Perkin Trans. 1 **1975**, 1401–1403.

(10) (a) Triebs, A.; Haberle, N. *Justus Liebigs Ann. Chem.* **1968**, *718*, 183–207. (b) Badger, M.; Jones, R. A.; Laslett, R. L. *Aust. J. Chem.* **1964**, *17*, 1028–1035.

(11) Boucher, L. J. *J. Am. Chem. Soc.* **1970**, *92*, 2725–2730.

(12) Adler, A. D.; Longo, F. R.; Kampas, F.; Kim, J. *J. Inorg. Nucl. Chem.* **1970**, *32*, 2443–2445.

(13) Buchler, J. H.; Eikelmann, G.; Puppe, L.; Rohbock, K.; Schneehage, H. H.; Weck, D. *Justus Liebigs Ann. Chem.* **1971**, *745*, 131–151.

(14) Kobayashi, H.; Yanagawa, Y. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 450–456.

(15) Summerville, D. A.; Jones, R. D.; Hoffman, B. M.; Basolo, F. *J. Am. Chem. Soc.* **1977**, *99*, 8195–8202.

(16) Gladney, J. D.; Swalen, H. M. Quantum Chemistry Program Exchange, No. 134, Indiana University, Bloomington, Ind.

(17) Lozos, G. P.; Hoffman, B. M.; Franz, C. G. Quantum Chemistry Program Exchange, No. 265, Indiana University, Bloomington, Ind.

(18) Blumberg, W. E. In "Magnetic Resonance in Biological Systems", Ehrenberg, A.; Malmström, B. G.; Vänngard, T., Ed.; Pergamon Press: Braunschweig, 1967; pp 119–133.

(19) McGarvey, B. R. *Transition Met. Chem.* **1967**, *3*, 89–200.

(20) Ferrante, R. F.; Wilerson, J. L.; Graham, W. R. M.; Weltner, W. Jr. *J. Chem. Phys.* **1977**, *67*, 5904–5913.

(21) Wertz, J. E.; Bolton, J. R. "Electron Spin Resonance, Elementary Theory and Practical Applications", McGraw-Hill: New York, N.Y., 1972, pp 140–143.

(22) Hoffman, B. M.; Mahoney, D., unpublished.

(23) Abragam, A.; Bleaney, B. "Electron Paramagnetic Resonance of Transition Metal Ions", Oxford University Press: London, 1970.

(24) McGarvey, B. R. *J. Chem. Phys.* **1964**, *41*, 3473–3758.

(25) Guilard, R.; Latour, J.; Lecomte, C.; Marchon, J.; Protas, J.; Ripoll, D. *Inorg. Chem.* **1978**, *17*, 1228–1237.

(26) Wayland, B. B.; Olson, L. W.; Siddiqui, Z. U. *J. Am. Chem. Soc.* **1976**, *98*, 94–98.

(27) Hansen, L. K.; Hoffman, B. M. In progress.

(28) Wayland, B. B.; Minkiewicz, J. V.; Abd-Elmageed, M. E. *J. Am. Chem. Soc.* **1974**, *96*, 2795–2801.

(29) Boucher, L. J. *Coord. Chem. Rev.* **1972**, *7*, 289–329.

(30) (a) Hanson, L. K.; Eaton, W. A.; Sligar, S. G.; Gunsalus, I. C.; Gouterman, M.; Connell, C. R. *J. Am. Chem. Soc.* **1976**, *98*, 2672–2674. (b) Chang, C. K.; Dolphin, D. *Ibid.* **1975**, *97*, 5948–5950. (c) Dawson, J. H.; Trudell, J. R.; Barth, G.; Linder, R. E.; Bunnenberg, E.; Djerassi, C.; Gouterman, M.; Connell, C. R.; Sayer, P. *ibid.* **1977**, *99*, 641–642, and references cited therein.

(31) Hoard, J. L. *Ann. N.Y. Acad. Sci.* **1973**, *206*, 18–31.

(32) (a) Hoffman, R.; Chen, M. M. L.; Elian, M.; Rossi, A. R.; Mingos, D. M. P. *Inorg. Chem.* **1974**, *13*, 2666–2675. (b) Hanson, L. K. Personal communication.

Pulse Radiolysis Studies of Decacarbonyldimanganese(0) and Halopentacarbonylmanganese(I). The Pentacarbonylmanganese(0) Radical

William L. Waltz,[*1] **Ortfried Hackelberg, Leon M. Dorfman,*** and **Andrew Wojcicki***

Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210. Received May 15, 1978

Abstract: The pulse radiolysis of $Mn_2(CO)_{10}$, $Mn(CO)_5Br$, and $Mn(CO)_5I$ in ethanol solution has been investigated. The $Mn(CO)_5$· radical, which was observed, exhibits an optical absorption band with a maximum at 830 nm and a molar absorption coefficient of $\epsilon_{830} = 800 \pm 80$ M^{-1} cm^{-1}. Absolute rate constants were determined for the reactions of the solvated electron with $Mn_2(CO)_{10}$ (9.1×10^9 M^{-1} s^{-1}), $Mn(CO)_5Br$ (1.0×10^{10} M^{-1} s^{-1}), and $Mn(CO)_5I$ (1.02×10^{10} M^{-1} s^{-1}). For the iodide system, $Mn(CO)_5$· is also formed by the reaction of α-ethanol radical with $Mn(CO)_5I$ (1.5×10^8 M^{-1} s^{-1}). The recombination of $Mn(CO)_5$· has a rate constant of $2k = 1.2 \times 10^9$ M^{-1} s^{-1}; $Mn_2(CO)_{10}$ is identified as a final product in the radiolysis of the halide complexes. $Mn(CO)_5$· reacts with O_2 (1.8×10^9 M^{-1} s^{-1}).

Introduction

Organotransition metal radicals represent a rapidly growing class of reactive intermediates.[2–7] They have been encountered, on numerous occasions, in chemical reactions leading to the formation and/or cleavage of metal–carbon, metal–hydrogen, and metal–metal bonds. A number of them have been implicated in catalysis by transition metal complexes.[8] Yet, recent developments notwithstanding, relatively little is known about their structure, spectroscopic properties, and elementary reactions.

