refers to the formal potential of a reversible couple, measured as the average of the cathodic and anodic peak potentials in CV experiments. The symbol $E_{1/2}$ refers to half-wave potentials measured at the RPE. Tetrabutylammonium chloride (Sigma) was dried under heated vacuum before use. Because of the small amounts of 1 available, a small-volume cell was employed in which volumes of 5 mL or less could be investigated by voltammetry (luggin probe reference tip) and bulk coulometry.

Samples of the anion radical of 2 were taken for ESR analysis by removal of electrolyzed solutions from the cell in the drybox, followed by rapid quenching in liquid nitrogen. All ESR spectra were measured at 77 K with DPPH used as a reference.

Results

Reduction of $Cp_3Co_3(CO)_3$. The carbonyl bonding mode of $Cp_3Co_3(CO)_3$ is known to be sensitive to matrix and solvent effects.[23,24,31] Cotton and co-workers have shown that the favored form in polar solvents such as THF is that of structure 3 which has one face-bridging CO and two edge-bridging CO's which bridge a single Co–Co bond. This isomer, which has been characterized by X-ray crystallographic methods,[24] is assumed to be that responsible for the electrochemistry reported in this paper. Spectroelectrochemical experiments are planned to investigate the solvent dependence of the voltammetric behavior, but results to date are included here in order to compare the Co_3 and Rh_3 clusters.

The reduction of this compound in glyme was reported to be a reversible one-electron process giving a monoanion partially characterized by ESR spectroscopy.[38] The reported spectrum is more likely that of the dinuclear monoanion $[Cp_2Co_2(\mu\text{-}CO)_2]^-$, which the following experiments show to be formed rapidly and in high yield through decomposition of the primary monoanion $[Cp_3Co_3(CO)_3]^-$.

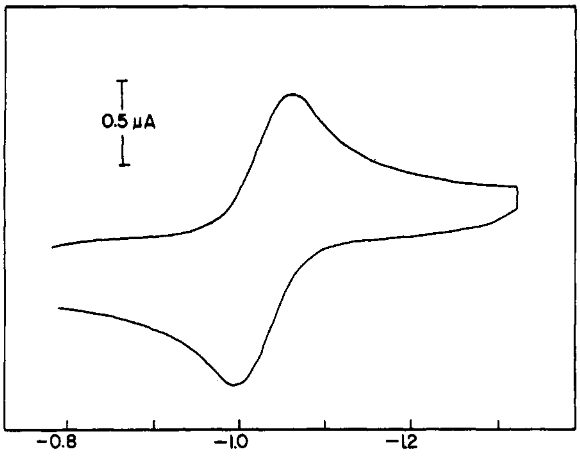

Figure 2. CV of 0.72 mM $Cp_3Co_3(CO)_3$ in DMF/0.1 M Bu_4NPF_6 at T = 238 K, v = 0.11 V/s, Pt bead electrode.

When solutions of $Cp_3Co_3(CO)_3$ in THF, DMF, or CH_3CN are scanned negatively at either Pt or Hg electrodes, two cathodic processes of one-electron height are observed (Figure 1). The wave slightly negative of −1.0 V gives 3^-. The height of the anodic wave for oxidation of 3^- to 3 on the reverse sweep depends on the scan rate. The second wave (E_{pc} = −1.9 V) is chemically irreversible and its height increases relative to the first as the scan rate increases (Table I). Over the same range of scan rates the anodic to cathodic current ratio increases for the first wave until the reversible value of i_a/i_c = 1.0 is reached when v > 0.5 V/s. ΔE_p values for this couple were about the same as those of $Cp_2Fe^{0/+}$ under comparable conditions (ca. 70 mV at v = 0.1 V/s in THF), consistent with nearly Nerstian charge transfer.

The decomposition rate of $[Cp_3Co_3(CO)_3]^-$ (3^-) was estimated from i_a/i_c values by the Nicholson method,[39] yielding an assumed first-order rate constant of k = 0.25 s^{-1} at T = 298 K. The half-life of 3^- is therefore ca. 2.6 s under these conditions.

The dinuclear monoanion $[Cp_2Co_2(\mu\text{-}CO)_2]^-$ so well characterized by Bergman and co-workers[40] is shown by electrochemistry and ESR to be the decomposition product of 3^-. The reversible couple $[Cp_2Co_2(\mu\text{-}CO)_2]/[Cp_2Co_2(\mu\text{-}CO)_2]^-$ has an E^0 of −0.74 V under these conditions (measured on an authentic sample). Peaks for this couple are observed on the reverse sweep of the first CV scan (anodic branch) and on the second forward sweep of a multiple scan experiment (cathodic branch) (Figure 1).

