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Ligand substitution at 19-electron organometallic centers. Electrocatalytic CO substitution reactions of (methylcyclopentadienyl)$Mn(CO)_2NO^+$ and (indenyl)$Mn(CO)_2NO^+$

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Abstract

(Methylcyclopentadienyl)$Mn(CO)NO^+$ ($\mathbf{1}^+$) undergoes a one-electron reduction at an electrode to give a 19-electron neutral radical that rapidly dissociates CO and dimerizes to yield $[(MeCp)Mn(CO)_2NO]_2$. In the presence of P-donor nucleophiles (L), the reduction of $\mathbf{1}^+$ initiates a rapid electron transfer catalyzed (ETC) CO substitution to give a quantitative yield of $(MeCp)Mn(CO)(L)NO^+$. The substitution reaction occurs via the 19-electron intermediate **1**, which dissociates CO in the rate limiting step with the following activation parameters: $\Delta H^* = 60 \pm 6$ kJ; $\Delta S^* = +37 \pm 15$ J K^{-1}. The 17-electron intermediate (MeCp)Mn(CO)NO is then trapped by the nucleophile to give the electron rich (MeCp)Mn(CO)(L)NO, which spontaneously transfers an electron to $\mathbf{1}^+$ to afford the final product and regenerate **1**. A variety of electrochemical techniques, including low temperature voltammetry and steady-state voltammetry with microelectrodes, was employed to quantitatively define the details of the reaction mechanism. The indenyl analogue of $\mathbf{1}^+$, (indenyl)$Mn(CO)_2NO^+$ ($\mathbf{2}^+$), was found to undergo ETC substitution reactions by the same dissociative mechanism and at approximately the same rate as $\mathbf{1}^+$. The conclusion is that the 'indenyl effect' does not operate in these 19-electron complexes. The rhenium complex $CpRe(CO)_2NO^+$ is reduced by one electron to give a relatively stable neutral radical that does not react with P-donor nucleophiles on the voltammetric time scale of 0.5 V s^{-1}. The conclusion is that CO dissociation from 19-electron complexes follows the reactivity order Mn ≫ Re.

Keywords: Electrocatalysis; Carbon monoxide substitution; Manganese complexes; Carbonyl complexes; Nitrosyl complexes; Cyclopentadienyl complexes; Indenyl complexes

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1. Introduction

In comparison to their 18-electron analogues, organometallic radicals with 17 or 19 electrons about the metal generally show greatly enhanced reactivity with respect to ligand substitution, migratory insertion and reductive elimination reactions. Advantage of this may be taken by the intentional generation of radical species to initiate stoichiometric and catalytic transformations [1–5]. One way to 'activate' 18-electron complexes in this manner is by oxidation or reduction. The former produces 17-electron species, which frequently can be identified spectroscopically, while the latter may generate transient 19-electron species, which have been only rarely characterized as such. With respect to ligand substitution, 17-electron complexes generally react rapidly by an associative pathway [3]. Little is known about ligand substitution at 19-electron centers, although it is often presumed that the mechanism is dissociative [2,4,5].

In this paper we are concerned with ligand substitution in 19-electron complexes formed by chemical or electrochemical reduction of 18-electron precursors. It is also possible to generate 19-electron species by *oxidation* in the presence of a potential ligand (L′). Scheme 1 summarizes the relevant chemistry with the key step being the 17*e* ↔ 19*e* interconversion. In either case, the more positive $E°$, the better the chance to 'see' a 19-electron complex. This is particularly true of reductions because an easily reduced (electron poor) M–L complex

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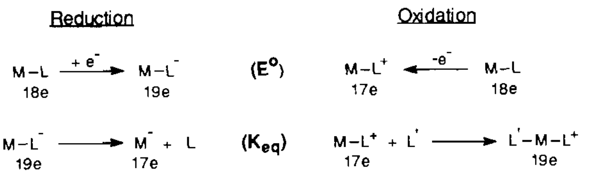
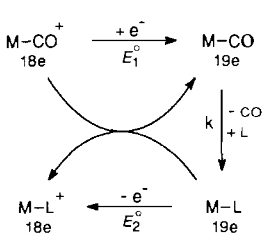


Scheme 1.



Scheme 2.

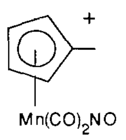
probably will not want to lose the ligand L after reduction (small K_{eq}). By the same token, a difficult to oxidize M–L will want to bind another ligand (large K_{eq}), but this will generally be followed by a second *spontaneous* oxidation of $L'–M–L^+$, so that the only *observed* species will be $L'–M–L^{2+}$. Thus, it is better to use reduction chemistry to study 19-electron complexes. However formed, 19-electron complexes are usually very reactive. For example, it is reported that $Mn(CO)_6$, $Mn(CO)_2(dppe)_2$ and $(arene)W(CO)_3(MeCN)^+$ dissociate a ligand with a half-life at room temperature of less than a microsecond [5b,c,e,6].

A number of substitution reactions at 18-electron centers has been found to be promoted by the presence of a catalytic amount of reducing agent, which can be a chemical or an electrode [2,7,8]. Thus, the rate of the overall reaction given in Eq. (1) can sometimes be enormously increased by the introduction of an electron transfer catalyzed (ETC) pathway. Scheme 2 gives the details of the ETC process.