A severe limitation on continued rapid progress in this field is the paucity of general methods of production and direct observation of such transient species in solution.[9] At present, transition metal centered radicals have been best generated by conventional photochemical or flash photolytic cleavage of metal–metal bonds in metal carbonyl complexes.[5–7,11–14]

$$L_n(CO)_mM\text{-}M(CO)_mL_n \xrightarrow{h\nu} 2L_n(CO)_mM\cdot \qquad (1)$$
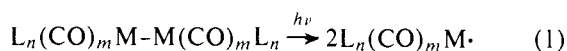
In these processes homolysis of the metal–metal bond is thought to occur via a $\sigma(M\text{-}M)$ to $\sigma^*(M\text{-}M)$ one-electron excitation.[15] The resultant short-lived radicals have been characterized indirectly either by spin trapping with nitroso compounds or by scavenging in halogen abstraction reaction with organic halides. Organotransition metal radical pathways have also been diagnosed by the observation of chemically induced dynamic nuclear polarization[16,17] and, less directly, by various methods of kinetic and stereochemical origin.[2]

The pulse radiolysis method[18,19] potentially represents a powerful and versatile alternative method to flash photolysis for the direct study of organotransition metal radicals in solution. Surprisingly, it has received little application toward these ends.[20] Attachment of the solvated electron to an appropriate organotransition metal compound is expected to produce a radical anion

$$L_nMX + e^-_{sol} \rightarrow L_nMX^- \qquad (2)$$

which may then undergo dissociation to generate a stable anion and the desired metal-centered radical.

$$L_nMX^- \rightarrow L_nM\cdot + X^- \qquad (3)$$
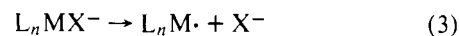
The present work was undertaken in a new program concerned with the application of pulse radiolytic methods to studies on a submicrosecond time scale of organotransition metal transients. The manganese carbonyls $Mn_2(CO)_{10}$ and $Mn(CO)_5X$ (X = Br, I) selected for this initial investigation represent two general classes of metal carbonyl compounds,

namely, metal–metal bonded dimers and the carbonyl halides. It may be anticipated that in combining with the solvated electron $Mn_2(CO)_{10}$ will use its $\sigma^*(M-M)$ orbital, causing dissociation into $Mn(CO)_5^-$ and $Mn(CO)_5\cdot$. Similarly, dissociative attachment of the solvated electron to $Mn(CO)_5X$ is expected, by analogy with the behavior of the organic halides,[21] to produce X^- and $Mn(CO)_5\cdot$. Thus, it appears that the desired $Mn(CO)_5\cdot$ radical is potentially accessible from several different types of compounds.

The $Mn(CO)_5\cdot$ radical has been generated in solution and indirectly characterized by several investigators.[5-7,11-13,22,23] It has a large rate constant for dimerization to form $Mn_2(CO)_{10}$.[12] The electronic spectrum of $Mn(CO)_5\cdot$ is unknown.[12] It is relevant to this investigation that a closely related, isoelectronic (d^7) analogue of the $Mn(CO)_5\cdot$ radical, the $Co(CN)_5^{3-}$ anion, is a well-characterized species.[24] It is quite stable toward dimerization in solution and it possesses a reasonably well-explored radical chemistry.[25,26] Its electronic spectrum has been recorded and interpreted.[24]

In this paper we report the generation of the $Mn(CO)_5\cdot$ radical by pulse radiolysis of $Mn_2(CO)_{10}$ and $Mn(CO)_5X$. Some physical and chemical properties of $Mn(CO)_5\cdot$ have been determined. All of these studies were conducted in ethanol solutions. Ethanol was selected as the solvent because the yield of e^-_{sol} is unity or higher[27-29] and the manganese carbonyls are sufficiently soluble. A number of radiolytic investigations have been carried out on ethanol, and the properties of the major radicals formed, e^-_{sol} and α-ethanol radical, have been well documented.[27-29]

Experimental Section

A. Pulse Radiolysis Apparatus and Procedures. The apparatus based on a Varian V-7715 A electron linac, delivering 4-MeV electrons, has been described previously.[18,19,30] The pulse radiolysis experiments were performed at 293 ± 1 K using a 2-cm quartz irradiation cell with a double pass of the analyzing light beam. Changes in the light level transmitted by the irradiated solutions were detected using photomultiplier tubes (RCA 7102 and 7200); these detectors and the associated electronic circuitry had a rise time of less than 70 ns. Appropriate light filters were used to minimize the extent of photolysis, and a shutter was employed to restrict the exposure to the analyzing light. The irradiation cell was constructed so that it could be filled and emptied of solution in the absence of air. The solutions were deaerated using argon gas (99.999%) in conjunction with a syringe technique similar to that of a published procedure.[31] For all sources of ethanol used in this work, the decay in deaerated solutions of the electron, which has an absorption band with a peak at 700 nm,[27b] closely approximated first-order kinetics. The apparent first-order rate constant for this process did, however, increase with increasing dose ($[e^-_{sol}]_{max} \simeq 1-7$ μM). This behavior and the range of half-lives found ($t_{1/2} \simeq 1-5$ μs) are in agreement with results reported by others.[29a,32] In this regard, corrections for the reaction of e^-_{sol} with the solvent system were made in determining the rate constants for the electron reactions for the manganese complexes and the molar absorption coefficient of the reaction product. This was done using the apparent first-order rate constant for the electron decay in the solvent system at the appropriate dose condition. In addition to the presence of e^-_{sol} in pulse-irradiated and deaerated ethanol, a transient was also observed in the region of 280–400 nm, which had the expected absorption level and kinetic properties of α-ethanol radical.[29b,32,33]

B. Materials. Decacarbonyldimanganese(0) was purchased from Strem Chemicals, Inc. Bromopentacarbonylmanganese(1), $Mn(CO)_5Br$, and the corresponding iodo compound, $Mn(CO)_5I$, were prepared by published procedures.[34,35] Samples of these compounds were purified by sublimation and stored in the dark in a refrigerator, generally under an argon atmosphere. Their IR and UV spectra were in good agreement with their reported spectra.[22,34-39] While $Mn(CO)_5Br$ decomposed slowly in absolute ethanol solutions (first half-life ca. 8 h)[40] and that of $Mn(CO)_5I$ even more slowly, solutions of these compounds were considered to be sufficiently stable for use under our conditions where the solutions were prepared and run within about a 4-h period. Solutions of $Mn_2(CO)_{10}$ were observed by their UV spectra to be unchanged over 3 days. All solutions were protected

from light as much as possible. Samples of absolute ethanol were obtained from two different sources. USP quality ethanol was purchased from I. M. C. Chemicals Group Inc., and distillation of this material under argon[32] was found to improve the lifetime of e^-_{sol}. Specially selected samples of absolute ethanol were generously supplied by U.S. Industrial Chemicals Co., and were used as received. This material had been analyzed by gas–liquid chromatography and UV spectrophotometric techniques. The only impurities identified were isopropyl and *sec*- and *tert*-butyl alcohols in the range of 1–10 ppm. Other chemicals and gases used were of reagent quality.

