Electrosynthesis of Hydridometal Carbonyls. Rapid Ligand Substitution in Transient Mn^0 Intermediates from the Reduction of Carbonylmanganese(I) Cations

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Unusually enhanced rates of multiple ligand substitutions are observed during the convenient synthesis of hydridomanganese complexes by the cathodic reduction of carbonylmanganese cations.

Electrochemistry offers a novel and potentially useful method for the preparation of various types of transition metal hydrides, especially by exploiting the reduction of the ubiquitous[1] carbonylmetal cations. In this report, we describe the successful electrosynthesis of hydridomanganese carbonyls and the unusual observation of facile, multiple ligand substitutions which can accompany the reduction of cationic manganese(I) carbonyls. For example, the electrolysis [E] of the mono-acetonitrile cation[2] $Mn(CO)_3(NCMe)(PMe_2Ph)_2^+$ [equation (1), L = PMe_2Ph or PPh_3] afforded excellent yields of the hydridomanganese complex $HMn(CO)_3(PMe_2Ph)_2$, as described in Table 1. Strikingly, the same hydridomanganese

$$Mn(CO)_3(MeCN)L_2^+ \xrightarrow{[E]} HMn(CO)_3L_2 + MeCN \quad (1)$$

complex was obtained when either the bis-acetonitrile, monophosphine analogue was reduced in the presence of merely 1 equiv. of L, equation (2), or even when the tris-acetonitrile

$$Mn(CO)_3(MeCN)_2L^+ + L \xrightarrow{[E]} HMn(CO)_3L_2 + 2\ MeCN \quad (2)$$

cation was reduced in the presence of the stoicheiometric 2 equiv. of L, equation (3). Moreover, the reductive substitu-

$$Mn(CO)_3(MeCN)_3^+ + 2L \xrightarrow{[E]} HMn(CO)_3L_2 + 3\ MeCN \quad (3)$$

tion of both L's is rapid since the results in Table 1 indicate that the bis-phosphine complex $HMn(CO)_3L_2$ was formed in *ca.* 50% yield when only 1 equiv. of L was employed in equation (3).

Cyclic voltammetry provides a clear insight into the mechanism of hydride formation and multiple ligand substitution. Thus for the series of the tricarbonylmanganese cations $Mn(CO)_3(MeCN)_{3-n}L_n^+$ in equations (1)—(3), the cyclic voltammograms in Figure 1 were recorded both in the presence (right-hand side) and in the absence (left-hand side) of added L. All the voltammograms show a principal reduction wave R corresponding to a *ca.* 1-electron addition, based on the calibration with ferrocene. On the return potential sweep, no oxidation wave was observed for the carbonylmanganese cations with $n = 0$ and $n = 1$ in the voltammograms (A) and (B), respectively. However, for the carbonylmanganese cation with $n = 2$, a pair of anodic waves P_2 and P_1 was observed in voltammogram (C) at E_p −0.32 and −0.94 V *vs.* saturated calomel electrode (S.C.E.). These two peaks were also observed for the cations with $n = 0$ and $n = 1$, but only in the presence of added L, as shown in voltammograms (A′) and (B′). Accordingly P_1 and P_2 must be associated with the phosphine-substituted product $Mn(CO)_3L_2^-$. The first wave P_1 is attributed to equation (4) and shows reversible electrochemical

$$Mn(CO)_3L_2^- - e \overset{P_1}{\rightleftharpoons} Mn(CO)_3L_2^{\bullet} \quad (4)$$

behaviour in the range of scan rates between 100 and 800 mV s^{-1} (see the dashed portion of the cyclic voltammograms).[4] The wave P_2 at E_p −0.32 V corresponds to the further oxidation of the phosphine-substituted radical to the corresponding cation. We attribute the irreversibility of P_2 to the instability of this co-ordinatively unsaturated cation toward solvation, equation (5) which is tantamount to the regeneration of the

$$Mn(CO)_3L_2^+ + MeCN \xrightarrow{fast} Mn(CO)_3(MeCN)L_2^+ \quad (5)$$

reactant cation for $n = 2$ in equation (1). The latter can be readily demonstrated independently by the cyclic voltammetry

