1634 *Organometallics* 1987, *6*, 1634–1639

Electrochemical Oxidation and Reduction of Methylene-Bridged Complexes of Manganese, Cobalt, and Rhodium†

William E. Geiger,* Thomas Gennett, and William K. McVicar

Department of Chemistry, University of Vermont, Burlington, Vermont 05405

Wolfgang A. Herrmann

Anorganisch-chemisches Institut der Technischen Universität Munchen, D-8046 Garching, Germany

Received December 10, 1986

The oxidation and reduction of a series of alkylidene-bridged dimetallic compounds containing Mn, Co, or Rh have been studied by electrochemical and spectroscopic techniques. Oxidation results in production of a cation radical whose stability depends on the identity of the metal in the complex and the nature of the bridge substituent. Among the dirhodium complexes, the one having bridging carbonyl groups gives the most stable cation. The cobalt and rhodium compounds are susceptible to attack by nucleophiles, and all cations decompose to give mononuclear products. One-electron reduction gives detectable anions in the case of Co and Rh compounds, but these anion radicals rapidly decompose. It is concluded that both oxidation and reduction weaken the M–C–M triangle, consistent with the description of these compounds as dimetallacyclopropanes.

Introduction

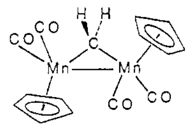
The chemical and physical properties of μ-bridged methylene transition-metal complexes are presently under intensive investigation.[1] Although the redox chemistry of this class of compounds has received scant attention, Connelly et al.[2] have made the interesting observation that oxidation of a μ-CH_2 complex of ruthenium that is also bridged by carbonyl and (diphenylphosphino)methane groups, $[Cp_2Ru_2(\mu\text{-}CO)(\mu\text{-}dppm)(\mu\text{-}CH_2)]$, to a dication results in rapid loss of a proton from the CH_2 group to give a μ-alkylidyne bridge that can be easily functionalized by nucleophiles.[2]

We wish to report electrochemical data on both the oxidation and reduction of a series of dimanganese, dicobalt, and dirhodium complexes containing μ-CRR′ bridges. In general, one-electron processes are observed which result in radical cations and anions having enough stability to be characterized by voltammetric methods and, in some cases, by electron spin resonance (ESR) or infrared (IR) spectroscopy. In no case, though, was the radical stable enough for isolation. Decomposition apparently takes place by fracture of the M–C–M triangle with formation of mononuclear complexes. The compounds studied are as shown, 1–7, and the shorthand notation used to describe them in the text is as listed.

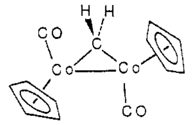
Experimental Section

Materials. The manganese and rhodium complexes 1 and 3–7 were prepared by literature methods,[3] as was $Cp_2Rh_2(CO)_2(\mu\text{-}CO)$.[4] The dicobalt complex 2 was supplied by Drs. R. G. Bergman and K. Theopold. Tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) was prepared by metathesis of Bu_4NI and NH_4PF_6 as described earlier.[5] Electrochemical solvents were purified as in earlier work.[5] KPF_6 (Aldrich) was recrystallized from water and vacuum dried.

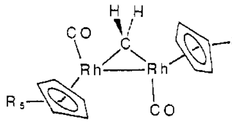
Electrochemical Procedures. Potentials are reported vs. the aqueous saturated calomel electrode (SCE). In some experiments (e.g. low-temperature electrolyses inside the drybox) a quasi-reference electrode (Pt or Ag) was used and potentials later referred to the SCE by comparing observed potentials to that of the $Cp_2Fe^{0/+}$ couple at the quasi-reference. Experiments were generally carried out under an atmosphere of nitrogen in a Vacuum Atmospheres drybox using instrumentation previously described.[5]



(1), $Mn_2(\mu\text{-}CH_2)$

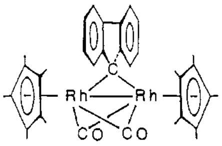


(2), $Co_2(\mu\text{-}CH_2)$

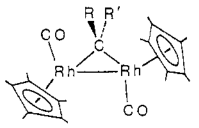


(3), R=H: $Rh_2(\mu\text{-}CH_2)$

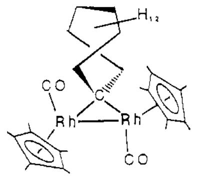
(4), R=CH_3: $^*Rh_2(\mu\text{-}CH_2)$



(5), $^*Rh_2(\mu\text{-fluorenyl})$



(6), R=H, R′=vinyl: $^*Rh_2(\mu\text{-}C_3H_4)$



(7), R–R′=cyclo-C_6H_{12}: $^*Rh_2(\mu\text{-}C_7H_{12})$

Each electrochemical study employed cyclic voltammetry (CV) measurements, and most systems were also studied by direct current polarography, bulk coulometry, voltammetry at the rotating platinum electrode (RPE), and in some cases double potential step chronoamperometry and pulse polarography. Rather than report the technical aspects of each series of voltammetric studies on each redox process, some generalizations may be made.

Each redox process noted for a compound was tested for diffusion control in CV experiments by observing the behavior of peak currents (i_p) as a function of scan rate (v), over at least 1 order of magnitude change in the latter. Over the range v = 0.03–0.5 V/s using small handmade Pt bead electrodes, we have found that the product $i_p/v^{1/2}$, which is constant for a diffu-

---

† Part 65 of the series "Transition Metal Methylene Complexes". Part 64: Herrmann, W. A.; Hörlein, R.; Barnes, C. E.; Weber, C.; Krüger, C.; Zielger, M. L. *J. Organomet. Chem.*, in press.

(1) For recent reviews, see: (a) Herrmann, W. A. *Adv. Organomet. Chem.* **1982**, *20*, 159. (b) Herrmann, W. A. *J. Organomet. Chem.* **1983**, *250*, 319. (c) Casey, C. P.; Audett, J. D. *Chem. Rev.* **1986**, *86*, 339.

