research. An Alfred P. Sloan Foundation Research Fellowship and a Union Carbide Innovation Recognition Program Award are appreciated by G.L.H. We thank Prof. Martin Minelli for very helpful discussions.

**Supplementary Material Available:** Experimental, spectroscopic, analytical, and crystallographic details, atomic coordinates, bond angles and distances, anisotropic thermal parameters, hydrogen atom coordinates (12 pages); observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

## Mechanism of CO Substitution in the 19-Electron Complex (MeCp)Mn(CO)$_2$NO

C. C. Neto, S. Kim, Q. Meng, and D. A. Sweigart*

*Department of Chemistry, Brown University Providence, Rhode Island 02912*

Y. K. Chung

*Department of Chemistry, Seoul National University Seoul 151-742, Korea*

*Received November 20, 1992*

Organometallic radicals containing 17 or 19 electrons about the metal have been recognized as playing an important role in a variety of transformations.[1] This is due in large part to the greatly increased rate of ligand substitution shown by the radicals when compared to 18-electron analogues. Ligand substitution at 17-electron centers generally follows an associative mechanism.[2] Very little quantitative information is available concerning ligand substitution at 19-electron centers, although it is often assumed that the mechanism is dissociative.[3,4] Of the two detailed mechanistic studies of 19-electron complexes reported to date, one 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.[5] A second study concerns dissociative CO substitution in Co(CO)$_3$L$_2$ (L$_2$ is 2,3-bis(diphenylphosphino)maleic anhydride).[6] In this case, however, it is known from recent ESR studies that the molecule is predominantly an 18-electron complex with a radical ligand; only 1.6% of the unpaired spin density is located on the metal.[7]

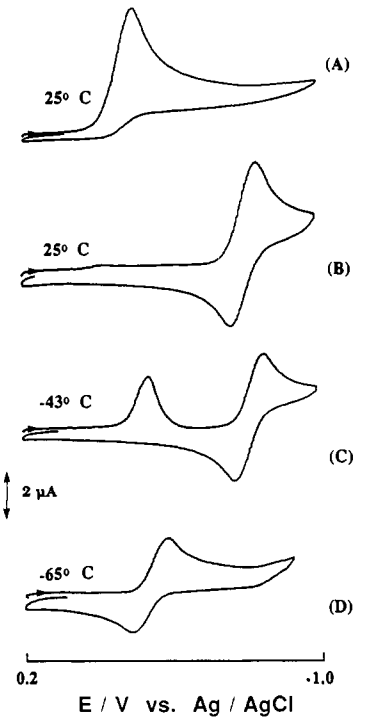
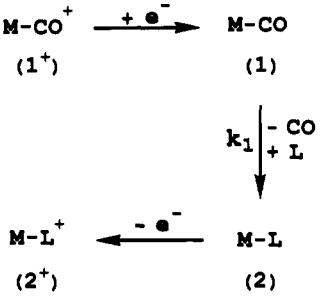



**Figure 1.** Cyclic voltammograms of 1.0 mM [(MeCp)Mn(CO)$_2$NO]PF$_6$ (**1**$^+$) in $CH_2Cl_2$/0.10 M $Bu_4NPF_6$ at the indicated temperatures with P(OEt)$_3$ present at a concentration of (A) 0 mM and (B–D) 10 mM. The working electrode was a 1.0 mm diameter glassy carbon disk, and the scan rate was 0.50 V/s. All potentials are relative to ferrocene $E_{1/2}$ = 0.52 V.

**Scheme I**




Herein it is shown that (MeCp)Mn(CO)$_2$NO$^+$ (**1**$^+$) undergoes efficient electron transfer catalyzed (ETC) substitution of CO by a range of P-donors (L = $PBu_3$, $PPh_3$, $P(OPh)_3$, $P(OEt)_3$, diphos, etc.) and that the initially formed 19-electron complex **1** reacts with L via a strictly dissociative pathway to give (MeCp)Mn(CO)(L)NO (**2**), which then is spontaneously oxidized to product **2**$^+$. Cyclic voltammetry of **1**$^+$ at 25 °C showed that the cathodic current due to the reduction of **1**$^+$ is completely suppressed in the presence of L and that new reversible couples at more negative potentials appear, which are due to **2**$^+$/**2**. A typical CV (with L = P(OEt)$_3$) is shown in Figure 1B. Proof of the identity of **2**$^+$ was provided by voltammetry of genuine samples[8] and by IR spectra obtained after bulk electrolysis of **1**$^+$ in the presence of 2 equiv of L; complete conversion to **2**$^+$ occurred after the passage of only 0.03 mol of electrons/mole of **1**$^+$.

