derivative with Mn(CO)$_5$X (X = Br or Cl) gave only (CH$_3$)$_3$SnMn(CO)$_5$.[11] Reaction of (CH$_3$)$_2$C=NOSn(CH$_3$)$_3$ with C$_5$H$_5$Mo(NO)$_2$Cl in diethyl ether gave an unidentified yellow solid suggested by its NMR spectrum to contain (CH$_3$)$_3$Sn groups but neither C$_5$H$_5$ nor (CH$_3$)$_2$C groups. Reaction of (CH$_3$)$_2$C=NOSn(CH$_3$)$_3$ with C$_5$H$_5$Fe(CO)$_2$Cl in boiling benzene gave only (CH$_3$)$_3$SnFe(CO)$_2$C$_5$H$_5$.[12] No tractable products were obtained from reactions of (CH$_3$)$_2$-C=NOSn(CH$_3$)$_3$ with Fe$_2$(CO)$_9$ or [Mo(NO)$_2$Cl$_2$]$_n$ in ethereal solvents at or near room temperature. These observations suggest that the range of transition metal systems to which (CH$_3$)$_2$C=NOSn(CH$_3$)$_3$ can transfer (CH$_3$)$_2$CNO groups is extremely limited and that in some cases this tin reagent instead transfers (CH$_3$)$_3$Sn or possibly (CH$_3$)$_3$SnO units to the transition metal system.

Registry No. Me$_2$CNOMo(CO)$_2$Cp, 61491-36-9; (CH$_2$)$_5$CNOMo(CO)$_2$Cp, 61813-21-6; (CH$_2$=CH)(Me)CNOMo-(CO)$_2$Cp, 61813-22-7; (Me$_2$C=CH)(Me)CNOMo(CO)$_2$Cp, 61813-23-8; CH$_2$=CH(CH$_2$)$_2$C(Me)NOMo(CO)$_2$Cp, 61813-24-9; Me$_2$CNOW(CO)$_2$Cp, 61813-25-0; (CH$_2$)$_5$CNOW(CO)$_2$Cp, 61813-26-1; (CH$_2$=CH)(Me)CNOW(CO)$_2$Cp, 61813-27-2; (Me$_2$C=CH)(Me)CNOW(CO)$_2$Cp, 61813-28-3; CH$_2$=CH-(CH$_2$)$_2$C(Me)NOW(CO)$_2$Cp, 61813-29-4; (CH$_3$)$_2$C=NOSn(CH$_3$)$_3$, 25092-71-1; (CH$_3$)$_2$C=CHC(CH$_3$)=NOSn(CH$_3$)$_3$, 61812-49-5; H$_2$C=CH(CH$_2$)$_2$C(CH$_3$)=NOSn(CH$_3$)$_3$, 61812-50-8; C$_5$H$_5$-Mo(CO)$_3$Cl, 12128-23-3; C$_5$H$_5$W(CO)$_3$Cl, 12128-24-4; mesityl oxide oxime, 2158-24-9; trimethyltin chloride, 1066-45-1; allylacetone oxime, 59239-06-4; ^{13}C, 14762-74-4.

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Electrochemical Studies on [Mn(CNR)$_6$]$^+$ Complexes

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The $E_{1/2}$ values for the processes [MnL$_6$]$^+$ $\rightleftarrows$ [MnL$_6$]$^{2+}$ + e$^-$ and [MnL$_6$]$^{2+}$ $\rightleftarrows$ [MnL$_6$]$^{3+}$ + e$^-$ (L = eleven aryl and four alkyl isocyanides) in dichloromethane were determined by cyclic voltammetry. The alkyl isocyanide complexes are easier to oxidize than the aryl isocyanide complexes in keeping with the better donor strength of these ligands. For the complexes of the aryl isocyanides there is substantial variation of $E_{1/2}$ values. A good correlation between $E_{1/2}$ values for complexes of meta- and para-substituted phenyl isocyanides and Hammett σ values is obtained.