Consistent with eqs 1–3 and the observed kinetics, the anodic wave owing to oxidation of $[Cp_2Co_2(\mu\text{-}CO)_2]^-$ becomes smaller as v increases. At high scan rates or low temperatures (Figure 2) the reduction of $Cp_3Co_3(CO)_3$ appears to be an uncomplicated one-electron process (eq 1).

$$Cp_3Co_3(CO)_3 + e^- \rightleftharpoons [Cp_3Co_3(CO)_3]^- \qquad E^0 = -1.03\ \text{V} \tag{1}$$

$$[Cp_3Co_3(CO)_3]^- + e^- \rightarrow [Cp_3Co_3(CO)_3]^{2-} \qquad E_{pc} = -1.9\ \text{V}\ (v = 0.1\ \text{V/s}) \tag{2}$$

$$[Cp_3Co_3(CO)_3]^- \rightarrow [Cp_2Co_2(\mu\text{-}CO)_2]^- + \text{“}CpCo(CO)\text{”} \tag{3}$$

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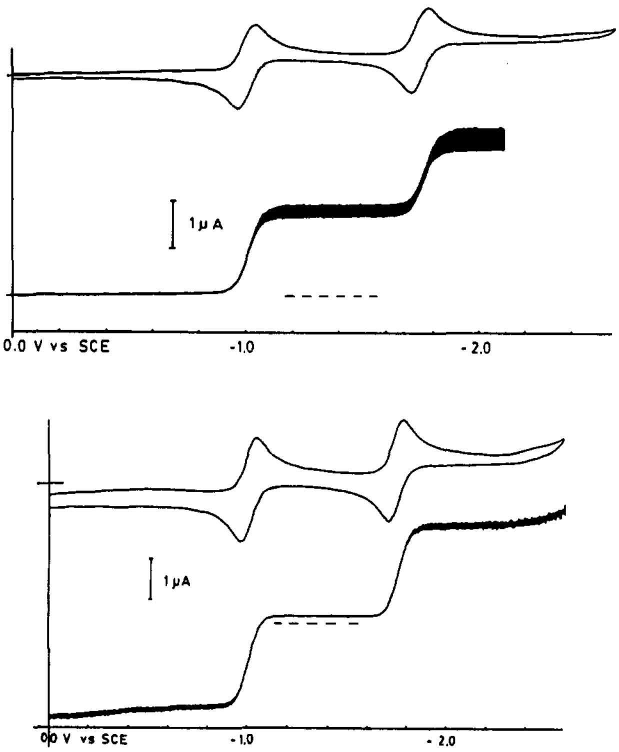

Figure 3. Top: Neutral C_{3v}-$Cp_3Rh_3(CO)_3$ (2) prior to electrolysis. Conditions were 0.52 mM 2 in THF/0.1 M Bu_4NPF_6, T = 283 K, Pt bead electrode, scan rate for CV = 0.20 V/s, for RPE = 0.04 V/s. Bottom: Scans after electrolysis at E_{appl} = −1.2 V, indicating stable 2^-. The dashed line gives the current zero in both experiments.

Bulk reduction of 3 with E_{app} = −1.2 V required 1.4 F of electrons, consistent with the overall stoichiometry of eq 4 which predicts 1.5 F. The major electrochemically

$$2Cp_3Co_3(CO)_3 + 3e^- \rightarrow 3[Cp_2Co_2(\mu\text{-}CO)_2]^- \qquad (4)$$

detectable product was that of the dinuclear complex $[Cp_2Co_2(\mu\text{-}CO)_2]^-$ (E^0 = −0.74 V), with a peak height approximately equal to that of the trinuclear starting material. A small (reversible) byproduct wave with E^0 ca. −1.3 V was also observed. Hence the dinuclear monoanion appears to be the major reduction product of $Cp_3Co_3(CO)_3$. The fully reduced solutions gave fluid ESR spectra identical with those reported for $[Cp_2Co_2(\mu\text{-}CO)_2]^-$ ($\langle a_{Co}\rangle$ = 48 G, 2 equivalent spins, $\langle g\rangle$ = 2.09).[40] Lower temperature electrolysis gave predominantly the cluster anion 3^-. At 238 K in DMF, only one electron was consumed (expt: 0.97 F) and only the CV waves for the $3/3^-$ couple were observed. Attempts to obtain ESR spectra of 3^- failed owing to formation of $[Cp_2Co_2(\mu\text{-}CO)_2]^-$ during the sample transfer.

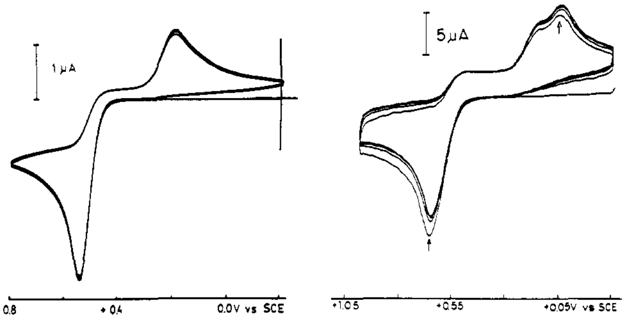

Figure 4. Oxidation of C_{3v}-$Cp_3Rh_3(CO)_3$ (2) in CH_2Cl_2/0.1 M Bu_4NPF_6. Top: Multiple cycle CV scans with v = 0.2 V/s. Conditions were 0.7 mM, T = 298 K, Pt electrode. Bottom: Multiple cycle CV scans with v = 10 V/s. Conditions were the same except that concentration was 0.47 mM.

