# LIGAND EFFECTS ON THE REDOX POTENTIALS OF METAL CARBONYLS

## RELATIONSHIP TO CO FORCE CONSTANTS IN MANGANESE(I) DERIVATIVES

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**Abstract**—The reversible oxidation potentials  $E^0$  of a single series of methylcyclopentadienyldicarbonylmanganese(I) derivatives  $\eta^5$ -MeCpMn(CO)<sub>2</sub>L are measured for a wide variety of ligand types, including L = alkyl and aromatic amines, alkyl cyanide and isocyanide, alkene, alkyl and aryl phosphines and phosphites. The relationship of  $E^0$  with the carbonyl force constants evaluated by the Cotton–Kraihanzel method is presented.

Oxidation and reduction are important properties of metal carbonyls since they can strongly influence the rates and course of reactions. For example, ligand substitutions and rearrangements of carbonylmetal derivatives have been shown to proceed rapidly when they are induced simply by either a one-electron oxidation or reduction.<sup>1-5</sup> As such. it is important to ascertain the functional relationship between the structure of metal carbonyl and its redox potential. Indeed Treichel et al.6,7 recognized a linear relationship between the potential  $E_{1/2}$  for the one-electron oxidation of a series of manganese carbonyls  $[Mn(CO)_{6-n}(CNR)_n]^+$  with the number of alkyl and aryl isocyanide ligands varying from 1 < n < 6. Moreover, Sarapu and Fenske<sup>8</sup> have analyzed the bonding properties of the methyl isocyanide and carbonyl ligands in  $[Mn(CO)_{6-n}(CNMe)_n]^+$  for 0 < n < 6 via approximate molecular orbital calculations, and have found that the values of  $E_{1/2}$  do correlate extremely well with the calculated HOMO energies. It is noteworthy that they found the approximate force constants for the carbonyl stretching frequencies v(CO) evaluated by the Cotton-Kraihanzel method9 to also correlate with the computed electron occupation of the carbonyl  $5\sigma$  and  $5\pi$  orbitals.

Similar relationships between the oxidation potential and the degree of substitution in the mixed carbonyl/acetonitrile complexes of chromium and tungsten, i.e.  $Cr(CO)_{6-n}(NCMe)_n$  and

 $W(CO)_{6-n}(NCMe)_n$ , have also been noted.<sup>10,11</sup> Several recent studies have discussed the correlation of the oxidation potentials of various metal carbonyl derivatives with the infrared data, particularly the carbonyl stretching frequencies.<sup>12-18</sup> Such studies have encompassed a variety of ligands, including such nitrogen-centred ones as dinitrogen, alkyl and aryl cyanides, ammonia, cyanide, thiocyanate, and azide, etc. in addition to carbon monoxide and the halides [12, 14]. The effects of phosphorus-centred ligands such as alkyl and aryl phosphines and phosphites on the potentials of metal carbonyls have also been examined.<sup>15,16</sup> In this context, the studies of Connelly and Kitchen<sup>16</sup> are particularly pertinent, since they showed that the oxidation potentials for the series of manganese carbonyls  $\eta^{5}$ -MeCpMn(CO)<sub>3,b</sub>L<sub>n</sub> with L = phosphorus(III) alkyls, aryls, alkoxides, phenoxides, etc. were directly related to the Cotton-Kraihanzel force constants derived from the carbonyl stretching frequencies.

In order to examine the general effect associated with the use of a wide variety of ligand types on the oxidation potential of a metal carbonyl, we focussed our attention on the mono-substitution products of  $\eta^{5}$ -MeCpMn(CO)<sub>3</sub>. The choice of this carbonylmetal system is particularly appropriate since the one-electron oxidation is usually reversible and allows the oxidation potential E<sup>0</sup> to be determined. Moreover, by focussing on a single carbonylmetal system, i.e.  $\eta^{5}$ -MeCpMn(CO)<sub>2</sub>L we hoped to minimize ambiguities related to the evaluation of the force constants based on the Cotton–Kraihanzel method.<sup>9</sup>