Manganese(I) complexes of organic isocyanides [Mn-(CNR)$_6$]$^+$ are known[1] to react with oxidizing agents such as HNO$_3$ giving the manganese(II) species [Mn(CNR)$_6$]$^{2+}$. The reverse reaction is effected by reducing agents including the free ligand itself; hence the synthesis of [Mn(CNR)$_6$]$^+$ complexes from reactions of an isocyanide and a manganese(II) salt is often encountered. Recently, electrochemical studies have been reported for [Mn(CNR)$_6$]$^+$ complexes. By using both dichloromethane[2] and acetonitrile,[3] $E_{1/2}$ values were obtained by cyclic voltammetry for two one-electron oxidation processes: [Mn(CNR)$_6$]$^+$ $\rightleftarrows$ [Mn(CNR)$_6$]$^{2+}$ + e$^-$; [Mn-(CNR)$_6$]$^{2+}$ $\rightleftarrows$ [Mn(CNR)$_6$]$^{3+}$ + e$^-$. The first oxidation is chemically reversible, with anodic and cathodic currents being equal. The second process is not, a consequence of decomposition of the unstable manganese(III) species.

In the earlier work[2,3] differences in the ease of oxidation of complexes of different ligands were noted. The $E_{1/2}$ value for the complex [Mn(CNCH$_3$)$_6$]PF$_6$ was found to be 0.38 V vs. SCE (in acetonitrile). Complexes of several aryl isocyanides, [Mn(CNR)$_6$]PF$_6$ (R = C$_6$H$_5$, p-CH$_3$C$_6$H$_4$, p-CH$_3$OC$_6$H$_4$, p-ClC$_6$H$_4$) had $E_{1/2}$ values between 0.68 and 0.95 V vs. SCE, indicating that oxidation is more difficult. A simple interpretation was accorded this observation, based on the relative donor abilities of alkyl and aryl isocyanides established some time ago by infrared studies.[4] In complexes of aryl isocyanides there is more negative charge withdrawal from the metal by π bonding due to extended conjugation into the aryl ring. The

extent of negative charge buildup on the metal center influences the energies of the HOMO (primarily metal d$_{xy}$, d$_{xz}$, d$_{yz}$) in the complex. In turn there is a direct correlation between HOMO energy and $E_{1/2}$ value.[5]

Variation with R of $E_{1/2}$ values for isoelectronic Cr(CNR)$_6$ complexes (R = aryl) was also noted in the earlier work.[2] Lack of alkyl isocyanide complexes of chromium(0) did not allow their inclusion in that study.

Work by McCleverty and co-workers[6] has further defined differences between isocyanide ligands in a series of complexes M(CO)$_{6-x}$(CNR)$_x$ (x = 1–3; M = Cr, Mo; R = CH$_3$, CH$_2$CH$_3$, CH(CH$_3$)$_2$, C$_6$H$_{11}$, C(CH$_3$)$_3$, p-CH$_3$C$_6$H$_4$, C$_6$H$_5$, p-ClC$_6$H$_4$); infrared, ultraviolet, NMR, and mass spectrometric data and electrochemical measurements were used to assess the effect of varying R and x in these systems. The electrochemical measurements showed that for the alkyl isocyanide complexes there are no significant differences in $E_{1/2}$ values, suggesting that alkyl isocyanide ligands are electronically alike. Among the aryl isocyanide complexes, which had higher $E_{1/2}$ values, there was a marked difference in $E_{1/2}$ values between species of the same stoichiometry; this was attributed to the inductive and/or mesomeric effects of aryl ring substituent group.

This work was carried out to extend consideration over a wider range of isocyanides, encompassing both the more commonly used alkyl isocyanides and also a wider range of substituted phenyl isocyanides. A linear free energy correlation

between $E_{1/2}$ values and aryl ring substituent parameters was also sought. Such a correlation was recently determined for $Cr(CNR)_6$ complexes.[7]

Experimental Section

The alkyl and aryl isocyanides used in this study were prepared by the literature methods from the corresponding formamides.[8] Several formamides were commercial samples; the rest were prepared from the amine and formic acid in toluene, distilling off the water as it formed. The $[MnL_6]^+$ complexes were prepared by the method of Sacco,[9] treating anhydrous MnI_2 in ethanol with the appropriate isocyanide. They were converted to the hexafluorophosphate salts by metathesis. The identities of these compounds, white or pale yellow species except for $[Mn(p-NCC_6H_4NC)_6]PF_6$ which was bright yellow and $[Mn(p-O_2NC_6H_4NC)_6]PF_6$ which was dark orange, were confirmed by infrared, NMR, and melting point data.

