sphere of $Ru_3(CO)_{11}(CO_2CH_3)^-$ in 90/10 THF/CH_3OH provide a strong support for the limiting dissociative pathway proposed previously on the basis of kinetics behavior.[5,6a] However, the $\Delta V^{\ddagger}$ values measured for the first substitution reaction of $Ru_3(CO)_{11}(CO_2CH_3)^-$ (eq 2) displayed a remarkable dependence on the solvent not paralleled by changes in the apparent rate law. A logical explanation would be a shift in mechanism for limiting dissociation in THF to a solvent-assisted displacement of CO in methanol, but the similarity of the donor numbers for the two solvents leads one to question why such a mechanism change would occur. An alternative proposal is that the dissociation of CO from $Ru_3(CO)_{11}(CO_2CH_3)^-$ would be accompanied by charge redistribution on the cluster leading to negative solvation contributions to $\Delta V^{\ddagger}$ owing to the much greater tendency of methanol to act as an acceptor. These and similar effects of solvent character on the reaction dynamics of metal cluster reactions are the subject of continuing investigation in these laboratories.

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Registry No. $HRu_3(CO)_{11}^-$, 77482-10-1; $Ru_3(CO)_{11}(CO_2CH_3)^-$, 90342-87-3; PPh_3, 603-35-0; $P(OCH_3)_3$, 121-45-9.

Electroreduction of Carbonylmanganese(I) Cations. Mechanism of Ligand Substitution and Hydride Formation via Manganese(0) Intermediates

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Hydridomanganese(I) complexes $(OC)_3MnL_2H$ are the principal products from a series of acetonitrile derivatives of carbonylmanganese cations, i.e., $(OC)_3Mn(NCMe)_nL_{3-n}^+$ (I), when the reductions are carried out electrochemically in the presence of added phosphines L. Cyclic voltammetric studies show that the conversion to the hydride can be formulated in three discrete stages. First, the carbonylmanganese cation such as $(OC)_3Mn(NCMe)_3^+$ with $n = 3$ undergoes an electrocatalytic ligand substitution with added L to form the bis(phosphine) complex $(OC)_3Mn(NCMe)L_2^+$ via labile 19-electron Mn(0) intermediates as in Scheme V. Second, the substitution product $(OC)_3Mn(NCMe)L_2^+$ is reduced to the Mn(0) radical $(OC)_3Mn(NCMe)L_2\cdot$ which is common to all cationic precursors irrespective of the degree of prior phosphine coordination in the precursor I (i.e., $n = 1, 2$). Third, the hydridomanganese product is derived by hydrogen atom transfer to the carbonyl ligand of the 19-electron intermediate $(OC)_3Mn(NCMe)L_2\cdot$ to form the formyl complex $(OC)_2Mn(NCMe)L_2CHO$, followed by the electrocatalytic extrusion of the coordinated ligand (MeCN) as in Scheme III. The third stage is established in the reductive conversion of the cationic $(OC)_4Mn(PPh_3)_2^+$ to the hydride $(OC)_3Mn(PPh_3)_2H$ by the observation of the intermediate $(OC)_3Mn(PPh_3)_2CHO$ during cyclic voltammetry. A competition to form the carbonylmanganate $(OC)_3MnL_2^-$ as a byproduct of reduction is also delineated.

Introduction

Electrochemistry offers a potentially useful method for the preparation of various types of transition metal hydrides, especially by exploiting the reduction of various types of carbonylmetal cations.[2,3] In a preliminary report,[4] we described the successful electrosynthesis of hydridomanganese carbonyls and the unusual observation of facile, multiple ligand substitutions which accompany the reduction of cationic manganese(I) carbonyls. As a part of our continuing studies of the electrocatalytic phenomena associated with metal carbonyls,[5] we wish to describe the use of transient electrochemical techniques, particularly cyclic voltammetry, to show how such reductive processes can occur via reactive paramagnetic intermediates.

Results

We have focussed our attention in this study on the reduction of a series of acetonitrile derivatives of tricarbonylmanganese(I) cations $(OC)_3Mn(NCMe)_nL_{3-n}^+$ (I), where L is a phosphine ligand and $n = 1$–3.

I. Electroreduction of Carbonylmanganese(I) Cations. A solution of the mono(acetonitrile) cation Ia ($n = 1$), $(OC)_3Mn(NCMe)(PMe_2Ph)_2^+$, as the PF_6^- or BF_4^- salt[6] in acetonitrile containing 0.1 M tetraethylammonium perchlorate (TEAP) is electroactive at a potential of −1.5 to −1.8 V vs. SCE. When a cathodic current of 20 mA was passed through the 4.2×10^{-2} M solution under galvanostatic conditions, a total charge of 1.3 coulombs was taken up per mole of I. Workup of the catholyte afforded

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(2) For example, see: (a) White, D. A. In *Organic Electrochemistry*, 2nd ed.; Baizer, M. M., Ed.; Marcel Dekker: New York, 1983; Chapter XVIII. (b) Kochi, J. K. *J. Organomet. Chem.* **1986**, *300*, 139.

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Table I. Galvanostatic Coulometry and Cyclic Voltammetry in the Reduction of $(OC)_3Mn(NCMe)_nL_{3-n}^+$ in the Presence of Added Phosphines L[a]

Mn(I) cation	added phosphine L (equiv)	E_p,[b] V vs. SCE	n_{app}[c]	product[d] (% yield)
$(OC)_3Mn(NCMe)_3^+$		−1.74	1.2	[e]
	PMe_2Ph (3)	−1.85	1.2	$(OC)_3MnL_2H$[f] (84)
	PMe_2Ph (2)	−1.85	1.2	$(OC)_3MnL_2H$[f] (82)
	PMe_2Ph (1)			$(OC)_3MnL_2H$[f] (38)
	PPh_3 (1)		1.2	$(OC)_3MnL_2H$[g]
	PPh_3 (2)		1.1	$(OC)_3MnL_2H$[g] (78)
	PPh_3 (3)		1.2	$(OC)_3MnL_2H$[g]
$(OC)_3Mn(NCMe)_2L^+$		−1.82		
	PMe_2Ph (1)	−1.85	1.3	$(OC)_3MnL_2H$[f] (74)
$(OC)_3Mn(NCMe)L_2^+$		−1.85	1.3	$(OC)_3MnL_2H$[f] (79)

[a] In acetonitrile containing 0.1 M TEAP at 25 °C. $C^0 = 5 \times 10^{-2}$ M for coulometry, 5×10^{-3} M for cyclic voltammetry. The counteranion is either PF_6^- or BF_4^-. [b] $v = 500$ mV s^{-1}. [c] Number of electrons consumed relative to I within $<\pm 0.1$. Fraction in excess of 1 corresponds to the yield of $(OC)_3MnL_2^-$ (III). [d] In addition to $(OC)_3MnL_2^-$ in yields equal to $100(n_{app} - 1)\%$. [e] Unidentified carbonylmanganese complex (IR 1940, 1905, 1880 cm^{-1}). [f] $(OC)_3Mn(PMe_2Ph)_2H$. IR (Nujol): 1950, 1908 cm^{-1}. ^1H NMR (C_6D_6): δ −7.9 [t, J(PH) = 27 Hz]. [g] $(OC)_3Mn(PPh_3)_2H$ by comparison of IR and ^1H NMR spectra of an authentic sample.[8]