(2) Connelly, N. G.; Forrow, N. J.; Gracey, B. P.; Knox, S. A. R.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1985**, 14.

(3) (a) Herrmann, W. A.; Reiter, B.; Biersack, H. *J. Organomet. Chem.* **1975**, *97*, 245. (b) Herrmann, W. A.; Huggins, J. M.; Reiter, B.; Bauer, Ch. *J. Organomet. Chem.* **1981**, *214*, C19. (c) Herrmann, W. A.; Bauer, Ch.; Kriechbaum, G.; Kunkely, H.; Ziegler, M. L.; Speth, D.; Guggolz, E. *Chem. Ber.* **1982**, *115*, 878. (d) Herrmann, W. A.; Huggins, J. M.; Bauer, Ch.; Smischek, M.; Pfisterer, H.; Ziegler, M. L. *J. Organomet. Chem.* **1982**, *226*, C59.

(4) Hill, R.; Knox, S. A. R. *J. Chem. Soc., Dalton Trans* **1975**, 2622.

(5) Tulyathan, B.; Geiger, W. E. *J. Am. Chem. Soc.* **1985**, *107*, 5960.

0276-7333/87/2306-1634$01.50/0

Table I. One-Electron Redox Potentials of Methylene-Bridged Complexes and Analogues[a]

complex[b]	oxidations	reductions
$Mn_2(\mu\text{-}CH_2)$ (**1**)	+0.53[c]	1.79[d] (υ = 0.48 V/s)
$Co_2(\mu\text{-}CH_2)$ (**2**)	+0.16[c]	−1.55[c]
$Rh_2(\mu\text{-}CH_2)$ (**3**)	+0.72[d] (υ = 0.10 V/s)	−1.72[c] −2.33[d] (υ = 0.25 V/s)
*$Rh_2(\mu\text{-}CH_2)$ (**4**)	+0.10[c]	
*$Rh_2(\mu$-fluorenyl) (**5**)	+0.05[c]	
*$Rh_2(\mu\text{-}C_3H_4)$ (**6**)	+0.07[c]	
*$Rh_2(\mu\text{-}C_7H_{12})$ (**7**)	+0.12[c]	

[a] Oxidation processes are reported in CH_2Cl_2 and reduction processes in THF; potentials vs. SCE. [b] For key to nomenclature, see drawings of structures 1–7. [c] $E°$ reported (chemically reversible process). [d] Peak potential reported (scan rate in parentheses), chemically irreversible.

sion-controlled wave,[6] decreases by about 10% for standards such as $Cp_2Fe^{0/+}$. This apparently arises from breakdown of linear diffusion (edge effects) at low scan rates. If the redox processes of the compounds under study displayed similar behavior, they were judged to be diffusion-controlled. Each compound was subjected to studies using CV scans as low as 0.02 V/s and as high as 50 V/s, as well as to reduced temperature experiments designed to stabilize radical ions. CV curves with $\upsilon > 0.5$ V/s were recorded on a digital recorder (Bascom Turner Model 4120). Although Hg electrodes were occasionally used, Pt was normally the electrode of choice for these compounds, and unless otherwise noted, data reported in this paper refer to reductions and oxidations at platinum.

Spectroscopic Instrumentation. ESR spectra were obtained with a modified Varian E-3 spectrometer, and DPPH was used as a *g* value standard. Since a single-cavity arrangement was available, ESR tubes containing the test radicals were dip-coated by a DPPH solution to provide simultaneous recording of the test spectrum and that of the standard. NMR spectra were recorded on a Bruker WM 250-MHz Fourier-transform instrument, and IR spectra were obtained with a Nicolet Series 6000 FT-IR spectrometer.

Results

Oxidations. I. $[CpMn(CO)_2]_2(\mu\text{-}CH_2)$ (1). The complex $Mn_2(\mu\text{-}CH_2)$ (**1**), which was the first stable CH_2-bridged transition-metal complex prepared,[7] exhibits a diffusion-controlled one-electron oxidation to a reasonably persistent cation radical via eq 1. An identical $E°$ (+0.53

$$Mn_2(\mu\text{-}CH_2) \rightleftarrows Mn_2(\mu\text{-}CH_2)^+ + e^- \qquad (1)$$

V: Table I lists potentials for all oxidations reported in this paper) was measured in several different solvents (THF, CH_2Cl_2, CH_3CN). CV scans gave evidence of electrochemical reversibility[8] (ΔE_p values were 60–68 mV for 50 mV/s < υ < 1500 mV/s) and a fully developed reverse wave (Figure 1) when υ > 100 mV/s.

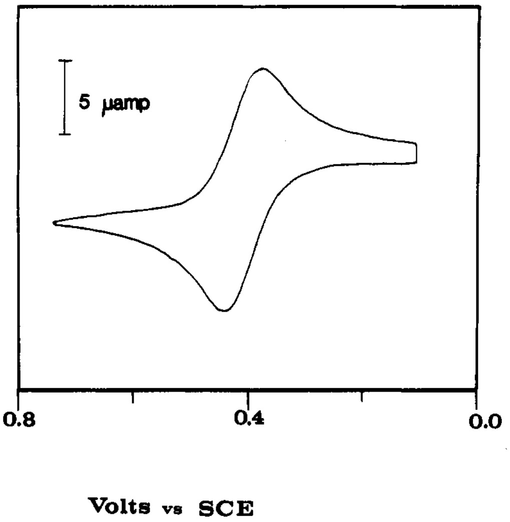


Figure 1. Cyclic voltammogram of oxidation of 6.9×10^{-4} M $[CpMn(CO)_2]_2(\mu\text{-}CH_2)$ (**1**) in CH_3CN at Pt electrode (υ = 230 mV/s).