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### **EXPERIMENTAL**

Synthesis of carbonylmanganese derivatives  $\eta^{5}$ -MeCpMn(CO)<sub>2</sub>L

The monosubstituted carbonylmanganese derivatives  $\eta^{5}$ -MeCpMn(CO)<sub>2</sub>L listed in Table 1 were prepared from  $\eta^{5}$ -MeCpMn(CO)<sub>2</sub>(THF), which was generated *in situ* by irradiation of a solution of the parent tricarbonyl complex in tetrahydrofuran (THF) under argon.<sup>19</sup>



The photochemical reactor consisted of a 300 cm<sup>3</sup> cylindrical flask with a 100 watt medium pressure Hg lamp contained in a quartz immersion well.

All preparative reactions and ligand exchange studies were carried out by benchtop manipulations under either a nitrogen or an argon atmosphere in Schlenk flasks. Many of the manganese complexes employed in this study are generally air

sensitive, both in the solid state as well as in solutions. In a typical procedure, a solution of 2 g of  $(\eta^5-C_5H_4Me)Mn(CO)_3$  in 300 cm<sup>3</sup> THF was deaerated, and irradiated for 50 min at 0°C. The IR spectrum of the solution indicated that  $\sim 90\%$ of the starting material was converted to  $(\eta^{5}-C_{5}H_{4}Me)Mn(CO)_{2}(THF)^{26}$  One equivalent of the appropriate ligand (L = py, MeCN, piperidine, PPh<sub>3</sub>,  $P(C_6H_4Me-p)_3$ ,  $P(C_6H_4Cl-p)_3$ P(OMe)<sub>3</sub>, P(OPh)<sub>3</sub>, PEt<sub>3</sub>, P(Me)Ph<sub>2</sub>, P(OMe)Ph<sub>2</sub>, CNCMe<sub>3</sub>, Me<sub>2</sub>-SO, AsPh<sub>3</sub>, and SbPh<sub>3</sub>) was added, and the solution stirred for several hours at ambient temperatures. During this period, the deep purple color of the tetrahydrofuran complex gave way to the yellow or orange color of the product. The THF was removed at reduced pressure, and the residue was taken up in ethyl ether. [When the product was not soluble in ether, chloroform was employed.] Filtration of the solution, followed by crystallization from a mixture of ether and hexane or chloroform and ethanol afforded crystalline products in 30–70% yield. For  $L = PEt_3$ and  $P(OMe)_3$ , the products were oils, which were purified by chromatography on Florisil according to the literature description.<sup>16</sup> For  $L = SO_2$ , sulphur dioxide gas (1 atm.) was bubbled through the solution of  $(\eta^5-C_5H_4Me)Mn(CO)_2$ 

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Table	1.	Methylcyclopentadienyldicarbonylmanganese(I) derivatives	
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L	IR†		m.p., °C‡ (lit)	Elemental analysis for new compounds					
				Found			Calc.		
		· 'a		С%	Н%	X%	C%	Н%	X%
1	СО	2024, 1946	oil						
2	PEt <sub>3</sub>	1937, 1874	oil [16]						
3	PPh <sub>3</sub>	1944, 1884	118-119 (119-120) [23]						
4	$P(C_6H_4Me-p)_3$	1939, 1879	184-186	70.38;	5.82		70.44	5.71	
5	$P(C_6H_4Cl-p)_3$	1946 1887	156-158	56.10;	3.45	(Cl, 19.28)	56.20	3.45	(Cl, 19.14)
6	$P(Me)Ph_2$	1940, 1878	57-58 (55-57) [24]			,			· · · ·
7	P(OMe)Ph <sub>2</sub>	1944, 1884	64-66	62.41	5.16		62.08	4.96	
8	P(OMe) <sub>3</sub>	1947, 1892	oil [16]						
9	P(OPh) <sub>3</sub>	1970, 1910	75-77 (75-76) [22]						
10	MeCN	1950, 1886	73 (dec)	52.07	4.26	(N, 6.34)	51.97	4.36	(N, 6.06)
11	NC₅H₅ (py)	1934, 1868	72–73 (75) [21]			,			
12	$HN(CH_2)_5$	1929, 1860	71–72 (71–73) [20]						
13	Norbornene	1969, 1910	65-66	63.56	6.00		63.38	6.03	
14	CNCMe <sub>3</sub>	1954, 1908	53-54.5	57.09	5.78	(N, 5.23)	57.15	5.90	(N, 5.13)
15	THF	1927, 1850§							
16	Me <sub>2</sub> SO	1960, 1896	64–66 (66) [25]						
17	SO <sub>2</sub>	2018, 1976	90 (dec) (73) [25]						
18	AsPh <sub>3</sub>	1941, 1881	117-119 (118-120) [16]						
19	SbPh3	1940, 1884	99–100	57.79	4.19		57.50	4.08	