(1) (a) *Organometallic Radical Processes*; Trogler, W. C., Ed.; Elsevier: Amsterdam, 1990. (b) Baird, M. C. *Chem. Rev.* **1988**, *88*, 1217. (c) Astruc, D. *Chem. Rev.* **1988**, *88*, 1189. (d) Tyler, D. R. *Prog. Inorg. Chem.* **1988**, *36*, 125. (e) Tyler, D. R. *Acc. Chem. Res.* **1991**, *24*, 325.

(2) (a) Basolo, F. *Polyhedron* **1990**, *9*, 1535. (b) Fox, A.; Malito, J.; Poë, A. *J. Chem. Soc., Chem. Commun.* **1981**, 1052. (c) Poë, A. *Trans. Met. Chem.* **1982**, *7*, 69. (d) Fawcett, J. P.; Jackson, R. A.; Poë, A. *J. Chem. Soc., Chem. Commun.* **1975**, 733. (e) Fawcett, J. P.; Jackson, R. A.; Poë, A. *J. Chem. Soc., Dalton Trans.* **1978**, 789. (f) Shi, Q.-Z.; Richmond, T. G.; Trogler, W. C.; Basolo, F. *J. Am. Chem. Soc.* **1984**, *106*, 71. (g) Kowaleski, R. M.; Basolo, F.; Trogler, W. C.; Gedridge, R. W.; Newbound, T. D.; Ernst, R. D. *J. Am. Chem. Soc.* **1987**, *109*, 4860. (h) Hershberger, J. W.; Klinger, Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 3771. (i) Herrinton, T. R.; Brown, T. L. *J. Am. Chem. Soc.* **1985**, *107*, 5700. (j) Turaki, N. N.; Huggins, J. M. *Organometallics* **1986**, *5*, 1703. (k) Cooley, N. A.; MacConnachie, P. T. F.; Baird, M. C. *Polyhedron* **1988**, *7*, 1965. (l) Watkins, W. C.; Macartney, D. H.; Baird, M. C. *J. Organomet. Chem.* **1989**, *377*, C52. (m) Zhang, Y.; Gosser, D. K.; Rieger, P. H.; Sweigart, D. A. *J. Am. Chem. Soc.* **1991**, *113*, 4062. (n) Watkins, W. C.; Jaeger, T.; Kidd, C. E.; Fortier, S.; Baird, M. C.; Kiss, G.; Roper, G. C.; Hoff, C. D. *J. Am. Chem. Soc.* **1992**, *114*, 907. (o) Poli, R.; Owens, B. E.; Linck, R. G. *Inorg. Chem.* **1992**, *31*, 662. (p) Song, L.; Trogler, W. C. *J. Am. Chem. Soc.* **1992**, *114*, 3355. (q) Meng, Q.; Huang, Y.; Ryan, W. J.; Sweigart, D. A. *Inorg. Chem.* **1992**, *114*, 4051.

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

(4) (a) Donovan, B. T.; Geiger, W. E. *J. Am. Chem. Soc.* **1988**, *110*, 2335. (b) Kuchynka, D. J.; Kochi, J. K. *Inorg. Chem.* **1988**, *27*, 2574. (c) Kuchynka, D. J.; Kochi, J. K. *Inorg. Chem.* **1989**, *28*, 855.

(5) Ruiz, J.; Lacoste, M.; Astruc, D. *J. Am. Chem. Soc.* **1990**, *112*, 5471.

(6) Mao, F.; Tyler, D. R.; Keszler, D. *J. Am. Chem. Soc.* **1989**, *111*, 130.

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

(8) The complexes **1**$^+$ and **2**$^+$ were synthesized by published procedures: Connelly, N. G.; Dahl, L. F. *J. Chem. Soc., Chem. Commun.* **1970**, 880. King, R. B.; Efraty, A. *Inorg. Chem.* **1969**, *8*, 2374. Typical IR bands in $CH_2Cl_2$ are as follows: **1**$^+$, 2116, 2077, 1845 cm$^{-1}$; **2**$^+$ (L = P(OEt)$_3$), 2047, 1803 cm$^{-1}$.

0002-7863/93/1515-2077$04.00/0 

Similarly, chemical reduction of $1^+$ with a trace of Na/Pb alloy afforded quantitative yields of $2^+$.