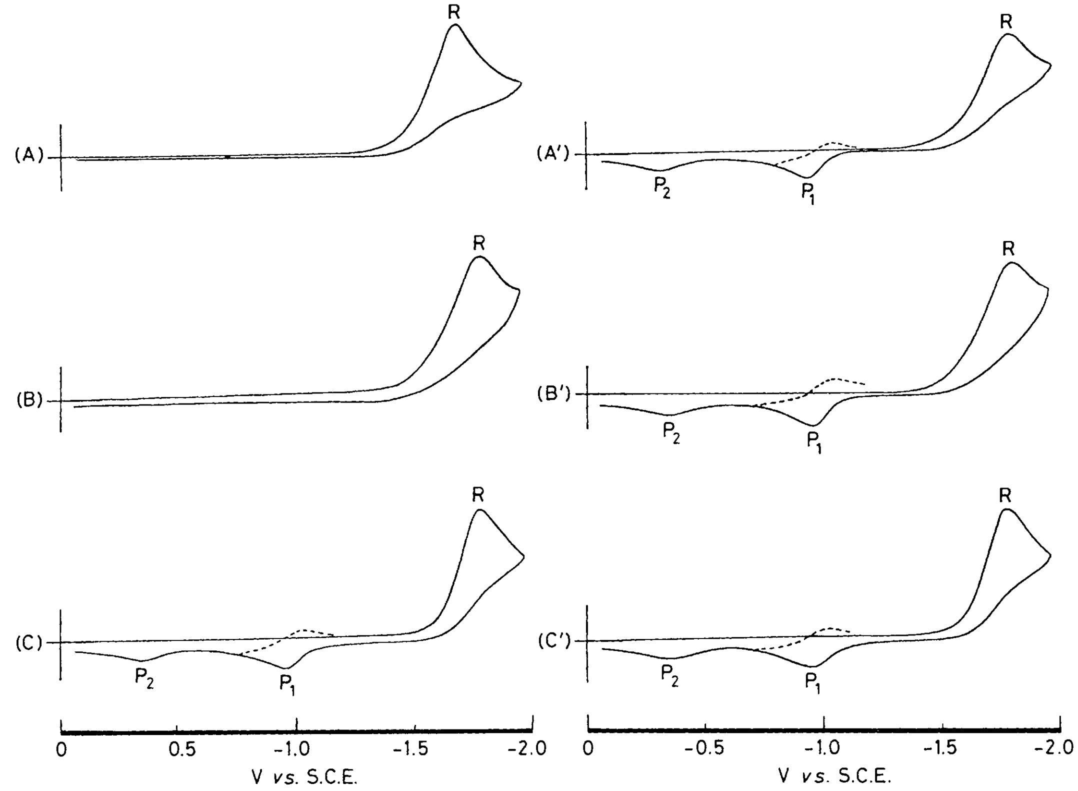

Figure 1. Initial negative scan cyclic voltammograms of (A) $Mn(CO)_3(NCMe)_3^+$, (B) $Mn(CO)_3(NCMe)_2(PMe_2Ph)^+$, and (C) $Mn(CO)_3(NCMe)(PMe_2Ph)_2^+$ in the absence (left) and in the presence (right) of 10 equiv. of added PMe_2Ph. Complex concentration 5×10^{-3} M in acetonitrile containing 0.1 M Et_4NClO_4 at 0.8 V s^{-1}.