Reduction of C_{3v}-$Cp_3Rh_3(CO)_3$ (2). The rhodium cluster with symmetrically disposed edge-bridging carbonyls gives rise to two cathodic processes, both of them Nernstian one-electron reductions which exhibit moderate to high chemical reversibility.[41] The reactions were studied in THF and in chloroalkane solvents, with the E^0 values of eqs 5 and 6 (Table I) being those measured in THF.

$$C_{3v}\text{-}Cp_3Rh_3(CO)_3 + e^- \rightleftharpoons [C_{3v}\text{-}Cp_3Rh_3(CO)_3]^- \qquad E^0_1 = -1.01\ V \qquad (5)$$

$$[C_{3v}\text{-}Cp_3Rh_3(CO)_3]^- + e^- \rightleftharpoons [C_{3v}\text{-}Cp_3Rh_3(CO)_3]^{2-} \qquad E^0_2 = -1.75\ V \qquad (6)$$

Bulk reduction at 298 K with E_{app} = −1.2 V in THF consumed 1.2 F as the solution went from gold to the dark green of 2^-. CV and RPE (rotating Pt electrode) scans (Figure 3) indicated about 90% conversion to the monoanion and a frozen sample of this solution gave an axial ESR spectrum with no hyperfine splittings ($g_\parallel$ = 2.0833, $g_\perp$ = 1.9885). We conclude that $[C_{3v}\text{-}Cp_3Rh_3(CO)_3]^-$ is quite persistent. The presence of a 2-fold excess of $P(OMe)_3$ in appeared to have no effect on the anion 2^-.

The *dianion* of 2 is more reactive. Bulk reduction of 0.5 mM C_{3v}-$Cp_3Rh_3(CO)_3$ at 283 K in THF with E_{app} = −1.95 V gave a dark red solution as 2.36 F were passed. CV scans after electrolysis showed about 10 waves in the potential range +1.0 to −2.0 V. The two principal reduction waves were reversible processes with approximately equal cathodic heights, E^0 values of −1.61 and −1.92 V. The cathodic peaks match fairly well those of the carbonyl-bridged dinuclear complex $Cp_2Rh_2(CO)_2(\mu\text{-}CO)$ which we measure at E_p = 1.58 and −1.92 V at 300 K. Assignment of this complex as a reduction product must be considred tentative since no confirming spectral information is available. However, one can say with reasonable assurance that two-electron reduction of the cluster C_{3v}-$Cp_3Rh_3(CO)_3$ leads to fragmentation of the cluster over a several minute time scale at 283 K. Confirming this, two-electron reduction in the presence of $P(OMe)_3$ leads to yet other electrochemical product waves.

Oxidation of C_{3v}-$Cp_3Rh_3(CO)_3$ (2). Anodic processes involving 2 were not a primary focus of this work, but the discovery of an oxidative electrocatalytic isomerization of 1 to 2 (vide infra) led us to survey the oxidation properties of 2. The oxidation of C_{3v}-$Cp_3Rh_3(CO)_3$ is diffusion controlled and electrochemically irreversible, but at least partially chemically reversible.

The limiting current in an RPE voltammogram of 2 ($E_{1/2}$ = + 0.55 V) was essentially twice that of its reduction. The overall two-electron oxidation was confirmed by coulometry. The anodic peak potential of 2 (+0.55 V at v = 0.1 V/s) shifted positive by 38 mV per 10-fold increase in scan rate, uncorrected for resistance errors.[42] A shift of 30 mV

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(41) Voltammetric diagnostics were obtained in an experiment employing 1:1 dichloromethane/1,2-dichloroethane as solvent (this mixture gives an ESR-quality frozen glass) over the CV scan rate range 0.05–0.50 V/s. Both reductions were diffusion controlled (constant $i_p/v^{1/2}$) and electrochemically reversible [ΔE_p and $E_p - Ep/2$ values equal to that of Cp_2Fe/Cp_2Fe^+ under same conditions (e.g., ΔE_p = 70 mV at v = 0.20 V/s; $E_p - Ep/2$ = 60–62 mV)]. The first reduction is chemically reversible (i_a/i_c = 1.00 ± 0.05 over range of v) whereas the dianion is slightly unstable under the same conditions (i_a/i_c = 0.86 at v = 0.05 V/s).

(42) Control experiments with $Cp_2Fe^{0/+}$ or $Cp_2Co^{0/+}$ under similar conditions give peak shifts of ca. 10 mV per decade in v.

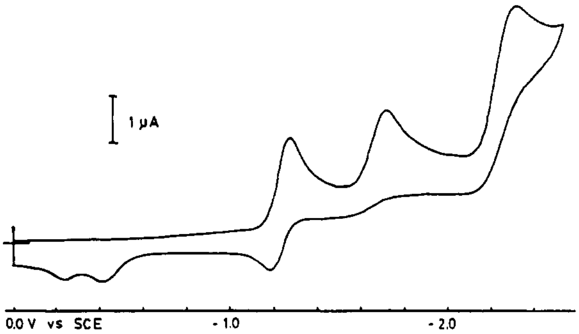

Figure 5. Reductions of C_s-$Cp_3Rh_3(CO)_3$ (1) in THF/0.1 M Bu_4NPF_6. Conditions were 0.35 mM, $T = 300$ K, $v = 0.20$ V/s, Pt electrode. The anodic waves at +0.2 V and +0.4 V arise from unassigned reduction products.

is expected for an irreversible process with $n = 2$, $\alpha = 0.5$.[43] $E_p - E_{p/2}$ was 45 mV, also consistent with αn near unity.[44] The reverse sweep at room temperature (Figure 4) showed one cathodic wave at + 0.2 V when the CV scan rate was below 0.2 V/s, but two cathodic features at higher sweep rates. The second product wave was also seen with slower scan rates at subambient temperatures.