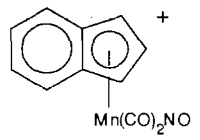
$$M–CO^+ + L \xrightarrow{e^-} M–L^+ + CO \qquad (1)$$

Reduction of $M–CO^+$ yields the labile 19-electron M–CO, which reacts rapidly with nucleophile L to give M–L. Generally, ligands that replace CO lead to a net increase in the electron density about the metal. This means that M–L is more easily oxidized than is M–CO, from which it follows that M–L formed during the reaction sequence will react with $M–CO^+$ in a cross redox reaction to give $M–L^+$ and M–CO, as shown in Scheme 2. Alternatively, heterogeneous electron transfer to $M–CO^+$ from an electrode with a potential near $E_1°$ leads to M–L, which then returns an electron to the electrode provided $E_1° > E_2°$. Thus, whether the electron transfer is homogeneous or heterogeneous, the overall substitution reaction in Eq. (1) is catalytic in electrons. The necessary conditions for efficient ETC catalysis are that the reduction potentials be in the order $E°(M–CO^+) > E°(M–L^+)$ and that the 19-electron radicals M–CO and M–L be sufficiently stable with respect to reactions other than substitution (e.g. decomposition) so that there can be many turnovers. The former requirement should be met for most reductions because departing ligands are usually replaced by ones that increase the electron density on the metal. Thus, catalytic reductive activation of organometallic complexes to ligand substitution should be common, whereas catalytic oxidative activation should be uncommon (but see Rcf. [3c,d]). It is possible that many substitution reactions of 18-electron complexes thought to occur by conventional dissociative or associative pathways in fact take place by an electron transfer catalyzed mechanism initiated by the presence of trace amounts of adventitious reductants or oxidants in solution.

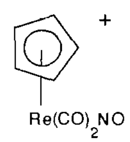
In this paper we report the reductive activation of complexes $\mathbf{1}^+$ and $\mathbf{2}^+$ to catalytic CO substitution by a variety of P-donor nucleophiles. A preliminary report of this work has already appeared [8]. The actual ligand substitution occurs at 19-electron intermediates according to Scheme 2. The indenyl complex $\mathbf{2}^+$ was selected for study in order to determine if an 'indenyl effect' operates in CO substitutions in 19-electron radicals. As is well known, the indenyl effect in 18-electron complexes can be extremely large [9]; for example, $(indenyl)Rh(CO)_2$ undergoes associative CO substitution about 10^8 times faster than does $(Cp)Rh(CO)_2$. The indenyl effect is one example of the general idea that accessibility of a transition state through ring slippage gets easier as the ligand conjugation increases. It is shown herein, however, that the increased π-hydrocarbon conjugation in $\mathbf{2}^+$ compared to $\mathbf{1}^+$ does not result in a substantial rate enhancement for CO substitution in the 19-electron neutral radical **2**.



$\mathbf{1}^+$



$\mathbf{2}^+$



$\mathbf{3}^+$

In addition to utilizing standard electrochemical techniques with conventional electrodes at ambient temperature, the present study benefited greatly from experiments performed at variable temperatures and with microelectrodes. Lowering the temperature in voltammetric experiments can greatly simplify observed behavior by slowing down the rates of chemical reactions of the radicals to values competitive with the experimental time scale [10]. Alternatively, the temperature may be kept at ambient and the voltammetric scan rate increased to match the time scale of the relevant chemical reactions. The latter procedure is often impeded by capacitive charging current and ohmic polarization distortions that become large when organic solvents are used. These effects can be alleviated to some extent by the use of microelectrodes of diameter 25 μm or less, although corrections for distortions are still required at very large scan rates [11].

A different approach is available by using microelectrodes (diameter ⩽10 μm) at low scan rates (e.g. 20 mV s^{-1}). Under these conditions, there is a *steady-state* current response [12]. The steady-state method is attractive because it is plagued with very little of the distortion effects noted above. A homogeneous chemical reaction coupled to the charge transfer can influence the steady-state wave and, as with any electrode, the rate of mass transport to the electrode compared to the chemical reaction rate determines the observed behavior. At a fixed temperature, the mass transport or diffusion rate is tuned until the observed current response is influenced by the chemical reaction being studied. With conventional electrodes, this means changing the scan rate. However, with microelectrodes under steady-state conditions, the diffusion rate is determined by the size of the electrode, so that the effective experimental 'time scale' is varied by changing the electrode size. Steady-state voltammetry with microelectrodes has been used to determine heterogeneous charge transfer rate constants [13], but applications to the mechanisms of homogeneous organometallic reactions are very few in number [14]. Herein, it is shown that low temperature steady-state voltammetry is a convenient technique with which to probe the quantitative mechanistic features of CO substitution at the 19-electron **1** and **2** and that agreement with transient data obtained with conventional electrodes is good.

2. Experimental

The complexes [(MeCp)Mn(CO)(L)NO]PF_6 (L= CO, PPh_3, $P(OEt)_3$, PBu_3) and [(MeCp)Mn(diphos)NO]PF_6 were synthesized from commercially available (MeCp)Mn$(CO)_3$ as previously described [15–17]. The indenyl analogues were similarly prepared from (indenyl)Mn$(CO)_3$ [18]. [CpRe$(CO)_2$NO]BF_4 ($\mathbf{3}^+$) and [CpRe(CO)(PPh_3)NO]BF_4 were made from CpRe$(CO)_3$ by published procedures [19]. Variable temperature voltammetric, bulk electrolysis and IR-OTTLE experiments employed standard potentiostatic control techniques [5e]. Inlaid disk microelectrodes were fabricated with platinum and gold wire of diameter 1–100 μm [20]. Steady-state voltammetry with microelectrodes of diameter ⩽10 μm was performed in a Faraday cage using a two-electrode configuration in conjunction with a Keithley model 427 current amplifier. Digital simulation of proposed mechanisms utilized the programs CVSIM [21] and DigiSim [22]. Extended Hückel and INDO/1 calculations were carried out on $\mathbf{1}^+$ and $\mathbf{2}^+$ using the CAChe set of computation programs developed by Tektronix. Molecules were constructed using the molecular editor, but bond distances and angles were constrained to be consistent with known structures [23]. A range of d-shell β values were explored (−18 to −25) in the INDO/1 calculations, with no significant effect on the calculated HOMO and LUMO.