Cyclic voltammetric measurements were made at 25 °C using a PAR Model 170 electrochemistry system. A three-electrode configuration was employed, using a stationary platinum bead working electrode, platinum spiral counterelectrode, and a saturated calomel (KCl(aq)) reference electrode. The system included compensation for internal resistive potential drop. Dichloromethane and dry acetonitrile were used as solvents with solutions ~5 × 10⁻³ M in complex. Tetrabutylammonium perchlorate (0.1 M) was employed as the base electrolyte. Sweep rates were varied from 50 to 200 mV/s to achieve optimum peak shapes. For the process $[MnL_6]^+ \rightleftharpoons [MnL_6]^{2+} + e^-$, anodic and cathodic peak currents were equal; for the second oxidation the anodic current exceeded the cathodic current. The peak separations for both processes were generally greater than 59 mV. The systems are probably quasi-reversible, with moderately slow electron transfer compared to the rate of potential change.[10] Electrochemical data are given in Table I.

Discussion

Manganese(I) complexes used in this study were prepared by the literature method[9] from anhydrous manganese(II) iodide and the isocyanide. The iodide or triiodide salts were converted to hexafluorophosphate salts since these anions are electroactive at moderate applied potentials; this was accomplished by simple metathesis reactions using NH_4PF_6. Prepared were eleven complexes of aryl isocyanides, [Mn-$(p-XC_6H_4NC)_6]PF_6$ (X = H, F, Cl, Br, CH₃, CN, OCH₃, NO₂), $[Mn(m-XC_6H_4NC)_6]PF_6$ (X = CF₃, CH₃), and $[Mn(o-CH_3C_6H_4NC)_6]PF_6$, and four complexes of alkyl isocyanides, $[Mn(CNR)_6]PF_6$ (R = CH₃, CH₂CH₃, CH₂C₆H₅, C(CH₃)₃). All were characterized by standard procedures.

Cyclic voltammetry for the complexes shows two sequential oxidations, corresponding to the known processes [Mn-$(CNR)_6]^+ \rightleftharpoons [Mn(CNR)_6]^{2+} + e^-$ and $[Mn(CNR)_6]^{2+} \rightleftharpoons [Mn(CNR)_6^{3+} + e^-.^{1-3}$ Current-potential scans for the first oxidation process show equal anodic and cathodic currents. The difference in anodic and cathodic peak potentials, $|E_{p,c} - E_{p,a}|$, exceeds 59 mV, the defined criterion for electrochemical reversibility; this difference varies with scan rate and is probably a consequence of the slow rate of electron transfer in the oxidation process.[10] This phenomenon is also seen in the electrochemical oxidations of $Cr(CNR)_6$ complexes.[11] The second oxidation is neither electrochemically nor chemically reversible.[2,3] Presumably $[Mn(CNR)_6]^{3+}$ rapidly decomposes after formation.

Difficulty in obtaining current-voltage traces was encountered with the complex $[Mn(p-O_2NC_6H_4NC)_6]PF_6$ which is only partially soluble in dichloromethane. The oxidized species is even less soluble, and it rapidly coats the electrode causing a decrease in the cathodic current after the first scan. The second oxidation, at quite high potential, is obscured by solvent breakdown.