Bulk oxidation of 2 at 253 K ($E_{appl} = +0.7$ V) gave 1.7 F and two product cathodic waves at $E_{pc} = +0.15$ V and + 0.05 V, matching the positions of product waves in low-temperature CV experiments. Reduction of the oxidized solution negative of both product waves ($E_{appl} = -0.2$ V) regenerated the original complex in about 65% yield, the current balance being made up by small cathodic peaks at −0.39, −0.85, −1.43, and −1.85 V. The oxidized solution reacts with $P(OMe)_3$ to give several new waves.

The oxidation product(s) of C_{3v}-$Cp_3Rh_3(CO)_3$ are as yet unidentified. However, the major product is shown to reform the original cluster upon rereduction, arguing against cluster fragmentation as the principal reaction route in oxidized 2. One possibility is opening of an edge of the cluster to give a linear Rh_3 moiety. We intend to pursue this interesting question. In the context of this paper, however, it is the general anodic characteristics of 2 and its $E_{1/2}$ value of +0.55 V (from RPE scans) that are most pertinent.

Reduction of C_s-$Cp_3Rh_3(CO)_3$ (1). This isomer shows the familiar pattern of two one-electron cathodic waves in THF. The first is diffusion-controlled and close to reversible in both the Nernstian and chemical senses. The ΔE_p value ($v = 0.1$ V/s) of 82 mV was slightly larger than that of either $Cp_2Fe^{0/+}$ or C_{3v}-$Cp_3Rh_3(CO)_3{}^{0/-}$. Furthermore, the value of i_a/i_c for this couple was marginally below that of a totally chemically reversible couple (0.93 with $v = 0.05$ V/s). A minimum half-life for 1^- of ca. 20 s is suggested by these data. The second cathodic wave of 1 was a one-electron process, chemically irreversible at temperatures down to 263 K ($v = 0.5$ V/s) (Figure 5). This is in contrast to 2, wherein reversibility is seen for the $[C_{3v}\text{-}Cp_3Rh_3(CO)_3]^-/[C_{3v}\text{-}Cp_3Rh_3(CO)_3]^{2-}$ couple. Scans to more negative potentials revealed a third reduction wave appearing to arise from the decomposition of the dianion.

Bulk electrolysis at the first reduction ($E_{appl} = -1.4$ V) gave an initial decrease of current with time, but a significant steady-state current, most likely arising from catalytic regeneration of the neutral reactant, invalidated the coulombic results. The electrolysis was discontinued after passage of 6 F. Cyclic voltammograms of the resulting solution showed the main peak at ca. −1.6, similar to that observed when the C_{3v} isomer is reduced to the dianion (vide ante). Apparently the anion 1^- undergoes irreversible reactions in parallel with regeneration of the neutral complex. Anion fragmentation is more rapid in the C_s isomer than in the C_{3v} isomer.

Oxidation of C_s-$Cp_3Rh_3(CO)_3$ (1). Cyclic voltammetry scans from 0 to +1 V vs. SCE for CH_2Cl_2 or THF solutions of 1 were identical with those of 2, appearing to suggest that the oxidations of the two isomers occurred at identical potentials. This implication runs counter to the observation that the reduction potentials differ by a rather large amount, 210 mV. Rather, it is now obvious that 1 is converted to 2 at the electrode surface when solutions of 1 are subjected to applied potentials more positive than ca. −0.1 V. The reaction is electrocatalytic, so no detectable current flows during the conversion (eq 7).

$$C_s\text{-}Cp_3Rh_3(CO)_3 \rightarrow C_{3v}\text{-}Cp_3Rh_3(CO)_3 \quad (7)$$

The clearest confirmation of the electrocatalytic conversion was obtained from bulk coulometry experiments. An E_{appl} of +0.22 or +0.24 V was employed. No anodic peak is observed in CV scans at this potential in solutions of 1. Nevertheless, within an average of ca. 300 s the solution changed color from the green of the C_s isomer (1) to the gold of the C_{3v} isomer (2). Coulometry indicated that only 0.03 F were passed in the reaction. CV scans before and after the electrolysis throughout the region +1 to −2 V indicated quantitative conversion from isomer 1 to isomer 2.

Chemical oxidation by Cp_2Fe^+ had a similar effect on solutions of the C_s isomer, although the catalytic efficiency was lower. Addition of 0.09 equiv of ferrocenium ion to CH_2Cl_2 solutions of 1 (5×10^{-4} M) resulted in complete conversion to the C_{3v} isomer 2, as monitored by optical spectroscopy[45] and voltammetry.

It is reasonable to assume that the oxidation of the C_s isomer occurs at a less positive potential than does the oxidation of the C_{3v} isomer, paralleling the shift in E^0 values for the reduction of these clusters. An anodic process might be therefore expected for 1 somewhere in the range of +0.2 to +0.4 V. In the event that this is a one-electron process, we may represent it by eq 8. If the isomerization reaction is rapid, the C_s cation would be converted to the C_{3v} cation (eq 9) in the electrode reaction layer. Finally, since E_{appl} would be negative of the E^0 for reduction of the C_{3v} *cation*, eq 10 would result in production of neutral 2.