The ETC process occurs as shown in Scheme I. The homogeneous cross reaction between **2** and $1^+$ to give $2^+$ and **1** is highly favored and accounts for most of the conversion of **2** to $2^+$. Of primary interest in this paper is the mechanism of CO substitution at the 19-electron center, reaction $1 \rightarrow 2$. In order to determine the rate, it is necessary to observe a cathodic current for the reduction of *both* $1^+$ and $2^+$. Figure 1 shows that temperature variation can be utilized to slow the CO substitution so that both cathodic waves can be observed. Thus, at 25 °C (Figure 1B) the rate is rapid compared to the CV time scale and all **1** formed at the electrode surface is rapidly converted to **2** (and then $2^+$), so that the only observed cathodic wave is due to $2^+$. Conversely, at −65 °C (Figure 1D) the only cathodic wave is due to $1^+$ because the rate of $1 \rightarrow 2$ is too slow for a substantial amount of **2** to form. At −43 °C (Figure 1C) the reaction rate and CV time scale are competitive and a reduction wave is observed for both $1^+$ and $2^+$; it was found that variation of the nucleophile concentration or external CO pressure had *no effect* on the CV under these conditions, indicating a rate independent of [L] and [CO]. Furthermore, CVs obtained at −43 °C with a variety of P-donors were very similar, which implies the *same* rate for all L. In other words, the mechanism is strictly dissociative, with the rate-determining step being CO loss from **1** to give the 17-electron intermediate, (MeCp)Mn(CO)NO, which is trapped rapidly and completely by nucleophile L.[9]

A digital simulation program[10] was used to determine the rate of $1 \rightarrow 2$. The simulations showed the CVs to be very sensitive to the rate constant for CO dissociation ($k_1$) but insensitive to the rate constant for the homogeneous cross reaction,[11] provided the latter is greater than ca. $10^4$ $M^{-1}$ $s^{-1}$. The rate constant $k_1$ was measured over the temperature range −30 to −50 °C with the following results: $\Delta H^{\ddagger} = 72 \pm 8$ kJ; $\Delta S^{\ddagger} = 90 \pm 15$ J $K^{-1}$; $k_1 = 11$ $s^{-1}$ at −43 °C. The entropy term clearly signals a dissociative process. The enthalpy term seems reasonable for the loss of $^1/_2$ bond order[1d,e,2a-e] in going from 19 $e^-$ to 17 $e^-$; by comparison, $\Delta H^{\ddagger}$ for CO dissociation from 18-$e^-$ complexes (loss of 1 bond order) is much higher: $Cr(CO)_6$, 162 kJ; $Fe(CO)_4PPh_3$, 178 kJ; $Co(CO)_2(NO)AsPh_3$, 142 kJ; $CpV(CO)_4$, 230 kJ.[12] It is therefore established that CO substitution in the 19-electron **1** is dissociative.

It is reasonable to inquire if **1** is really a 19-electron complex or whether the odd electron is localized in ligand orbitals (especially the nitrosyl). An ESR study[13] of $CpM(CO)_2NO^-$ (M = Cr, Mo), which is isoelectronic with $CpMn(CO)_2NO$, is directly relevant to this question. This study showed that the NO ligand bends and acquires ca. 40% of the unpaired spin density 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 can be reasonably described as 19-electron complexes. It is highly likely that $(MeCp)Mn(CO)_2NO$ (**1**) is similarly best formulated as a 19-electron complex. The simple observation that complex **1** reacts by a dissociative mechanism also argues against the possibility that **1** is a 17-electron complex (with the NO ligand being a 1-electron donor) because 17-electron complexes always react by an associative mechanism unless steric factors dominate.[2a,g,14]

In order to assess the increase in substitution rate in 19-electron compared to 18-electron complexes, the direct reaction of $1^+$ with several phosphines was studied. It was found that the reaction to give $2^+$ is clean, but the rates were difficult to reproduce. Sometimes, but not always, an induction period was observed and the rates (in the dark under $N_2$) varied by a factor of 10 for ostensibly the same reaction conditions (e.g., $1 \text{ h} \leq t_{1/2} \leq 10$ h with $[1^+] = 10^{-3}$ M and $[PPh_3] = 10^{-2}$ M). This suggests the possibility that the rate of conversion of $1^+$ to $2^+$ may be determined by the presence of adventitious reductants that initiate an ETC process. In accordance with this is the observation by McCleverty[15] that normally slow CO substitution in $1^+$ becomes rapid in the presence of a catalytic amount of reducing agent $NEt_3$.

