# Anodic Catalysis of the Isomerization of a Metal Carbonyl Cluster

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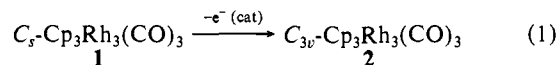*Burlington, Vermont 05452*
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We report two results of electrochemical studies of trirhodium clusters of the type $Cp_3Rh_3(CO)_3$, $Cp = \eta^5\text{-}C_5H_5$. Our original purpose was to measure the one-electron reduction potentials of the isomers C_s $Cp_3Rh_3(\mu_2\text{-}CO)_2(CO)$, 1, and C_{3v} $Cp_3Rh_3(\mu_2\text{-}CO)_3$, 2. Since the former has one terminal carbonyl ligand and two

1, C_s isomer   2, C_{3v} isomer
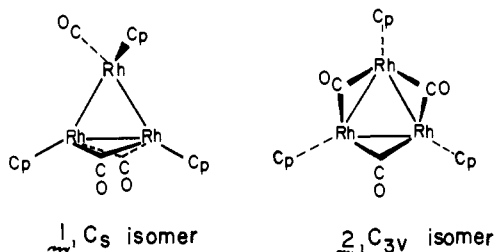
edge-bridging CO's,[1] where the latter has only edge-bridging CO's,[2] a comparison of the $E°$ values would allow a quantitative test of the long-standing hypothesis[3] that bridging carbonyls are more effective at withdrawing negative charge from metal centers than are terminal carbonyls. This hypothesis is confirmed by our measurements. In the process, however, we discovered that the isomerization of 1 to 2 is rate-enhanced by well over 1 000 000-fold when catalyzed by anodic electron transfer. To our knowledge, this is the first report of an electron-transfer-catalyzed isomerization of a metal cluster complex. The results may be relevant to the preferred orientations of adsorbed carbon monoxide on metal surfaces.

Both 1 and 2 are reduced reversibly to stable monoanions [cyclic voltammetry (CV), coulometry, ESR[4]] in THF, the reversible reduction potential of the C_{3v} isomer being 210 mV positive of that of the C_s isomer (2: −1.01 V; 1: −1.22 V vs SCE). This suggests that the increased π^* acceptor ability of the extra bridging CO in 2 is more important in the 49 e$^-$ monoanions than in the 48 e$^-$ neutral clusters.

Unusual behavior was observed when the initial potential was varied before CV scans of solutions of 1. If the negative scan is initiated at potentials negative of ca. +0.20 V, only the reversible 1e$^-$ reduction wave of the C_s isomer is observed (Figure 1, top). More positive rest potentials result in the appearance of the reduction wave of the C_{3v} isomer, at the expense of the C_s wave (Figure 1, middle and bottom). Thus, with applied potentials between +0.25 and +0.45 V, 1 is converted to 2 at the electrode surface. Since no anodic waves are observed when scanning from 0 to +0.45 V, the conversion is accomplished with virtually *no current flow* and is therefore *catalytic* in the quantity of electricity used (eq 1).[5]

$$C_s\text{-}Cp_3Rh_3(CO)_3 \xrightarrow{-e^- \text{ (cat)}} C_{3v}\text{-}Cp_3Rh_3(CO)_3 \quad (1)$$
$$\phantom{C_s\text{-}Cp_3Rh_3(CO)_3}\mathbf{1} \mathbf{2}$$

Consistent with this hypothesis, bulk oxidation of a solution of 1 with E_{app} = +0.22 V gave complete conversion to 2 with only

(1) Paulus, E. F.; Fischer, E. O.; Fritz, H. P.; Schuster-Woldan, H. *J. Organomet. Chem.* **1967**, *10*, P3.

(2) (a) Paulus, E. F. *Acta Crystallog.* **1969**, *25B*, 2206. (b) Mills, O. S.; Paulus, E. F. *J. Organomet. Chem.* **1967**, *10*, 331. (c) Farone, F.; Schiavo, S. L.; Bruno, G.; Piraino, P.; Bombieri, G. *J. Chem. Soc., Dalton Trans.* **1983**, 1813.