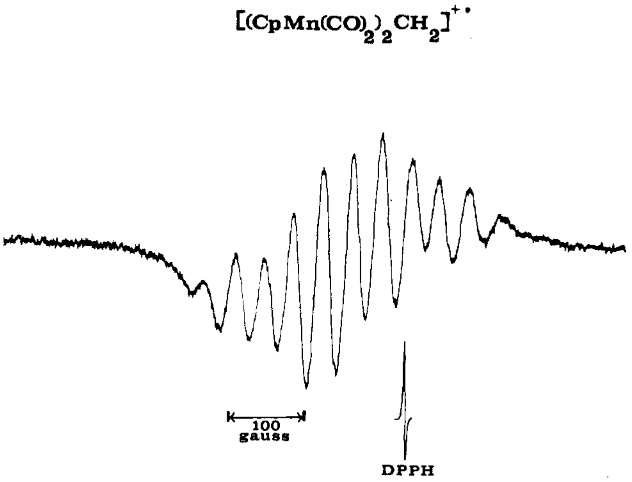


Figure 2. Fluid solution ESR spectrum of $(1)^+$ at 213 K in CH_2Cl_2.

The cation radical $(1)^+$ slowly decomposes, as indicated in slow sweep CV[9] or bulk coulometry experiments. Electrolysis at a Pt basket with an applied potential positive of the oxidation wave of $Mn_2(\mu\text{-}CH_2)$ released 1.8 F when the oxidation was performed at 298 K. The yellow electrolysis solution exhibited a reversible wave with $E°$ = +0.26V and was ESR-active. A six-line spectrum was observed, due to interaction with a *single* metal (^{55}Mn, $I = {}^5/_2$). The same spectrum was observed after oxidation of $CpMn(CO)_3$.[10] Lower temperature electrolysis (248 K) in CH_2Cl_2 or CH_3CN gave 1.0 F and a dark green solution of $(1)^+$ in about 80% yield, but ESR still displayed the six-line decomposition spectrum. Clean production of $(1)^+$ was finally achieved by mixing CH_2Cl_2 solutions of $[(p\text{-}BrC_6H_4)_3N]^{+}$[11] and the neutral dimanganese compound just above their melting points (ca. 180 K). Warming the solution to 210 K gave the 11-line fluid solution spectrum of Figure 2 consistent with interaction of the unpaired electron with two ^{55}Mn centers, $\langle a \rangle_{Mn}$ = 38 G and $\langle g \rangle$ = 2.053.

As these experiments suggest, the dimanganese cation radical was too reactive to isolate in pure form. It was obtained mixed with the neutral starting material in the following experiment. Electrolysis at 248 K in CH_3CN using 0.1 M KPF_6 as supporting electrolyte was followed by immediate removal of solvent in vacuo and extraction by CH_2Cl_2 (KPF_6 is insoluble in CH_2Cl_2), removal of CH_2Cl_2, and washing with hexane. The hexane-insoluble portion gave strong IR bands in CH_2Cl_2 at 2010 and 1977 cm^{-1} which disappeared upon standing, as the bands for

---

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

(7) Herrmann, W. A.; Reiter, B.; Biersack, H. *J. Organomet. Chem.* **1975**, *97*, 245.

(8) Besides CV data, other evidence of fast charge transfer comes from the slope of a plot of potential vs. log $[(i_l - i)/i]$ from RPE scans, which was 60 mV.

(9) i_c/i_a ratios fell below 0.9 when υ < 0.05 V/s.

(10) $\langle a \rangle_{Mn}$ = 92 G; $\langle g \rangle$ = 2.006. This spectrum did not disappear after electrolyzed solutions were left open to the air for hours. It was identical with that found after electrolytic or Ag^+ oxidation of $CpMn(CO)_3$ and is likely due to a Mn^{2+} decomposition product.

(11) Tris(*p*-bromophenyl)amine(1+/0) has a $E°$ of ca. +1.1 V in this medium: Schmidt, W.; Steckhan, E. *Chem. Ber.* **1980**, *113*, 577.

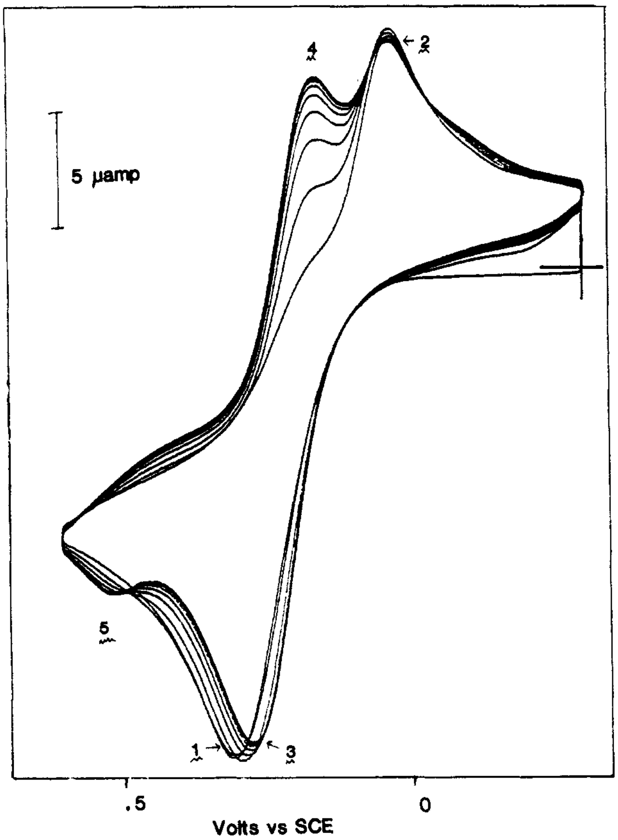


Figure 3. Repetitive CV scans of oxidation of 6.9 × 10^{-4} M $[CpCo(CO)]_2(\mu\text{-}CH_2)$ (**2**) in CH_3CN at Pt electrode (v = 500 mV/s). The scan was initiated at −0.3 V. See text for identification of numbered peaks.

the neutral $[CpMn(CO)_2]_2(\mu\text{-}CH_2)$ grew in (ν_{CO} = 1955 and 1925 cm^{-1}).[12] The shift to higher frequency for the hexane-insoluble portion (average 53 cm^{-1}) is consistent with the positive charge on the radical.

