arise because at a synthetic level it is still a problem to engineer reaction chemistry to give reasonable yields of isolatable species that may be expected to exhibit features that would be helpful in the assessment of these bonding considerations, whether they be "hypercloso" or "isocloso". At present we would prefer to spend time addressing these synthetic problems.

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Contribution from the Department of Chemistry,
Massachusetts Institute of Technology,
Cambridge, Massachusetts 02139

Photochemistry of (η^5-C$_5$H$_5$)$_2$M$_2$(CO)$_3$ (M = Co, Rh) in Low-Temperature Organic Glasses: Generation of [(η^5-C$_5$H$_5$)M(μ-CO)]$_2$

F. Ruth Anderson and Mark S. Wrighton*

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We wish to report that near-UV irradiation of (η^5-C$_5$H$_5$)$_2$M$_2$(CO)$_3$ (M = Co, Rh) in low-temperature hydrocarbon matrices results in rapid and clean loss of CO to produce the metal-metal-double-bonded, doubly CO-bridged product [(η^5-C$_5$H$_5$)M(μ-CO)]$_2$. Compounds containing a simple 2e metal-metal bond have been shown to generally yield metal-centered radicals upon photolysis.[1] However, even though metal-centered radicals may dominate the photoproducts in fluid solutions, recent results have shown that photolysis of metal-metal-bonded compounds in rigid matrices may yield products resulting from expulsion of a 2e-donor ligand. Although the photolysis of the compounds Mn$_2$(CO)$_{10}$,[2] (η^5-C$_5$H$_5$)Fe$_2$(CO)$_4$,[3] and (η^5-C$_5$H$_5$)$_2$W$_2$(CO)$_6$[4] in fluid solutions results in the formation of radicals arising from net metal-metal bond homolysis, irradiation of these same compounds in rigid matrices gives only the CO loss products Mn$_2$(CO)$_9$,[5] (η^5-C$_5$H$_5$)$_2$Fe$_2$(μ-CO)$_3$,[6] and (η^5-C$_5$H$_5$)$_2$W$_2$(CO)$_5$,[7] respectively.

Our interest in the (η^5-C$_5$H$_5$)$_2$M$_2$(CO)$_3$ compounds was sparked by reports that irradiation of (η^5-C$_5$H$_5$)Co(CO)$_2$ in rigid matrices results in formation of [(η^5-C$_5$H$_5$)Co(μ-CO)]$_2$.[8,9] Prolonged photolysis of (η^5-C$_5$H$_5$)Co(CO)$_2$ in fluid solution yields small amounts of the thermally unstable [(η^5-C$_5$H$_5$)Co(μ-CO)]$_2$,[10] but the dominant product is (η^5-C$_5$H$_5$)$_2$Co$_2$(CO)$_3$.[11] Irradiation of ~1 mM (η^5-C$_5$H$_5$)Rh(CO)$_2$ at 93 K in a rigid methylcyclohexane matrix results in the formation of an alkane oxidative-addition product (η^5-C$_5$H$_5$)Rh(CO)(H)(C$_7$H$_{13}$), although at higher concentrations (>5 mM) an additional product, [(η^5-C$_5$H$_5$)Rh(μ-CO)]$_2$, is formed.[9] At room temperature the irradiation of (η^5-C$_5$H$_5$)Rh(CO)$_2$ in alkane solution results in formation of (η^5-C$_5$H$_5$)$_2$Rh$_2$(CO)$_3$.[12] The crystal structure of (η^5-C$_5$H$_5$)$_2$Rh$_2$(CO)$_3$ reveals that the molecule contains a metal-metal bond and is singly bridged and that the (η^5-C$_5$H$_5$) groups are trans to each other.[12] We were interested in determining whether the [(η^5-C$_5$H$_5$)M(μ-CO)]$_2$ complexes observed in the matrix studies could be the products of photolysis of the metal-metal-single-bonded dimers (η^5-C$_5$H$_5$)$_2$M$_2$(CO)$_3$. Though no quantitative data were provided, it has been previously noted that irradiation at room temperature of the related complex (η^5-C$_5$Me$_5$)$_2$Rh$_2$(CO)$_3$ results in formation of [(η^5-C$_5$Me$_5$)Rh(μ-CO)]$_2$.[13] Irradiation of (η^5-C$_5$Me$_5$)Co(CO)$_2$ and (η^5-C$_5$Me$_5$)Rh(CO)$_2$ at room temperature results in [(η^5-C$_5$Me$_5$)Co(μ-CO)]$_2$ and [(η^5-C$_5$Me$_5$)Rh(μ-CO)]$_2$,[14,15] respectively. We now report that photoreaction according to eq 1 occurs rapidly and cleanly at low temperature,