$$C_s\text{-}Cp_3Rh_3(CO)_3 \rightleftharpoons [C_s\text{-}Cp_3Rh_3(CO)_3]^+ + e^- \quad (8)$$

$$[C_s\text{-}Cp_3Rh_3(CO)_3]^+ \rightarrow [C_{3v}\text{-}Cp_3Rh_3(CO)_3]^+ \quad (9)$$

$$[C_{3v}\text{-}Cp_3Rh_3(CO)_3]^+ + e^- \rightleftharpoons C_{3v}\text{-}Cp_3Rh_3(CO)_3 \quad (10)$$

The result of eqs 8–10 is conversion from 1 to 2 without net passage of current, with the electrode reaction layer containing 2 and the bulk of solution containing 1. If the conversion at the electrode surface is complete, positive- or negative-going CV scans have exclusively the voltammetric characteristics of 2, the isomer with only bridging CO's. In the ECE sequence of eqs 8–10 we have written the oxidation steps as one-electron processes, although there is no proof of the anodic stoichiometry. In the event

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(43) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 706.

(44) Adams, R. N. *Electrochemistry at Solid Electrodes*; Marcel Dekker: New York, 1969; p 136.

(45) The diagnostic optical bands in CH_2Cl_2: 1, $\lambda_{max} = 318$ nm ($a_M = 1.35 \times 10^4$ M^{-1} cm^{-1}) and 280 nm (1.15×10^4); 2, 396 nm (5.66×10^4) and 285 nm (2.60×10^4).

that the cross-reaction of eq 11 comes into play, reduction

$$[C_{3v}\text{-}Cp_3Rh_3(CO)_3]^+ + C_s\text{-}Cp_3Rh_3(CO)_3 \rightleftharpoons C_{3v}\text{-}Cp_3Rh_3(CO)_3 + [C_s\text{-}Cp_3Rh_3(CO)_3]^+ \quad (11)$$

of the C_{3v} cation might also be accomplished by a homogeneous charge-transfer reaction. However, the conversion from 1 to 2 appears to be too fast to have the homogeneous reaction contribute to a major extent.[46]

Several approaches were used in an effort to estimate the E^0 or $E_{1/2}$ value for oxidation of 1. In principle, sufficiently fast linear scans from negative to positive potentials can outrun the rate of the cation isomerization (eq 9) and result in the appearance of a new anodic wave arising from eq 8. Scans up to 10 V/s did *not* show the onset of new waves between 0 and + 0.45 V. Preliminary simulations of the ECE mechanism of eqs 8–10 were performed by P. H. Rieger under the assumption that E^0 for eq 8 is 300 mV negative of that of eq 10. These calculations showed that a measurable anodic wave would arise if the rate of eq 9 is lower than ca. 10^5 s^{-1}. Hence we take this as a tentative lower limit for the rate of the isomerization of the cation $[C_s\text{-}Cp_3Rh_3(CO)_3]^+$. Confidence in this number is tempered by the fact that the simulations did not take the cross-reaction of eq 11 into account.

An anodic wave for oxidation of 1 should also be observed if the electrocatalytic chain is interrupted by decomposition of the cation of either the C_s or C_{3v} isomer. For example, if the C_{3v} cation reacts with a nucleophile (eq 12), then 2^+ will not be reduced in eq 10 (or eq 11) and the oxidation of 1 would result in net passage of current through the equations

$$C_s\text{-}Cp_3Rh_3(CO)_3 \rightleftharpoons [C_s\text{-}Cp_3Rh_3(CO)_3]^+ + e^-$$

$$[C_s\text{-}Cp_3Rh_3(CO)_3]^+ \rightarrow [C_{3v}\text{-}Cp_3Rh_3(CO)_3]^+$$

$$[C_{3v}\text{-}Cp_3Rh_3(CO)_3]^+ + \text{Nuc} \rightarrow \text{products} \quad (12)$$

Preliminary experiments of this type have been performed. CV experiments on CH_2Cl_2 solutions of 1 containing $[Bu_4N][Cl]$ revealed an anodic wave with a peak potential of +0.38 V. No conclusion can be made on the question of whether the catalytic cycle is being interrupted by reaction of the C_{3v} cation (eq 12) or of the C_s cation (eq 13). It is significant, however, that the potential of the new

$$[C_s\text{-}Cp_3Rh_3(CO)_3]^+ + \text{Nuc} \rightarrow \text{products} \quad (13)$$

peak is about 200 mV negative of the C_{3v} anodic wave, in concert with the shift seen in the one-electron reductions of the two isomers (vide ante).

Finally, an attempt was made to probe the relative concentrations of 1 and 2 in the electrode reaction layer for different static applied potentials in solutions of 1. In this approach, the potential was held for 15 s at a potential between −0.2 and +0.6 V, then rapidly scanned to more negative potentials (Figure 6), terminating about −1.5 V. The cathodic peak currents for 2 (E_{pc} = −1.03 V) and 1 (E_{pc} = −1.24 V) were used to calculate the relative amounts of the two isomers near the electrode surface. This experiment was repeated for other values of E_{app}. A figure in our earlier communication[32] gave the amount of C_{3v} isomer 2 as a function of applied potential. Current for the isomerized cluster 2 begins to appear when $E_{appl} > 0$ V and increases until a plateau is reached ($E_{appl} > +0.4$ V).[47] The midpoint of this plot was + 0.25 V, which may be taken as another estimate of $E_{1/2}$ for the oxidation of the C_s isomer. Qualitatively, since the isomerization reaction facilitates the oxidation of 1, this estimate of the $E_{1/2}$ should be negative of the true E^0 of eq 8.