C. Determination of Dissolved Oxygen Concentrations. Based upon the apparent rate constant for the electron decay at low doses and the rate constant for the reaction of e^-_{sol} with O_2 $[k_{e+O_2} = (1.9 \pm 0.3) \times 10^{10}$ M^{-1} $s^{-1}]$,[32] an upper limit to the concentration of residual oxygen in deaerated ethanol solutions was estimated to be 10 μM. In experiments directed at investigating the reactivity of the manganese transient toward O_2, the value of k_{e+O_2} also served as a means to determine the concentration of added oxygen as follows. A deaerated solution of pure ethanol was saturated with O_2. Aliquots from this oxygenated stock solution were injected by syringe into deaerated solutions containing $Mn_2(CO)_{10}$ and into deaerated ethanol. The concentration of added O_2 in ethanol was then calculated from the apparent first-order rate constants for the electron decay in the presence and absence of O_2. This procedure was done in triplicate, and served as the basis for determining the oxygen concentrations in the stock solution and in the solutions containing $Mn_2(CO)_{10}$.

D. Pulse Radiolysis Dosimetry. These measurements were made using the absorption of e^-_{sol} at 700 nm (ϵ 15 000 M^{-1} cm^{-1})[27b] or the application of the aqueous ferrocyanide dosimeter.[41] The latter technique involves observing the formation of a stable product, $Fe(CN)_6^{3-}$ (ϵ_{420nm} 1040 M^{-1} cm^{-1}), and is consequently a somewhat more reliable procedure than that based upon the electron absorption, particularly at high dose rates where the electron decay is rapid. The response of aqueous 5 mM $K_4Fe(CN)_6$ solutions saturated with N_2O was used in determining the molar absorption coefficients for the transients arising from the reactions of e^-_{sol} with the manganese complexes. The dose per pulse was typically in the range of 1–5 $\times$ 10^{17} eV/g.

Results and Discussion

A. Studies of $Mn_2(CO)_{10}$. On pulse irradiation of deaerated ethanol solutions containing 200–400 μM $Mn_2(CO)_{10}$, the decay of e^-_{sol} was found to be concurrent with the formation of a transient absorbing in the region of 680–1030 nm (Figure 1). No significant level of absorption was observed in the region of 680–440 nm.[42] Saturation of such solutions with N_2O, a facile scavenger of e^-_{sol},[28] completely eliminated the transient absorption. This feature indicates that not only is the transient associated with the reaction of the electron but also that the α-ethanol radical, the other principal radical present in both deaerated and N_2O-saturated solutions, did not give rise to this transient. Concentration studies where the concentration of $Mn_2(CO)_{10}$ was greatly in excess of that for e^-_{sol} showed that the kinetics of the decay of e^-_{sol} were independent of wavelength over the wavelength region in which the 830-nm transient overlaps the absorption of e^-_{sol}, and in which e^-_{sol}, of course, dominates the absorption. The kinetics were first order with respect to $Mn_2(CO)_{10}$ concentration, yielding a rate constant of $(9.1 \pm 1.0) \times 10^9$ M^{-1} s^{-1} for the reaction of e^-_{sol} with $Mn_2(CO)_{10}$.

The transient absorption shown in Figure 1 decayed on the millisecond time scale without the formation of an observable product in the region of 440–1030 nm[42] and without alteration in the shape of the band. This decay obeyed second-order kinetics; a representative plot of $1/A$ vs. time for the decay is shown in Figure 2. The slopes of such lines were normalized by multiplying by the factor A_λ/A_{830}. These normalized slopes indicated that the decay rate was invariant with wavelength (790–900 nm) as well as being independent of dose (factor of 2) and of the source of ethanol used. The slopes did, however, decrease slightly from the first to the third pulse and thereafter remained the same from the fourth to the 16th pulse; the total amount of $Mn_2(CO)_{10}$ reacting at this stage was ca. 10%. In

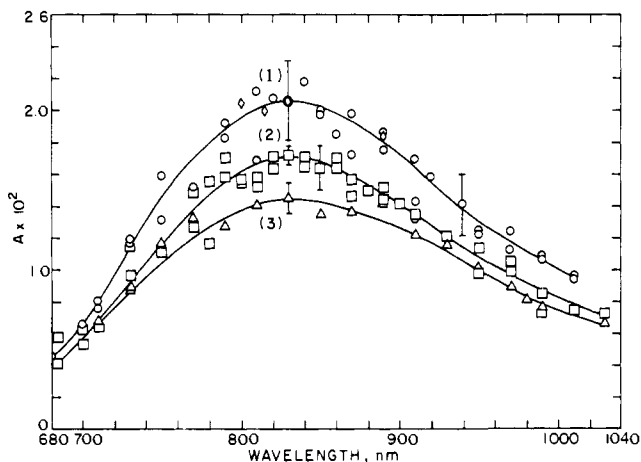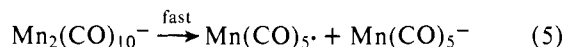**Figure 1.** Transient spectra on pulse irradiation of manganese complexes in ethanol. Curve 1: deaerated solution of $[Mn(CO)_5I] = 308$ μM and $[e^-_{sol}]_{max} \simeq 5.5$ μM, $t = 3.4$ μs (O); (◊) deaerated solution of $[Mn(CO)_5Br] = 307$ μM at $t = 3.2$ μs—points normalized to curve 1 at 830 nm. Curve 2: deaerated solution of $[Mn_2(CO)_{10}] = 288$ μM and $[e^-_{sol}]_{max} \simeq 5.9$ μM, $t = 4.0$ μs (□). Curve 3: N_2O-saturated solution of $[Mn(CO)_5I] = 320$ μM, $t = 42$ μs (△). Same dose level as curve 1. Light path = 4 cm.

this work, results obtained from the fourth to the 12th pulse were made use of.