$$(\eta^5\text{-C}_5\text{H}_5)_2\text{M}_2(\text{CO})_3 \xrightarrow[\text{MCH}]{h\nu,\ 93\ \text{K}} [(\eta^5\text{-C}_5\text{H}_5)\text{M}(\mu\text{-CO})]_2 + \text{CO} \tag{1}$$

establishing CO loss as the only efficient photoreaction of (η^5-C$_5$H$_5$)$_2$M$_2$(CO)$_3$ in a low-temperature rigid matrix.

Experimental Section

Instruments. IR spectra were recorded by using either a Nicolet 7199 or 60SX Fourier transform interferometer. UV-vis spectra were obtained with the use of either a Cary 17 spectrophotometer or a Hewlett-Packard 8451A diode array spectrophotometer. Low-temperature IR and UV-vis spectra were obtained by using a Specac Model P/N 21000 variable-temperature cell with CaF$_2$ outer windows using liquid N$_2$ as the coolant. A small hole drilled into the metal portion of the sample cell accommodates the junction end of a copper-constantan thermocouple. Irradiations were carried out with use of either a 450-W medium-pressure Hanovia Hg lamp with a quartz, H$_2$O-cooled jacket or a Bausch and Lomb SP 250-W high-pressure Hg lamp. The Bausch and Lomb lamp was used with a 10-cm H$_2$O filter with Pyrex windows to filter out IR and deep-UV irradiation.

Chemicals. Hexane was distilled from CaH$_2$ under N$_2$ before use. Methylcyclohexane (MCH) was distilled from Na under Ar before use. CH$_2$Cl$_2$ was chromatographic grade and deoxygenated before use. Generally, all manipulations of organometallic compounds were carried out under N$_2$ or Ar by using a Vacuum Atmospheres drybox or conventional Schlenk-line techniques. The known[11] (η^5-C$_5$H$_5$)$_2$Co$_2$(CO)$_3$ was prepared by irradiation (General Electric Blacklight bulbs) of a dilute (~0.03 M) hexane solution of (η^5-C$_5$H$_5$)Co(CO)$_2$. The solvent was stripped and the residue chromatographed on alumina. (η^5-C$_5$H$_5$)Co(CO)$_2$ was eluted with hexane, after which (η^5-C$_5$H$_5$)$_2$Co$_2$(CO)$_3$ was eluted with CH$_2$Cl$_2$. The solvent was then removed by vacuum. A similar procedure was used for the preparation of the known[12] (η^5-C$_5$H$_5$)$_2$Rh$_2$(CO)$_3$. [(η^5-C$_5$Me$_5$)Rh(μ-CO)]$_2$ was prepared according to the literature method.[17]

Results and Discussion

Figure 1 shows IR spectral changes resulting from near-UV irradiation of (η^5-C$_5$H$_5$)$_2$Co$_2$(CO)$_3$ and (η^5-C$_5$H$_5$)$_2$Rh$_2$(CO)$_3$ in methylcyclohexane glasses at 93 K. The terminal (1965 cm^{-1}) and bridging (1812 cm^{-1}) CO bands of (η^5-C$_5$H$_5$)$_2$Co$_2$(CO)$_3$ can be seen to decrease upon irradiation. Free CO (2132 cm^{-1})[18] is produced upon consumption of (η^5-C$_5$H$_5$)$_2$Co$_2$(CO)$_3$, as well as a material with a strong CO absorption in the bridging region at 1792 cm^{-1}, which is assigned to the doubly bridged dimer

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* To whom correspondence should be addressed.