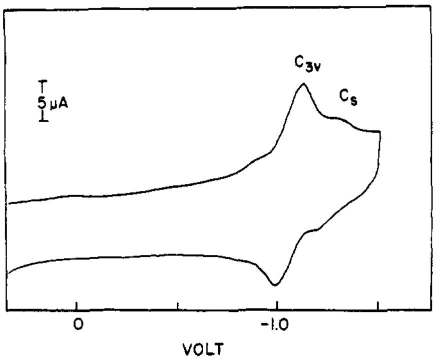

Figure 6. Cathodic scan of 0.35 mM 1 (C_s isomer) in CH_2Cl_2/0.1 M Bu_4NPF_6 with rest potential that allows conversion of 1 to 2 in electrode reaction layer. Conditions were T = 298 K, Pt electrode, v = 20 V/s.

Discussion

Reductions. Comparing the kinetic stabilities of the three monoanions studied, we find in order of increasing stability $[Cp_3Co_3(CO)_3]^- < [C_s\text{-}Cp_3Rh_3(CO)_3]^- < [C_{3v}\text{-}Cp_3Rh_3(CO)_3]^-$. The half-life of the tricobalt anion (2.6 s at 298 K) is at least one order of magnitude lower than that of either isomer of the trirhodium anions. The lifetime of the less stable trirhodium anion, $[C_s\text{-}Cp_3Rh_3(CO)_3]^-$, is somewhere between the CV timescale (ca. 20 s) and the bulk electrolysis timescale (ca. 600 s). The decomposition products appear to involve cluster fragmentation, as demonstrated in the Co_3 case by formation of $[Cp_2Co_2(\mu\text{-}CO)_2]^-$ and as implied by the multitude of product waves, including one assigned to $Cp_2Rh_2(CO)_2(\mu\text{-}CO)$, formed upon electrolysis of 1.

The LUMO of 48e⁻ triangular clusters has been shown to be an a_2 symmetry orbital which is antibonding among the metals.[4–6,1j] Addition of an electron to this orbital weakens the trimetallic framework and produces anions with a tendency toward scission of one M–M bond or outright fragmentation, as has been observed in other studies.[5a,2] The increased stability of the Rh_3 cluster anions (compared to the Co_3 anion) is explicable in terms of increased M–M bond strength for the heavier metal. Thermochemical measurements suggest an increase of ca. 20 kJ mol^{-1} for Rh–Rh over Co–Co bonds.[48] A second factor that may be operative in the greater kinetic stability of the trirhodium anions is the increased carbonyl π-acidity expected from more efficient π-back-bonding from Rh compared to Co.[49] A broader study is needed to distin-

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(46) At potentials positive of the E^0 of $1^{0/+}$ the concentration of C_s-$Cp_3Rh_3(CO)_3$ (1) is very small close to the electrode, limiting the extent of Eq 11. A longer-lived cation 2^+ would diffuse into the bulk of solution, where the concentration of (unelectrolyzed) 1 is much higher, leading to a larger contribution from eq 11.

(47) This experiment would be best conducted by using a fresh solution to obtain each data point because when $E_{appl} > E^0(1^{0/+})$ a "minielectrolysis" occurs at the electrode during the 15-s hold at the rest potential. For noncatalytic mechanisms this causes no difficulties, but for a catalytic process with a reasonably high chain length, some change of concentrations can occur in the body of solution. This was observed, and a procedure correcting for this effect was employed which simply assumed that the amount of isomer 2 in the bulk of solution before a scan from a given potential was proportional to the raw i_p for isomer 2 times the rest time at that potential. Details are given in ref 36.

(48) Connor, J. A. See: ref 11, pp 358–363.

(49) Holland, G. F.; Ellis, D. E.; Tyler, D. R.; Gray, H. B.; Trogler, W. C. *J. Am. Chem. Soc.* 1987, *109*, 4276.

guish between these two factors.

Separate comparison can be made between the kinetic stabilities of the anions of the C_{3v} and C_s trirhodium isomers, which of course contain the same trimetallic core but differ in disposition of the CO ligands. $[C_{3v}\text{-}Cp_3Rh_3(CO)_3]^-$ (2^-) is stable indefinitely under N_2, in contrast to 1^-, which apparently fragments completely within minutes. The increased kinetic stability of the former may arise from the superior ability of the three symmetrical bridging CO's to withdraw negative charge from the metal core. In contrast, the C_s anion has fewer bridging carbonyls to withdraw charge. Moreover, the disposition of *two* CO's bridging *one* M–M bond in 1^- creates an unequal charge distribution in the cluster. The charge density built up on the unique metal (with the terminal CO) might weaken the adjacent M–M bond or make it more susceptible to electrophilic attack.

As implied in the foregoing discussion, bridging CO's are generally assumed to have a π-acidity superior to that of terminal CO's. This property has consequences for the rates and mechanisms of metal carbonyl reactions.[16,50] From the E^0 values of the 0/1- couples of 1 and 2, one can obtain a quantitative measure of the effect of carbonyl geometry on the thermodynamic stabilization of the cluster anion. Consistent with qualitative expectations, the C_{3v} isomer is reduced 210 mV positive of the C_s isomer. In thermochemical language, this amounts to a stabilization of ca. 20 kJ mol^{-1}. It must be kept in mind that an E^0 value depends on the *difference* in energies of the oxidized and reduced forms of the couple. Thus the more positive E^0 of the C_{3v} isomer means that the extra bridging CO stabilizes 2^- relative to 2 to a greater extent than does the CO arrangement on the other isomer stabilizes 1^- relative to 1. Therefore, although the increased π-acidity of the three CO bridges in 2 is undoubtedly operative in both redox states, it is more effective when removing charge from the anion than from the neutral complex.