(3) (a) Cotton, F. A.; Troup, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 1233. (b) Muetterties, E. L.; Rhodin, T. N.; Band, E.; Brucker, C. F.; Pretzer, W. R. *Chem. Rev.* **1979**, *79*, 91. (c) Colton, R.; McCormick, M. J. *Coord. Chem. Rev.* **1980**, *31*, 1. (d) Braterman, P. S. *Struct. Bonding* **1972**, *10*, 57.

(4) Mevs, J. M. Ph.D. Thesis, University of Vermont, 1988.

(5) This is an example of electron-transfer chain catalysis (ETC). Numerous examples are found in the leading references: Saveant, J. M. *Acc. Chem. Res.* **1980**, *13*, 323. Chanon, M. *Acc. Chem. Res.* **1987**, *20*, 214.
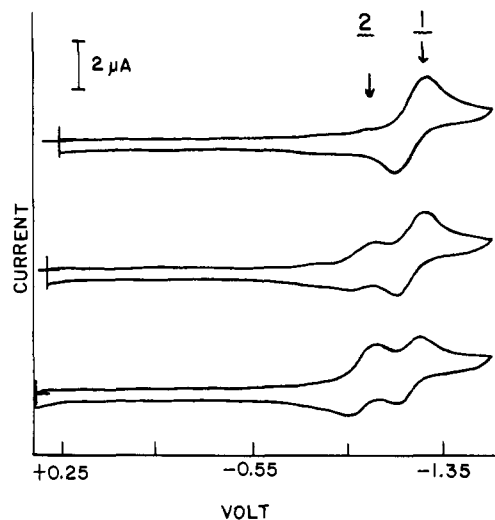
Figure 1. CV scans at a Pt electrode of 3.5×10^{-4} M 1 in THF, with beginning potentials of +0.25 V (top), +0.30 V (middle), and +0.35 V (bottom). Conditions: T = 298 K, v = 0.20 V/s. The small feature at about +0.30 V is due to an impurity.
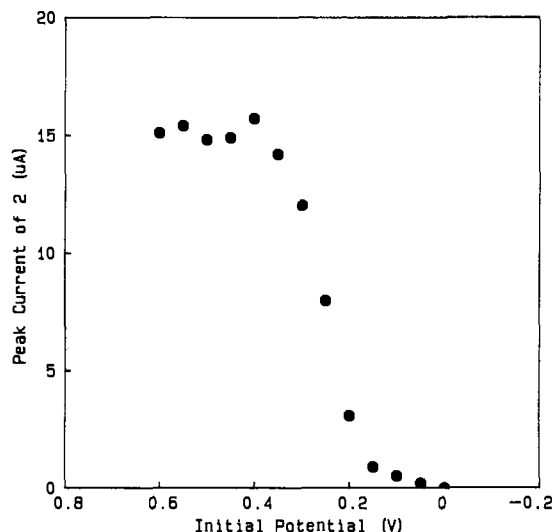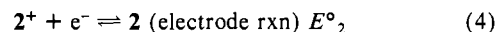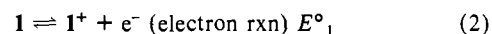
Figure 2. Plot of the corrected current height of the reduction wave of 2 obtained from CV scans of ca. 3×10^{-4} M 1 in THF using different initial potentials, T = 298 K, v = 10 V/s, after 15-s application of initial potential. The current height is corrected for the amount of isomer 2 generated in scans with initial potentials positive of the $E_{1/2}$ value of 1. See ref 4.

0.03 F. Catalytic amounts of ferrocenium ion also accomplished the isomerization. Equation 2–4 account for these observations.

$$\mathbf{1} \rightleftharpoons \mathbf{1}^+ + e^- \text{ (electron rxn)} \; E°_1 \quad (2)$$

$$\mathbf{1}^+ \rightarrow \mathbf{2}^+ \; k_{isom} \quad (3)$$

$$\mathbf{2}^+ + e^- \rightleftharpoons \mathbf{2} \text{ (electrode rxn)} \; E°_2 \quad (4)$$