Table II. Spectral Properties of Carbonylmanganese Compounds

	IR spectrum		^1H NMR spectrum	
Mn compd	solv	ν, cm^{-1}	solv	δ
$(OC)_3Mn(NCMe)_3^+PF_6^-$	$CHCl_3$[a]	ν(CN) 2328, 2300 ν(CO) 2060, 1982	CD_2Cl_2	2.4 (s)
$(OC)_3Mn(NCMe)_2(PMe_2Ph)^+BF_4^-$	CH_2Cl_2[a]	ν(CN) 2326, 2297 ν(CO) 2059, 1982, 1954		
$(OC)_3Mn(NCMe)(PMe_2Ph)_2^+PF_6^-$	$CHCl_3$[a]	ν(CN) 2325, 2290 ν(CO) 2034, 1972, 1945		
$(OC)_3Mn(PMe_2Ph)_2H$	Nujol[7]	ν(CO) 1950, 1908	C_6D_6	−7.9 (t)[e]
$(OC)_3Mn(PMe_2Ph)_2^-$	Nujol[13]	ν(CO) 1800, 1750		
$(OC)_4Mn(PPh_3)_2^+PF_6^-$ (trans)	CH_2Cl_2[b]	ν(CO) 2046, 2000		
$(OC)_3Mn(PPh_3)_2^-PPN^+$	THF[c]	ν(CO) 1940, 1846, 1815		
$(OC)_3Mn(PPh_3)_2^-Na^+$	Nujol	ν(CO) 1780		
$(OC)_3Mn(PPh_3)_2H$			$CDCl_3$[d]	−7.2 (t)[f]

[a] Reference 6. [b] Reference 9. [c] Reference 10. [d] Reference 8. [e] J(PH) = 27 Hz. [f] J = 33 Hz.

the neutral hydride derivative II in 79% yield according to the partial stoichiometry in eq 1 (Table I). Compound

$$\underset{\text{Ia}}{(OC)_3Mn(NCMe)(PMe_2Ph)_2^+} \xrightarrow{[+e]} \underset{\text{II}}{(OC)_3Mn(PMe_2Ph)_2H} \quad (1)$$

II was readily identified by its characteristic carbonyl bands at 1950 and 1908 cm^{-1} in the IR spectrum and the hydride resonance at δ −7.9 [t, J(PH) = 27 Hz] in the ^1H NMR spectrum (Table II).[7]

Strikingly, the *same* hydridomanganese complex was obtained in 82% yield when the tris(acetonitrile) complex Ic (n = 3) was reduced in the presence of added PMe_2Ph in stoichiometric amounts (i.e., 2 equiv). Control exper-

$$\underset{\text{Ic}}{(OC)_3Mn(NCMe)_3^+} + 2PMe_2Ph \xrightarrow{[+e]} \underset{\text{II}}{(OC)_3Mn(PMe_2Ph)_2H} \quad (2)$$

iments demonstrated that the tris(acetonitrile) complex Ic did not react with either PMe_2Ph or PPh_3 in the absence of a cathodic current. Therefore, the ligand substitution into II must have occurred during electroreduction. Moreover, the reductive incorporation of both phosphines in eq 2 was rapid since only II was formed in ca. 40% yield when only 1 equiv of PMe_2Ph was added. No product corresponding to the incorporation of one phosphine was observed.

When 1 equiv of PMe_2Ph was present during the electroreduction of the bis(acetonitrile) complex Ib (n = 2), the hydride II was again isolated in excellent yields (74%) according to the partial stoichiometry in eq 3.

$$\underset{\text{Ib}}{(OC)_3Mn(NCMe)_2(PMe_2Ph)^+} + PMe_2Ph \xrightarrow{[+e]} \underset{\text{II}}{(OC)_3Mn(PMe_2Ph)_2H} \quad (3)$$

In other words, the same bis(phosphine) hydride II was obtained from the reduction of each of the homologous carbonylmanganese cations Ia–c. In every case the full complement of phosphine ligands was incorporated into the carbonylmanganese hydride. Equivalent results obtained when the tris(acetonitrile) complex Ic was treated with various amounts of triphenylphosphine to produce the corresponding bis(phosphine) hydride, i.e., eq 4.

$$\underset{\text{Ic}}{(OC)_3Mn(NCMe)_3^+} + 2PPh_3 \xrightarrow{[+e]} (OC)_3Mn(PPh_3)_2H \quad (4)$$

Finally the reduction of the tris(acetonitrile) complex Ic in the absence of added phosphine yielded an unidentified manganese carbonyl showing prominent carbonyl bands at 1940, 1905, and 1880 cm^{-1} in the IR spectrum. The preparative results are summarized in Table I.

II. Cyclic Voltammetry of the Carbonylmanganese (I) Cations Ia–c with and without the Phosphine Additive (L = PMe_2Ph). The appearance of a single hydridomanganese carbonyl II as the common reduction product of the homologous cations Ia–c could be investigated by transient electrochemical methods. Among these,

(7) Compare with the spectra of the related triphenylphosphine derivative.[8]

(8) Ugo, R.; Bonati, F. *J. Organomet. Chem.* **1967**, *8*, 189.

(9) Angelici, R. J.; Brink, R. W. *Inorg. Chem.* **1973**, *12*, 1067.

(10) Faltynek, R. A.; Wrighton, M. S. *J. Am. Chem. Soc.* **1978**, *100*, 2701.

(11) For the significance of these changes, see Discussion.

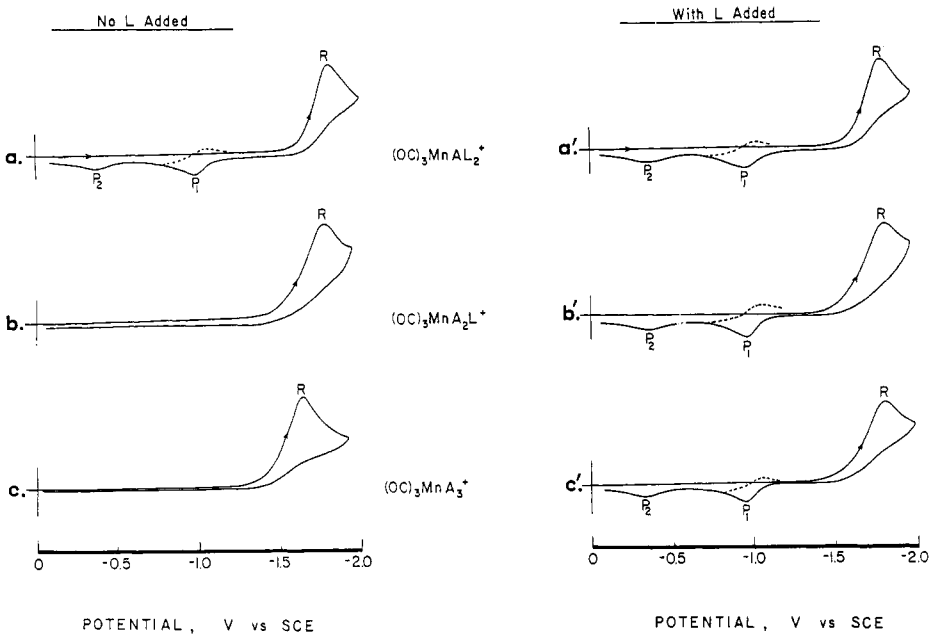

Figure 1. Initial negative scan cyclic voltammograms of (a) *fac*-$(OC)_3Mn(NCMe)(PMe_2Ph)_2^+$ (Ia), (b) *fac*-$(OC)_3Mn(NCMe)_2(PMe_2Ph)^+$ (Ib), and (c) *fac*-$(OC)_3Mn(NCMe)_3^+$ (Ic) in the absence (left column) and in the presence (right column) of 10 equiv of added PMe_2Ph. Cation concentration 5×10^{-3} M in acetonitrile containing 0.1 M TEAP at 800 mV s^{-1}.