3. Results and discussion

At a scan rate of 0.5 V s^{-1} and temperature of 23 °C, complex $\mathbf{1}^+$ is reduced in a chemically irreversible one-electron step in CH_2Cl_2/TBAPF_6 under N_2 (Fig. 1). Slight reversibility appears at 0 °C and becomes complete below −60 °C. Under an atmosphere of CO at 0.5 V s^{-1}, the reduction of $\mathbf{1}^+$ is much more reversible, being partially so at 23 °C and completely at 0 °C. (The reduction potentials for $\mathbf{1}^+$ and all other complexes investigated are listed in Table 1). It is known [15,16] that chemical reduction of $\mathbf{1}^+$ in the absence of potential nucleophiles leads to loss of CO and formation of the dimer [(MeCp)Mn(CO)NO$]_2$. By using an IR-OTTLE cell, we confirmed that the electrochemical reduction of $\mathbf{1}^+$ at a gold minigrid also cleanly produces the dimer. The observed inhibition of the rate of this process when the atmosphere is changed from N_2 to CO suggests that the rate limiting step is CO dissociation from the radical species **1** (vide infra). The reduction of the

Table 1
Reduction potentials of manganese and rhenium dienyl complexes in dichloromethane at 23 °C [a]

Complex	$E_{1/2}$ [a]	Complex	$E_{1/2}$ [b]
(MeCp)Mn$(CO)_2NO^+$	−0.29	(indenyl)Mn$(CO)_2NO^+$	−0.17
(MeCp)Mn(CO)[P$(OPh)_3$]NO^+	−0.60	(indenyl)Mn(CO)[P$(OPh)_3$]NO^+	−0.46
(MeCp)Mn(CO)[P$(C_2H_4CN)_3$]NO^+	−0.60		
(MeCp)Mn(CO)(PPh_3)NO^+	−0.76	CpRe$(CO)_2NO^+$	−0.38
(MeCp)Mn(CO)[P$(OEt)_3$]NO^+	−0.77	CpRe(CO)PPh_3)NO^+	−0.90
(MeCp)Mn(CO)(PBu_3)NO^+	−0.86	CpRe(diphos)NO^+	−1.54
(MeCp)Mn(diphos)NO^+	−1.30		

[a] Electrolyte was 0.10 M TBAPF_6; the anion was PF_6^- for all manganese complexes and BF_4^- for all rhenium complexes.
[b] All potentials are relative to ferrocene $E_{1/2}=0.50$.

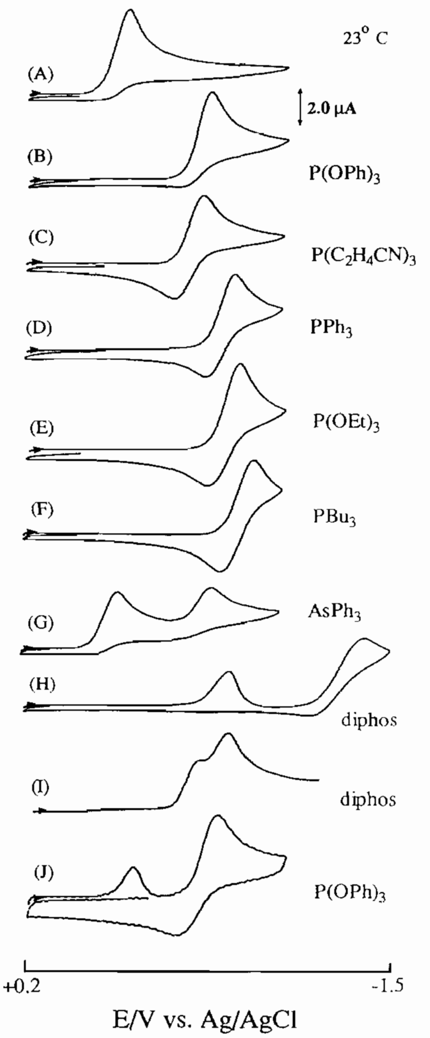


Fig. 1. Cyclic voltammograms of 1.0 mM $[(MeCp)Mn(CO)_2NO]PF_6$ ($\mathbf{1}^+$) in CH_2Cl_2/0.10 M Bu_4NPF_6 under N_2 at 23 °C. (B)–(J) contained the following nucleophiles: (B) 0.003 M $P(OPh)_3$, (C) 0.05 M $P(C_2H_4CN)_3$, (D) 0.05 M PPh_3, (E) 0.005 M $P(OEt)_3$, (F) 0.002 M PBu_3, (G) 0.050 M $AsPh_3$, (H) 0.01 M diphos, (I) 0.0006 M diphos, (J) 0.003 M $P(OPh)_3$. The working electrode was a 1 mm diameter platinum disk and the scan rate was 0.5 V s^{-1} for (A)–(I); for (J) a 100 μm diameter platinum electrode was used and the scan rate was 50 V s^{-1}. All potentials are relative to ferrocene $E_{1/2}=0.50$ V.

indenyl complex $\mathbf{2}^+$ under N_2 and at 0.5 V s^{-1} is similar to that of $\mathbf{1}^+$, being irreversible at 23 °C and reversible below −50 °C. As was found with **1**, an atmosphere of CO retards the decomposition of **2** so that the electrochemical wave attains some reversibility, even at 23 °C. In sharp contrast to the behavior of the manganese complexes, the rhenium complex $\mathbf{3}^+$ is reduced by one-electron with complete chemical reversibility at 23 °C under N_2. The half-life of the radical **3** must be at least 100 times that of **1** and **2**.