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Table I. Spectroscopic Data for Relevant Complexes[a]

	T, K	IR, cm^{-1} (ϵ, M^{-1} cm^{-1})	UV–vis, nm (ϵ, M^{-1} cm^{-1} or rel abs)
$(\eta^5\text{-}C_5H_5)_2Co_2(CO)_3$	298	1965 (6500), 1812 (3700)	400 (7000), 290 (10 000)
$[(\eta^5\text{-}C_5H_5)Co(\mu\text{-}CO)]_2$	93	1792 (8400)	590 (13 500), 395 (21 000)
$[(\eta^5\text{-}C_5Me_5)Co(\mu\text{-}CO)]_2$[b]	298	1760	610 (10 000), 410 (21 000)
$(\eta^5\text{-}C_5H_5)_2Rh_2(CO)_3$	298	1981 (9000), 1834 (3700)	330 (11 000), 440 (1200)
$[(\eta^5\text{-}C_5H_5)Rh(\mu\text{-}CO)]_2$	93	1778 (10 000)	550 (30 000), 330 (46 000)
$[(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}CO)]_2$	298	1747	580 (0.3), 345 (1.0)

[a] All spectra reported in methylcyclohexane, unless otherwise noted. [b] Reference 14. Spectra reported in hexane.

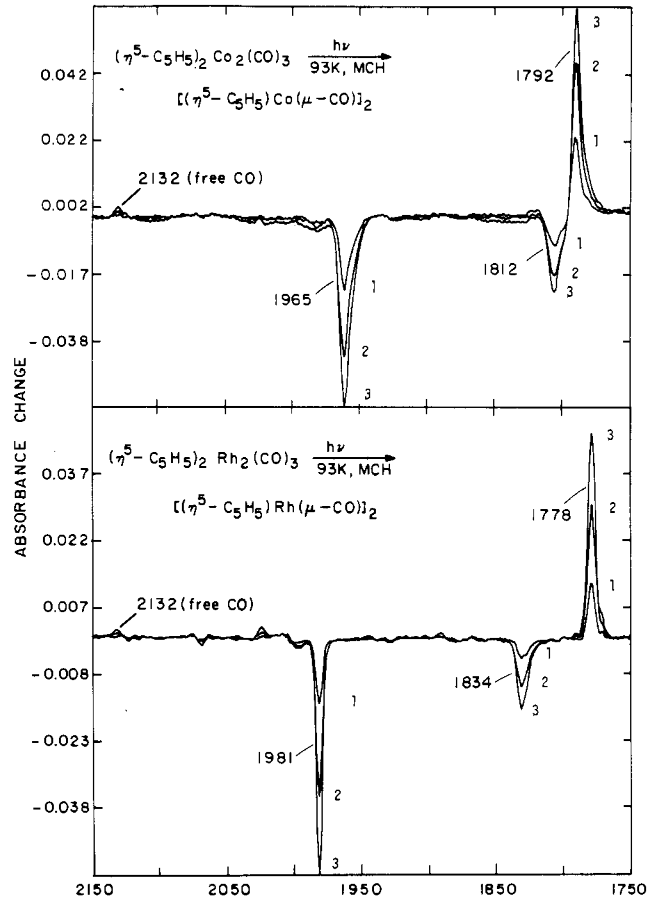

Figure 1. (Top) IR difference spectra at 93 K upon photolysis of ~1 mM $(\eta^5\text{-}C_5H_5)_2Co_2(CO)_3$ in methylcyclohexane. The curves are for (1) 5, (2) 10, and (3) 15 s of irradiation corresponding to 10, 20, and 30% consumption, respectively, to generate $[(\eta^5\text{-}C_5H_5)Co(\mu\text{-}CO)]_2$ (1792 cm^{-1}). (Botton) IR difference spectrum at 93 K upon irradiation of ~1 mM $(\eta^5\text{-}C_5H_5)_2Rh_2(CO)_3$ in methylcyclohexane. The curves are for (1) 60, (2) 120, and (3) 180 s of photolysis corresponding to 4, 10, and 15% consumption, respectively, to produce $[(\eta^5\text{-}C_5H_5)Ru(\mu\text{-}CO)]_2$ (1778 cm^{-1}). The small peak appearing at ~2020 cm^{-1} has not been identified and may be due to photolysis of an impurity associated with declining bands at ~2000 and ~2070 cm^{-1}.