cyclic voltammetry was especially useful in providing insight into the mechanism of hydride formation and multiple ligand substitution. Thus for the series of tricarbonylmanganese cations $(OC)_3Mn(NCMe)_nL_{3-n}^+$ in eq 1–3, the initial negative scan cyclic voltammograms in Figure 1 were recorded both in the presence (right-hand side) and in the absence (left-hand side) of added phosphine L. All the voltammograms showed a principal reduction wave R corresponding to a ca. one-electron addition, based on the calibration of the cathodic current with ferrocene.[5] With the exception of slight peak broadenings and some minor peak shifts,[11] all the cathodic waves were the same. However, the cyclic voltammograms were largely distinguished when the linear potential sweeps were reversed at ~−2.0 V. Thus the voltammogram (a) from the mono(acetonitrile) cation Ia on the reverse potential (positive) scan showed the appearance of a pair of anodic waves P_1 and P_2 at −0.94 and −0.32 V vs. SCE, respectively. By contrast, no such CV waves were observed in cyclic voltammograms (b) and (c) derived from the bis- and tris(acetonitrile) cations Ib and Ic, respectively. The limited magnitudes of the anodic peak currents of the CV waves P_1 and P_2 indicate that they are associated with a side product formed in 20–30% yield. Indeed the anodic wave of the major product II was shifted to positive potentials beyond +0.5 V and was irreversible at scan rates up to 10 V s^{-1}.

The identity of the byproduct responsible for the CV waves P_1 and P_2 was established in the following way. The cyclic voltammograms of the bis- and tris(acetonitrile) cations Ib and Ic were reexamined in the presence of phosphine L = PMe_2Ph. As shown in parts b′ and c′ of Figure 1, the same anodic waves P_1 and P_2 were evident. Accordingly, P_1 and P_2 must be associated with the phosphine-substituted $Mn(CO)_3L_2^-$ (III) which is indeed the reported byproduct in Table I (footnote *d*). We attribute the first wave P_1 at −0.94 V to its oxidation in eq 5. The dashed portions of the cyclic voltammograms

$$\underset{\text{III}}{(OC)_3MnL_2^-} \underset{P_1}{\overset{[-e]}{\rightleftharpoons}} (OC)_3MnL_2\cdot \qquad (5)$$

indicate a reversible electrochemical behavior in the range

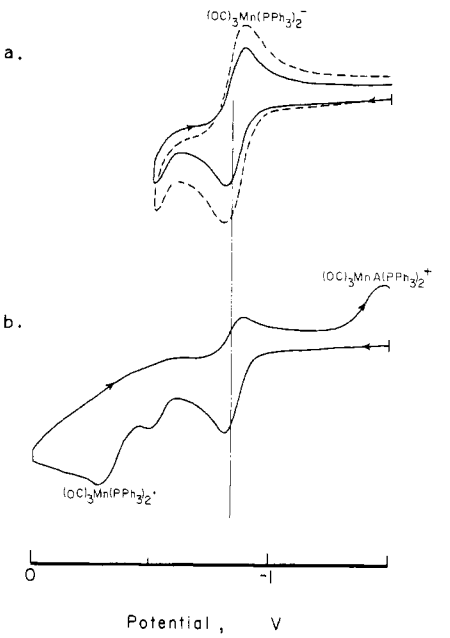

Figure 2. Initial positive scan cyclic voltammograms of 5×10^{-3} M $(OC)_3Mn(PPh_3)_2^-Na^+$ in acetonitrile containing 0.1 M TEAP: (a) scan reversed at −0.5 V for 500 (—) and 1000 (- - -) mV s^{-1}; (b) scan reversed at 0 V for 500 mV s^{-1}.

of scan rates between 100 and 800 mV s^{-1}.[12] Such an assignment of P_1 to the oxidation of $(OC)_3MnL_2^-$ was confirmed by the observation of the same anodic wave when an authentic sample[13] of $(OC)_3MnL_2^-Na^+$ was oxidized (see Figure 2a). The second wave P_2 at −0.32 V then corresponds to the further oxidation of the bis(phosphine)-substituted radical to the corresponding cation in eq 6. We attribute the irreversibility of P_2 to the insta-

(12) The reversibility of the CV wave P_1 indicates that the radical $(OC)_3MnL_2\cdot$ is stable[14] on the CV time scale.
(13) Hieber, W.; Höfler, M.; Muschi, J. *Chem. Ber.* **1965**, *98*, 311.
(14) See: (a) Walker, H. W.; Brown, T. L. *J. Am. Chem. Soc.* **1982**, *104*, 4007. (b) Kidd, D. R.; Cheng, C. P.; Brown, T. L. *J. Am. Chem. Soc.* **1978**, *100*, 4103. (c) See also: McCullen, S. B.; Brown, T. L. *J. Am. Chem. Soc.* **1982**, *104*, 7496. Brown, T. L. *Ann. N. Y. Acad. Sci.* **1980**, *80*, 333.

$$(OC)_3MnL_2^{\bullet} \xrightarrow[P_2]{[-e]} (OC)_3MnL_2^{+} \quad (6)$$

bility of this coordinatively unsaturated cation toward solvation, i.e., eq 7. The overall transformation is tan-

$$Mn(CO)_3L_2^{+} + MeCN \xrightarrow{fast} Mn(CO)_3L_2(NCMe)^{+} \quad (7)$$

tamount to the regeneration of the reactant cation Ia (n = 1). This was readily demonstrated independently by cyclic voltammetry of the bis(phosphine)manganate(I) salt III shown in Figure 2b.

It is noteworthy that the reactant wave R corresponding to the reduction of the mono(acetonitrile) complex Ia was partially restored in the voltammograms only after scanning the potential in the positive direction beyond −0.3 V (i.e., after the anodic wave P_2). The same CV behavior was observed in a completely reduced solution of $(OC)_3Mn(NCMe)L_2^{+}$.

It is important to note that the anodic peak currents in P_1 and P_2 in the cyclic voltammograms b′ and c′ from the bis- and tris(acetonitrile) cations (Ib and Ic, respectively) in Figure 1 were comparable to the anodic currents obtained in the direct voltammetry of the mono(acetonitrile) cation $(OC)_3Mn(NCMe)L_2^{+}$ (Ia) in the absence of any added phosphine (see Figure 1a′). The formation of $(OC)_3MnL_2^{-}$ in 20–30% yields following the bulk reduction of the carbonylmanganese(I) cations Ia–c corresponds to the fraction in excess of 1 in the coulometry (see Table I, column 4). The identity of the carbonylmanganate $(OC)_3MnL_2^{-}$ was confirmed by its characteristic carbonyl absorptions at 1800 and 1750 cm^{-1} in the IR spectrum. Finally the acidification of the catholyte with hydrogen chloride afforded only the hydridomanganese complex II in high yields.