It is clear from the foregoing that the absorption band with a peak at 830 nm is representative of a single species. From the evidence subsequently developed we identify this absorption band with the $Mn(CO)_5\cdot$ radical formed in the dissociative electron attachment:

$$e^-_{sol} + Mn_2(CO)_{10} \rightarrow Mn_2(CO)_{10}^- \qquad (4)$$

$$Mn_2(CO)_{10}^- \xrightarrow{fast} Mn(CO)_5\cdot + Mn(CO)_5^- \qquad (5)$$

The second-order decay which follows this is ascribed to

$$Mn(CO)_5\cdot + Mn(CO)_5\cdot \rightarrow Mn_2(CO)_{10} \qquad (6)$$
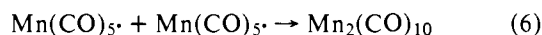
a reaction which has been proposed under other circumstances.[6,7,11,12,22,38]

The molar absorption coefficient of $Mn(CO)_5\cdot$ at the maximum, ϵ_{830}, was determined using aqueous ferrocyanide dosimetry in the following manner. The value of ϵ_{830} was calculated using the amount of $Fe(CN)_6^{3-}$ formed in the aqueous dosimetry solution and the following G values (yield of radical/100 eV): $G(e^-_{aq}) = G(OH) = 2.8$; $G(e^-_{sol}) = 1.0$.[27b,43] In this calculation, allowance was also made for the fact that only about 90% of e^-_{sol} reacted with $Mn_2(CO)_{10}$ under our conditions. The average value of ϵ_{830} for four determinations was 800 ± 80 M^{-1} cm^{-1} so that the second-order rate constant for the transient decay was found to be $2k_6 = (1.1 \pm 0.2) \times 10^9$ M^{-1} s^{-1} on the assumption that the only reaction of the $Mn(CO)_5\cdot$ occurring was reaction 6.

To investigate the reactivity of $Mn(CO)_5\cdot$ toward O_2, 0.3 mM solutions of $Mn_2(CO)_{10}$ were injected with oxygen in the range of 40-70 μM (see Experimental Section). At these oxygen levels, less than 32% of the electron formed would react with O_2. Addition of oxygen caused a marked increase in the rate of the disappearance of the transient but without the formation of an observable product. The decay kinetics of this process could now be described by first-order kinetic behavior. A plot of the observed first-order rate constant vs. concentration of added oxygen is presented in Figure 3. From the slope of this line, the rate constant was found to be 1.8×10^9 M^{-1} s^{-1}, presumably due to the reaction

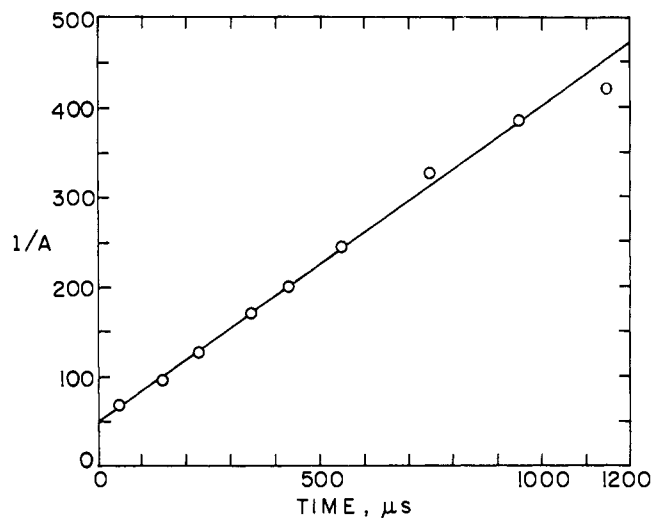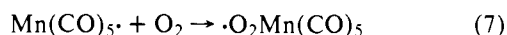$$Mn(CO)_5\cdot + O_2 \rightarrow \cdot O_2Mn(CO)_5 \qquad (7)$$

Figure 2. Second-order kinetic plot for decay of transient at 830 nm. Data recorded on the eighth pulse of $[Mn_2(CO)_{10}] = 287$ μM. Plot covers 3 half-lives of the reaction.
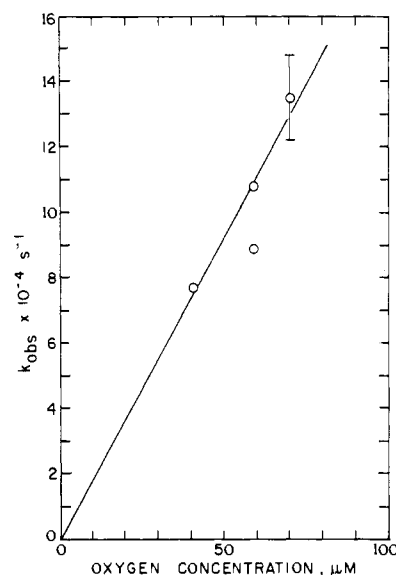

Figure 3. Plot of observed first-order rate constant for decay of transient from the reaction of e^-_{sol} and $Mn_2(CO)_{10}$ vs. concentration of added oxygen. $[Mn_2(CO)_{10}] = 300$ μM. Slope = 1.8×10^9 M^{-1} s^{-1}.

While this reaction has not previously been investigated in detail, the presumed product has been detected.[44]

B. Studies of $Mn(CO)_5Br$. On pulse irradiation of solutions containing 190-300 μM $Mn(CO)_5Br$, the disappearance of e^-_{sol} coincided with the formation of an intermediate having an optical absorption band with λ_{max} 830 nm (Figure 1) and a molar absorption coefficient of 690 M^{-1} cm^{-1}, which is, within experimental error, the same as was obtained in reaction 5. As in the $Mn_2(CO)_{10}$ case, the addition of N_2O as an electron scavenger eliminated the occurrence of the transient. The rate constant associated with the decay of the electron was determined as $(1.0 \pm 0.3) \times 10^{10}$ M^{-1} s^{-1}. In analogy to reactions 4 and 5, these reactions are

$$e^-_{sol} + Mn(CO)_5Br \rightarrow Mn(CO)_5Br^- \qquad (8)$$

$$Mn(CO)_5Br^- \xrightarrow{fast} Mn(CO)_5\cdot + Br^- \qquad (9)$$
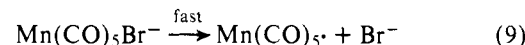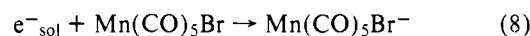
The $Mn(CO)_5\cdot$ radical decayed via second-order kinetics (740-870 nm) with a value of $2k_6 = (1.0 \pm 0.2) \times 10^9$ M^{-1}