Taken together, these data indicate that the dimanganese compound yields a cation radical which probably retains the basic structure of a methylene bridging the two metals, with the carbonyls remaining terminal. The cation $(1)^+$ is prone to re-formation of the neutral starting compound and to decomposition to mononuclear side products.

II. $[CpCo(CO)]_2(\mu\text{-}CH_2)$ (2). Electrochemical oxidation of this compound was studied in THF and CH_3CN[13] and provides an interesting example of how CV results can be deceiving if the response is not measured over a range of scan rates. Slow CV scans in CH_3CN gave an anodic wave (E_{p_a} = +0.30 V) and return cathodic wave (E_{p_c} = +0.17 V) *appearing* to comprise a chemically reversible couple. However, at faster sweep rates, the wave at +0.17 V disappeared and a new cathodic wave appeared at E_{p_c} = +0.02 V. Repetitive CV scans also show this effect (Figure 3). The first scan at v = 500 mV/s shows the anodic peak due to the oxidation of **2**, E_{p_a} = +0.30 V (peak 1 in Figure 3), and the coupled cathodic peak[14] (peak 2 in Figure 3) at E_{p_c} = +0.02 V. Subsequent scans result in a negative shift of the anodic peak until it reaches a value of +0.23 V (peak 3, Figure 3) under steady state conditions and the appearance of a new cathodic feature with E_{p_c} = +0.17 V (peak 4, Figure 3). Waves 3 and 4 constitute a new reversible couple ($E°$ = +0.20 V, ΔE_p = 60 mV) at the same potential[14] as that of $CpCo(NCCH_3)_3{}^{+/2+}$, the latter apparently being formed smoothly in the oxidation of the dinuclear complex. The small wave at E_{p_a} = +0.50 V (wave 5 in Figure 3) is assigned to $CpCo(CO)_2$, which is oxidized at this potential in this medium.[15] Waves 3 and 4 appear even if the potential is not scanned through wave 5, so the half-sandwich complex $CpCo(NCCH_3)_3{}^+$ can be formed directly from the dinuclear cation rather than requiring intermediate formation of $CpCo(CO)_2$. At temperatures below 250 K the waves due to $CpCo(NCCH_3)_3{}^{+/2+}$ and the oxidation of $CpCo(CO)_2$ are not observed in CV scans down to v = 50 mV/s, leaving only waves 1 and 2 of Figure 3. Since peaks 1 and 2 constitute a chemically reversible couple, we use the average of their potentials to compute $E°$ for **2** (Table I). It cannot be assumed, however, that significant structural changes do not occur in this redox process.

Table II. Approximate Half-Lives of Dirhodium Methylene-Bridged Cation Radicals Observed in This Work

cation radical	half-life (298 K)[a]
$*Rh_2(\mu\text{-fluorenyl})^+$, $(5)^+$	stable ($t_{1/2}$ > 10 min)
$*Rh_2(\mu\text{-}CH_2)^+$, $(4)^+$	17 s
$*Rh_2(\mu\text{-}C_7H_{12})^+$, $(7)^+$	0.13 s
$*Rh_2(\mu\text{-}C_3H_4)^+$, $(6)^+$	0.01 s
$Rh_2(\mu\text{-}CH_2)^+$, $(3)^+$	<0.01 s

[a] Calculated from CV data using assumed first-order rate constants derived from the method of Nicholson (*Anal. Chem.* **1965**, *37*, 1351).

Bulk coulometry at a Pt electrode in CH_3CN at 263 K (E_{app} = +0.50 V) released 3.2 F as the solution changed from red to pink and then finally to yellow. Voltammetry of the final solution showed it to contain Co^{2+} and Cp_2Co^+,[16] consistent with what is known[14,16] about the disproportionation of $CpCo(NCCH_3)^{2+}$ and with the approximate overall oxidation mechanism (2) in which

$$[CpCo(CO)]_2(\mu\text{-}CH_2) \rightarrow Cp_2Co^+ + Co^{2+} + 2CO + 3e^- + \text{organic products} \quad (2)$$

"organic products" arise from the (unknown) fate of the methylene group. Thus, oxidation of $[CpCo(CO)]_2(\mu\text{-}CH_2)$ leads to rapid cleavage of the methylene bridge and formation of mononuclear products.

III. Oxidation of Dirhodium Complexes. Five dirhodium complexes, **3**–**7**, were investigated, each showing a diffusion-controlled one-electron oxidation over the range of 0 to +0.8 V in CH_2Cl_2 (Table I). The stabilities of the resulting cation radicals varied greatly, but only in one case, **3**, was the radical too unstable to be detected by high sweep rate CV experiments. Lifetimes of the radicals calculated from CV measurpments are listed in Table II.

The fluorenyl-bridged complex **5** not only gives the most stable cation radical but also oxidizes to a dication as well (Figure 4), establishing the electron-transfer series in eq 3.

$$*Rh_2(\mu\text{-fluorenyl})^0 \overset{e^-}{\rightleftharpoons} [*Rh_2(\mu\text{-fluorenyl})]^+ \overset{e^-}{\rightleftharpoons} [*Rh_2(\mu\text{-fluorenyl})]^{2+} \quad (3)$$

Oxidation of **5** by 1 equiv of Cp_2Fe^+ in cold 1:1 CH_2Cl_2/1,2 dichloroethane gave a deep purple solution of $(5)^+$. Freezing this solution resulted in an ESR signal with a rhombic **g** tensor, g_1 = 2.089, g_2 = 2.056, and g_3 = 1.991, confirmed by comparison with a simulated spectrum. No

---

[12] Small additional peaks were present at ν_{CO} = 2028 and 1935 cm^{-1}, which were identical with those of the decomposition product formed by anodic oxidation of $CpMn(CO)_3$ in an identical control experiment.