The $E_{1/2}$ values ($^1/_2[E_{p,c} + E_{p,a}]$) for the first oxidation process are solvent dependent. Most measurements were made in dichloromethane; a few were also studied in acetonitrile. The complex $[Mn(p-NCC_6H_4NC)_6]PF_6$ was run only in acetonitrile due to its insolubility in the former solvent. The

Table I. Voltammetric Data for $[MnL_6]PF_6$ Complexes

Complex	$^1/_2[E_{p,c} + E_{p,a}],^a$ V	$E_{p,c} - E_{p,a}$, mV	Process
$[Mn(p-O_2NC_6H_4NC)_6]PF_6^b$	1.31	60	1+ → 2+
$[Mn(m-CF_3C_6H_4NC)_6]PF_6$	1.14	80	1+ → 2+
	1.99	150	2+ → 3+
$[Mn(p-BrC_6H_4NC)_6]PF_6$	1.05	70	1+ → 2+
	1.91	140	2+ → 3+
$[Mn(p-ClC_6H_4NC)_6]PF_6^c$	1.04	160	1+ → 2+
	$(0.89)^d$		
	1.90	200	2+ → 3+
	$(1.79)^d$		
$[Mn(p-FC_6H_4NC)_6]PF_6$	0.99	175	1+ → 2+
	1.88	240	2+ → 3+
$[Mn(p-CH_3C_6H_4NC)_6]PF_6^c$	0.93		1+ → 2+
	$(0.76)^d$		
	1.83		2+ → 3+
	$(1.69)^d$		
$[Mn(m-CH_3C_6H_4NC)_6]PF_6$	0.98	200	1+ → 2+
	1.92	230	2+ → 3+
$[Mn(o-CH_3C_6H_4NC)_6]PF_6$	1.05	200	1+ → 2+
	2.00	300	2+ → 3+
$[Mn(p-NCC_6H_4NC)_6]PF_6^c$	1.10^d	80	1+ → 2+
	1.92^d		2+ → 3+
$[Mn(C_6H_5NC)_6]PF_6^c$	1.01		1+ → 2+
	$(0.83)^d$		
	1.91		2+ → 3+
	$(1.77)^d$		
$\{Mn(p-CH_3OC_6H_4NC)_6]PF_6^c$	0.81		1+ → 2+
	$(0.69)^d$		
	1.68		2+ → 3+
	$(1.55)^d$		
$[Mn(CNCH_3)_6]PF_6^c$	0.47		1+ → 2+
	1.59		2+ → 3+
$[Mn(CNCH_2CH_3)_6]PF_6$	0.47	50	1+ → 2+
	1.63	110	2+ → 3+
$[Mn(CN-t-Bu)_6]PF_6$	0.56	80	1+ → 2+
	1.68		2+ → 3+
$[Mn(CNCH_2C_6H_5)_6]PF_6$	0.56	76	1+ → 2+
	1.68		2+ → 3+

^{a} Average of cathodic and anodic peak potentials vs. SCE (KCl(aq)); solutions in CH_2Cl_2 (5 × 10⁻³ M) with Bu_4NClO_4 (0.1 M) as supporting electrolyte. ^{b} Low solubility did not allow all of the complex to dissolve; rapid electrode coating required a single scan at a higher rate. ^{c} Voltammetric data previously reported. Data in CH_2Cl_2 are from ref 2; CH_3CN data are from 3. ^{d} Solutions in CH_3CN (5 × 10⁻³ M) with Bu_4NClO_4 (0.1 M) as supporting electrolyte.

differences in $E_{1/2}$ values between these solvents for similar compounds are almost constant, with the $E_{1/2}$ values in acetonitrile 0.12–0.18 V lower. The difference could arise as a consequence of the different liquid junction potentials at the aqueous SCE reference electrode; alternatively it could be a consequence of differences in solvent polarity leading to different energetics of solvation of the cations.

As anticipated, complexes of alkyl isocyanides have lower $E_{1/2}$ values than do complexes of aryl isocyanides, a consequence of the higher net donor ability of these ligands.[4] There is only a small variation among the four complexes investigated; $E_{1/2}$ values are in the range 0.47–0.56 V vs. SCE in dichloromethane. The $E_{1/2}$ values for the complexes of aryl isocyanides are higher and span a wider range of values; the lowest value for $E_{1/2}$ (1+ → 2+) in dichloromethane is for the complex $[Mn(p-CH_3OC_6H_4NC)_6]PF_6$, 0.81 V, whereas the highest found here occurs for $[Mn(O_2NC_6H_4NC)_6]PF_6$, 1.31 V vs. SCE. Undoubtedly, judicious choice of aryl substituent groups could have extended this observed range of $E_{1/2}$ values over a still broader range.