 $\dagger$ Carbonyl stretching frequencies in cm<sup>-1</sup>.

<sup>‡</sup>Melting points are uncorrected.

§The IR spectrum was recorded in THF.

The IR spectrum of this compound is reported in Ref. 26.

(THF) in THF with rapid stirring. The reaction was complete at room temperature within a few minutes. Crystallization of the product from a mixture of ether and hexane afforded orange crystals in 53% yield based on  $(\eta^{5}-C_{5}H_{4}Me)$ Mn(CO)<sub>3</sub>. Since THF is not readily displaced from  $(\eta^{5}-C_{5}H_{4}Me)Mn(CO)_{2}(THF)$  by norbornene,  $(\eta^{5}-C_{5}H_{4}Me)Mn(CO)_{2}(norbornene)$  was prepared directly by the irradiation of  $(\eta^{5}-C_{5}H_{4}Me)Mn(CO)_{3}$ (2.0 g) in 300 cm<sup>3</sup> of toluene containing a 20-fold excess of norbornene. The product was purified by crystallization from *n*-heptane, and obtained in 59% yield.

The microanalyses included in Table 1 were performed either by Midwest Microlabs, Ltd., Indianapolis, Indiana, or by Galbraith Laboratories, Inc., Knoxville, Tennessee.

The infrared spectra of the series of  $\eta^{5}$ -MeCpMn(CO)<sub>2</sub>L were measured in heptane solution on a Perkin-Elmer model 298 spectrophotometer.

Electrochemical measurements were performed on a Princeton Applied Research Model 173 potentiostat equipped with a Model 176 current-tovoltage converter, which provided a feedback compensation for ohmic drop between the working and reference electrodes. The high impedance voltage follower amplifier (PAR Model 178) was mounted external to the potentiostat to minimize the length of the connection to the reference electrode for low noise pickup. Cyclic voltammetry was carried out in a cell designed according to Van Duyne and Reilley.<sup>27</sup> The configuration of this cell is convenient for low temperature experiments since the lower portion of the cell containing the working solution could be easily submerged in the desired cold bath contained in a Dewar flask. The distance between the Pt electrode and the tip of the salt bridge was less than 2 mm to minimize ohmic drop. The reference electrode was isolated from the cold bath and maintained at room temperature  $(\sim 25^{\circ}C)$ . The voltammograms were recorded on a Houston Series 2000 X-Y recorder. CV scans were measured several minutes after agitation to ensure thermal equilibration. Electrode aging was not a serious problem in this study. Between experiments the platinum wire was soaked briefly in concentrated nitric acid, rinsed with distilled water, and dried at 110°C.