Note that the formal potentials in eq 2 and 4 are those of the 47e$^-$/48e$^-$ processes. The experimental observations require (a) $E°_1 < E°_2$ and (b) k_{isom} to be very large. Note that the reduction of $\mathbf{2}^+$ to 2 may occur either by heterogeneous electron transfer from the electrode (eq 4) or through the homogeneous cross reaction of eq 5. However, if the isomerization (eq 3) is very

$$\mathbf{2}^+ + \mathbf{1} \rightleftharpoons \mathbf{1}^+ + \mathbf{2} \quad (5)$$

rapid, $\mathbf{2}^+$ will not have time to diffuse into solution to be reduced by 1.[6] Therefore, it seems likely that eq 2–4 describe the catalytic cycle.[7]

(6) Feldberg, S. W. *J. Phys. Chem.* **1971**, *75*, 2377.

A lower limit for the isomerization rate of the 47e$^-$ monocation (eq 3) is ca. 10^5.[8] Since the thermal isomerization of **1** to **2** is very slow at room temperature,[9] removing an electron from **1** speeds up its isomerization rate by at least a factor of 10^6 and probably by much more.

In an attempt to estimate $E°_1$, the formal potential of the couple **1**/**1$^+$**, a series of fast linear scans to negative potentials was made on solutions of **1** beginning from different initial potentials, E_{app}. This experiment varies from that of Figure 1 only in the rapidity of the potential scan, 10 V/s, which "freezes" the electrode reaction layer during the scan. The peak heights of the two reduction waves are then proportional to the steady-state concentrations of **1** and **2** at the electrode surface. Figure 2 shows that a plot of the C_{3v} isomer reduction wave height increases approximately sigmoidally as a function of E_{app}, analogous to a potentiometric curve. The midpotential of this plot, +0.25 V, is analogous to an $E_{1/2}$ value and was taken as an estimate of $E°_1$. The $E_{1/2}$ for **2**, directly measured at the rotating platinum electrode, is +0.55 V, consistent with the requirements of eq 2 and 4.[10]

The mechanism whereby **1** is isomerized to **2** so much more easily in the 47e$^-$ cations than in the 48e$^-$ neutral complexes may include a third isomer, **3**, with two edge-bridging and one face-

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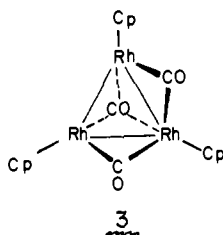
bridging CO groups. Analysis of the ^{13}C NMR behavior of **1**[6] suggests that **3** is an energetically accessible intermediate in the fluxionality of the C_s isomer. However, since **1** and **2** do not share a common intermediate in their fluxional rearrangements,[6,8] structure **3** cannot convert to **2** in the 48e$^-$ species. We postulate that the conversion of **3$^+$** to **2$^+$** is favored in the 47e$^-$ cations, perhaps facilitated by increased delocalization of positive charge over all three metals in the isomer with the face-bridging CO. Thus, we propose the following route for the anodic catalytic isomerization of **1** to **2**. Since 48e$^-$ clusters with the ground-state structure **3** are known,[12] this mechanistic hypothesis will be tested.

$$ 1 \xrightarrow{-e^-} 1^+ \rightarrow 3^+ \rightarrow 2^+ \xrightarrow{+e^-} 2 $$
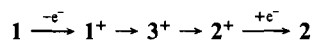
This result shows that the structural preferences of carbonyls bound to metal clusters may be dramatically affected by the electron count (or charge) of the cluster. Since the above trirhodium clusters have been proposed as having particular relevance to CO adsorbates on metal surfaces,[13] our data suggest that the type of bonding of CO to a metal surface may be influenced or controlled by the oxidation state level of the metal.

Studies of *Stemona* Alkaloids. Total Synthesis of (+)-Croomine

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The roots and rhizomes of plants of Stemonaceae (*Stemona* and *Croomia*) produce a rich alkaloidal extract. Herbal teas have been used in Chinese folk medicine as "concocts" for pulmonary tuberculosis, bronchitis, and pertussis as well as to rid the human body of ringworm and intestinal parasites. Furthermore, extracts and dried plant materials are used throughout Eastern Asia to rid livestock of ticks and mites. Thus far, 14 highly oxygenated, polycyclic alkaloids have been determined, mostly as a result of X-ray diffraction studies.[1] Croomine[2] (**1**) and stemospironine[3]

Croomine (1)   Stemospironine (2)
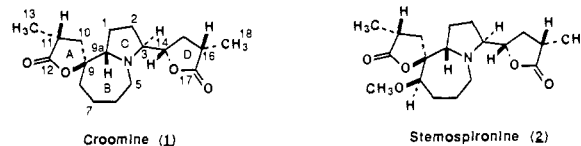
(**2**) are prototypical examples of this family of compounds, all of which characteristically contain the 1-azabicyclo[5.3.0]decane nucleus. Herein we report the first synthesis within this novel class of alkaloids by communication of our recent total synthesis of (+)-croomine (**1**).