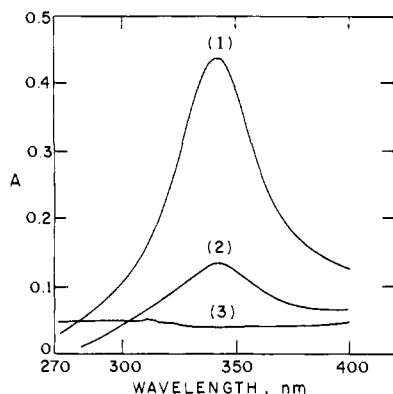**Figure 4.** Absorption spectra of irradiated Mn(CO)₅Br solutions recorded on a Cary 17 spectrophotometer. Curves: 1, deaerated solution; 2, N₂O-saturated solution; 3, base line with unirradiated Mn(CO)₅Br solution as reference. [Mn(CO)₅Br] = 302 μM (before irradiation); total transient concentration ≃ 28 μM (ca. 4.7 μM per pulse). Light path = 1 cm.

s⁻¹, in excellent agreement with the result for the decacarbonyl system.[45]

To investigate the final products formed upon irradiation of Mn(CO)₅Br solutions, such solutions were pulse irradiated in the *dark* six times so that the total concentration of the electron product was ca. 28 μM (ca. 4.7 μM per pulse). This was done in both the presence and absence of N₂O. The near-UV spectra of the pulsed materials were recorded on a Cary 17 spectrophotometer with the unirradiated solutions serving as the reference. These spectra are reproduced in Figure 4. In the deaerated medium, there occurred a band with a peak at 342 nm. While the absorption level of this band was somewhat less than that anticipated on the basis of the amount of e⁻ₛₒₗ formed (see below), the location of the peak and the half-width of the band indicated that it represented, predominantly, the presence of Mn₂(CO)₁₀. The effect of the addition of N₂O in largely suppressing the band pointed out that it derived principally from the reaction of e⁻ₛₒₗ. Two features suggested, however, the presence of other unidentified products: the fact that there was some residual absorption in the N₂O saturated solutions and that while the location of the peak at 342 nm in the deaerated medium remained unchanged over several hours, the absorption at both tails of the band decreased with time.

Pulse radiolysis experiments were also conducted to determine if the growth of Mn₂(CO)₁₀ coincided with the decay of Mn(CO)₅·. Owing to the absorption of Mn(CO)₅Br (peak at 382 nm), these efforts were severely hindered by the photolysis of Mn(CO)₅Br upon exposure to light below 450 nm from the monitoring lamp. At 364 nm, which was chosen to try to minimize these complications, a relatively stable product was observed to be formed over the same time scale (millisecond) as that for the disappearance of the Mn(CO)₅·. On addition of N₂O, the growth in absorption was now somewhat less and took slightly longer to reach its maximum development. While on a qualitative basis, the growth in near-UV absorption occurred concurrently with the Mn(CO)₅· decay in the near-IR region, clearly more than one process was being monitored at 364 nm.

C. Studies of Mn(CO)₅I. Irradiation of deaerated ethanol solutions containing 177–425 μM Mn(CO)₅I resulted in the rapid disappearance of e⁻ₛₒₗ and the concurrent formation of a transient again having the same spectral features as that formed by the electron reactions with Mn(CO)₅Br and Mn₂(CO)₁₀ (Figure 1). The rate constant for the reaction of e⁻ₛₒₗ and Mn(CO)₅I was determined to be (1.02 ± 0.06) × 10¹⁰ M⁻¹ s⁻¹.

However, in the case of the Mn(CO)₅I there was an additional reaction forming Mn(CO)₅· which did not occur with

the other two compounds. From about 3.4 μs (at which point the amount of electron remaining was negligible) to ca. 15 μs, there was a slight increase in the absorption level without alteration in the shape of the band. Clearly there was an additional reaction giving rise to Mn(CO)₅·. This effect was most pronounced in experiments involving N₂O solutions. In the presence of N₂O, the electron will react with N₂O to yield hydroxyl radical.[28] Under our conditions, OH is very rapidly scavenged by ethanol to form α-ethanol radical[43] so that this is now the principal radical species present at the end of the irradiation period. In this situation, since the electron was now scavenged by N₂O, there occurred only the slower growth in absorption covering the region of 680–1030 nm. The absorption spectrum, which developed over a period of ca. 40 μs, is presented in Figure 1. While the maximum level of absorption was about 70% of that encountered in the absence of N₂O, the peak at 830 nm and its band shape were the same. The evidence suggests that this slower process is

$$CH_3\dot{C}HOH + Mn(CO)_5I \rightarrow Mn(CO)_5\cdot + CH_3CHIOH$$

(10)
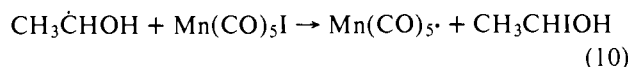
The rate of this process was independent of wavelength (730–970 nm) and increased with increasing concentration of Mn(CO)₅I (177–425 μM). The rate curves were found to fit a first-order rate law. However, the rate constants obtained from these rate curves were sensitive to dose level (ninefold), the value tending to be lower at high concentrations of Mn(CO)₅I and low doses. This dose dependence would be consistent with the occurrence, in competition with reaction 10, of

$$CH_3\dot{C}HOH + CH_3\dot{C}HOH \rightarrow products$$

(11)

At the highest concentration of Mn(CO)₅I used (425 μM), the value of k_{10}^{obsd} ranged from 4.2 to 1.6 × 10⁸ M⁻¹ s⁻¹ for the ninefold variation in dose. Extrapolation of the rate constants to zero dose yields a value of k_{10} = 1.5 × 10⁸ M⁻¹ s⁻¹. Oxygen, which scavenges organic free radicals such as alcohol radicals,[46] completely eliminates this reaction.