### **RESULTS AND DISCUSSION**

The electrochemical behaviour of the manganese carbonyls in Table 1, was examined by cyclic voltammetry (CV) carried out at a stationary platinum microelectrode in acetonitrile solutions containing 0.1 M tetraalkylammonium perchlorates as supporting electrolytes. The initial anodic scans for the cyclic voltammorgrams of the pyridine, triphenylphosphine, and carbon monoxide derivatives of MeCpMn(CO)<sub>2</sub>L in Fig. 1 are all characterized by ratios of the anodic and cathodic currents  $(i_p^{a}/i_pc)$  of unity and by anodic and cathodic peak separations  $(E_p^{a} - E_p^{c})$  of near 60 mV for reversible one-electron processes, i.e.

$$MeCpMn(CO)_{2}L \stackrel{E^{0}}{\leftarrow} MeCpMn(CO)_{2}L^{+} + e^{-}.$$
 (2)

Hereafter the average value  $(E_p^a + E_p^c)/2$  will be taken as the measure of the oxidation potential  $E^{0.28}$ 

The cyclic voltammetry of the piperidine and pyridine derivatives could not be examined in acetonitrile solutions owing to a rapid electrocatalytic ligand substitution described elsewhere.<sup>29</sup> Accordingly, the cyclic voltammograms for these complexes were recorded for acetone solutions containing 0.1 M TEAP. The difference in solvent effects between acetonitrile and acetone on  $E^0$  for these complexes appears to be minimal since an examination of several alkyl and aryl phosphine and phosphite complexes indicated the values of  $E^0$  to be virtually solvent independent.

The magnitude of the reversible oxidation potentials  $E^0$  of the series of MeCpMn(CO)<sub>2</sub>L listed in Table 2 is strongly dependent upon the nature of the coordinated ligand L. Thus the nitrogencentred ligands such as amines and nitriles effect the most negative values in the range.  $-0.04 \text{ V} < \text{E}^{0} < 0.19 \text{ V}$ . The reversible potentials of alkyl and aryl phosphine complexes are clustered around  $0.5 \pm 0.1$  V, but those of corresponding phosphites are significantly more positive. Among carbon-centred ligands, the values of  $E^0$ become progressively more positive in the order: alkene (norbornene, 0.44 V) < isocyanide (tert-BuNC,  $0.53 \text{ V} \ll \text{carbon}$  monoxide (1.15 V). In-



Fig. 1. Variation in  $E^0$  for various MeCpMn(CO)<sub>2</sub>L as shown by the reversible cyclic voltammograms recorded at 100 mV s<sup>-1</sup> in acetonitrile containing 0.1 M tetraethylammonium perchlorate at 22°C [CO derivative measured at 200 mV s<sup>-1</sup> and  $-28^{\circ}$ C].

	L	Solvent	Epox	E <sup>0</sup>	i <sub>p</sub> <sup>a</sup> /i <sub>p</sub> <sup>c</sup>
			(V)	(V)	•••
1	со	MeCN <sup>e</sup>	1.15	1.10	1.0
2	PEt <sub>3</sub>	Me <sub>2</sub> CO	0.44	0.40	1.0
3	PPh₃	MeCN	0.55	0.52	1.0
4	PPh3	Me <sub>2</sub> CO	0.55	0.52	1.0
5	P(C <sub>6</sub> H <sub>4</sub> Me-p) <sub>3</sub>	MeCN	0.53	0.50	1.0
6	P(C <sub>6</sub> H <sub>4</sub> Cl-p) <sub>3</sub>	MeCN	0.64	0.60	1.0
7	P (Me) Ph <sub>2</sub>	MeCN	0.53	0.49	1.0
8	P(OMe)Ph <sub>2</sub>	MeCN	0.65	0.62	1.0
9	P(OMe) <sub>3</sub>	MeCN	0.72	0.68	1.0
10	P(OPh) <sub>3</sub>	MeCN	0.91	0.85	1.0
11	MeCN	Me <sub>2</sub> CO <sup>b</sup>	0.18	0.12	1.0
12	MeCN	CH <sub>2</sub> C1 <sub>2</sub> C	0,20	0.15	1.0
13	MeCN	MeCN	0.22	0.19	1.0
14	NC <sub>5</sub> H <sub>5</sub> (py)	Me <sub>2</sub> CO	0.14	0.11	1.0
15	HN(CH <sub>2</sub> ) <sub>5</sub>	Me <sub>2</sub> CO	0.02	-0.04	1.1
16	norbornene	MeCNd	0.49	0 44	1 1
17	CNCMe <sub>1</sub>	MeCN	0.58	0.53	1.0
18	CNCMe <sub>3</sub>	Me <sub>2</sub> CO	0.59	0.54	1 0
19	THF	THEF	0.09	h	
20	Me <sub>2</sub> SO	MeCN	0.73	h	
21	S02	Me <sub>2</sub> CO	1,06 <sup>g</sup>	h	
22	AsPh	MeCN	0.55	h	
23	SbPh <sub>3</sub>	MeCN	0.65	h	