From the onset of our investigations, we had sought to develop a strategy involving preliminary construction of a branched acyclic carbon chain to be followed by timely consecutive ring closures of each heterocycle (A → B → C → D). Since the methyl substituents of croomine (C_{13} and C_{18}) could be incorporated into the carbon framework beginning with (*S*)-(+)-methyl 3-hydroxy-2-methylpropionate and (*R*)-(–)-methyl 3-hydroxy-2-methylpropionate, respectively, we sought to establish the correct relative configurations of the β-amino alcohol of C_9 and C_{9a} at an early stage. Moreover, it was imperative to utilize a surrogate amino functionality, which would withstand several oxidations throughout the route. This necessary protection was assured by our selection of azide for introduction of the nitrogen unit at C_{9a}.

The carbon framework of croomine was assembled as summarized in Scheme I.[4] Acylation of the terminal acetylene **3**[5]

(7) In the terminology of Hawley and Feldberg, eq 2–4 describe an ECE process "without nuance". See: Hawley, M. D.; Feldberg, S. W. *J. Phys. Chem.* **1966**, *70*, 3459.

(8) This estimate is based on the lack of anodic waves between 0 and +0.45 V up to v = 100 V/s, and finite difference theoretical simulations of an ECE process. We thank Dr. P. H. Rieger for a copy of the simulation program.

(9) Lawson, R. J.; Shapley, J. R. *Inorg. Chem.* **1978**, *17*, 772.

(10) $E_{1/2}$ is quoted instead of $E°$ because the oxidation of **2** is electrochemically irreversible but chemically reversible. Details will be published later.

(11) Lawson, R. J.; Shapley, J. R. *J. Am. Chem. Soc.* **1976**, *98*, 7433.

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(13) Reference 3b, pp 129–130.

(1) (a) Xu, R.-S.; Lu, Y.-J.; Chu, J.-H.; Iwashita, T.; Naoki, H.; Naya, Y.; Nakanishi, K. *Tetrahedron* **1982**, *38*, 2667. (b) Nakanishi, K.; Goto, T.; Ito, S.; Natori, S.; Nozoe, S. *Natural Products Chemistry*; Academic Press: New York, 1975; Vol. 2, pp 292–293. (c) Koyama, H.; Oda, K. *J. Chem. Soc. B* **1970**, 1330. (d) Iizuka, H.; Irie, H.; Masaki, N.; Osaki, K.; Uyeo, S. *Chem. Commun.* **1973**, 125. (e) Irie, H.; Masaki, N.; Ohno, K.; Osaki, K.; Taga, T.; Uyeo, S. *Chem. Commun.* **1970**, 1066.

(2) Noro, T.; Fukushima, S.; Ueno, A.; Litaka, Y.; Saiki, Y. *Chem. Pharm. Bull.* **1979**, *27*, 1495.

(3) Sakata, K.; Aoki, K.; Chang, C.-F.; Sakaurai, A.; Tamura, S.; Mukakoshi, S. *Agric. Biol. Chem.* **1978**, *42*, 457. We have noted that stemospironine (**2**) appears to have virtually identical physical and spectral data as subsequently reported for stemonidine.[1a] The marked similarities suggest that a direct comparison of these two alkaloids is necessary. Stemospironine (**2**) was assigned by X-ray diffraction.

(4) All yields are reported for purified samples. Each compound has been fully characterized by optical rotation, infrared, ^{1}H NMR, ^{13}C NMR, and high-resolution mass spectral data. Selected combustion analyses have also been obtained. Complete experimental details will be forthcoming in a full account of this work.