In both deaerated and N₂O-saturated solutions, the decay of Mn(CO)₅· obeyed second-order kinetics, leading to a rate constant of $2k_6$ = (1.2 ± 0.3) × 10⁹ M⁻¹ s⁻¹ in deaerated solution and $2k_6$ = (1.2 ± 0.4) × 10⁹ M⁻¹ s⁻¹ in N₂O-saturated solution based on ϵ_{830} = 800 M⁻¹ cm⁻¹, in excellent agreement with the values obtained in Mn(CO)₅Br and Mn₂(CO)₁₀ systems.[47] In point of fact, the iodide data represent a particularly favorable situation for the evaluation of $2k_6$ for the following reason. The occurrence of reaction 10 removes the α-ethanol radical and diminishes the possibility of the cross-reaction:
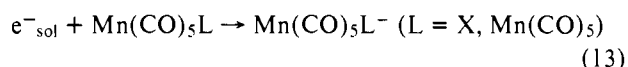
$$CH_3\dot{C}HOH + Mn(CO)_5\cdot \rightarrow (CH_3CHOH)Mn(CO)_5$$

(12)
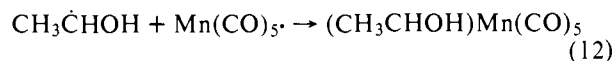
so that the second-order decay in the iodide case represents only reaction 6.[48]

The final products formed upon irradiation of Mn(CO)₅I solutions in the presence and absence of N₂O were investigated in the same manner as for Mn(CO)₅Br experiments. The UV spectra of the irradiated solutions exhibited a pronounced band (similar to Figure 4) with a peak at 342 nm, characteristic of Mn₂(CO)₁₀. Two features were encountered which differed in detail from the case of Mn(CO)₅Br. In addition to the spectra being relatively stable in time, the amount of Mn₂(CO)₁₀ in N₂O-saturated solution was now about 85% that in deaerated media. Furthermore, the concentrations of Mn₂(CO)₁₀ for deaerated (21 μM) and N₂O-saturated (18 μM) conditions were greater than that expected (14 μM) on the basis of the amount of e⁻ₛₒₗ produced and the occurrence of reaction 6. This fact is consistent with the occurrence of reaction 10 in addition to the generation of the radical by re-
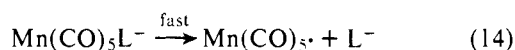
action of e^-_{sol}. The observation that the yield in deaerated solution is greater than in N_2O-saturated solution is expected on the basis of the competition between reactions 10 and 11.

In the case of $Mn(CO)_5Br$, it should be pointed out that the yield of $Mn_2(CO)_{10}$ in deaerated media was lower than that expected. This suggests the possibility that the cross-reaction, 12, does occur. Processes analogous to that of 12 are known; for example, $Cr^{2+}(aq)$ reacting with a variety of alcohol radicals to yield Cr–C bonded species,[20] and similar behavior for $Co(CN)_5^{3-}$, which is isoelectronic with $Mn(CO)_5$·, have been reported.[26] The difference in behavior of the bromide system from the iodide system, with regard to the role of reaction 12, is presumably a manifestation of the lower rate of the reaction analogous to 10 in the bromide system. This is not unexpected; for example, the reaction of methyl halide with sodium atom shows the same effect.[49]

D. Additional Facets. Our observation that the reaction of the electron with all three complexes gives rise to the same transient (λ_{max} 830 nm), and that its decay is second order, resulting in $Mn_2(CO)_{10}$ as a product, identifies the transient as $Mn(CO)_5$·. It is formed by

$$e^-_{sol} + Mn(CO)_5L \rightarrow Mn(CO)_5L^- \quad (L = X, Mn(CO)_5)$$
(13)

followed by

$$Mn(CO)_5L^- \xrightarrow{fast} Mn(CO)_5\cdot + L^-$$
(14)

$Mn_2(CO)_{10}^-$ and $Mn(CO)_5Br^-$ have been observed in ESR experiments on γ-irradiated solids of $Mn_2(CO)_{10}$ and $Mn(CO)_5Br$ at 77 K where the unpaired electrons are largely confined to the σ^* Mn–Mn and Mn–Br bonds, respectively.[50] Our observation of concurrent decay of e^-_{sol} and formation of the 830-nm band makes it clear that in room temperature solution reaction 14 is very fast. Owing to solubility limitations of the complexes in ethanol, it was not possible to resolve reaction 14 from 13. We can only say that the rate constant, k_{14}, is greater than 10^7 s^{-1} and may, indeed, be much greater. It is also noteworthy that $Mn(CO)_5$· is also generated in a reaction, 10, which is less likely to involve the formation of an anion. We have also established that the reaction of the electron with free carbon monoxide did not give rise to an observable product in the region 450–950 nm; the transient then cannot be an electron adduct of CO.

The rate constant for the recombination of $Mn(CO)_5$· in ethanol, $2k_6 = 1.2 \times 10^9$ M^{-1} s^{-1}, may be compared with literature values[12] for this reaction in cyclohexane and in tetrahydrofuran, obtained by flash photolysis of $Mn_2(CO)_{10}$. The data obtained by observation of the re-formation of $Mn_2(CO)_{10}$ give $4k = 7.7 \times 10^9$ M^{-1} s^{-1} in cyclohexane and $4k = 3.8 \times 10^9$ M^{-1} s^{-1} in tetrahydrofuran, both at 293 K. These values were calculated from data given in the dissertation of Hughey.[51] On a comparative basis, our value of $k = 6.0 \times 10^8$ M^{-1} s^{-1} (ethanol) is in fairly good agreement with the values $k = 1.9 \times 10^9$ M^{-1} s^{-1} (cyclohexane) and $k = 9.5 \times 10^8$ M^{-1} s^{-1} (tetrahydrofuran). As different solvents were used these variations likely reflect viscosity effects and specific solvation effects.

A further feature of note in regard to the assignment of the transient with a peak at 830 nm to $Mn(CO)_5$· is its similarity to the isoelectronic $Co(CN)_5^{3-}$. This free-radical species is sensitive to oxygen and exhibits an absorption band in the near IR (λ_{max} 966 nm, ϵ_{max} 233 M^{-1} cm^{-1}).[24a] The structure of $Co(CN)_5^{3-}$ in solution is assigned to that of square pyramidal; this is based in part upon the expected absence of an absorption band above ca. 500 nm if $Co(CN)_5^{3-}$ exhibited trigonal-bipyramidal form.[24a] Theoretical calculations[52] and results from low-temperature matrix isolation–infrared experiments[10] indicate a square pyramidal structure for $Mn(CO)_5$·. The loca-

tion of the absorption band at 830 nm implies that its structure *in solution* may also be of the square pyramidal type.

