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FACILE HALIDE REPLACEMENT IN ELECTRON RICH COMPLEXES

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Summary

Reactions of MnL_5X or $Mn(CO)L_4X$ compounds (L = several aryl isocyanides, X = halide) with $AgPF_6$ give $[MnL_6]PF_6$ or $[Mn(CO)L_5]PF_6$ respectively. These reactions are presumed to occur with initial halide extraction to give an intermediate solvated species $[MnL_5solv]^+$ or $[Mn(CO)L_4solv]^+$ which can subsequently decompose or scavenge free L from solution to give the products observed. Addition of an alternative potential ligand L' allows preparation of mixed ligand species $[MnL_5L']PF_6$ or $[Mn(CO)L_4L']PF_6$ (L = MeNC, ^tBuNC, py). Cyclic voltammetric studies on the various complexes have been carried out, and results correlated with infrared data and with theory.

Introduction

In earlier work on isocyanide derivatives of metals we prepared a variety of manganese carbonyl halide derivatives, $Mn(CO)_{5-n}(CNR)_nX$ ($n = 1 \rightarrow 5$; R = Me, Ph; X = Cl, Br, I), by thermal reactions of $Mn(CO)_5X$ and isocyanide [1]. These complexes can be converted into cationic complexes, $[Mn(CO)_{6-n}(CNR)_n]^+$ by replacement of halide ion by CO, this reaction usually requiring the assistance of a halide acceptor such as $AlCl_3$. Further reactions of the more fully substituted complexes, either $Mn(CO)(CNR)_4X$ or $Mn(CNR)_5X$, with CNR often led to replacement of halide by the ligand, generating $[Mn(CO)(CNR)_5]X$, respectively [1]; these reactions do not require a halide acceptor. Contrast between halide replacement in $Mn(CNR)_5X$ and carbonyl replacement in $Mn(CO)_5X$ is noted here because it anticipates the work to be discussed in this paper.

Electrochemical studies on $[Mn(CO)_{6-n}(CNR)_n]^+$ complexes defined two oxidative processes, sequential one electron losses to give $[Mn(CO)_{6-n}(CNR)_n]^{2+}$ and $[Mn(CO)_{6-n}(CNR)_n]^{3+}$. The ease of these oxidations, measured as $E_{1/2}$ values, is dependent on the extent of isocyanide substitution, n; $E_{1/2}$ values decrease by ∿0.4v per substitution. The ease of oxidation also depends on the choice of isocyanide, with complexes of alkyl isocyanides being easier to oxidize than similar complexes of aryl isocyanides. There is a smaller dependence on geometry of substitution [2]. These results correlate qualitatively with the extent of negative charge buildup on the metal; in turn, this is related to the donor ability of the ligands. Molecular orbital calculations, bearing out this relationship, show that the $E_{1/2}$ value is directly related to the energy of the highest occupied molecular orbitals in the complex; these orbitals are primarily metal (dxy, dxz, dyz) in character [3]. We have designated metal isocyanide complexes as "electron rich", to identify the charge buildup on the metal. Our design is to elaborate on the unique chemistry of such complexes of which oxidative behavior is only one facet; and to define similarities and differences in analogous complexes of isocyanides and carbonyls.

Among the complexes investigated in this general study are the species $Mn(CO)_{5-n}(CNR)_nX$, (particularly those with n = 4,5). The $E_{1/2}$ values for these complexes are particularly low. For example $Mn(CNPh)_5X$ (X = Cl, Br) complexes have $E_{1/2}$ values of ∿0.3 v vs. SCE, for the process $Mn(CNPh)_5X \rightleftarrows Mn(CNPh)_5X]^+ + e$; in contrast the $E_{1/2}$ value for the one-electron oxidation of $[Mn(CNPh)_6]PF_6$ in the same solvent is 0.80v [1]. Expecting a facile chemical oxidation of $Mn(CNPh)_5X$, the reactions of these compounds with $AgPF_6$ a known oxidizing agent were carried out. However the isolated product here was $[Mn(CNPh)_6]PF_6$, arising from preferential halide abstraction by Ag^+ [4]. We have now elaborated further on this facile halide abstraction reaction. Herein we report results of this study.

Experimental

All reactions were run under a nitrogen atmosphere. Melting points were determined using a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were taken on a Beckman IR-10, using dichloromethane solutions. Nuclear magnetic resonance spectra were obtained on a JEOL MH-100 instrument. Nmr and infrared spectral data are given in Table I.