Table 1. Electrochemical reduction of $Mn(CO)_3(NCMe)_{3-n}(PMe_2Ph)_n^+$.[a]

Mn^I Cation	Added L^b			
n (conc. M)	L	(no. of equiv.)	Q^c/C	Product
0 (5×10^{-2})	PPh_3	(2)	1.1	$HMn(CO)_3(PPh_3)_2$[d,e]
		(3)	1.2	$HMn(CO)_3(PPh_3)_2$[d]
		(1)	1.2	$HMn(CO)_3(PPh_3)_2$[d,f]
		(0)	1.2	[f]
	PMe_2Ph	(2)	1.2	$HMn(CO)_3(PMe_2Ph)_2$[g,h]
		(3)	1.2	$HMn(CO)_3(PMe_2Ph)_2$[g]
1 (5×10^{-2})	PMe_2Ph	(1)	1.3	$HMe(CO)_3(PMe_2Ph)_2$[g]
2 (1×10^{-2})	none		1.5	$HMn(CO)_3(PMe_2Ph)_2$[g]

[a] By galvanostatic coulometry of either the BF_4^- or the PF_6^- salt (ref. 2) in acetonitrile containing 0.1 M tetraethylammonium perchlorate as supporting electrolyte at 25 °C, unless stated otherwise. [b] Relative to Mn^I cation. [c] Total charge passed per equiv. Mn^I cation. Fraction in excess of 1 attributed to $Mn(CO)_3L_2^-$, observed by its i.r. spectrum (1800 and 1750 cm^{-1}) in entries 1—3. [d] Identified by i.r. and n.m.r. spectral comparison with an authentic sample (ref. 3). [e] Isolated yield, 78%. [f] Unidentified manganese carbonyl complex formed with a characteristic i.r. spectrum (1940, 1905, and 1880 cm^{-1}). [g] I.r.: 1950, 1908 cm^{-1} (in Nujol), ^1H n.m.r.: δ —7.9 (C_6D_6) [t, J(PH) 27Hz]. [h] Isolated yield, 82%.

of a completely prereduced solution of $Mn(CO)_3(MeCN)L_2^+$, in which it is noteworthy that the reactant wave R is partially restored in the voltammogram only after scanning the potential in the positive direction beyond −0.3 V (*i.e.* after wave P_2).

To develop an understanding of these results, we note that the 1-electron reduction of the carbonylmanganese(I) cations actually corresponds to the production of manganese(0) species. Since similar organometallic radicals are known to be highly labile to ligand substitution,[5] the initial reduction of the carbonylmanganese cation can be followed by a rapid sequence of ligand-substitution steps, equations (6)—(8).†

$$Mn(CO)_3(MeCN)_3^+ + e \longrightarrow Mn(CO)_3(MeCN)_3^{\bullet} \qquad (6)$$

$$Mn(CO)_3(MeCN)_3^{\bullet} + L \xrightarrow{\text{fast}} Mn(CO)_3(MeCN)_2L^{\bullet} + MeCN \qquad (7)$$

$$Mn(CO)_3(MeCN)_2L^{\bullet} + L \xrightarrow{\text{fast}} Mn(CO)_3(MeCN)L_2^{\bullet} + MeCN \qquad (8)$$

The production of $Mn(CO)_3L_2^-$ for equation (4) and the ultimate production of the hydridomanganese carbonyls $HMn(CO)_3L_2$ in equations (1)—(3) then proceed from the manganese(0) species, equations (9) and (10).[6] It appears from

$$Mn(CO)_3(MeCN)L_2^{\bullet} \xrightarrow{+e} Mn(CO)_3L_2^- + MeCN \qquad (9)$$

$$\quad \longrightarrow HMn(CO)_3L_2, \textit{ etc.} \text{ (ref. 7)} \qquad (10)$$

the ratios of peak currents in Figure 1 that the relative amounts of equations (9) and (10) are *ca.* 1:5, which also

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† Associative or dissociative mechanisms for the rapid ligand substitutions in equations (7) and (8) are as yet undefined.

accords with the bulk coulometric results in Table 1. This mechanistic formulation identifies manganese(0) radicals as the reactive intermediates responsible for the formation of the hydridomanganese products in the facile electroreduction of carbonylmanganese(I) cations.

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