A linear free energy relationship was anticipated between the $E_{1/2}$ data and aryl ring substituent parameters. A good correlation of $E_{1/2}$ data with Hammett σ constants for a series of $Cr(CNR)_6$ complexes had been observed earlier,[7] and similar correlations have been found for other organometallic

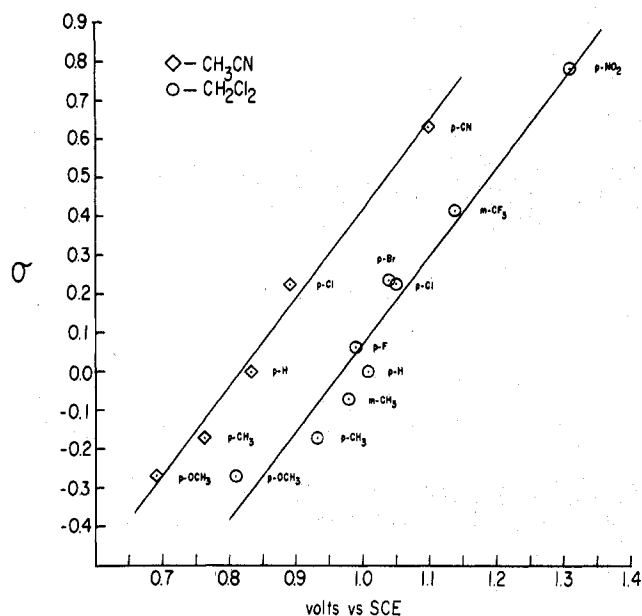**Figure 1.** Plot of σ vs. $E_{1/2}$ for complexes of the type [Mn(p-XC$_6$H$_4$NC)$_6$]PF$_6$ and [Mn(m-XC$_6$H$_4$NC)$_6$]PF$_6$.

systems.[12-15] Least-squares analysis of these data produced an excellent correlation of $E_{1/2}$ (in dichloromethane) vs. Hammett σ_p or σ_m.[16] For the equation $\sigma = -2.20 + 2.27E_{1/2}$ a data correlation coefficient of 0.98 was obtained.[16] Graphically, this fit of the data is shown in Figure 1. Data for $E_{1/2}$ values in acetonitrile are also illustrated in this figure.

A value of ρ, the reaction parameter, can easily be calculated from the equation $\Delta E_{1/2} = 6\rho\sigma$, where the factor of 6 arises from the influence of six ligand groups. The value of ρ is +0.0734. A large majority of ρ values for electrochemical processes are positive. The order of magnitude of this value, reflecting the proximity of the substituent group to the reaction center (the metal), is similar to the value seen for the Cr-(CNR)$_6$ oxidations.[7]

It may be noted that neither inductive nor resonance parameters adequately correlate with the $E_{1/2}$ data. Also of interest is the fact that ν(CN) values for the aryl complexes were found at approximately 2090 cm^{-1}, essentially invariant to the substituent groups. In contrast, values of ν(CO) usually show a substantial variation with different ligands; in the series [Mn(CO)(CNR)$_4$L]$^+$ there is a good correlation between ν(CO) and $E_{1/2}$.[17] The ν(CN) invariance arises because the π^* ligand acceptor orbital is substantially a π^* ring orbital, perturbed by the substituent group.[18] There is little C–N antibonding character associated with this orbital; consequently ν(CN) is not much influenced by the π interaction.

Interpretation of the $E_{1/2}$–Hammett σ constant relationship is straightforward. The net charge donation to the metal from the ligand is a consequence of balance of σ (donor) and π (acceptor) functions of the ligand. The Hammett σ reflects

a summation of both σ and π effects attributed to the substituent groups. Undoubtedly the balancing of σ- and π-bonding effects (in essence, the electroneutrality principle) has much to do to force a good accord of $E_{1/2}$ values and substituent group parameters.

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