TABLE I. INFRARED AND PROTON MAGNETIC RESONANCE DATA

Compound		IR $(cm^{-1})^a$		NMR[b]
		C≡N	C≡O	τ multiplicity (intensity)
1	$[Mn(CNC_6H_4Me)_5py]PF_6$	2100m,sh 2075s 2040m		1.15d(2) 2.24,2.56m(3) 2.68s(16) 2.84s(4) 7.62s(15)
2	$[Mn(CNPh)_5(CNMe)]PF_6$	2200vw 2140w 2070vs		2.60s(25) 6.44s(3)
3	$[Mn(CO)(CNC_6H_4Me)_5]PF_6$	2200vw 2090vs	1995s	
4	$[Mn(CO)(CNC_6H_4Me)_4(CNBu^t)]PF_6$	2140w 2100vs	1985	2.80s(16) 7.64s(12) 8.44s(9)
5	$[Mn(CO)(CNC_6H_4Me)_4(CNMe)]PF_6$	2160w 2100vs	1980s	2.76m(16) 6.40s(3) 7.64s(12)
6	$[Mn(CO)(CNC_6H_4Me)_4py]PF_6$	2090vs	1945m,b	1.24d(2) 2.24,2.56(3) 2.76m(16) 7.64s(12)
7	$[Mn(CO)(CNC_6H_4Me)_4(o\text{-}H_2NC_6H_4Me)]PF_6$	2090s	1935w,b	2.80s 3.08s (20) 5.72s(2) 7.64s(15)

[a] Low resolution data (±5 cm^{-1}), Beckman IR-10, CH_2Cl_2 solution.

[b] $CDCl_3$ solvent; tetramethylsilane internal standard $\tau = 10$.

Electrochemical measurements were made using a three-electrode configuration, employing a stationary platinum bead working electrode, and saturated calomel (KCl) reference electrode. Voltage and current functions were controlled using a Princeton Applied Research Electrochemistry System, Model 170, incorporating compensation for internal resistive potential drop. Dichloromethane was used as solvent with the solute concentration $\sim 5 \times 10^{-3}$ M. Tetrabutylammonium perchlorate (0.1 M) was employed as the supporting electrolyte. Voltammetric data are presented in Table II.

TABLE II. VOLTAMMETRIC DATA FOR PROCESS $[MnL_n]^+ \rightleftarrows [MnL_n]^{2+} + e$

Compound	$1/2[E_{p,c}+E_{p,a}]^a$	$\lvert E_{p,c}-E_{p,a} \rvert^b$
1 $[Mn(CNC_6H_4Me)_5py]PF_6$	0.62 v	200 mV
	(1.6 v	200 mV)[c]
2 $[Mn(CNPh)_5(CNMe)]PF_6$	0.93 v	170 mV
	(1.87 v	250 mV)[c]
3 $[Mn(CO)(CNC_6H_4Me)_5]PF_6$	1.21 v	200 mV
4 $[Mn(CO)(CNC_6H_4Me)_4(CNBu^t)]PF_6$	1.18 v	210 mV
5 $[Mn(CO)(CNC_6H_4Me)_4(CNMe)]PF_6$	1.16 v	220 mV
6 $[Mn(CO)(CNC_6H_4Me)_4py]PF_6$	1.09 v	280 mV
7 $[Mn(CO)(CNC_6H_4Me)_4(o\text{-}H_2NC_6H_4Me)]PF_6$	1.04 v	260 mV

[a] Cathodic and anodic peak potentials in volts *vs*. SCE (saturated calomel electrode, aq. KCl). Solutions in CH_2Cl_2 (5×10^{-3}M) with $[Et_4N][ClO_4]$ (0.1 M) as base electrolyte.

[b] Although the peak separations do not meet the required 0.06 v needed for one-electr reversible systems, anodic and cathodic currents are equal. These separations are changed by varying the scan rates, suggesting a quasi-reversible system [9].

[c] Voltammetric data for process $[MnL_5L']^{2+} \rightleftarrows [MnL_5L]^{3+} + e$.

The aryl isocyanides used in this study were prepared by reaction of the appropriate formamide with triphenylphosphine, carbon tetrachloride and triethylamine [5]. Methyl and t-butyl isocyanides were also prepared by the method given in Organic Syntheses [6]. The $Mn(CO)_5X$ compounds (X = Cl, Br) were prepared by the literature method [7]. The preparations of $Mn(CO)(CNPh)_4Br$ and $Mn(CNPh)_5Cl$ from $Mn(CO)_5X$ and the isocyanide were reported earlier in the literature [1]. A by-product of the former reaction, $Mn(CNPh)_5Br$, not previously described in our earlier work, was also obtained in small yield. The preparations of $Mn(CNC_6H_4Cl)_5Cl$, $Mn(CNC_6H_4Me)_5Cl$, and $Mn(CO)(CNC_6H_4Me)_4X$ (X = Br, Cl) were also accomplished by similar reactions of the ligand and $Mn(CO)_5X$. Details of these preparations are described elsewhere [8].