Finally, we note that one of the important features of organometallic reactions is the reactivity dependence on the metal in a triad. Within the context of this paper, it was found that $CpRe(CO)_2NO^+$ is reversibly reduced at the same potential as $1^+$, but unlike **1**, $CpRe(CO)_2NO$ is *completely unreactive* (on the CV time scale) toward P-donor nucleophiles. This shows that the reactivity with respect to CO dissociation in these 19-electron complexes follows the order Mn ≫ Re, which likely reflects the stronger M–CO bond in the heavier transition metal.[16]

**Acknowledgment.** This work was supported by a grant from the National Science Foundation (No. CHE-8821588). We are grateful to Prof. P. H. Rieger for helpful discussions.

(9) With the weak nucleophile $AsPh_3$, a rate retardation occurred when the atmosphere was changed from $N_2$ to CO, showing that CO can compete with $AsPh_3$ for the reaction intermediate. When no nucleophile is present, it is known from previous work that the chemical reduction of $1^+$ with $NEt_3$ or $NaBH_4$ leads to simple dimerization to afford $[(MeCp)Mn(CO)(NO)]_2$: James, T. A.; McCleverty, J. A. *J. Chem. Soc., Dalton Trans.* **1970**, 850. King, R. B.; Bisnette, M. B. *Inorg. Chem.* **1964**, *3*, 791.

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

(11) Multiple scan CVs showed that the rate constant must be greater than $10^4$ $M^{-1}$ $s^{-1}$.

(12) Howell, J. A. S.; Burkinshaw, P. M. *Chem. Rev.* **1983**, *83*, 557.

(13) Geiger, W. E.; Rieger, P. H.; Tulyathan, B.; Rausch, M. D. *J. Am. Chem. Soc.* **1984**, *106*, 7000.

(14) Kowaleski, R. M.; Basolo, F.; Trogler, W. C.; Ernst, R. D. *J. Am. Chem. Soc.* **1986**, *108*, 6046.

(15) James, T. A.; McCleverty, J. A. *J. Chem. Soc., Dalton Trans.* **1970**, 850.

(16) The same reactivity order obtains with (arene)$M(CO)_3$ (M = Mn, Re): Neto, C. C.; Baer, C. D.; Chung, Y. K.; Sweigart, D. A. Submitted for publication.

## Sensitive Detection of Catalytic Species without Chromophoric Substrates

James W. Lane, Xingfang Hong, and Alan W. Schwabacher*

*Department of Chemistry*
*Iowa State University*
*Ames, Iowa 50011*

*Received December 2, 1992*

The development of antibodies as catalysts[1a,b] has allowed preparation of enzymelike materials that catalyze reactions with predetermined specificity. Monoclonal antibodies to transition-state analogues[1c] catalyze reactions as enzymes do: by preferentially binding and stabilizing the transition state.[1d] These catalysts are selected from a large repertoire of structures, initially by screening for antibodies that bind antigen, and then, usually after expensive scaleup, for activity.[2] Screening directly for activity, rather than binding, would be particularly valuable, considering that many of the most efficient antibody catalysts operate by mechanisms for which the eliciting antigens were not good transition-state analogs.[3]

Efficient screening of antibody activity is critical to the identification of catalysts,[2] and sensitive assays can greatly facilitate

(1) (a) Tramontano, A.; Janda, K.; Lerner, R. *Science* **1986**, *234*, 1566–1570. (b) Pollack, S. J.; Jacobs, J. W.; Schultz, P. G. *Science* **1986**, *234*, 1570. (c) Jencks, W. P. *Catalysis in Chemistry and Enzymology*; McGraw-Hill: New York, 1969; p 288. (d) Pauling, L. *Am. Sci.* **1948**, *36*, 51.

(2) (a) *Catalytic Antibodies, Ciba Foundation Symposium 159*; Wiley: Chichester, 1991. (b) Lerner, R. A.; Benkovic, S. J.; Schultz, P. G. *Science* **1991**, *252*, 659–667. (c) Tarasow, T.; Hilvert, D. In *Protein Engineering and Design: An Introduction*; Wrede, P., Schneider, G., Eds.; Walter de Gruyter: New York, in press.

(3) (a) Martin, M. T.; Napper, A. D.; Schultz, P. G.; Rees, A. R. *Biochemistry* **1991**, *30*, 9757–9761. (b) Wirsching, P.; Ashley, J. A.; Benkovic, S. J.; Janda, K. D.; Lerner, R. A. *Science* **1991**, *252*, 680–685. (c) Janda, K. D.; Lerner, R. A.; Tramontano, A. *J. Am. Chem. Soc.* **1988**, *110*, 4835–4837.

0002-7863/93/1515-2078$04.00/0 