[13] **2** appeared to decompose in CH_2Cl_2.

[14] Koelle, U. *J. Organomet. Chem.* **1980**, *184*, 379.

[15] Gennett, T., unpublished results, Mt. Holyoke College.

[16] The analysis was similar to that reported previously: Moraczewski, J.; Geiger, W. E. *Organometallics* **1982**, *1*, 1385.

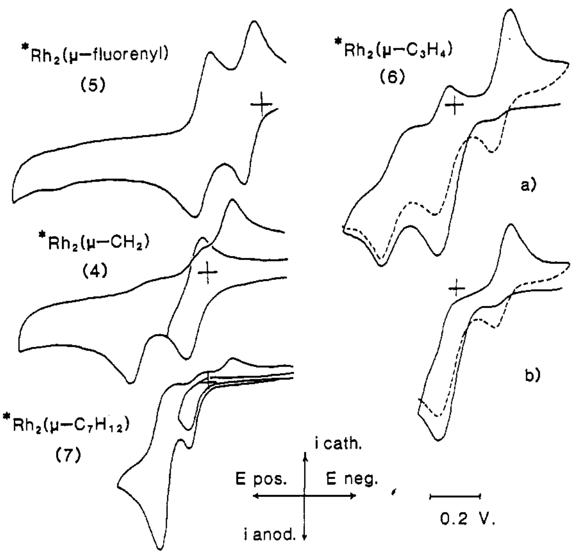


Figure 4. Representative CV scans at Pt electrode (v = 200 mV/s) for four rhodium complexes. Dotted lines give results of positive-going ramp of second cycle. The cross mark gives the zero current/voltage position. Peak currents are about 1 μA. Curves a and b for $*Rh_2(\mu\text{-}C_3H_4)$ refer to scans through the second and first waves, respectively.

Rh hyperfine splittings were observed. Among the methylene-bridged compounds studied here, 5 is the only complex with bridging carbonyls, and this may account in part for its stability upon oxidation. We will return to this point in the Discussion.

The least stable cation radical was obtained from oxidation of 3, which has an unsubstituted CH_2 bridge. Bulk electrolyses were consistent with a one-electron oxidation, but attempts to recover electrolysis products were unsuccessful. The CH_2-bridged complex having the pentamethylcyclopentadienyl ligand 4, $*Rh_2(\mu\text{-}CH_2)$, was studied in detail because its oxidation products were more stable than those of its Cp analogue.

$*Rh_2(\mu\text{-}CH_2)$ (4), $E°$ = +0.09 V, displays a chemically reversible one-electron process giving $(4)^+$. Careful studies of peak potentials in CH_2Cl_2 established that the electron transfer is quasi-reversible at a platinum electrode, having a minimum ΔE_p of 80 mV, corrected for resistance effects,[17] when v = 0.03 V/s. $(4)^+$ is unstable at room temperature. This was established both by CV and by double potential step chronoamperometry, which suggested a half-life of 5–10 s for $(4)^+$. Bulk electrolysis of 4 gave 1.0 F at either 298 or 233 K. Cold solutions from the lower temperature electrolysis gave ESR and IR spectra consistent with a cation radical (ESR, $g_{\parallel}$ = 2.145, $g_{\perp}$ = 2.036; IR, ν_{CO} = 2054 cm^{-1}), but these spectra cannot be assigned with certainty to $(4)^+$. Neutral 4 could be regenerated from the cold red electrolysis solution in about 20% overall yield by bulk reduction at −0.2 V. Solutions of 4 oxidized at 298 K did not show IR activity in the carbonyl region, so the major decomposition products of $(4)^+$ do not contain CO.

The remaining two dirhodium complexes 6 and 7 were investigated more briefly. The vinyl derivative 6 forms a short-lived cation, $(6)^+$, in a couple that is chemically reversible only at CV scan rates above 20 V/s ($E°$ = +0.07 V). Oxidative electrolysis of 6 gave a product with a reversible wave at $E°$ = −0.25 V which was not identified.

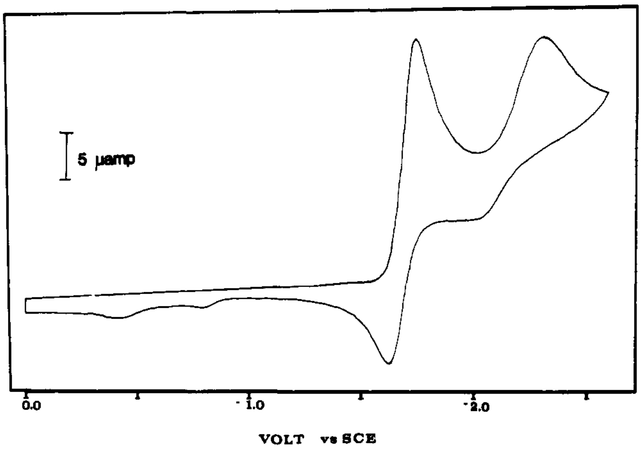


Figure 5. CV of reduction of 6.9 × 10^{-4} M $[CpRh(CO)]_2(\mu\text{-}CH_2)$ (3) in CH_3CN at Pt electrode (v = 300 mV/s; T = 258 K).

The cyclohexyl derivative 7 behaves quite similarly to the unsubstituted analogue 4 except that higher CV scan rates are needed to achieve reversibility ($E°$ = +0.12 V, reversible at v = 5 V/s). At slower sweep rates, waves arising from decomposition products of $(7)^+$ are observed (Figure 4), at least one of which (cathodic wave at −1.4 V) is also observed from the decomposition of $(4)^+$, again implying splitting of the methylene bridge.