The reduction of $\mathbf{1}^+$ at 23 °C in the presence of nucleophiles produced the CVs shown in Fig. 1. At a scan rate of 0.5 V s^{-1}, all nucleophiles except $AsPh_3$ led to the complete disappearance of the voltammetric wave due to the reduction of $\mathbf{1}^+$ and the appearance of a new couple at a more negative potential. IR spectra recorded after completion of the electrochemical experiments indicated that no reaction had occurred between $\mathbf{1}^+$ and the nucleophiles in the bulk solution. Bulk electrolysis at a platinum basket electrode showed that the passage of ~0.02 mol of electrons per mole of $\mathbf{1}^+$ at a potential corresponding to the voltammetric wave in Fig. 1(A) was sufficient to convert all of $\mathbf{1}^+$ to the CO substituted product, $(MeCp)Mn(CO)(L)NO^+$. In other words, the substitution reaction is electrocatalytic (Scheme 2). Accordingly, the voltammetric reduction waves in Fig. 1(B)–(H) were assigned to the respective $(MeCp)Mn(CO)(L)NO^+$ complexes, and this was confirmed by comparison to the behavior of genuine samples. The reaction with the bidentate donor diphos ($Ph_2PCH_2CH_2PPh_2$) merits special comment. Fig. 1(H) shows two reduction waves, which we interpret as due to single and double CO substitution, the latter being observed with diphos because of its chelating ability. The more negative of the two waves in Fig. 1(H) matches that found with a genuine sample of $(MeCp)Mn(diphos)NO^+$. When the diphos concentration was less than that of $\mathbf{1}^+$, the first reduction wave split as shown in Fig. 1(I). The less negative component of the split wave vanished as [diphos] was increased beyond [$\mathbf{1}^+$]. A likely explanation is that single CO substitution in the radical M–CO (**1**) let to a mixture of $M\text{–}P{\sim}P^+$ and $M\text{–}P{\sim}P\text{–}M^{2+}$ species, the latter being formed because there was insufficient diphos to convert all M–CO to the former. The less negative of the two split waves is assigned to reduction of the *dicationic* species.

The absence of a reduction wave due to $\mathbf{1}^+$ when P-donor nucleophiles are present implies that formation of the dimer $[(MeCp)Mn(CO)NO]_2$ cannot compete with CO substitution. With $AsPh_3$, however, the wave due to $\mathbf{1}^+$ was only partially suppressed, indicating that CO substitution and dimer formation are competitive (Fig. 1(G)). Experiments with P-donor nucleophiles under an atmosphere of CO gave results identical to those under N_2. In contrast, with $AsPh_3$ the wave due to $\mathbf{1}^+$ increased and that due to $(MeCp)Mn(CO)(AsPh_3)NO^+$ decreased under CO, showing that $AsPh_3$ and CO compete for reaction with an intermediate.

Fig. 1(J) shows that the reduction wave for $\mathbf{1}^+$ reappears in the presence of $P(OPh)_3$ if the scan rate is increased to 50 V s^{-1}. Similar behavior was found with all of the P-donors studied and was independent of the CO pressure. Furthermore, at 50 V s^{-1} the reduction of $\mathbf{1}^+$ alone was partially chemically reversible. These observations suggest that species **1**, produced initially upon reduction of $\mathbf{1}^+$, reacts in a rate determining step to give an intermediate that is scavenged by nucleophile to yield $(MeCp)Mn(CO)(L)NO^+$ as the final product. As discussed below, the intermediate in question is almost certainly the 17-electron radical (MeCp)Mn(CO)NO.

While variation of the scan rate can be a useful way to probe reaction mechanisms, in the present study it proved far more convenient to alter the relevant time scales by lowering the temperature. Fig. 2 shows some CVs obtained at −43 °C. Note that the reduction wave for $\mathbf{1}^+$ is approximately equal in magnitude to that for $(MeCp)Mn(CO)(L)NO^+$. It is the rate of the M–CO→M–L step in Scheme 2 that determines the relative height of these two reduction waves. At 23 °C, this rate is fast compared to the CV time scale at 0.5 V s^{-1}, and as a consequence no wave is observed for $\mathbf{1}^+$ in the presence of P-donor nucleophiles. However, at −43 °C the reaction rate is sufficiently slowed to make it comparable in magnitude to the CV time scale, with the result that a wave for $\mathbf{1}^+$ is observed. Inspection of Fig. 2 reveals that the CVs are very similar for all P-donor nucleophiles, even though they span a wide range of basicities and cone angles. In addition, it was found that a tenfold variation in the nucleophile concentration or switching from an N_2 to a CO atmosphere had no effect on the CVs. It may be concluded from this that the rate of CO substitution by L in the 19-electron **1** is independent of [CO], [L] and the nature of L. In other words, the mechanism is strictly dissociative, with the rate limiting step being CO dissociation from **1** to give the 17-electron (MeCp)Mn(CO)NO, which is trapped rapidly and completely by L.