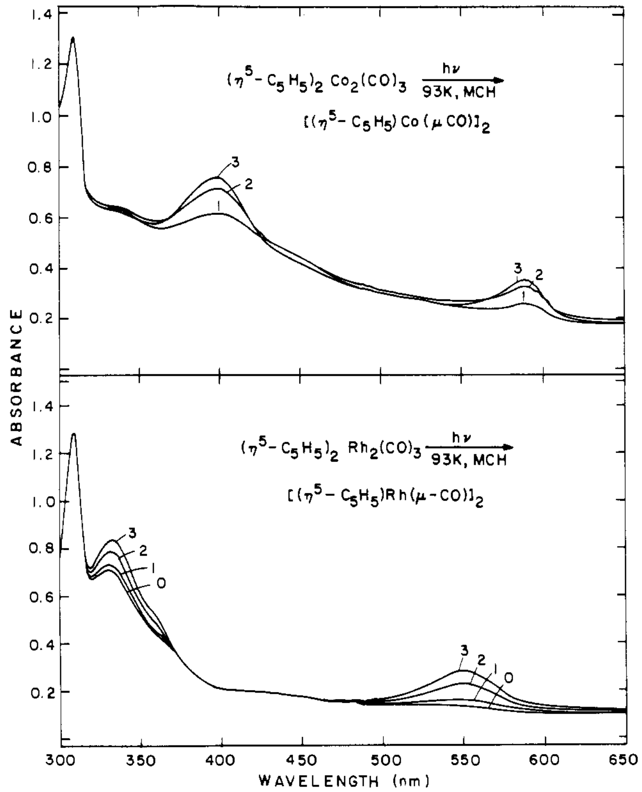

Figure 2. (Top) UV–vis spectral changes upon photolysis of $(C_5H_5)_2Co_2(CO)_3$ in methylcyclohexane at 93 K. Curves are for (1) 5, (2) 10, and (3) 15 s of photolysis. (Bottom) UV–vis spectral changes upon photolysis of $(\eta^5\text{-}C_5H_5)_2Rh_2(CO)_3$ in methylcyclohexane at 93 K. Curves are for (1) 60, (2) 120, and (3) 180 s of photolysis. The spectra correspond to the same samples used to record the IR spectral changes shown in Figure 1. The large peak at 310 nm is due to the CaF$_2$ windows of the cell.

$[(\eta^5\text{-}C_5H_5)Co(\mu\text{-}CO)]_2$. Since the absorptivity of CO in methylcyclohexane matrices is known to be ϵ = 400 M^{-1} cm^{-1},[19] the low temperature spectral changes can be used to determine the amount of free CO generated compared to the amount of $(\eta^5\text{-}C_5H_5)_2Co_2(CO)_3$ consumed. The results are consistent with the loss of one molecule of CO per molecule of $(\eta^5\text{-}C_5H_5)_2Co_2(CO)_3$ consumed. Irradiation of $(\eta^5\text{-}C_5H_5)_2Rh_2(CO)_3$ under the same conditions produces spectral changes similar to those for the Co complex. The metal-containing product displays a single CO band in the bridging region (1778 cm^{-1}). Again, there is one molecule of CO produced for every starting molecule consumed. The known compounds $[(\eta^5\text{-}C_5H_5)Co(\mu\text{-}CO)]_2$, $[(\eta^5\text{-}C_5Me_5)Co(\mu\text{-}CO)]_2$, and $[(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}CO)]_2$ all have single CO absorptions in the bridging region, as shown in Table I. These facts lead to the assignment of the metal-containing product of photolysis of $(\eta^5\text{-}C_5H_5)_2Rh_2(CO)_3$ as $[(\eta^5\text{-}C_5H_5)Rh(\mu\text{-}CO)]_2$. Neither of the $(\eta^5\text{-}C_5H_5)_2M_2(CO)_3$ species irradiated produces any carbonyl absorptions attributable to terminal CO's. Accordingly, eq 1 gives the photochemistry at low temperature.