For at least 3, it has been shown that potential nucleophiles are important in the decomposition of the cation. When CH_3CN is added to a CH_2Cl_2 solution of 3, the chemical reversibility is lost as the oxidation wave shifts negative and a new reduction grows in. CV, IR, and bulk oxidation in CH_3CN are consistent with the demise of $(3)^+$ to give non-CO-containing products. Variation in the rates of decomposition of several of the cations has been attributed to solvent preparation, which presumably provided a source of trace H_2O. Additionally the identification of $CpCo(NCCH_3)_3^+$ as an oxidation product of 2 in CH_3CN must arise from this type of chemistry. We conclude that electrochemical activation of the stable μ-CH_2 compounds has been achieved but that the stabilities of the resulting cations were not suitable for detailed study.

Reductions. IV. $[CpMn(CO)]_2(\mu\text{-}CH_2)$ (1). This compound undergoes an irreversible (Table I) reduction in CH_3CN, THF, DMF, and CH_2Cl_2. E_{p_c} was −1.79 V in CH_3CN at a Pt electrode using v = 480 mV/s, and the reduction was irreversible at temperatures as low as 230 K and scan rates to 1 V/s. A dc polarogram gave $E_{1/2}$ = −1.62 V in CH_3CN and a diffusion current constant of 5.64 μA mM^{-1} mg$^{-2/3}$ s$^{1/2}$, almost twice that of the one-electron standard $Cp_2Co^{+/0}$ (I = 3.33), suggesting that electroactive products are formed in the decomposition reaction of the monoanion, $[Mn_2(\mu\text{-}CH_2)]^-$. The reverse CV sweep showed oxidation waves at −0.63 and −0.25 V arising from uncharacterized decomposition products.

V. $[CpRh(CO)]_2(\mu\text{-}CH_2)$ (3). Two reduction waves were observed for this complex, the first ($E°$ = −1.72 V) involving the one-electron reduction to a reasonably persistent anion (eq 4). This process is not fully reversible

$$Rh_2(\mu\text{-}CH_2) + e^- \rightleftarrows [Rh_2(\mu\text{-}CH_2)]^- \qquad (4)$$

in either the electrochemical (charge transfer) or chemical sense. CV scans at either Hg or Pt in CH_3CN display a ratio of i_a/i_c less than 1.0 unless fast sweep rates or subambient temperatures (Figure 5) are employed. ΔE_p values increase from about 105 to about 175 mV at Hg electrodes over the scan rate range v = 40–800 mV/s, indicating a standard heterogeneous electron-transfer rate of about 10^{-2} cm/s. The half-life of the anion radical at 295 K is about

---

[17] ΔE_p (v = 0.03 V/s) was measured over a concentration range of 4 of 0.058–0.74 mM. ΔE_p values were linear with concentration, and extrapolation to zero concentration (zero iR loss) gave 80 mV. This value was occasionally observed experimentally at low concentrations by using a small Pt bead electrode. $Cp_2Fe^{0/+}$ gave ΔE_p = 65–70 mV under these conditions.

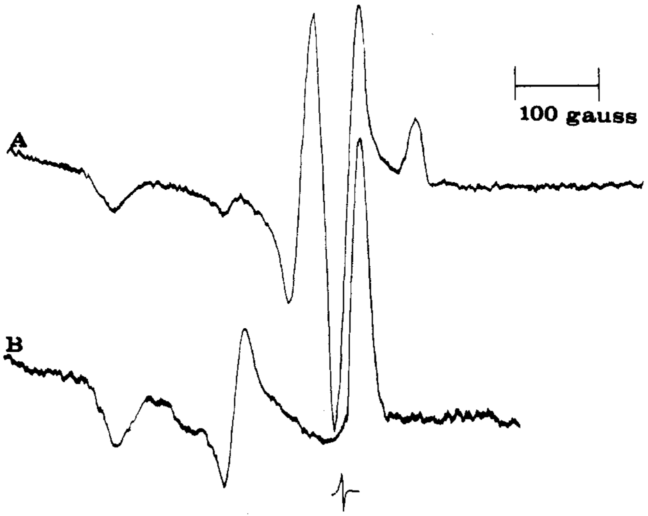


Figure 6. Frozen solution (173 K) ESR spectra following cathodic (−1.8 V) reduction of 3 in CH_3CN: (A) sample taken when electrolysis was approximately half-complete; (B) sample from (A) after thawing and refreezing.

3 s. The second reduction wave (Table I) apparently involving a one-electron reduction from the monoanion to a dianion is irreversible under a variety of solvent, temperature, and scan rate conditions.

The first reduction (eq 4) was studied by a variety of electrochemical methods, including conventional dc polarography[18] pulse and reverse pulse polarography,[19] variable sweep rate CV, and bulk coulometry. Each method verified that the dirhodium monoanionic complex is unstable.

Bulk electrolysis of $Rh_2(\mu\text{-}CH_2)$ at 248 K in THF or CH_3CN at −1.8 V consumed a total of 1.8 F as the color cahanged from orange to green. After electrolysis, rotating platinum electrode (RPE) voltammograms indicated that the monoanion was present at about 15% of the original concentration of starting material, with a second, larger, wave at −0.37 V.[20] Samples taken for ESR during electrolysis showed the presence of at least two radicals. Spectrum B in Figure 6 was dominant in samples taken late in the electrolysis or when the ESR sample tube was thawed and then refrozen and is apparently due to a decomposition product. Samples removed less than halfway through electrolysis and immediately frozen have features at $g = 1.945$ and ca. 2.02 (spectrum A in Figure 6) which may be due to $[Rh_2(\mu\text{-}CH_2]^-$ or a secondary radical arising from its decay.[21]

VI. $[CpCo(CO)]_2(\mu\text{-}CH_2)$ (2). Reduction of $Co_2(\mu\text{-}CH_2)$ resulted in a monoanion slightly more stable than that of its rhodium analogue. In THF two reversible reductions were observed for 2 ($E°_1 = -1.55$ V and $E°_2 = -1.96$ V), corresponding to the reactions in eq 5 and 6. The two