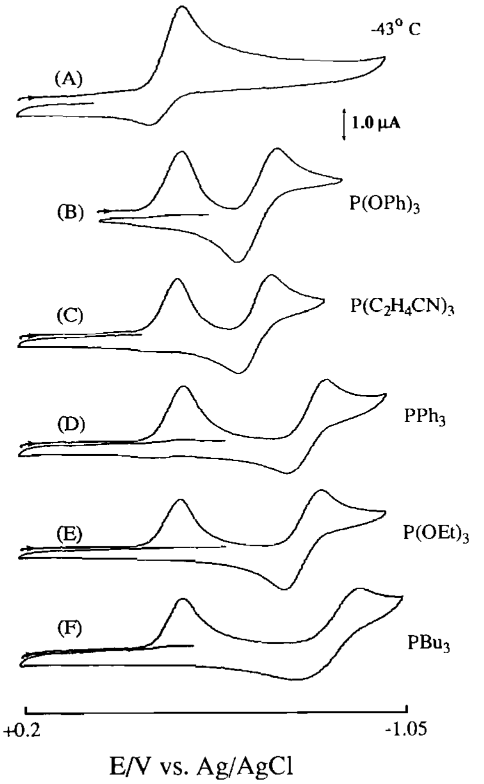


Fig. 2. Cyclic voltammograms of 1.0 mM $[(MeCp)Mn(CO)_2NO]PF_6$ ($\mathbf{1}^+$) in CH_2Cl_2/0.10 M Bu_4NPF_6 under N_2 at −43 °C. (B)–(F) contained the following nucleophiles: (B) 0.02 M $P(OPh)_3$, (C) 0.01 M $P(C_2H_4CN)_3$, (D) 0.01 M PPh_3, (E) 0.02 M $P(OEt)_3$, (F) 0.01 M PBu_3. The working electrode was a 1 mm diameter glassy carbon disk and the scan rate was 0.5 V s^{-1}. All potentials are relative to ferrocene $E_{1/2}=0.50$ V.

Digital simulations of the CVs in Fig. 2 according to the mechanism in Scheme 2 were performed in order to determine the rate constant (k) for CO dissociation from **1**. As expected, the simulations showed the CVs to be very sensitive to the value of k. The homogeneous disproportionation or cross reaction $M\text{–}L + M\text{–}CO^+ \rightarrow M\text{–}L^+ + M\text{–}CO$ is highly exoergic and accounts for much of the conversion of M–L to $M\text{–}L^+$. Simulations showed, however, that the rate constant for the cross reaction (k_2) has little effect on the first CV cycle, provided k_2 is greater than $\sim 10^4\ M^{-1}\ s^{-1}$. The influence of k_2 is most evident on the second cycle. If $k_2 \geqslant 10^5\ M^{-1}\ s^{-1}$, the cross reaction effectively removes $M\text{–}CO^+$ from the vicinity of the electrode so that the first reduction wave (at −43 °C) vanishes on the second cycle. This is the behavior found experimentally (see Fig. 2) and we therefore conclude that $k_2 \geqslant 10^5\ M^{-1}\ s^{-1}$ at −43 °C. The rate constant k was measured over the temperature range −25 to −54 °C with $P(OEt)_3$ as the nucleophile. A standard Eyring plot gave the following activation parameters [1] for CO dissociation from the 19-electron **1**: $\Delta H^{\neq} = 60 \pm 6$ kJ; $\Delta S^{\neq} = +37 \pm 15\ J\ K^{-1}$. Although it was not possible to evaluate the rate constant for the trapping of the 17-electron intermediate by the P-donor nucleophiles to give M–L, a comparison of experiment with digital simulations indicates that these rate constants must be greater than $10^5\ M^{-1}\ s^{-1}$ at −43 °C.

The rate constant k for CO dissociation from **1** was also determined using steady-state voltammetry with microelectrodes. Typical results are given in Fig. 3. At 23 °C, the addition of nucleophile, which in this case was $P(OPh)_3$, caused the steady-state wave to shift negative to that expected for $(MeCp)Mn(CO)[P(OPh)_3]NO^+$ (Fig. 3(B)). There was, of course, no reaction in the bulk solution. The shift in the steady-state wave is completely analogous to that which obtains at a macroelectrode at room temperature (e.g. (Fig. 1(A) and (B)) and shows that the rate of the substitution M–CO→M–L is rapid compared to the rate of diffusion of $\mathbf{1}^+$ and **1** to/from the microelectrode. At −43 °C the substitution reaction is slowed sufficiently in comparison to the diffusion rate so that two steady-state waves are seen (Fig. 3(C)); the *same* solution gave the

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[1] The activation parameters reported in the present study are somewhat different from those reported in a preliminary communication [8]. The latter were calculated from a more restricted data set over a narrower temperature range.

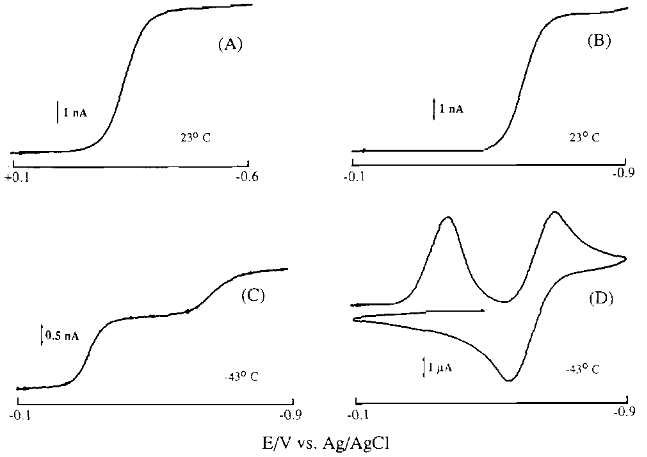

Fig. 3. Cyclic voltammograms of 2.0 mM [(MeCp)Mn(CO)$_2$NO]PF$_6$ (1^+) in CH$_2$Cl$_2$/0.10 M Bu$_4$NPF$_6$ under N$_2$ at the indicated temperatures. (B)–(D) contained 0.020 M P(OPh)$_3$. The working electrode for the steady-state CVs (A)–(C) was a 10 μm diameter gold disk and the scan rate was 20 mV s^{-1}. The working electrode for CV (D) was a 1 mm diameter glassy carbon disk and the scan rate was 0.5 V s^{-1}. All potentials are relative to ferrocene $E_{1/2}=0.50$ V.

CV in Fig. 3(D) at a macroelectrode. The rate constant k determines the relative heights of the two steady-state waves. Digital simulations yielded a value of k as 10 ± 2 s^{-1} at −43 °C. This is essentially the same value implied by the transient CV in Fig. 3(D) and, of course, also matches the results discussed above with P(OEt)$_3$ as the nucleophile (Fig. 2).