Additional characterization of $[(\eta^5\text{-}C_5H_5)Rh(\mu\text{-}CO)]_2$ formed by irradiation of $(\eta^5\text{-}C_5H_5)_2Rh_2(CO)_3$ is provided by the UV–vis spectral changes accompanying the irradiation. The metal–metal double-bonded compounds $[(\eta^5\text{-}C_5H_5)Co(\mu\text{-}CO)]_2$, $[(\eta^5\text{-}C_5Me_5)Co(\mu\text{-}CO)]_2$,[14] and $[(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}CO)]_2$[17] all display two strong absorptions, one between 350 and 400 nm, and another between 500 and 610 nm. When $(\eta^5\text{-}C_5H_5)_2Rh_2(CO)_3$ is irradiated in alkane matrices at 93 K, the product exhibits absorptions at 330 and 550 nm (Figure 2) similar to $[(\eta^5\text{-}C_5H_5)Rh(\mu\text{-}CO)]_2$ with its absorbances at 345 and 580 nm. The substitution of C_5H_5 for C_5Me_5 results in a shift of the absorbances toward shorter wavelengths. Photoexcitation of $(\eta^5\text{-}C_5H_5)_2Co_2(CO)_3$ in a methylcyclohexane matrix results in a product with strong absorbances at 395 and 590 nm, which are associated with $[(\eta^5\text{-}C_5H_5)Co(\mu\text{-}CO)]_2$.

Although $[(\eta^5\text{-}C_5H_5)Rh(\mu\text{-}CO)]_2$ can be produced in low-temperature glasses, it is thermally unstable above ~200 K. Efforts to isolate this material have failed, resulting either in decomposition or back-reaction with CO upon warming to produce

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either $(\eta^5\text{-}C_5H_5)_2Rh_2(CO)_3$ or $(\eta^5\text{-}C_5H_5)Rh(CO)_2$. Thus, although $[(\eta^5\text{-}C_5H_5)Rh(\mu\text{-}CO)]_2$ has for several years been the object of seculation and interest,[17b] it is not surprising that this compound has not been previously observed. The analogous $[(\eta^5\text{-}C_5H_5)Co(\mu\text{-}CO)]_2$ is known to be thermally unstable to give $[(\eta^5\text{-}C_5H_5)Co(CO)]_3$.[10] For both cobalt and rhodium, the $[(\eta^5\text{-}C_5Me_5)M(\mu\text{-}CO)]_2$ complexes, although very sensitive to oxygen, appear to be more robust than their $[(\eta^5\text{-}C_5H_5)M(\mu\text{-}CO)]_2$ analogues.

Assignment of the electronic transition leading to labilization of the CO ligand of $(\eta^5\text{-}C_5H_5)_2M_2(CO)_3$ is not straightforward. Generally, a $\sigma \rightarrow \sigma^*$ absorption is observed for any system that contains a simple 2e metal–metal bond.[1] CNDO calculations performed for $(\eta^5\text{-}C_5H_5)_2Rh_2(CO)_3$ have led to the conclusion that the two highest occupied molecular orbitals are those related to the Rh–Rh and Rh(μ-CO)Rh bonds and that these are very close in energy.[20] Our results suggest that the lowest excited state has substantial M–CO antibonding character. While quantum yields have not been measured, the $(\eta^5\text{-}C_5H_5)_2M_2(CO)_3$ complexes are exceedingly photosensitive. In our hands the complexes are sufficiently photosensitive that their formation cannot be detected upon irradiation of the mononuclear $(\eta^5\text{-}C_5H_5)M(CO)_2$ species in a 93 K methylcyclohexane matrix. Rather, the dinuclear $[(\eta^5\text{-}C_5H_5)M(\mu\text{-}CO)]_2$ species appear to be prompt products. The extreme photosensitivity of $(\eta^5\text{-}C_5H_5)_2M_2(CO)_3$ suggests that their accumulation upon irradiation of $(\eta^5\text{-}C_5H_5)M(CO)_2$ in low-temperature matrices is unlikely. The structural rearrangement necessary to form $[(\eta^5\text{-}C_5H_5)M(\mu\text{-}CO)]_2$ from the tricarbonyl is likely similar to that for the conversion of the trans isomer of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ to $(\eta^5\text{-}C_5H_5)_2Fe_2(\mu\text{-}CO)_3$.[5] It is evident that such rearrangement is possible at very low temperatures. Interestingly, irradiation of $Fe_2(CO)_9$, which is triply CO-bridged,[21] in a low-temperature matrix gives CO loss, but the $Fe_2(CO)_8$ is formed as a mixture of bridged and unbridged isomers.[22]