We conclude from these studies that the complete stoichiometry for the cathodic reduction of the mono(acetonitrile) cation Ia is given by eq 8. Essentially the

$$(OC)_3Mn(NCMe)L_2^{+} \xrightarrow[-MeCN]{[\sim 1.2e]} \begin{cases} \xrightarrow{\sim 80\%} (OC)_3MnL_2H \quad II \\ \xrightarrow{\sim 20\%} (OC)_3MnL_2^{-} \xrightarrow{HCl} II \quad III \end{cases} \quad (8)$$

same relative amounts of II and III were formed when the bis- and tris(acetonitrile) cations Ib and Ic were reduced in the presence of added phosphine, i.e., eq 9.

$$(OC)_3Mn(NCMe)L_{2(3)}L_{1(0)}^{+} + 1(2)L \xrightarrow[-2(3)MeCN]{[\sim 1.2e]} \begin{cases} \xrightarrow{\sim 80\%} II \\ \xrightarrow{\sim 20\%} III \end{cases} \quad (9)$$

The striking similarity between the reductive substitutions in eq 8 and 9, both in terms of the total charge consumed (see n in Table I) and the relative amounts of II and III, suggests that a common intermediate is involved. This point is further strengthened when one considers that the anodic CV waves P_1 and P_2 in Figure 1a from the reduction of the bis(phosphine) cation Ia are identical with those in Figure 1c′ from the unsubstituted cation Ic in the presence of added phosphine—especially with regard to both the peak positions and the peak currents. Thus, whatever the mechanism for reductive substitution may be, the same intermediate pertains to all cations I. Therefore we examined the electroreduction of the bis(triphenylphosphine) analogue $(OC)_4Mn(PPh_3)_2^{+}$ (IV) in some detail.

III. Transient Electrochemistry of $(OC)_4Mn(PPh_3)_2^{+}$. Evidence for the Formyl Complex as a Reaction Intermediate. The cyclic voltammetry of $(OC)_4Mn(PPh_3)_2^{+}$ (IV) was carried out under the same conditions as described above for the mono(acetonitrile) analogue Ia. Thus the initial negative scan cyclic voltammogram of $(OC)_4Mn(PPh_3)_2^{+}$ (IV) in acetonitrile containing 0.1 M TEAP in Figure 3a showed the first cathodic wave at E_p = −1.56 V (which was irreversible at a scan rate of 1000 mV s^{-1}).[15] Moreover, when the initial negative scan was continued to a more negative potential of −3.0 V, a pair of additional cathodic waves R_1 and R_2 (E_p = −2.55 and −2.85 V) were visible, as shown in Figure 3b.[16] The pronounced third cathodic wave R_2 was readily ascribed to the further reduction of hydridomanganese product by comparison with the behavior of an authentic sample[8] shown in Figure 3c.

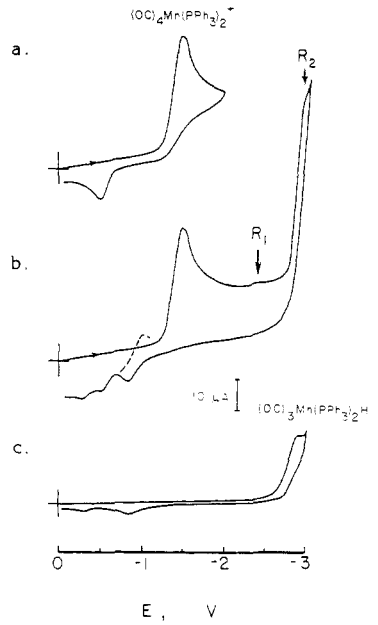

Figure 3. Initial negative scan cyclic voltammograms of 5×10^{-3} M $(OC)_4Mn(PPh_3)_2^{+}$ in acetonitrile containing 0.1 M TEAP at 25 °C with the scan reversed at (a) −2.0 V and (b) −3.0 V for 1.0 V s^{-1}. (c) Cyclic voltammogram of 5×10^{-3} M $(OC)_3Mn(PPh_3)_2H$ under the same conditions as (b).

The second cathodic peak R_1, which is barely discernible in Figure 3b, became more pronounced when the cyclic voltammogram was conducted at lower temperatures. Indeed Figure 4a shows that the cathodic peak at E_p = −2.55 V has grown considerably at −30 °C. An authentic sample of the formyl complex V was prepared by the hydridic reduction of IV,[18] i.e., eq 10. The cyclic voltam-

$$(OC)_4Mn(PPh_3)_2^{+} + Li(C_2H_5)_3BH \rightarrow \underset{IV}{} \quad \underset{V}{(OC)_3Mn(PPh_3)_2CHO} \quad (10)$$

mogram of V is shown in Figure 4b. The comparison of Figure 4b with Figure 4a indicates that the cathodic wave R_1 indeed results from the formyl intermediate V. Note that the magnitude of the cathodic peak current in Figure 4b corresponds to 0.2 coulomb/mol of the formyl complex charged. The limited cathodic current is associated with

(15) The anodic wave at E_p = −0.49 V arises from $(OC)_4MnPPh_3^{-}$ by comparison with that of an authentic sample, which was prepared by the reduction of $[(OC)_4Mn(PPh_3)]_2$ with sodium amalgam.

(16) The anodic waves at E_p = −0.79 and −0.35 V arise from $(OC)_3Mn(PPh_3)_2^{-}$ and $(OC)_3Mn(PPh_3)_2^{\bullet}$. The origins of these species[15] will be reported separately.[17]

(17) Kuchynka, D. J.; Amatore, C.; Kochi, J. K. *Inorg. Chem.*, in press.

(18) Tam, W.; Lin, G. Y.; Gladysz, J. A. *Organometallics* **1982**, *1*, 525.

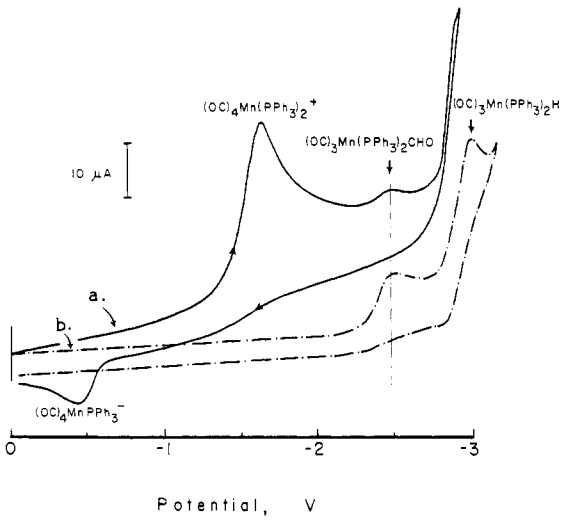

Figure 4. (a) Initial negative scan cyclic voltammogram of 5×10^{-3} M $(OC)_4Mn(PPh_3)_2^+$ in acetonitrile containing 0.1 M TEAP at −30 °C with scan rate of 1.0 V s^{-1}. (b) Cyclic voltammogram of 5×10^{-3} M $(OC)_3Mn(PPh_3)_2CHO$ under the same conditions (-·-·-).

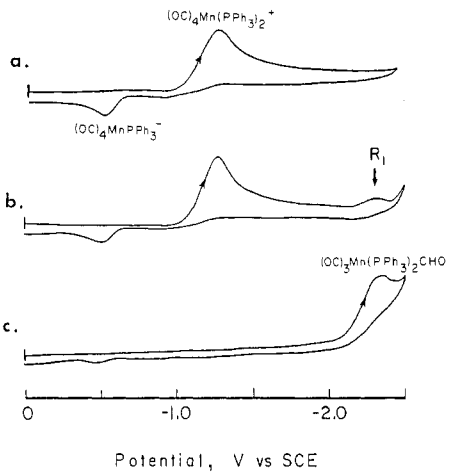

Figure 5. Initial negative scan cyclic voltammograms of 5×10^{-3} M $(OC)_4Mn(PPh_3)_2^+PF_6^-$ in THF containing 0.2 M TBAP at a scan rate of 500 mV s^{-1}: (a) no *n*-Bu_3SnH; (b) 8×10^{-2} M *n*-Bu_3SnH added. (c) The cyclic voltammogram of 5×10^{-3} M $(OC)_3Mn(PPh_3)_2CHO$ under the same conditions as (b).

the spontaneous appearance of the new wave at −2.9 V due to the hydridomanganese complex II. It is important to emphasize that the formyl complex V is unstable at room temperature (vide infra).