In this study, the technique of pulse radiolysis has been used to directly detect and characterize the free radical, $Mn(CO)_5$·, formed through the reactions of e^-_{sol} and α-ethanol radical with two types of manganese carbonyl compounds. This species is representative of a broad class of radicals of general importance to organometallic and polymer chemistry. As such, this work illustrates the potential usefulness of pulse radiolysis (and associated radiation chemistry) to kinetic investigations into these areas.

References and Notes

(1) On leave from the Department of Chemistry and Chemical Engineering and the Saskatchewan Accelerator Laboratory, University of Saskatchewan, Saskatoon, Canada.
(2) Lappert, M. F.; Lednor, P. W. *Adv. Organomet. Chem.* **1976**, *14*, 345–399.
(3) Kochi, J. K. *Acc. Chem. Res.* **1974**, *7*, 351–360.
(4) Krusic, P. J.; Fagan, P. J.; San Filippo, Jr., J. *J. Am. Chem. Soc.* **1977**, *99*, 250–252.
(5) Hudson, A.; Lappert, M. F.; Nicholson, B. K. *J. Chem. Soc., Dalton Trans.* **1977**, 551–554.
(6) Abrahamson, H. B., Wrighton, M. S. *J. Am. Chem. Soc.* **1977**, *99*, 5510–5512, and references cited therein.
(7) Kidd, D. R.; Brown, T. L. *J. Am. Chem. Soc.* **1978**, *100*, 4095–4103, and references cited therein.
(8) Bamford, C. H. "Reactivity, Mechanism, and Structure in Polymer Chemistry", Vol. 3, A. D. Jenkins and A. Ledwith, Ed.; Wiley-Interscience: New York, N.Y., 1974; p 52, and references cited therein.
(9) In contrast, a number of transition metal carbonyl and related radicals have been generated and characterized by infrared spectroscopy in solid matrices at cryogenic temperatures.[10]
(10) Huber, H.; Kündig, E. P.; Ozin, G. A.; Poë, A. J. *J. Am. Chem. Soc.* **1975**, *97*, 308–314.
(11) Hallock, S. A.; Wojcicki, A. *J. Organomet. Chem.* **1973**, *54*, C27–C29.
(12) (a) Hughey, IV, J. L.; Anderson, C. P.; Meyer, T. J. *J. Organomet. Chem.* **1977**, *125*, C49–C52. (b) Hughey, IV, J. L. Ph.D. Dissertation, University of North Carolina (Chapel Hill), 1975.
(13) Huffadine, A. S.; Peake, B. M.; Robinson, B. H.; Simpson, J.; Dawson, P. A. *J. Organomet. Chem.* **1976**, *121*, 391–403.
(14) Laine, R. M.; Ford, P. C. *Inorg. Chem.* **1977**, *16*, 388–391.
(15) (a) Levenson, R. A.; Gray, H. B.; Ceasar, G. P. *J. Am. Chem. Soc.* **1970**, *92*, 3653–3658. (b) Levenson, R. A.; Gray, H. B. *ibid.* **1975**, *97*, 6042–6047.
(16) Kramer, A. V.; Osborn, J. A. *J. Am. Chem. Soc.* **1974**, *96*, 7832–7833.
(17) Sweany, R. L.; Halpern, J. *J. Am. Chem. Soc.* **1977**, *99*, 8335–8337.
(18) Matheson, M. S.; Dorfman, L. M. "Pulse Radiolysis", MIT Press: Cambridge, Mass., 1969.
(19) Dorfman, L. M. "Techniques of Chemistry", Vol. VI, Part II, G. G. Hammes, Ed.; Wiley: New York, N.Y., 1974; pp 463–519.
(20) Cohen, H.; Meyerstein, D. *Inorg. Chem.* **1974**, *13*, 2434–2443.
(21) Hart, E. J.; Anbar, M. "The Hydrated Electron", Wiley-Interscience: New York, N.Y., 1970; pp 138–141, 144–151.
(22) (a) Wrighton, M. S.; Ginley, D. S. *J. Am. Chem. Soc.* **1975**, *97*, 2065–2072. (b) Ginley, D. S.; Wrighton, M. S. *ibid.* **1975**, *97*, 4908–4911.
(23) Krusic, P. J.; Stoklosa, H.; Manzer, L. E.; Meakin, P. *J. Am. Chem. Soc.* **1975**, *97*, 667–669.
(24) (a) Alexander, J. J.; Gray, H. B., *J. Am. Chem. Soc.* **1967**, *89*, 3356–3357, and references cited therein. (b) Caulton, K. G. *Inorg. Chem.* **1968**, *7*, 392–394.
(25) Kwiatek, J.; Seyler, J. K. *Adv. Chem. Ser.* **1968**, *70*, 207–232.
(26) Chock, P. B.; Halpern, J. *J. Am. Chem. Soc.* **1969**, *91*, 582–588, and references cited therein.
(27) (a) Taub, I. A.; Dorfman, L. M. *J. Am. Chem. Soc.* **1962**, *84*, 4053–4059. (b) Dorfman, L. M. *Adv. Chem. Ser.* **1965**, *50*, 36–44.
(28) (a) Akhtar, S. M. S.; Freeman, G. R. *J. Phys. Chem.* **1971**, *75*, 2756–2762. (b) Freeman, G. R. *Actions Chim. Biol. Radiat.* **1970**, *14*, 73–134.
(29) (a) Fletcher, J. W.; Richards, P. J.; Seddon, W. A. *Can. J. Chem.* **1970**, *48*, 1645–1650. (b) *ibid.* **1970**, *48*, 3765–3768.
(30) Felix, W. D.; Gall, B. L.; Dorfman, L. M. *J. Phys. Chem.* **1967**, *71*, 384–392.
(31) Reference 21, Chapter 9.
(32) Taub, I. A.; Harter, D. A.; Sauer, Jr., M. C.; Dorfman, L. M. *J. Chem. Phys.* **1964**, *41*, 979–985.
(33) Simic, M.; Neta, P.; Hayon, E. *J. Phys. Chem.* **1969**, *73*, 3794–3800.
(34) King, R. B. "Organometallic Synthesis", Vol. I, "Transition Metal Compounds", J. J. Eisch and R. B. King, Ed.; Academic Press: New York, N.Y., 1965; pp 174–175.