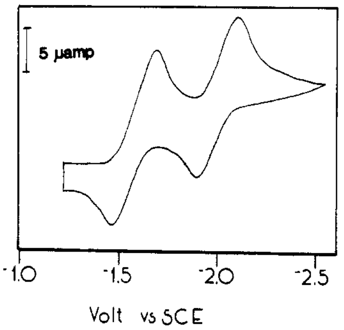


Figure 7. CV of reduction of 8.5×10^{-4} M $[CpCo(CO)]_2(\mu\text{-}CH_2)$ (2) in THF at Pt electrode (v = 100 mV/s).

$$Co_2(\mu\text{-}CH_2) + e^- \rightleftarrows [Co_2(\mu\text{-}CH_2)]^- \quad (5)$$

$$[Co_2(\mu\text{-}CH_2)]^- + e^- \rightleftarrows [Co_2(\mu\text{-}CH_2)]^{2-} \quad (6)$$

waves gave ΔE_p values of about 120 mV at a Pt electrode when v = 280 mV/s. This ΔE_p data is quoted for a solution fairly concentrated in the dicobalt complex (almost 1 *m*M: see Figure 7) and was typical for reversible charge transfers (e.g. Cp_2Co^+/Cp_2Co) under these conditions. The monoanion appears to be moisture-sensitive, since CV scans after addition of 10 mM water to the THF solution resulted in irreversibility of the first wave and virtual disappearance of the second.

Bulk coulometric reduction past the first wave also demonstrated the instability of $[Co_2(\mu\text{-}CH_2)]^-$. Electrolysis of a 8×10^{-4} M solution at −1.7 V at a Pt basket at 273 K consumed 1.00 F as the color changed from red to yellow-brown. CV and RPE scans after electrolysis showed that in addition to ca. 50% yield of $[Co_2(\mu\text{-}CH_2)]^-$, a second reversible couple was present ($E°$ = −0.69 V), also in about 50% yield (by relative current heights). This matches the $E°$ measured[22] for the carbonyl-bridged dimer $[CpCo(\mu\text{-}CO)]_2^{0/-}$, an assignment confirmed by the presence of a 15-line ESR spectrum with $\langle a\rangle_{Co}$=48G and $\langle g\rangle$ = 2.09, identical with that reported[22] for $[CpCo(\mu\text{-}CO)]_2^-$. Back-electrolysis at −0.30 V gave about an equal yield of the methylene-bridged starting material and neutral $[CpCo(\mu\text{-}CO)]_2$. The latter is known to be formed rapidly from $CpCo(CO)_2^-$,[22] so we believe that $\{[CpCo(CO)]_2(\mu\text{-}CH_2)\}^-$ cleaves off the methylene bridge, giving transient $CpCo(CO)_2^-$, which goes to form $[CpCo(\mu\text{-}CO)]_2^-$.

Discussion

All three dimetal systems (Mn, Co, Rh) give one-electron redox processes to radical anions and cations, the electron-transfer series involving 33-/34-/35-electron complexes. Although the potentials involved are relatively mild, the odd-electron species are in general unstable, prone to formation of mononuclear decomposition products.

Two independent studies of the bonding in μ-methylene compounds have emphasized the cyclopropane-like bonding in these molecules. A six-electron, three-center bond is partly responsible for the stability of the M–C–M bridge.[23,24] Hofmann calculated that 3 has two high-lying filled orbitals, one of which is mainly π_{xy} bonding between the rhodium atoms and the other being antibonding be-

---

(18) I = 3.01 in CH_3CN, close to that of the $Cp_2Co^{+/0}$ standard.

(19) The ratio of the reverse current to the forward current plateau increased from 0.64 to 0.85 when the mercury drop time was decreased from 2.0 to 0.5 s, indicating partial decomposition of $(3)^-$ at longer experiment times. See: Osteryoung, J.; Talmor, D.; Hermolin, J.; Kirowa-Eisner, E. *J. Phys. Chem.* **1981**, *85*, 285.

(20) This wave falls at the same potential as that of the dimer $[CpRh(\eta^4\text{-}C_5H_5)]_2$, which may arise from disproportionation of $(3)^-$. See: El Murr, N.; Sheats, J. E.; Geiger, W. E.; Holloway, J. D. L. *Inorg. Chem.* **1979**, *18*, 1443.

(21) The possibility of the mononuclear anion radical $CpRh(CO)_2^-$ being responsible for some of the features of Figure 5A should be considered. Although this radical is extremely unstable, some features of A match those of the pentaphenylcyclopentadienyl analogue $[(C_5Ph_5)Rh(CO)_2]^-$, which has $g_1 = 2.019$, $g_2 = 2.005$, and $g_3 = 1.945$ (Connelly, N. G.; Geiger, W. E.; Lane, G. A.; Raven, S. J.; Rieger, P. H. *J. Am. Chem. Soc.* **1986**, *108*, 6219). The lack of Rh hyperfine splitting for the g_3 (high field) features is, however, in contrast to appreciable splitting (7.5×10^{-4} cm^{-1}) observed for $[(C_5Ph_5)Rh(CO)_2]^-$.

(22) Schore, N. E.; Ilenda, C. S.; Bergman, R. G. *J. Am. Chem. Soc.* **1977**, *99*, 1781 and references therein.

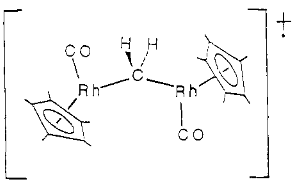
(23) Hofmann, P. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 554.

