Electrocatalysis of Ligand Substitution in Metal Carbonyls. Thermodynamics of a Chain Process.

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Electrocatalysis of ligand substitution in carbonylmanganese derivatives proceeds by a cationic chain mechanism, and the driving force for each step in the catalytic cycle can be evaluated.

We report a novel method for the ligand substitution of stable metal carbonyls such as $(\eta^5\text{-}C_5H_4Me)Mn(CO)_2(NCMe)$, hereafter referred to as $(MeCN)\{M\}$ where $\{M\} = (\eta^5\text{-}$

$C_5H_4Me)Mn(CO)_2$. Ligand substitution in equation (1) was complete within 10 min at 22 °C upon the application of a slight anodic current through the solution with the aid of

Pt electrodes [E] at a potential of -0.06 V vs. S.C.E. (saturated calomel electrode). Other carbonylmanganese

$$\text{(MeCN)}\{M\} + \text{PPh}_3 \xrightarrow[\text{0.1 M-TEAP-MeCN}]{[E]} \text{(Ph}_3\text{P)}\{M\} + \text{MeCN} \quad (1)$$
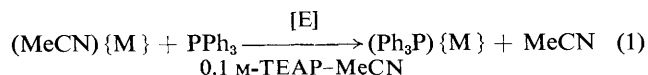
derivatives listed in Table 1 reacted with various nucleophiles under similar conditions. In each case, it is noteworthy that no ligand substitution was observed in the absence of current. The material balance among the substitution products† (identified by comparison with authentic samples[1]) was essentially quantitative. Most importantly, the high current efficiencies (>250) indicate the participation of catalytic cycles with exceedingly long kinetic chain lengths.

The mechanism of electrocatalysis can be directly related to the reversible 1-electron oxidation of the manganese carbonyls listed in Table 2.[2] For example, a solution of (MeCN){M} was first oxidized partially at 0.10 V until only 2% was converted into the corresponding cation. Addition of 1 equiv. of PPh$_3$ to this solution led spontaneously to an excellent yield of the substitution product (Ph$_3$P){M}, as noted by the immediate change in colour followed by isolation. Indeed the participation of the cation (MeCN){M}$^+$ as the catalytically active species can be observed during a cyclic voltammetric (C.V.) scan. Figure 1 illustrates how the C.V. of (MeCN){M} is drastically altered in the presence of either 1 or 9 equiv. of PPh$_3$. It is particularly noteworthy that the originally reversible C.V. wave for (MeCN){M} becomes irreversible in the presence of PPh$_3$. Such an observation accords with an electrochemical EC mechanism, in which the cation (MeCN){M}$^+$ is rapidly intercepted by PPh$_3$ (equation 2).[3] Furthermore, the chain character of the ligand
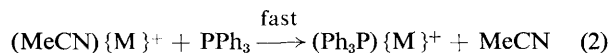
$$\text{(MeCN)}\{M\}^+ + \text{PPh}_3 \xrightarrow{\text{fast}} \text{(Ph}_3\text{P)}\{M\}^+ + \text{MeCN} \quad (2)$$

Figure 1. Single-scan cyclic voltammograms of 1.0 $\times$ 10^{-3} M (η^5-C$_5$H$_4$Me)Mn(CO)$_2$(NCMe) in acetonitrile containing 0.1 M-TEAP at a scan rate of 200 mV s^{-1} and 22 °C. The C.V. waves of the reactant (R) and product (P) are indicated for solutions contaning (a) 0, (b) 1, and (c) 9 equiv. of added PPh$_3$.

Table 1. Electrocatalytic substitution of manganese carbonyls (η^5-C$_5$H$_4$Me)Mn(CO)$_2$L by nucleophiles L′.[a]

L	L′	Potential[b]	(η^5-C$_5$H$_4$Me)-Mn(CO)$_2$L′, yield (%)[c]	Coulometry[d]
MeCN	PPh$_3$	-0.06	100	1013
MeCN	Bu^{t}NC	-0.12	95	365
Pyridine	PPh$_3$	-0.12	96	260

[a] With 4 $\times$ 10^{-2} M (η^5-C$_5$H$_4$Me)Mn(CO)$_2$L and L′ in 12 ml of MeCN containing 0.1 M tetraethylammonium perchlorate (TEAP) at 22 °C. [b] Constant anodic current of 100 μA was applied until the i.r. spectrum of the anolyte revealed complete ligand substitution. Initial potential in V vs. S.C.E. [c] By quantitative i.r. spectrophotometry. [d] Current efficiency in moles of product per Faraday of charge passed.