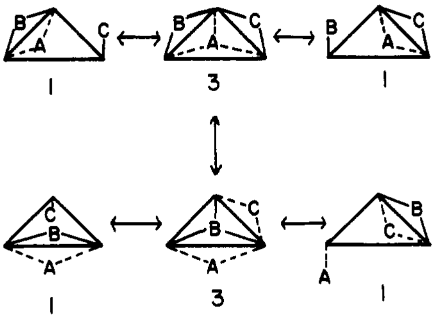
Electrocatalytic Oxidation. Electron-transfer catalyzed (ETC) reactions became well known in organometallic chemistry during the past decade. The most in-depth exploration has involved ligand substitutions,[51] but other reactions, including stereoisomerization, have also been enhanced.[52] The electrode-catalyzed anodic isomerization of 1 to 2 is a still-rare example of an ETC cluster geometry change. The rate of the isomerization of 1^+ to 2^+ could not be measured because positive-sweep scans of 1 up to v = 10 V/s showed only the peak assigned to 2. Given the literature report that the thermal conversion of 1 to 2 requires 0.5 h in boiling benzene, we estimate a rate enhancement for isomerization in the cation of at least 10^5.[53]

The difficulty of obtaining workable amounts of pure 1 limited our mechanistic studies on the catalytic process, but the data unequivocally establish the fact of the electrode-catalyzed reaction and lead us to speculate on the reason for the enormous acceleration of the isomerization in the 47e$^-$ cation.[54]

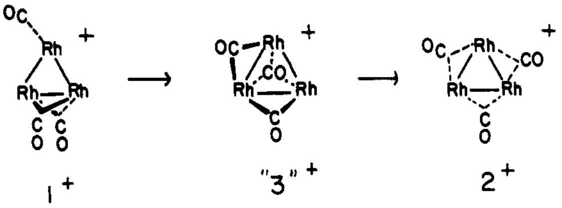
In our earlier communication we postulated that isomer 3, which has two edge-bridging and one face-bridging CO's, might be an anodic intermediate (eq 14). Isomers 2 and

$$1 \rightarrow 1^+ \rightarrow 3^+ \rightarrow 2^+ \rightarrow 2 \qquad (14)$$

3 have been shown to be in equilibrium for tricobalt clusters,[23,24] and 3 has been postulated to be an intermediate in the fluxional behavior of 1 (see Lawson and Shapley[29]):

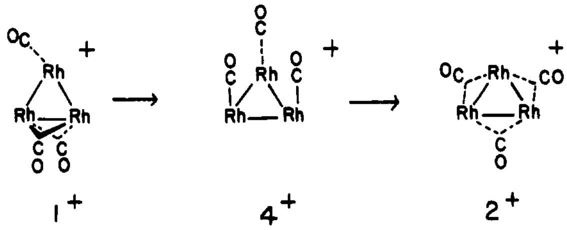


It is important to note that the ^{13}C NMR studies of ref 29 rule out the possibilities that the observed fluxionality of 1 involves 2 or that the fluxional behavior of 2 involves 1. There is negligible thermal interconversion between the two neutral isomers at room temperature. However, since isomers 3 and 1 must lie fairly close in energy,[29,55] oxidation of 1 might favor 3^+, which could then isomerize to 2^+:



This mechanism would result in equal distribution of charge around the cluster framework. However, the idea of replacing a triply bridging CO (in 3^+) with a doubly bridging CO (in 2^+) appears to run counter to the idea that higher cluster electron density favors more highly bridging CO's.

Another possibility, suggested to us by Dr. Allan Pinhas, is that 1^+ rearranges to 2^+ via the all-terminal CO isomer 4^+:



Studies on other, synthetically more accessible, analogues are underway in an attempt to answer some of the

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(50) (a) Vahrenkamp, H. *Struct. Bonding (Berlin)* **1977**, *32*, 1. (b) Shriver, D. F. *Inorg. Chem.* **1974**, *13*, 499. (c) Tyler *Acc. Chem. Res.* **1984**, *17*, 61. (d) Shriver, D. F.; Sailor, M. J. *Acc. Chem. Res.* **1988**, *21*, 374.

(51) See, for example, leading references: (a) Kochi, J. *J. Organometal. Chem.* **1986**, *300*, 139. (b) Therien, M. J.; Trogler, W. C. *J. Am. Chem. Soc.* **1988**, *110*, 4942. (c) Astruc, D. *Angew. Chem. Int., Ed. Engl.* **1988**, *27*, 643.

(52) (a) Chanon, M. *Acc. Chem. Res.* **1987**, *20*, 214. (b) Geiger, W. E. *Prog. Inorg. Chem.* **1985**, *33*, 275.

(53) We estimated a lower limit of the 47e$^-$ vs 48e$^-$ rate enhancement as 10^6 in an earlier communication on the basis of the misstated maximum sweep rate of 100 V/s. In fact, the highest v was 10 V/s. Note also that this concept assumes that the E^0 values of the 0/+ couples are sufficiently different for 1 and 2 that their anodic peaks would be resolved in linear scan voltammetry experiments.