The formyl complex V can be generated in higher yields when the electrochemical reduction of the bis(phosphine) cation IV was carried out in the presence of an active hydrogen donor such as tri-*n*-butylstannane.[19] For example, Figure 5a shows an irreversible cathodic wave at $E_p = -1.37$ V ($v = 500$ mV s^{-1}) for the room-temperature reduction of IV in tetrahydrofuran (THF) containing 0.2 M tetra-*n*-butylammonium perchlorate (TBAP).[20] The same CV reduction carried out in the presence of *n*-Bu_3SnH is shown in Figure 5b. The appearance of a new cathodic wave R_1 at $E_p = -2.37$ V ($v = 500$ mV s^{-1}) grows in importance as the amount of *n*-Bu_3SnH is increased. The new cathodic wave (which corresponds to R_1 in Figure 3b) can be readily assigned to the neutral formyl complex $(OC)_3Mn(PPh_3)_2CHO$ (V) by comparison with that in Figure 5c of an authentic sample prepared by hydridic reduction of the bis(phosphine) cation IV.

Discussion

The hydridomanganese complex II is produced together with the analogous carbonylmanganate III from the electroreduction of the carbonylmanganese(I) cations Ia–c with high current efficiencies. Moreover the ready protonation of III allows the hydridomanganese complex to be isolated as the sole product in essentially quantitative yields.

I. Mechanism of the Reduction of the Carbonylmanganese(I) Cations I. The electroreduction of the carbonylmanganese cations is unusual in several ways. First, an extensive replacement of the coordinated acetonitrile by added phosphine accompanies the reductive conversion of the carbonylmanganese cations. Second, the formation of only products of bis(phosphine) substitution from the reduction of the tris(acetonitrile) complex Ic, even in the presence of a stoichiometric deficiency of added phosphine, indicates that the substitution of the second acetonitrile occurs considerably faster than the first (vide infra).

To develop an understanding of these results, we note that the one-electron reduction of the carbonylmanganese(I) cations actually corresponds to the production of the 19-electron manganese(0) species, e.g., eq 11. Since similar carbonylmanganese(0) radicals are

$$(OC)_3Mn(NCMe)_3^+ + e \rightarrow (OC)_3Mn(NCMe)_3\cdot \quad (11)$$

known to be highly labile,[21] the ligand substitution of the coordinated acetonitrile by phosphine (L) follows in rapid sequence, viz., eq 12 and 13. The production of the hydridomanganese complex II in eq 1–3 and the carbonylmanganate III in eq 5 then proceeds from the 19-electron manganese(0) species VI by reduction and hydrogen transfer, i.e., Scheme I. According to this formulation, the bis(phosphine) radical VI is the intermediate which is common to all the carbonylmanganese cations I. The manner in which it is partitioned in Scheme I is the same for all carbonylmanganese(I) cations Ia–c, irrespective of the degree of prior phosphine substitution, in accord with the comparison of the experimental results in eq 8 and 9. In Scheme I, the route to the hydridomanganese complex II in eq 15 requires no additional electrons, whereas that leading to the carbonylmanganate III in eq 14 requires one more electron. Thus the apparent number of electrons consumed ($n \simeq 1.2$ in Table I) agrees with the relative amounts of I and II produced of ca. 1:4.

$$(OC)_3Mn(NCMe)_3\cdot + L \xrightarrow{\text{fast}} (OC)_3Mn(NCMe)_2L\cdot + MeCN \quad (12)$$

$$(OC)_3Mn(NCMe)_2L\cdot + L \xrightarrow{\text{fast}} (OC)_3Mn(NCMe)L_2\cdot + MeCN \quad (13)$$

Scheme I

$$(OC)_3Mn(NCMe)L_2\cdot \text{ (VI)} \xrightarrow{+e} (OC)_3MnL_2^- \text{ (III)} \quad (14)$$

$$(OC)_3Mn(NCMe)L_2\cdot \text{ (VI)} \xrightarrow{[H]} (OC)_3MnL_2H \text{ (II)} \quad (15)$$

(19) See, e.g.: Lusztyk, J.; Lusztyk, E.; Maillard, B.; Lunazzi, L.; Ingold, K. U. *J. Am. Chem. Soc.* **1983**, *105*, 4475.

(20) For the stabilization of the formyl complex by *n*-Bu_3SnH at room temperature see: Narayanan, B. A.; Amatore, C. A.; Kochi, J. K. *Organometallics* **1984**, *3*, 802.

(21) Compare the studies by Brown and co-workers in ref 14. See also: Meyer, T. J.; Caspar, J. V. *Chem. Rev.* **1985**, *85*, 187. Stiegman, A. E.; Tyler, D. R. *Coord. Chem. Rev.* **1985**, *63*, 217.

An alternative formulation involves the 17-electron carbonylmanganese radical VII as the common intermediate formed by the loss of a coordinated acetonitrile, i.e., eq 16 and 17. However this possibility is inconsistent with

$$(OC)_3Mn(NCMe)L_2^+ \xrightarrow{-MeCN} \underset{VI}{} \qquad \underset{VII}{(OC)_3MnL_2\cdot} \begin{cases} \xrightarrow{+e} (OC)_3MnL_2^- & (16) \\ \xrightarrow{[H]} (OC)_3MnL_2H & (17) \end{cases}$$

the persistence of $(OC)_3MnL_2\cdot$ generated from the anodic oxidation of $(OC)_3MnL_2^-$. Thus the reversible cyclic voltammogram in Figure 2a indicates that the 17-electron radical VII is not the precursor responsible for the formation of the hydridomanganese complex V under reaction conditions.[22]

Let us now consider the mechanism by which the 19-electron radical in Scheme I is converted to the carbonylmanganate ion III and the hydridomanganese complex II in eq 14 and 15, respectively.

A. Formation of the Carbonylmanganate (I) Ion III. The production of $(OC)_3MnL_2^-$ (III) from the 19-electron radical VI in Scheme I requires overall an electron accession and an acetonitrile loss. Of the two formal possibilities for the sequence by which these steps occur, we favor the prior loss of acetonitrile or ECE mechanism in Scheme II for several reasons. *First*, the alternative EEC mechanism involving initial electron accession would require that the 19-electron radical VI is reduced to the hexacoordinate 20-electron anion more readily than the parent cation I, which is an unlikely possibility.[25] By contrast, electron accession to the 17-electron radical VII formed in Scheme II occurs readily as shown by the reversible cyclic voltammograms in Figure 2a. Second, it is seen from the invariance of the cyclic voltammograms of the mono(acetonitrile) cation Ia that the relative yields of II and III are independent of the scan rate. This indicates that (electron) molecularity of the branching reactions for $(OC)_3Mn(NCMe)L_2\cdot$ in Scheme I are identical. Since the formation of the hydridomanganese complex II does not involve an electron accession (vide infra), it follows that the formation of the carbonylmanganate does not involve an EEC mechanism. We thus propose that the ECE sequence in Scheme II, which is analogous to that previously presented[17] for the reduction of the analogous cation $(OC)_5MnL^+$, pertains to the formation of the carbonylmanganate ion III.