Acknowledgment. We thank the National Science Foundation for support of this research.

Registry No. $(\eta^5\text{-}C_5H_5)_2Co_2(CO)_3$, 53450-14-9; $(\eta^5\text{-}C_5H_5)_2Rh_2(CO)_3$, 65138-21-8; $[(\eta^5\text{-}C_5H_5)Co(\mu\text{-}CO)]_2$, 58496-39-2; $[(\eta^5\text{-}C_5H_5)Rh(\mu\text{-}CO)]_2$, 82397-01-1; $[(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}CO)]_2$, 69728-34-3.

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Contribution from the Department of Chemistry,
Howard University, Washington, D.C. 20059,
Department of Health and Natural Sciences,
Benedict College, Columbia, South Carolina 29204,
and National Bureau of Standards,
Gaithersburg, Maryland 20899

Kinetics of the Reduction of Manganese(III) Myoglobin by Dithionite

Robert Langley, Peter Hambright,* Kenneth Alston,
and P. Neta

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Due to its stability in the neutral and basic pH ranges, dithionite ($S_2O_4^{2-}$) has been used to study the kinetics and mechanisms of reactions of numerous metalloproteins,[1-6] metalloporphyrins,[7-14] dioxygen,[15] and classical Werner complexes.[16-19] We report the kinetics of reduction of manganese(III)-substituted myoglobin (Mn^{III}–Mb) into its Mn^{II}–Mb form with dithionite. The metalloporphyrin self-exchange rate constants and potentials are used to predict the relative reduction rates of Fe^{III}–Mb and Mn^{III}–Mb by SO_2^-.

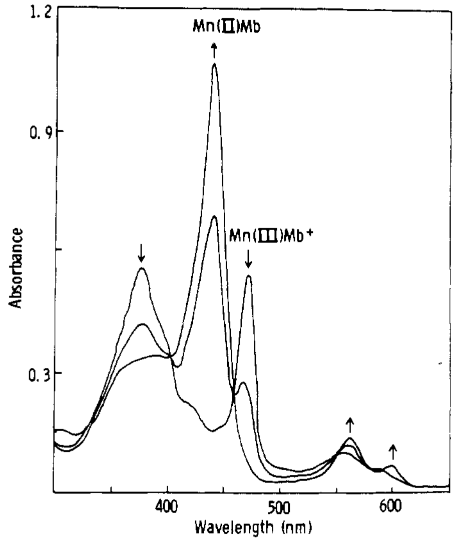

Figure 1. Absorption spectra of Mn^{III}–Mb and Mn^{II}–Mb; pH = 7.

Experimental Section

Manganese(III) myoglobin was prepared from manganese(III) protoporphyrin IX and purified sperm whale metomyoglobin by procedures[20] similar to those used for Co^{III}–Mb[3] and stored frozen at pH 7.3. The absorption bands of Mn^{III}–Mb were essentially the same as those reported by other workers.[21-23] For comparison with Fe^{III}–Mb[4] and Co^{III}–Mb,[3]

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* To whom correspondence should be addressed at Howard University.

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