(54) We assume that the oxidation of the C_s isomer 1 is a one-electron process at short times. However, since oxidation of 1 is not directly observed, the stoichiometry of the anodic process is not proven. The anodic voltammetry of the C_{3v} isomer is that of a two-electron overall process.

(55) Extended Hückel molecular orbital calculations on this type of cluster do not easily yield information on the preferred isomers owing to the complexity of the calculated energy surfaces. See refs 5a and 14 as well as: Pinhas, A. R.; Albright, T. A.; Hofmann, P.; Hoffmann, R. *Helv. Chim. Acta* **1980**, *63*, 29.

mechanistic questions raised by these observations.[56]

Summary

(1) The trinuclear cluster $Cp_3Co_3(CO)_3$ (**3**) undergoes a one-electron reduction but the resulting anion is not as stable as proposed in the earlier literature[38] ($t_{1/2}$ = 2.6 s at 298 K). Fragmentation follows, yielding the dinuclear monoanion $[Cp_2Co_2(\mu\text{-}CO)_2]^-$.

(2) The two known isomers of $Cp_3Rh_3(CO)_3$, namely C_s-$Cp_3Rh_3(CO)_3$ (**1**) and C_{3v}-$Cp_3Rh_3(CO)_3$ (**2**) undergo one-electron reduction to a persistent (**1**) or stable (**2**) monoanion. No isomeric interconversion was noted in the monoanions. A second reversible reduction occurs with 2^-, whereas 1^- was reduced irreversibly. The order of increasing kinetic stabilities of the monoanions is $[Cp_3Co_3(CO)_3]^- < [C_s\text{-}Cp_3Rh_3(CO)_3]^- < [C_{3v}\text{-}Cp_3Rh_3(CO)_3]^-$. The rhodium clusters 1^- and 2^{2-} eventually fragment to apparent dinuclear complexes and other products.

(3) The E^0 value for reduction of the C_{3v} rhodium cluster is 210 mV positive of that of the C_s isomer, consistent with the more facile removal of electron density from the metal core by the additional doubly bridging CO in **2**.

(4) The trirhodium C_s isomer is converted to the C_{3v} isomer in an efficient electron-transfer-catalyzed anodic process. The chain length is about 30 under electrochemical conditions. The thermal isomerization rate is minimally 10^5 higher in the 47e$^-$ monocation than in the 48e$^-$ neutral complex.

Acknowledgment. We gratefully acknowledge support of this research by the National Science Foundation (Grant Nos. CHE 8303974 and 8603728) and by the donors of the Petroleum Research Fund, administered by the American Chemical Society. We also thank Johnson Matthey Co. for a generous loan of Rh, J. R. Shapley for a gift of **2** which facilitated initial studies, P. H. Rieger for a digital simulation of the isomerization reaction scheme (Gosser, D. K.; Rieger, P. H. *Anal. Chem.* **1988**, *60*, 1159), W. A. Herrmann for a sample of $Cp_2Rh_2(CO)_3$, and C. Amatore and A. Pinhas for helpful discussions.

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Intramolecular Coordination at Silicon. The Small Effect of Equatorial Ligands upon the Stability of Pentacoordinated Organosilanes

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Received July 18, 1990

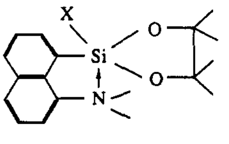
The molecular structure of 2-[8-(dimethylamino)-1-naphthyl]-4,4,5,5-tetramethyl-1,3,2-dioxasilacyclopentane (**1a**, X = H) determined by X-ray diffraction, shows this fused system to adopt a trigonal-bipyramidal geometry with the pinacol ring spanning equatorial–apical positions, the equatorial substituent (X = H) being orthogonal to the apical dimethylamino coordinated ligand. Functional pentacoordinated organosilanes derived from **1** (X = H, F, Cl, OCOR, OPh, Ph) model the trigonal-bipyramidal (tbp) intermediates which have been postulated in nucleophilic substitution with retention at silicon, with X, the leaving group, in the equatorial position of the tbp, and the coordinated nitrogen as the apical incoming nucleophile. ^{1}H NMR dynamic spectroscopy shows the formation of diastereomeric pentacoordinated organosilanes, and the energy barrier for their thermal interconversion is a measure of the intramolecular coordination. Despite the large electronic changes in the equatorial X substituents, the activation energy is only slightly dependent on the nature of this ligand ($\Delta G^{\ddagger}$ = 15–20 kcal mol^{-1}). The results confirm kinetic studies and ab initio calculations. The nature of the equatorial ligand has in general little effect on the energy level of the tbp species.

Introduction

The stereochemistry of tetracoordinated silicon compounds containing chiral centers has been extensively studied during the last decade.[1] The results support the formation of pentacoordinated species as intermediates or transition states in nucleophilic displacement reactions (Scheme I).

The reactions which give inversion at the silicon center are believed to occur (process A) through the attack of the nucleophile (Nu) at 180° relative to the leaving group (X) with formation of a trigonal-bipyramidal (tbp) structure, Nu and X being in apical positions. Two possible retention mechanisms (process B or process C) have been discussed in the literature.[2,3] Both involve adjacent attack on the

Chart I



1 (X=H)

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