B. Formation of the Hydridomanganese Complex II. It could be argued that the hydridomanganese complex

Scheme II

$$(OC)_3Mn(NCMe)L_2^+ \xrightarrow{[+e]} (OC)_3Mn(NCMe)L_2\cdot \qquad (18)$$

$$(OC)_3Mn(NCMe)L_2\cdot \longrightarrow (OC)_3MnL_2\cdot + MeCN \qquad (19)$$

$$(OC)_3MnL_2\cdot \xrightarrow{[+e]} (OC)_3MnL_2^- \qquad (20)$$

II is formed via a direct proton transfer to the carbonylmanganate ion III, as indicated in eq 21.[26] That this is

$$\underset{III}{(OC)_3MnL_2^-} + H^+ \rightarrow \underset{II}{(OC)_3MnL_2H} \qquad (21)$$

not the case is readily shown by the requirement of substantially less than two electrons (see n_{app} in Table I). Furthermore the presence of deliberately added water had no effect on the yield of II from the electroreduction of Ia.[27] On the basis of our earlier studies,[17] we propose that hydridomanganese arises via a formyl intermediate as outlined in Scheme III.[28] This formulation involves (a) the

Scheme III

$$(OC)_3Mn(NCMe)L_2\cdot \xrightarrow{[+e]} (OC)_3Mn(NCMe)L_2\cdot \qquad (22)$$

$$(OC)_3Mn(NCMe)L_2\cdot + SH \rightarrow (OC)_2Mn(NCMe)L_2CHO + S\cdot \qquad (23)$$

$$(OC)_2Mn(NCMe)L_2CHO \rightarrow (OC)_3MnL_2H + MeCN \qquad (24)$$

occurrence of hydrogen atom transfer to the 19-electron radical in eq 23 followed by (b) the loss of an acetonitrile ligand during the reorganization of the formyl intermediate to the hydridomanganese product in eq 24. Indeed we have recently demonstrated the feasibility of both processes in some related systems.[30,31] As a model for the carbonylmanganese cations pertinent to this study, we scrutinized the electroreduction of the related bis(phosphine) cation $(OC)_4Mn(PPh_3)_2^+$ (IV) since the corresponding formyl complex $(OC)_3Mn(PPh_3)_2CHO$ is known.[20] Indeed Figures 3 and 4 show that the formyl complex $(OC)_3Mn(PPh_3)_2CHO$ is formed as an intermediate during the course of the reduction of IV. Furthermore its increasing importance in the presence of an active hydrogen atom donor tri-*n*-butylstannane in Figure 5 supports the homolytic nature of its formation, i.e., eq 25.

$$(OC)_4Mn(PPh_3)_2\cdot + n\text{-}Bu_3SnH \rightarrow (OC)_3Mn(PPh_3)_2CHO + n\text{-}Bu_3Sn\cdot \qquad (25)$$

The sizeable magnitude of the formyl cathodic wave during the reduction of $(OC)_4Mn(PPh_3)_2^+$ in Figure 4a compared to that observed from an authentic sample of $(OC)_3Mn(PPh_3)_2CHO$ in Figure 4b demonstrates that it is formed in 30–50% yields at −30 °C. Thus the formation of $(OC)_3Mn(PPh_3)_2CHO$ in major amounts is consistent with the path for its formation in Scheme III.

The cyclic voltammogram of the formyl complex $(OC)_3Mn(PPh_3)_2CHO$ in Figure 4b also shows that the corresponding hydridomanganese derivative $(OC)_3Mn$-

(22) The yield of hydridomanganese complex according to the path in eq 17 is predicted by be[23] $[II] = 100k_2^{1/2}/(k_1^{1/2} + k_2^{1/2})$ where k_1 is the first-order rate constant for acetonitrile loss from VI and k_2 is the pseudo-first-order rate constant for hydrogen transfer at suitably high concentrations of hydrogen donor. Since the CV wave of $(OC)_3MnL_2^-$ is reversible (see Figure 2), $k_2 < 1\ s^{-1}$.[24] On the other hand, $k_1 \gtrsim 4 \times 10^3\ s^{-1}$ since the CV of Ia is irreversible up to 100 V s^{-1}. Thus [II] is <2%, and at least 98% of III would be obtained according to this mechanism.

(23) Amatore, C.; Saveant, J. M. *J. Electroanal. Chem.* **1981**, *123*, 203.

(24) Nadjo, L.; Saveant, J. M. *J. Electroanal. Chem.* **1973**, *48*, 113.

(25) See also the discussion in ref 17.

(26) (a) The acid required for such a protonation must have an acid strength of $pK_a < 7$, which is an upper limit for that of the conjugate acid $HMn(CO)_3L_2$. Thus the acid strength of the parent hydridomanganese $HMn(CO)_5$ of 8×10^{-8} [See: King, R. B.; Eisch, J. J. *Organometallic Synthesis*; Academic: New York, 1965; Vol. I] is a lower limit. (b) Cf. Zotti, G.; Zecchin, S.; Pilloni, *J. Organomet. Chem.* **1983**, *246*, 61 and Moore, E. J.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 2257.

(27) However, see ref 26.

(28) In Scheme III, SH is any hydrogen donor including the supporting electrolyte and the solvent. In order to balance the charge requirement, S· should disappear in a homolytic coupling and/or disproportionation. In acetonitrile/TEAP, we found no products derived from the cyanomethyl radical. In pivalonitrile/TBAP, significant amounts of butene-1 were detected, suggesting the formation and occurrence of $[CH_3CH_2CH_2\dot{C}HNBu_3^+ \rightarrow CH_3CH_2CH{=}CH_2 + Bu_3N\cdot^+]$[29] which derives from the attack on the supporting electrolyte.

(29) (a) Klingler, R. J.; Huffman, J. C.; Kochi, J. K. *Inorg. Chem.* **1981**, *20*, 34. (b) Compare also: M'Halla, F.; Pinson, J.; Saveant, J. M. *J. Am. Chem. Soc.* **1980**, *102*, 4120. Sofranko, J. A.; Eisenberg, R.; Kampmeier, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 1163.

(30) Narayanan, B. A.; Kochi, J. K. *J. Organomet. Chem.* **1984**, *272*, C49.

(31) Narayanan, B. A.; Amatore, C.; Casey, C. P.; Kochi, J. K. *J. Am. Chem. Soc.* **1983**, *105*, 6351.