(35) Hallock, S. A. Ph.D. Dissertation, The Ohio State University, 1974, p 90.
(36) Gray, H. B.; Billig, E.; Wojcicki, A.; Farona, M. *Can. J. Chem.* **1963**, *41*, 1281–1288.
(37) Blakney, B. G.; Allen, W. F. *Inorg. Chem.* **1971**, *10*, 2763–2770.
(38) Bamford, C. H.; Burley, J. W.; Coldbeck, M. *J. Chem. Soc., Dalton Trans.* **1972**, 1846–1852.
(39) Wrighton, M. *Chem. Rev.* **1974**, *74*, 401–430.
(40) While this process has not been studied in detail, UV spectral analysis indicates that the products are not those of $Mn_2(CO)_{10}$ or $[Mn(CO)_4Br]_2$, the latter being the reported product in benzene.[38]
(41) Waltz, W. L.; Akhtar, S. S.; Eager, R. L. *Can. J. Chem.* **1973**, *51*, 2525–2529.
(42) Owing to the strong near UV absorption of $Mn_2(CO)_{10}$ solutions, it was not feasible to observe at wavelengths below ca. 440 nm.
(43) Dorfman, L. M.; Adams, G. E. *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.* **1973**, No. 46.
(44) Fieldhouse, S. A.; Fullam, B. W.; Neilson, G. W.; Symons, M. C. R. *J. Chem. Soc., Dalton Trans.* **1974**, 567–569.
(45) Data for the $Mn(CO)_5Br$ case was that taken from the fourth to the eighth

pulse because, as in the case of $Mn_2(CO)_{10}$, the decay rate decreased slightly from the first to the third pulse.
(46) Adams, G. E.; Michael, B. D.; Willson, R. L. *Adv. Chem. Ser.* **1968**, *81*, 289–308.
(47) In contrast to the transient behavior in the cases of $Mn_2(CO)_{10}$ and $Mn(CO)_5Br$, the decay rate of the transient for the $Mn(CO)_5I$ system was relatively insensitive to the number of irradiation pulses.
(48) Kidd and Brown[7] have proposed that $Mn(CO)_5$· can undergo rapid loss of CO; under our conditions, the decay of $Mn(CO)_5$· is second order. In addition, Hudson and co-workers[5] have proposed that $Mn(CO)_5$· can react with $Mn_2(CO)_{10}$ by electron transfer; however, our results indicate that if this reaction can occur it is much slower than reaction 6 under our conditions.
(49) Von Hartel, H.; Polanyi, M. *Z. Phys. Chem. (Frankfurt am Main)* **1930**, *11B*, 97–138.
(50) Anderson, O. P.; Symons, M. C. R. *J. Chem. Soc., Chem. Commun.* **1972**, 1020–1021.
(51) Reference 12b, p 124.
(52) Elian, M.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 1058–1076.

Preparation of Chemically Derivatized Platinum and Gold Electrode Surfaces. Synthesis, Characterization, and Surface Attachment of Trichlorosilylferrocene, (1,1'-Ferrocenediyl)dichlorosilane, and 1,1'-Bis(triethoxysilyl)ferrocene

Mark S. Wrighton,* Michael C. Palazzotto, Andrew B. Bocarsly, Jeffrey M. Bolts, Alan B. Fischer, and Louis Nadjo

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. Received May 15, 1978

Abstract: The synthesis and characterization of three ferrocene-centered, hydrolytically unstable, surface derivatizing reagents and their attachment to pretreated (anodized) Pt and Au electrode surfaces are described. Trichlorosilylferrocene (I) has been isolated from the reaction of $SiCl_4$ and lithioferrocene; (1,1'-ferrocenediyl)dichlorosilane (II) has been isolated from the reaction of $SiCl_4$ and 1,1'-dilithioferrocene; and 1,1'-bis(triethoxysilyl)ferrocene (III) has been isolated from reaction of $ClSi(OEt)_3$ with 1,1'-dilithioferrocene. The species I, II, and III have been fully characterized by ^1H NMR, mass, and UV–vis spectra and elemental analyses. All are moisture sensitive and are capable of derivatizing anodized Pt surfaces. Detailed studies for derivatization of anodized Au using II are described. In many respects the properties of derivatized Au electrodes parallel those for derivatized Pt. Such derivatized electrodes exhibit persistent cyclic voltammetric waves at a potential expected for an electroactive ferrocene derivative. Greater than monolayer coverages are found in each case, as determined by the integration of the cyclic waves. The cyclic voltammetric parameters are as expected for a reversible, one-electron, surface-attached electroactive system except that the peak widths are broader than theoretical. This is attributed to chemically distinct ferrocene centers resulting from the oligomerization of the derivatizing reagent during the derivatization procedure.

In a recent preliminary account we outlined the chemical derivatization of anodized Pt electrode surfaces using trichlorosilylferrocene (I), which resulted in the persistent attachment of polymeric, reversibly electroactive ferrocene.[1] Also, we have shown that (1,1'-ferrocenediyl)dichlorosilane (II) is capable of derivatizing n-type semiconducting Si photoelectrodes,[2] illustrating the first example of photoelectroactive surface-attached species. These studies have added to a growing literature of chemically derivatized electrode surfaces.[3-17]

Elaboration of the number and types of chemical derivatizing procedures is seemingly a necessary step in the illustration and understanding of fundamental and practical consequences of the resulting surfaces. In this article we wish to report the synthesis and characterization of I, II, and 1,1'-bis(triethoxysilyl)ferrocene (III) and their use as derivatizing reagents for anodized Pt electrode surfaces. We also report the first derivatized Au electrodes using II as the derivatizing reagent, and outline a procedure for the surface pretreatment of Au that leads to successful derivatization. The structures

of the three derivatizing reagents are shown below. A qualitative comparison of the behavior of the resulting derivatized surfaces is made.

Results and Discussion

1. Preparation of Compounds. The compounds presented here are, by design, extremely moisture sensitive. Therefore, care must be taken in the exclusion of moisture in their preparation and subsequent handling. It should be noted that compounds I and II seem to react with glass over a period of time even when kept at low temperatures (−10 °C). Because of this problem, in order to obtain satisfactory analysis, the samples were purified immediately before being sent for analysis, sealed in plastic ampules under dry nitrogen, and analyzed as quickly as possible. This slow decomposition also requires that the compounds be purified before use in electrochemical studies.

All three complexes which we have prepared have been characterized by elemental analyses and the results are satisfactory. The mass spectral characterization provides a quick