Having established that CO substitution in the 19-electron (MeCp)Mn(CO)$_2$NO is dissociative, the reactivity of (MeCp)Mn(CO)(PPh$_3$)NO (**4**) was briefly investigated. It was found that $\mathbf{4}^+$, under N$_2$ or CO at 23 °C, is reduced in a chemically irreversible manner at a scan rate of 0.5 V s^{-1}. Bulk electrolysis experiments established that the product of the reduction of $\mathbf{4}^+$ is the dimer [(MeCp)Mn(CO)NO]$_2$, suggesting that **4** readily dissociates PPh$_3$. In accordance with this, it was found that the CVs of $\mathbf{4}^+$ become reversible when free PPh$_3$ is added to the solution. No doubt this occurs because PPh$_3$ dissociative from **4** is reversible and excess PPh$_3$ can in this way inhibit the net rate of transformation to the dimer.

The electroactivation of the indenyl complex $\mathbf{2}^+$ to CO substitution was studied to see what effect, if any, an increase in the π-conjugation from C$_5$H$_4$Me to C$_9$H$_7$ would have on the reactivity of the radical intermediate **2**. In view of the magnitude of the 'indenyl effect' operating in 18-electron systems [9], it seemed likely that the radicals **1** and **2** would differ significantly in stability/reactivity. This turned out not to be the case. As expected, $\mathbf{2}^+$ reduces at a slightly less negative potential than does $\mathbf{1}^+$ (see Table 1). As mentioned above, the effect of scan rate, temperature and CO pressure on the chemical reversibility of the $\mathbf{2}^+/\mathbf{2}$ couple is very similar to that found with $\mathbf{1}^+/\mathbf{1}$, allowing the conclusion that changing from C$_5$H$_4$Me to C$_9$H$_7$ has minimal effect on the stability of the neutral radicals. The reduction of $\mathbf{2}^+$ in the presence of the nucleophile P(OPh)$_3$ produced the CVs shown in Fig. 4. Neither variation of the P(OPh)$_3$ concentration nor the CO pressure affected the CVs in Fig. 4(B), (D). It follows, for the reasons detailed above, that the mechanism of CO substitution in **2** is dissociative. An analysis of the data at −45 °C implies a rate constant for CO dissociation of $k=15$ s^{-1}. This is rather close to the value of k for **1** (estimated as 7 s^{-1} at −45 °C).

It is generally thought that the indenyl effect in 18-electron systems is due to easier 'ring slippage' in C$_9$H$_7$ compared to C$_5$H$_5$ (or C$_5$H$_4$Me), which facilitates an associative substitution pathway. Our finding that **1** and **2** react by a dissociative pathway suggests that the dienyl rings do not slip when $\mathbf{1}^+$ and $\mathbf{2}^+$ are reduced. If the bonding had changed to η^3 in the radicals, one would expect the resultant 17-electron complexes to react with nucleophiles by an associative mechanism [3]. It is our belief that slippage will rarely occur in 19-electron complexes. An examination of the LUMO of $\mathbf{1}^+$ and $\mathbf{2}^+$, calculated using both extended Hückel and INDO/1 methods, showed that (i) the localization is essentially all on the metal and NO ligand with none on the dienyl ligand and (ii) the LUMO of $\mathbf{1}^+$ is almost identical to that of $\mathbf{2}^+$. These results naturally lead to the expectation that **1** and **2** would dissociate a CO ligand with similar facility [2].

The fact that **1** and **2** react by a dissociative mechanism is a strong argument against the possibility that, upon reduction of $\mathbf{1}^+$ and $\mathbf{2}^+$, the metal attains a 17-electron count through slippage of a dienyl or nitrosyl ligand.

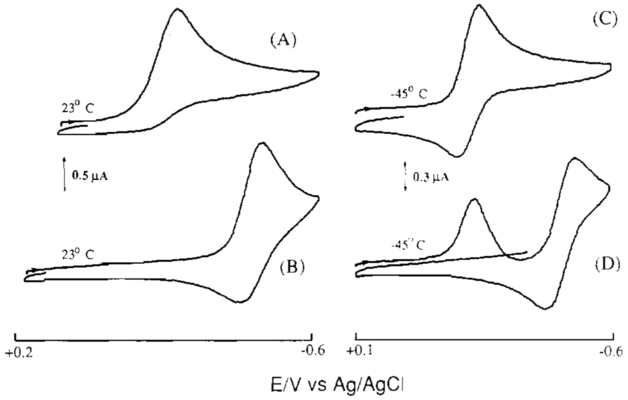

Fig. 4. Cyclic voltammograms of 0.35 mM [(indenyl)Mn(CO)$_2$NO]PF$_6$ (2^+) in CH$_2$Cl$_2$/0.10 M Bu$_4$NPF$_6$ under N$_2$ at the indicated temperatures. (B) and (D) contained P(OPh)$_3$ at concentrations of 0.003 and 0.05 M, respectively. The working electrode was a 1 mm diameter glassy carbon disk and the scan rate was 0.5 V s^{-1}. All potentials are relative to ferrocene $E_{1/2}=0.50$ V.

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[2] Calculations on (dienyl)Fe(CO)$_3{}^+$ analogues with C$_5$H$_5$ and C$_9$H$_7$ ligands suggest that greatly different CO dissociation rates should obtain in the 19-electron radicals, as is known to be the case [24].