(24) Calabro, D. C.; Lichtenberger, D. L.; Herrmann, W. A. *J. Am. Chem. Soc.* **1981**, *103*, 6852.

tween the metals but bonding between the metals and the CH_2 bridge.[23] The latter may be the half-occupied orbital in the $(Rh_2(\mu\text{-}CH_2))^+$ radicals. This would account for the facile fragmentation of the M–C–M bridge upon oxidation. In support of this, we note that the LUMO of **3** is shown to be the antibonding partner of this orbital.[23] Hence, occupation of this orbital by the extra electron in the radical anions should also lead to extrusion of the CH_2 bridge and formation of mononuclear products. We have no direct evidence of this in the anions, but formation of $[CpCo(\mu\text{-}CO)]_2^-$ in the reduction of **2** is consistent with this decomposition route.

Substituent effects on $E°$ potentials are roughly as expected. Substitution of *Cp for Cp (in **4** vs. **3**) results in lowering of the neutral/cation potential by ca. 600 mV, consistent with shifts reported for other $\eta^5\text{-}C_5R_5$ complexes.[25] Perhaps more interestingly, the anodic peak potential for oxidation of the CH_2-bridged complex **3** (+0.72 V) is slightly *positive* of that observed for oxidation of the CO-bridged analogue $[CpRh(CO)]_2(\mu\text{-}CO)$, +0.65 V.[26] This is in concert with calculations and experiments which have shown that the CH_2 bridge is highly effective at withdrawing charge from the dimetal center.[23,24,27,28]

There is a possibility that upon oxidation the cation radical undergoes significant weakening or rupture of the M–M bond, giving an intermediate like that drawn below for the dirhodium monocation:



There is precedence for this kind of structure from the irradiation of $Mn_2(CO)_{10}$. γ-Irradiation of single crystals of the neutral metal carbonyl resulted in formation of $\{[(CO)_4Mn]_2(\mu\text{-}CO)\}^-$, which was identified by ESR studies under cryogenic conditions.[29] This anion is isoelectronic with $(1)^+$. We do not favor an "opened" M–C–M bridge in our dimanganese system because we believe that it would lead to a carbonyl-bridged complex in the next step. IR data on the cation radical of the dimanganese complex $(1)^+$ demonstrates that all carbonyl remain terminal in the oxidized species.

It is noteworthy that in the series of dirhodium complexes the cation derived from the doubly CO-bridged complex **5** is by far the most stable. This observation is similar to that reported by Connelly et al.,[2] who showed that cations of CH_2-bridged ruthenium complexes were stabilized by a diphosphine ligand which spanned the two metal atoms.

Conclusions

1. Methylene-bridged complexes undergo reversible one-electron processes to anions and cations at very accessible potentials.
2. In the absence of other bridging ligands, extrusion of the CH_2 bridge apparently occurs from radical cations, leading to rapid formation of mononuclear products.
3. ESR of $\{[CpMn(CO)]_2(\mu\text{-}CH_2)\}^+$ indicates equivalent interaction with two Mn atoms, implying delocalization in the Mn–C–Mn bridge. The carbonyls remain terminal in the cation.
4. The instability of the M–C–M bridge to oxidation is similar to that observed in the anodic behavior of cyclopropanes[30] and further supports the formulation of these complexes as dimetallacyclopropanes.[31]

Acknowledgment. We are grateful for the financial support of the donors of the Petroleum Research Fund, administered by the American Chemical Society, and of the National Science Foundation (NSF CHE83-03974). We also thank the Johnson Matthey Corp. for a generous loan of rhodium salts. W.A.H. acknowledges financial support of this work by the Deutsche Forschungsgemeinschaft and the German Federal Ministry of Research (BMFT), Bonn.

Registry No. **1**, 57603-41-5; $\mathbf{1}^{\cdot +}$, 108919-03-5; **2**, 77674-08-9; **3**, 65138-22-9; **4**, 76582-86-0; **5**, 76550-38-4; $\mathbf{5}^{\cdot +}$, 108919-04-6; **6**, 76687-29-1; **7**, 108919-02-4; $[CpCo(\mu\text{-}CO)]_2$, 58496-39-2; $[CpCo(\mu\text{-}CO)]_2^-$, 58543-12-7; $CpCo(NCCH_3)_3^{2+}$, 73065-79-9; $CpCo(CO)_2$, 12078-25-0; $[(p\text{-}BrC_6H_4)_3N]^+$, 37881-41-7.

---

(25) a) Koelle, U.; Fuss, B.; Rajasekharan, M. V.; Ramakrishna, B. L.; Ammeter, J. H.; Böhm, M. C. *J. Am. Chem. Soc.* **1984**, *106*, 4152. (b) Astruc, D.; Hamon, J.; Althoff, G.; Roman, E.; Batail, P.; Michaud, P.; Mariot, J.; Varret, F.; Cozak, D. *J. Am. Chem. Soc.* **1979**, *101*, 5445.

(26) Oxidation of $[CpRh(CO)]_2(\mu\text{-}CO)$ is irreversible in CH_2Cl_2 at $v >$ 1 V/s. At slower sweep rates, cathodic waves due to electroactive products were observed. Attempted isolation of these products by anodic oxidation or by ferrocenium oxidation was unsuccessful.

(27) Clemente, D. A.; Biagini, M. C.; Rees, B.; Herrmann, W. A. *Inorg. Chem.* **1982**, *21*, 3741.

(28) Xiang, S. F.; Chen, H. W.; Eyermann, C. J.; Jolly, W. L.; Smit, S. P.; Theopold, K. H.; Bergman, R. G.; Herrmann, W. A.; Petit, R. *Organometallics* **1982**, *1*, 1200.

(29) Lionel, T.; Morton, J. R.; Preston, K. F. *Inorg. Chem.* **1983**, *22*, 145.

(30) Gassman, P. G.; Yamaguchi, R. *J. Am. Chem. Soc.* **1979**, *101*, 1308. Shono, T.; Matsumura, Y. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 2861; *J. Org. Chem.* **1970**, *35*, 4157.

(31) For a comprehensive study of the thermolytic behavior of μ-alkylidene complexes, see: Schäfer, A.; Herrmann, W. A. *J. Organomet. Chem.* **1985**, *297*, 229.