Table 2. The cyclic voltammetric parameters of  $\eta^{5}$ -MeCpMn(CO)<sub>2</sub>L<sup>a</sup>

<sup>a</sup> Cyclic voltammetry performed at a Pt microelectrode with solutions 10<sup>-3</sup> M in substrate and 0.1 N in supporting electrolyte (tetraethylammonium perchlorate for MeCN or acetone, tetrabutylammonium perchlorate for THF or CH<sub>2</sub>Cl<sub>2</sub>). Unless otherwise noted, the scan rate was 100 mV s<sup>-1</sup> and T = 22 °C. Potentials reported relative to the Cp<sub>2</sub>Fe/Cp<sub>2</sub>Fe<sup>+</sup> couple taken to have  $(E_p^{OX} + E_p^{red})/2 = 0.31$  V in all solvents. <sup>b</sup> Scan rate = 50 mV s<sup>-1</sup>, T = -55 °C. <sup>c</sup> Scan rate = 800 mV s<sup>-1</sup>. <sup>d</sup> Scan rate = 200 mV s<sup>-1</sup>, T = -50 °C. <sup>e</sup> Scan rate = 200 mV s<sup>-1</sup>, T = -28 °C. <sup>f</sup> Scan rate = 30 mV s<sup>-1</sup>. <sup>g</sup> Value difficult to reproduce owing to the rapid deactivation of the Pt electrode. Experimental error in voltage is ± 0.01 V. <sup>h</sup> Irreversible CV wave.

deed the potential of the carbon monoxide complex MeCpMn(CO)<sub>3</sub> is the most positive of the derivatives listed in Table 2. We can deduce from these trends that the ease with which various MeCpMn(CO)<sub>2</sub>L are oxidized is qualitatively dependent on the  $\sigma$ -donor property of L and by its  $\pi$ -acidity. For example, among complexes with nitrogen ligands, E<sup>0</sup> becomes progressively more negative with increasing base strengths of L in the order: acetonitrile < pyridine ≪ piperidine. Moreover, we infer from the significantly more negative value of  $E^0$  for MeCpMn(CO)<sub>2</sub>-(CNBu-t) compared to the  $E^0$  for MeCpMn(CO)<sub>3</sub> that the ligand basicities are in the order: t-butyl isocyanide > carbon monoxide, as elaborated by Sarapu and Fenske<sup>8</sup> for the series of  $Mn(CO)_{6-n}(CNMe)_{n+1}$ .

From the IR data presented in Table 1, we applied the method of Cotton and Kraihanzel<sup>9</sup> to derive the carbonyl force constants for these

carbonyl-manganese complexes. The derived force constants k(CO) are listed in Table 3, and they are plotted vs the reversible oxidation potentials in Fig. 2. The extensive scatter of the points indicate no general correlation of k(CO) with  $E^0$  for this single series of carbonylmanganese derivatives. However a closer inspection reveals a limited correlation among the various phosphorus(III) ligands. Thus the arbitrary line drawn in Fig. 2 includes only those phosphine and phosphite ligands with a correlation coefficient of 0.86 [30]. The complexes derived from the nitrogen-centred ligands such as piperidine, pyridine and acetonitrile as well as the carbon-centred ligands such as *t*-butyl isocyanide, norbornene and carbon monoxide clearly lie beyond any reasonable relationship with those containing phosphorus(III) ligands.31