In a more general sense one may ask if reduction of the 18-electron cations is centered on the metal or the ligands. Our MO calculations show the LUMO in **1**$^+$ and **2**$^+$ to be 50% or more metal based. However, these results were not optimized with respect to possible ligand slippage. Of more relevance to this question is the published ESR study of $CpMn(CO)_2NO^-$ ($M = Cr$, Mo), which is isoelectronic with $CpMn(CO)_2NO$ [25]. This study showed that some NO ligand bending occurs when $CpM(CO)_2NO$ is reduced to the anion. However, a large amount (>50%) of the unpaired spin density is localized on the metal, so that the radical anions are best described as 19-electron complexes. It is highly likely that **1** and **2** are similarly best formulated as 19-electron complexes.

In order to explore the dependence of the CO substitution rate on the metal, the rhenium complex **3**$^+$ was investigated. At room temperature under N_2 or CO and at a scan rate of 0.5 V s^{-1}, **3**$^+$ was found to undergo a *reversible* one-electron reduction at a potential similar to that of **1**$^+$. The reduction product, $CpRe(CO)_2NO$, was *completely unreactive* on the CV time scale towards P-donor nucleophiles. Thus, the order of reactivity with respect to CO dissociation in these 19-electron complexes follows the order $Mn \gg Re$. The same reactivity order was found for CO substitution in the 19-electron $(arene)M(CO)_3$ ($M = Mn$, Re) [7] and is most likely due to a stronger M–CO bond in the rhenium complexes. Interestingly, *oxidation* of $(dienyl)M(CO)_3$ complexes ($M = Mn$, Re) produces 17-electron species that undergo *associative* CO substitution with a reactivity order $Re \gg Mn$ [26].

There have been two detailed mechanistic studies of 19-electron complexes reported to date. One [27] showed that the arene in (arene)Fe(Cp) is replaced by phosphines via an *associative* pathway; it is likely, however, that successive arene ring slippage occurs to avoid the formation of 21-electron intermediates. A second study [28] concerned dissociative CO substitution in $Co(CO)_3L_2$ (L_2 is 2,3-bis(diphenylphosphino)maleic anhydride). In this case, however, recent ESR studies have shown [29] that the molecule is predominantly an 18-electron complex with a radical ligand. The study reported herein is the first quantitative mechanistic investigation of CO substitution in genuinely 19-electron complexes. One conclusion of our work is that rapid dissociative substitution in 19-electron intermediates, formed as the result of the presence of trace amounts of reductants, may sometimes, and perhaps frequently, provide a viable alternative to the standard associative or dissociative mechanism of substitution in 18-electron complexes. A good example of this is provided by the observation [16] that normally slow CO substitution in **1**$^+$ becomes rapid in the presence of a catalytic amount of reducing agent NEt_3.

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References

[1] W.C. Trogler (ed.), *Organometallic Radical Processes*, Elsevier, Amsterdam, 1990.

[2] (a) G.J. Bezems, P.H. Rieger and S. Visco, *J. Chem. Soc., Chem. Commun.*, (1981) 265; (b) C.M. Arewgoda, B.H. Robinson and J. Simpson, *J. Chem. Soc., Chem. Commun.*, (1982) 284; (c) A. Darchen, C. Mahé and H. Patin, *J. Chem. Soc., Chem. Commun.*, (1982) 243; (d) M. Arewgoda, P.H. Rieger, B.H. Robinson, J. Simpson and S. Visco, *J. Am. Chem. Soc., 104* (1982) 5633; (e) D. Miholova and A.A. Vlcek, *J. Organomet. Chem., 279* (1985) 317; (f) K. Hinkelmann, F. Mahlendorf, J. Heinze, H.-T. Schacht, J.S. Field and H. Vahrenkamp, *Angew. Chem., Int. Ed. Engl., 26* (1987) 352.

[3] (a) J.P. Fawcett, R.A. Jackson and A. Poë, *J. Chem. Soc., Dalton Trans.*, (1978) 789; (b) A. Poë, *Transition Met. Chem., 7* (1982) 69; (c) J.W. Hershberger, R.J. Klinger and J.K. Kochi, *J. Am. Chem. Soc., 105* (1983) 61; (d) P.M. Zizelman, C. Amatore and J.K. Kochi, *J. Am. Chem. Soc., 106* (1984) 3771; (e) Q.-Z. Shi, T.G. Richmond, W.C. Trogler and F. Basolo, *J. Am. Chem. Soc., 106* (1984) 71; (f) T.R. Herrinton and T.L. Brown, *J. Am. Chem. Soc., 107* (1985) 5700; (g) N.N. Turaki and J.M. Huggins, *Organometallics, 5* (1986) 1703; (h) R.M. Kowaleski, F. Basolo, W.C. Trogler, R.W. Gedridge, T.D. Newbound and R.D. Ernst, *J. Am. Chem. Soc., 109* (1987) 4860; (i) M.C. Baird, *Chem. Rev., 88* (1988) 1217; (j) N.A. Cooley, P.T.F. MacConnachie and M.C. Baird, *Polyhedron, 7* (1988) 1965; (k) F. Basolo, *Polyhedron, 9* (1990) 1535; (l) W.C. Watkins, T. Jaeger, C.E. Kidd, S. Fortier, M.C. Baird, G. Kiss, G.C. Roper and C.D. Hoff, *J. Am. Chem. Soc., 114* (1992) 907; (m) L. Song and W.C. Trogler, *J. Am. Chem. Soc., 114* (1992) 3355; (n) Q. Meng, Y. Huang, W.J. Ryan and D.A. Sweigart, *Inorg. Chem., 31* (1992) 4051; (o) R. Poli, B.E. Owens and R.G. Linck, *Inorg. Chem., 31* (1992) 662.

[4] (a) D.R. Tyler, *Prog. Inorg. Chem., 36* (1988) 125; (b) D. Astruc, *Chem. Rev., 88* (1988) 1189; (c) D.R. Tyler and F. Mao, *Coord. Chem. Rev., 97* (1990) 119; (d) D.R. Tyler, *Acc. Chem. Res., 24* (1991) 325.