Table 2. Cyclic voltammetry of (η^5-C$_5$H$_4$Me)Mn(CO)$_2$L.[a]

L	E_p^a/V vs. S.C.E.[b]	E^0/V vs. S.C.E.[c]	$i_p^a/i_p^{c,d}$
PPh$_3$	0.56	0.52	1.0
Bu^{t}NC	0.58	0.54	1.0
MeCN	0.22	0.19	1.0
Pyridine[e]	0.16	0.11	1.0
MeCN[e,f]	0.18	0.12	1.0

[a] In MeCN containing 0.1 M TEAP with a Pt microelectrode at a scan rate of 200 mV s^{-1} at 22 °C, unless indicated otherwise. [b] Anodic peak potential. [c] Calibrated relative to E^0 (ferrocene) = 0.31 V. [d] Ratio of anodic and cathodic peak currents. [e] In acetone. [f] At scan rate of 50 mV s^{-1} at -55 °C.
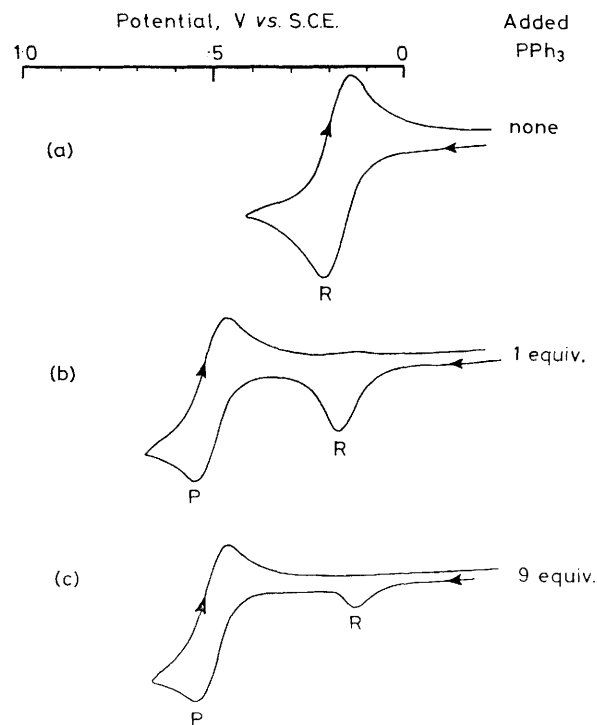
† Satisfactory elemental analyses and spectral data were obtained for all new compounds.

substitution is also indicated in Figure 1(c) by the marked diminution of the anodic peak current of (MeCN){M}, which reflects its rapid, *catalytic* disappearance at the electrode, a result consistent with the coulometry (Table 1). The chain mechanism is completed by equation (3), which, together with equation (2), represent the two steps in the catalytic
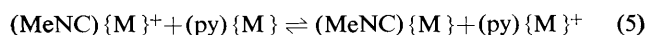
$$\text{(Ph}_3\text{P)}\{M\}^+ + \text{(MeCN)}\{M\} \to \text{(Ph}_3\text{P)}\{M\}$$
$$+ \text{(MeCN)}\{M\}^+ \quad (3)$$
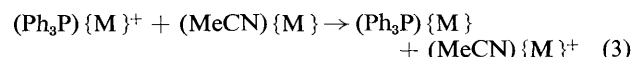
cycle required for the overall stoicheiometry in equation (1).[4,5]

The reversibility of ligand substitution can be readily assessed by the electrocatalytic method. For example, (py){M} (py = pyridine) can be readily interconverted with (MeCN){M} to give an equilibrium mixture by starting with either component. Employing quantitative i.r. spectrophotometry, we determined the equilibrium constant K_{eq} to be

$$\text{(py)}\{M\} + \text{MeCN} \underset{}{\overset{K_{eq}}{\rightleftharpoons}} \text{(MeCN)}\{M\} + \text{py} \quad (4)$$
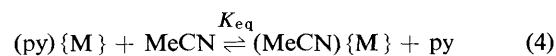
1.1 $\times$ 10^{-2}, *i.e.*, the driving force (ΔG) is 10.9 kJ mol^{-1} for equation (4). From the reversible reduction potentials (Table 2), a driving force of -0.8 kJ mol^{-1} is derived for the electron transfer process in equation (5). The completion of

$$\text{(MeNC)}\{M\}^+ + \text{(py)}\{M\} \rightleftharpoons \text{(MeNC)}\{M\} + \text{(py)}\{M\}^+ \quad (5)$$

$$\text{(py)}\{M\}^+ + \text{MeCN} \rightleftharpoons \text{(MeNC)}\{M\}^+ + \text{py} \quad (6)$$

the thermochemical cycle allows the evaluation of ΔG for the substitution step in equation (6) as 11.7 kJ mol^{-1}.

References

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2 *Cf.* N. G. Connelly and M. D. Kitchen, *J. Chem. Soc., Dalton Trans.*, 1977, 931.

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4 For other cationic chain mechanisms, see J. W. Hershberger, R. J. Klingler, and J. K. Kochi, *J. Am. Chem. Soc.*, in the press.

5 Chain mechanisms have also been recently proposed for ligand substitutions of metal carbonyls induced by *reduction:* G. J. Bezems, P. H. Rieger, and S. Visco, *J. Chem. Soc., Chem. Commun.*, 1981, 265; D. P. Summers, J. C. Luong, and M. S. Wrighton, *J. Am. Chem. Soc.*, 1981, **103**, 5238.