The oxidation potentials of a series of chromium

#### Redox potentials of metal carbonyls

	L	k(CO) (mdyn Å <sup>-1</sup> )		L	k (CO) (medyn Å <sup>-1</sup> )
1	со	15.71	11	NC <sub>5</sub> H <sub>5</sub> (py)	14.60
2	PEt <sub>3</sub>	14.66	12	HN(CH <sub>2</sub> )5	14.50
3	PPh <sub>3</sub>	14.80	13	norbornene	15.19
4	P(C <sub>6</sub> H <sub>4</sub> Me-p) <sub>3</sub>	14.72	14	CNCMe <sub>3</sub>	15.06
5	P(C <sub>6</sub> H <sub>4</sub> C1-p) <sub>3</sub>	14.83	15	THF	14.41
6	P (Me) Ph <sub>2</sub>	14.72	16	Me <sub>2</sub> SO	15.01
7	$P(OMe)Ph_2$	14.80	17	S02	16.10
8	P(OMe) <sub>3</sub>	14.88	18	AsPh <sub>3</sub>	14.75
9	P(OPh)₃	15.20	19	SbPh 3	14.76
10	MeCN	14.86			

Table 3. Carbonyl force constants for  $\eta^{5}$ -MeCpMn(CO)<sub>2</sub>L<sup>a</sup>

<sup>8</sup> Experimental force constant error:  $\pm$  0.02 mdyn Å<sup>-1</sup>



Fig. 2. Relationship between  $E^0$  of MeCpMn(CO)<sub>2</sub>L and the Cotton-Kraihanzel carbonyl force constant for various ligands L containing phosphorus(III) centres, nitrogen centres (pip = piperidine, py = pyridine), and carbon centres as labelled. The least squares line is arbitrarily drawn only through the phosphorus(III) derivatives, see text.

carbonyls with the  $Cr(CO)_5$  moiety bound to a variety of ligands L are also known [3, 32]. Figure 3 shows the relationship between the oxidation potentials of the manganese dicarbonyls Me-CpMn(CO)<sub>2</sub>L with those of the corresponding chromium pentacarbonyls (OC)<sub>5</sub>CrL for some of the representative ligands included in Fig. 2. The reasonable correlation is consistent with HOMO energies of both series of complexes which are affected in similar ways by amine, phosphine,



Fig. 3. Comparative effects of phosphorus(III)-, nitrogen-, and carbon-centred ligands on  $E^0$  on the series of MeCpMn(CO)<sub>2</sub>L and (OC)<sub>5</sub>CrL. [Data for *t*-Bu-NC(OC)<sub>5</sub>Cr taken from Ref. 18.]

isocyanide and carbonyl ligands with different  $\sigma$ and  $\pi$ -bonding characteristics. However the small slope indicates that the effect in the chromium carbonyls is attenuated to about a half of that in the manganese carbonyls. Thus the carbonyl force constants in (OC)<sub>5</sub>CrL are also unlikely to be measures of their oxidation potentials when a broad series of donors are considered. In this connection, the recent empirical approach by Chatt *et al.*<sup>13</sup> to the prediction of redox potentials based on linear free energy relationships appears to be a more inclusive method.

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- 30. The least squares slope is  $1.14 \text{ mdyn } \text{\AA}^{-1} \text{V}^{-1}$  with an intercept of  $14.2 \text{ mdyn } \text{\AA}^{-1}$ .
- 31. The anodic CV peak potential  $E_p$  (measured at a scan rate of 100 mV s<sup>-1</sup>) shows a similar correlation with k(CO), and includes all the derivatives listed in Table 1. The line for the phosphorus(III) ligands has a slope of 1.08 mdyn Å<sup>-1</sup>V<sup>-1</sup> with an intercept of 14.1 mdyn Å<sup>-1</sup>. The correlation coefficient of 0.94 is slightly better than that in Fig. 2.
- 32. See also Ref. 12.