[5] (a) B.T. Donovan and W.E. Geiger, *J. Am. Chem. Soc., 110* (1988) 2335; (b) D.J. Kuchynka and J.K. Kochi, *Inorg. Chem., 27* (1988) 2574; (c) *28* (1989) 855; (d) O.B. Ryan, M. Tilset and V.D. Parker, *J. Am. Chem. Soc., 112* (1990) 2618; (e) Y. Zhang, D.K. Gosser, P.H. Rieger and D.A. Sweigart, *J. Am. Chem. Soc., 113* (1991) 4062.

[6] D.J. Kuchynka, C. Amatore and J.K. Kochi, *Inorg. Chem., 25* (1986) 4087.

[7] C.C. Neto, C.D. Baer, Y.K. Chung and D.A. Sweigart, *J. Chem. Soc., Chem. Commun.*, (1993) 816.

[8] C.C. Neto, S. Kim, Q. Meng, D.A. Sweigart and Y.K. Chung, *J. Am. Chem. Soc., 115* (1993) 2077.

[9] (a) M.E. Rerek, L.-N. Ji and F. Basolo, *J. Chem. Soc., Chem. Commun.*, (1983) 1208; (b) M.E. Rerek and F. Basolo, *Organometallics, 2* (1983) 372; (c) L.-N. Ji, M.E. Rerek and F. Basolo, *Organometallics, 3* (1984) 740; (d) M.E. Rerek and F. Basolo, *J. Am. Chem. Soc., 106* (1984) 5908; (e) H. Bang, T.J. Lynch and F. Basolo, *Organometallics, 11* (1992) 40.

[10] (a) P. O'Brien and D.A. Sweigart, *J. Chem. Soc., Chem. Commun.*, (1986) 198; (b) N.J. Stone, D.A. Sweigart and A.M. Bond, *Organometallics, 5* (1986) 2553; (c) L.K. Safford and M.J. Weaver, *J. Electroanal. Chem., 331* (1992) 857.

[11] R.M. Wightman and D.O. Wipf, *Acc. Chem. Res., 23* (1990) 64.

[12] (a) R.M. Wightman and D.O. Wipf, *Electroanal. Chem., 15* (1989) 267; (b) C.D. Baer, C.A. Camaioni-Neto, D.A. Sweigart, A.M. Bond, T.F. Mann and G.A. Tondreau, *Coord. Chem. Rev., 93* (1989) 1; (c) A.M. Bond, K.B. Oldham and C.G. Zoski, *Anal. Chim. Acta, 216* (1989) 177.

[13] Y. Zhang, C.D. Baer, C. Camaioni-Neto, P. O'Brien and D.A. Sweigart, *Inorg. Chem., 30* (1991) 1682.

[14] (a) C.G. Zoski, D.A. Sweigart, N.J. Stone, P.H. Rieger, E. Mocellin, T.F. Mann, D.R. Mann, D.K. Gosser, M.M. Doeff and A.M. Bond, *J. Am. Chem. Soc., 110* (1988) 2109; (b) C. Amatore and F. Pflüger, *Organometallics, 9* (1990) 2276.

[15] R.B. King and M.B. Bisnette, *Inorg. Chem., 3* (1964) 791.

[16] T.A. James and J.A. McCleverty, *J. Chem. Soc., Dalton Trans.,* (1970) 850.

[17] (a) N.G. Connelly and L.F. Dahl, *J. Chem. Soc., Chem. Commun.,* (1970) 880; (b) R.B. King and A. Efraty, *Inorg. Chem., 8* (1969) 2374; (c) H. Brunner, *Z. Anorg. Allg. Chem., 368* (1969) 120.

[18] R.B. King and A. Efraty, *J. Organomet. Chem., 23* (1970) 527.

[19] (a) C.P. Casey, M.A. Andrews, D.R. McAlister and J.E. Rinz, *J. Am. Chem. Soc., 102* (1980) 1927; (b) W. Tam, G. Lin, W. Wong, W.A. Kiel, V.K. Wong and J.A. Gladysz, *J. Am. Chem. Soc., 104* (1982) 141.

[20] C.D. Baer, N.J. Stone and D.A. Sweigart, *Anal. Chem., 60* (1988) 188.

[21] (a) D.K. Gosser and P.H. Rieger, *Anal. Chem., 60* (1988) 1159; (b) D.K. Gosser and F. Zhang, *Talanta, 38* (1991) 715.

[22] *DigiSim 1.0 Program*, Bioanalytical Systems, Inc., West Lafayette, IN.

[23] S.D. Ittel, J.F. Whitney, Y.K. Chung, P.G. Williard and D.A. Sweigart, *Organometallics, 7* (1988) 1323.

[24] K.P. Pevear, M.M. Banazak Holl and D.A. Sweigart, submitted for publication.

[25] W.E. Geiger, P.H. Rieger, B. Tulyathan and M.D. Rausch, *J. Am. Chem. Soc., 106* (1984) 7000.

[26] Y. Huang and D.A. Sweigart, unpublished results.

[27] J. Ruiz, M. Lacoste and D. Astruc, *J. Am. Chem. Soc., 112* (1990) 5471.

[28] F. Mao, D.R. Tyler and D. Keszler, *J. Am. Chem. Soc., 111* (1989) 130.

[29] (a) F. Mao, D.R. Tyler, A.L. Rieger and P.H. Rieger, *J. Chem. Soc., Faraday Trans., 87* (1991) 3113; (b) F. Mao, D.R. Tyler, M.R.M. Bruce, A.E. Bruce, A.L. Rieger and P.H. Rieger, *J. Am. Chem. Soc., 114* (1992) 6418.