$(PPh_3)_2H$ is quantitatively generated upon reduction. However the magnitude of the cathodic peak current of the formyl wave corresponds to a charge consumption of only 0.2 electron. This behavior is indicative of an electrocatalytic extrusion of carbon monoxide, i.e., eq 26, where

$$(OC)_3Mn(PPh_3)_2CHO \xrightarrow{[E]} (OC)_3Mn(PPh_3)_2H + CO \quad (26)$$

[E] represents the cathode. Furthermore the retardation of this electrocatalytic conversion of n-Bu_3SnH (compare the ~1-electron wave at 25 °C in Figure 5d with the ~0.2-electron wave at −30 °C in Figure 4b) suggests that a free radical chain process is operative. Indeed such a pathway has been delineated with several formyl complexes, and the homolytic propagation sequence is summarized in Scheme IV (where M· represents a carbonyl-

Scheme IV

$$MCO\cdot \longrightarrow M\cdot + CO \quad (27)$$

$$M\cdot + MCHO \rightarrow MH + MCO\cdot \text{ etc.} \quad (28)$$

metal radical).[31,32] As applied to the formylmanganese intermediate involved in this study, the transient radical M· in Scheme IV is $(OC)_3MnL_2$·, which is the same as derived from acetonitrile loss in Scheme II. Since $(OC)_3MnL_2$· is readily reduced at the potentials extant in the electroreduction (see Figure 2a), the involvement in Scheme IV would imply a rate constant in eq 28 which is incompatible with its stability. On the other hand the comparison of the anodic waves in Figure 3 with those in Figure 4 shows clearly that in the presence of the formyl complex, the reduction of hydridomanganese II does not yield significant amounts of its decomposition product $Mn(CO)_3P_2^-$. This suggests the participation of an electron-transfer step,[33] e.g., eq 29, which coupled with eq 30,[34] leads to an overall extrusion of carbon monoxide from the formyl intermediate. The initiation of this chain process would occur by the primary reduction of the formyl complex at the cathode, i.e., eq 31.

$$(OC)_3MnL_2H^{\cdot-} + (OC)_3MnL_2CHO \rightarrow (OC)_3MnL_2H + (OC)_3MnL_2CHO^{\cdot-} \quad (29)$$

$$(OC)_3MnL_2CHO^{\cdot-} \rightarrow (OC)_3MnL_2H^{\cdot-} + CO \quad (30)$$

$$(OC)_3MnL_2CHO \xrightarrow{[+e]} (OC)_3MnL_2CHO^{\cdot-} \quad (31)$$

II. Mechanism of Ligand Substitution during the Electroreduction of Carbonylmanganese Cations. The mechanistic formulation in Scheme I identifies the 19-electron radical VI as the common intermediate leading to hydridomanganese II and carbonylmanganate III. However, there is some ambiguity as to how VI is formed. On one hand, the stoichiometric reduction of the tris(acetonitrile) cation Ic followed by rapid ligand substitution by added phosphine (as indicated in eq 11–13) requires an overall consumption of one-electron to produce each VI. A close inspection of the cyclic voltammograms in Figure 1 does not support this conclusion. For convenience, the cathodic waves are reproduced in Figure 6 as a superposition of the ones from (a) tris(acetonitrile)

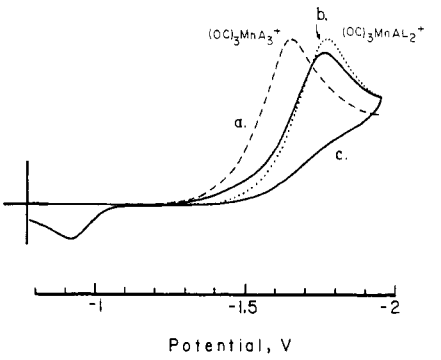

Figure 6. Superposition of the cathodic CV peaks in the reduction of (a) $(OC)_3Mn(NCMe)_3^+$ (- - -), (b) $(OC)_3Mn(NCMe)_3^+$ plus 10 equiv of PMe_2Ph added (···), and (c) $(OC)_3Mn(NCMe)(PMe_2Ph)_2^+$ (—) under conditions given in Figure 1.

Scheme V

$$(OC)_3Mn(NCMe)_3\cdot + 2L \rightarrow (OC)_3Mn(NCMe)L_2\cdot + 2MeCN \quad (12,13)$$

$$(OC)_3Mn(NCMe)L_2\cdot + (OC)_3Mn(NCMe)_3^+ \rightarrow (OC)_3Mn(NCMe)L_2^+ + (OC)_3Mn(NCMe)_3\cdot \quad (32)$$

complex Ic alone, (b) Ic with 10 equiv of added PMe_2Ph, and (c) the mono(acetonitrile) complex Ia alone. At the foot of the cathodic waves (in the region of −1.3 V), the cathodic currents in (a) and (b) are comparable. However at a slightly more negative potential of −1.5 V the cathodic current in (a) is much smaller than that in (b). As the full CV wave develops in (b), it is akin to that observed in (c) for the mono(acetonitrile) cation. This behavior is typical for an electrocatalytic process in which the tris(acetonitrile) complex Ic is almost quantitatively converted to the mono(acetonitrile) cation Ia in the potential range from beyond −1.5 V. Owing to the rather small difference of the cathodic peak potentials of $\Delta E_p = 0.12$ V between Ic and Ia, the electrocatalytic wave of the reactant is simply merged with that of the product, without the peak resolution which has been observed in other systems.[5] Accordingly, the propagation sequence for the ligand substitution is presented as an electron-transfer chain mechanism shown in Scheme V.[35] Note that the involvement of the electron-transfer reaction in eq 32 [or its heterogeneous analogue $(OC)_3Mn(NCMe)L_2\cdot \xrightarrow{[-e]} (OC)_3Mn(NCMe)L_2^+$] is required to account for the decrease in the cathodic current in the potential range (−1.5 ± 0.2 V) where the ligand substitution is achieved.[36] This leads to an overall consumption of charge which approaches zero for the electrocatalytic process in Scheme V. A similar mechanism also pertains to the ligand substitution of the bis(acetonitrile) complex Ib.

Summary and Conclusion

The electroreduction of carbonylmanganese(I) cations I constitutes a simple and efficient procedure for the preparation of the hydridomanganese complexes II. Ini-

(32) (a) Sumner, C. E.; Nelson, G. O. *J. Am. Chem. Soc.* **1984**, *106*, 432. (b) Paonessa, R. S.; Thomas, N. C.; Halpern, J. *J. Am. Chem. Soc.* **1985**, *107*, 4333.

(33) Cf. Narayanan, B. A.; Amatore, C.; Kochi, J. K. *Organometallics* **1986**, *5*, 926.

(34) Cf. (a) Casey, C. P.; Neumann, S. M.; Andrews, M. A.; McAlister, D. R. *Pure Appl. Chem.* **1980**, *52*, 625. Casey, C. P.; Andrews, M. A.; Rinz, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 741. (b) Gladysz, J. A. *Adv. Organomet. Chem.* **1982**, *20*, 1. (c) The apparent role of n-Bu_3SnH in retarding the decarbonylation is not understood.

(35) A quantitative analysis of the electrocatalytic kinetics[5] is discouraged by the small difference in ΔE_p and the irreversible CV waves. Thus we are unable to state definitely whether the ligand substitution of the 19-electron radicals in eq 12 and 13 occurs by an associative or dissociative mechanism. We favor the latter since the associative process would proceed via an electron-supersaturated 21-electron intermediate or transition state. For the microscopic reverse of the dissociative mechanism in some related carbonylmetal cation radicals, see ref 5.

(36) This driving force for electron transfer is exergonic since the product radical $(OC)_3Mn(NCMe)L_2$· is unstable in a potential range which is less negative than that of the cathodic wave of the reactant cation.

tially, the carbonylmanganese cations undergo a facile ligand substitution under electrocatalytic conditions in Scheme V. Thus the tris(acetonitrile) cation Ic in the presence of stoichiometric amounts of phosphine (PMe_2Ph or PPh_3) affords quantitative yields of the mono(acetonitrile) cation Ia with a charge consumption close to zero. The further reduction of the cation leads to the 19-electron carbonylmanganese radical VI which is subsequently partitioned to the hydridomanganese complex II and the carbonylmanganate according to Scheme I. The stepwise mechanisms for the reduction and hydrogen atom transfer are summarized in Schemes II and III, respectively.

Experimental Section

Materials. The carbonylmanganese cations $(OC)_3Mn(NCMe)_3^+$ either as the hexafluorophosphate or tetrafluoroborate salt,[6] $(OC)_3Mn(NCMe)_2(PMe_2Ph)^+BPh_4^-$,[6] $(OC)_3Mn(NCMe)(PMe_2Ph)_2^+PF_6^-$,[6] and $(OC)_4Mn(PPh_3)_2^+PF_6^-$,[9] were prepared as described in the literature. The hydridomanganese complex $(OC)_3Mn(PPh_3)_2H$ was prepared according to Ugo and Bonatis' procedure.[8] Triphenylphosphine (Matheson, Coleman and Bell) was sublimed prior to use. Dimethylphenylphosphine was prepared from $PhPCl_2$ (Arapahoe) and methylmagnesium iodide.[37] Tri-*n*-butylstannanes, *n*-Bu_3SnH and *n*-Bu_3SnD, were prepared by literature procedures.[38] Lithium triethylborohydride (Aldrich, 1 M in THF) was used as received. Acetonitrile (Fisher, reagent grade) was repurified by refluxing it (1000 g) over $KMnO_4$ (15 g) and powdered P_2O_5 (5 g) for 2 h. The mixtures was filtered, and the colorless liquid was treated with diethylenetriamine (6 g) and fractionated at high reflux through a 15-plate Oldershaw column under an argon atmosphere. The absorbance at 200 nm was less than 0.1 in a 1-cm cuvette. The purified acetonitrile was stored in a Schlenk flask under argon. Tetraethylammonium perchloride (TEAP from G. F. Smith Chemical) was used as received. Tetra-*n*-butylammonium perchlorate (TBAP from G. F. Smith Chemical Co.) was recrystallized twice from ethyl acetate and dried in vacuo overnight at room temperature.

^1H and ^{13}C NMR spectra were recorded on a JEOL FX90Q spectrometer. IR spectra were recorded on either a Perkin-Elmer 1330 or a Nicolet DX10 spectrometer. All manipulations were carried out under an atmosphere of argon or prepurified nitrogen in the dark, unless specified otherwise.

Electrochemical Measurements. Bulk electrochemistry was performed on a Princeton Applied Research (PAR) Model 173 potentiostat equipped with a Model 176 current-to-voltage converter which provided feedback compensation for ohmic drop between the working and reference electrodes. The charge passed during prereduction or the oxidatively induced experiments were measured with a PAR Model 179 digital coulometer. The voltage follower amplifier (PAR Model 178) was mounted external to the potentiostat with a minimum length of high impedance connection to the reference electrode to ensure minimum or low noise pickup. Some of the bulk electrolyses were conducted with a Vacuum Atmosphere glovebox in which the electrodes were connected to the voltage follower amplifier by means of wires running through an Apiezon W wax seal constructed in an air-tight Cajon pipe fitting mounted in a utility port. Coulometry was conducted in a three-compartment cell in which the working and counter electrodes were separated by a Nafion (Du Pont) membrane, and a platinum gauze basket was the working electrode. Cyclic voltammograms were obtained with an *iR*-compensated potentiostat of local construction, coupled with a PAR Model 175 universal programmer. The electrochemical cell was constructed according to Van Duyne and Reilley.[39] The distance between the platinum working electrode and the tip of the salt bridge was <5 mm. The SCE reference electrode was connected through a capacitor to a platinum wire electrode located between the working and counter electrodes to facilitate *iR* compensation of the ohmic drop in the nonaqueous solutions. All operations and manipulations were conducted under argon or prepurified nitrogen with 0.2 M tetra-*n*-butylammonium perchlorate (TBAP) as the supporting electrolyte in tetrahydrofuran or methylene chloride.

Electrosynthesis of the Hydridomanganese Complex II. In a typical procedure, a mixture of 85 mg (0.21 mmol) of $(OC)_3Mn(NCMe)_3^+PF_6^-$ and 70.2 mg (2 equiv) of PMe_2Ph was dissolved in 5 mL of acetonitrile containing 0.1 M TEAP. The bulk electrolysis was carried out with a cathodic current of 20 mA at −1.5 V at constant current. When the potential reached −1.8 V, 1.2 coulombs of charge was passed. The catholyte was transferred with the aid of a Teflon cannula into a Schlenk flask containing 20 mL of ether saturated with HCl gas, and the mixture was stirred for 15 min. The solvent was removed in vacuo, and the residue was chromatographed over florisil using a 10:1 v/v mixture of dichloromethane and ether. The hydrido complex $(OC)_3Mn(PMe_2Ph)_2H$ was isolated as a colorless solid: 71 mg (82%); ^1H NMR (C_6D_6) δ −7.9 (t, $J(PH)$ = 27 Hz); IR (Nujol) ν_{CO} 1950, 1908 cm^{-1}.

Electroreduction of $(OC)_4Mn(PPh_3)_2^+PF_6^-$ (IV). The carbonylmanganese cation $(OC)_4Mn(PPh_3)_2^+PF_6^-$ (100 mg, 0.12 mmol) was dissolved in 10 mL of THF containing 0.2 M TBAP. A constant cathodic current of 10 mA was passed through the solution until the electrode potential increased from −1.15 to −1.40 V. During the electrolysis, the solution turned yellowish brown and the IR spectrum showed the presence of bands at 1940, 1905, 1890, 1850, and 1810 cm^{-1}. The bands at 1905 and 1890 cm^{-1} were assigned to $(OC)_3Mn(PPh_3)_2H$, and those at 1940, 1850 and 1810 cm^{-1} were attributed to $(OC)_4Mn(PPh_3)^-$. The reduction of $(OC)_4Mn(PPh_3)_2^+$ in the presence of stannane was carried out as follows. A mixture of 100 mg (0.12 mmol) of $(OC)_4Mn(PPh_3)_2^+PF_6^-$ and 175 mg (5 equiv) of *n*-Bu_3SnH was dissolved in 10 mL of THF. A constant cathodic current of 10 mA was passed through the solution until the potential shifted from −1.15 to −1.40 V. During the electrolysis, the solution turned dark yellow and a yellow solid precipitated from solution. The catholyte was transferred with the aid of a Teflon cannula into a Schlenk flask and evaporated to dryness. The residue was extracted with 20-mL portions of dichloromethane. Chromatography on a Florisil column yielded 92 mg of a light yellow solid. The ^1H NMR spectrum of the compound in C_6D_6 showed a triplet resonance at δ −6.87 (J = 33 Hz) and a broad singlet at δ 0.16 as well as aromatic resonances at δ 7.1–7.8 (m).

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Registry No. Ia, 52745-57-0; Ia·PF_6, 104911-21-9; Ib·BF_4, 104911-20-8; Ic·PF_6, 54039-60-0; Ic·BF_4, 68928-06-3; II, 86708-28-3; III, 104911-22-0; IV·PF_6, 70083-76-0; V, 70083-79-3; VI (L = PMe_2Ph), 104911-23-1; VI (L = PPh_3), 104911-24-2; $(OC)_3Mn(PPh_3)_2H$, 16972-17-1; $(OC)_3Mn(PPh_3)_2^-Na^+$, 14244-50-9; $(OC)_4Mn(PPh_3)^-$, 53418-18-1; *n*-Bu_3SnH, 688-73-3.

(37) Davis, W. C. *J. Chem. Soc.* **1937**, 527.
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(39) Van Duyne, R. P.; Reilley, C. N. *Anal. Chem.* **1972**, *44*, 142.