Reaction of $Mn(CNPh)_5Br$ and $AgPF_6$. To a solution of $Mn(CNPh)_5Br$ (0.65g, 1.0 mmol) in 100 ml THF was added $AgPF_6$ (0.40 g; 1.5 mmol). The solution was stirred at 25° for 2 hr, evaporated, and the residue extracted with CH_2Cl_2. Addition of hexane to the CH_2Cl_2 solution precipitated 0.60 g of white needle-like crystals. The compound has the same melting point (264°C) and infrared spectrum as the known complex, $[Mn(CNPh)_6]PF_6$ [1] (83% yield, based on PhNC available. The yield can be increased by adding PhNC to the system).

Found: C, 61.25,; H, 3.78; N, 10.48. $C_{42}H_{30}N_6PF_6Mn$ calcd. C, 61.6; H, 3.68; N, 10.25%.

Reaction of $Mn(CNC_6H_4Cl)_5Cl$ and $AgPF_6$. Reaction as above gave $[Mn(CNC_6H_4Cl)_6]PF_6$ as pale-yellow crystals in 34% yield. The infrared spectrum, mp, and voltammetry data confirm the identity of this known compound [1].

Reaction of $Mn(CO)(CNPh)_4Br$ and $AgPF_6$. The reaction of these reagents, carried out in the manner described above, gave pale yellow crystalline $[Mn(CO)(CNPh)_5]PF_6$ in 51% yield. The mp, infrared spectrum, and cyclic voltammetry data were identical with data on this known compound [1].

It was determined that by adding additional ligand improved yields in each of these reactions could be obtained. In turn, this suggested that mixed ligand complexes could be obtained by running these reactions in the presence of other ligands. These reactions are described below.

Preparation of $[Mn(CNPh)_5(CNMe)]PF_6$. Solid $AgPF_6$ (0.30g, 1.2 mmol) was added to a suspension of $Mn(CNPh)_5Cl$ (0.60g, 1.0 mmol) in 25 ml MeNC. The mixture was heated to 50° for 2 hr to dissolve the reactants, then stirred at 25° for 16 hr. The MeNC was distilled off and collected. The residue was extracted with chloroform and 0.40 g of white cubes precipitated by addition of heptane (53% yield). mp 172-174°C.

Found: C, 58.81; H, 3.60; N, 10.50. $C_{37}H_{28}N_6F_6PMn$ calcd: C, 58.80; H, 3.71; N, 11.10.

Preparation of $[Mn(CNC_6H_4Me)_5(pyr)]PF_6$. This compound was prepared in the same way as the previous one, substituting pyridine for MeNC. The reaction residue was extracted with dichloromethane; the solvent was evaporated and the crude product crystallized from acetone/ether in 25% yield. mp 183-185°C.

Found: C, 62.32; H, 5.65; N, 8.90. $C_{45}H_{40}N_6F_6PMn$ calcd. C, 62.50; H, 4.66; N, 9.72%.

Preparation of a Series of $[Mn(CO)(CNC_6H_4Me)_4L]PF_6$ Complexes. a) L = MeNC. The general procedure is illustrated by this example. To a solution of $Mn(CO)(CNC_6H_4Me)_4Cl$ (0.30 g, 0.50 mmol) in 25 ml MeNC was added $AgPF_6$ (0.15 g, 0.60 mmol). The reaction was refluxed for 12 hr, the MeNC was removed, and the residue extracted with dichloromethane. Addition of heptane to the filtrate resulted in the precipitation of 0.20 g of white cubes of $[Mn(CO)(CNC_6H_4Me)_4(CNMe)]PF$ (54%). m.p. 201-203°C.

Found: C, 57.02; H, 4.07; N, 9.60. $C_{35}H_{31}N_5OF_6PMn$ calcd: C, 56.99; H, 4.23; N, 9.50%.

Also prepared by this method were compounds with the following ligands L:

b) L = $CNBu^t$. Obtained as clear rectangles from dichloromethane/hexane in 80% yield after reaction in $CNBu^t$ at 50°C for 24 hr. mp. 182-184°C.

Found: C, 58.40; H, 4.77; N, 8.85. $C_{38}H_{37}N_5OF_6PMn$ calcd: C, 58.54; H, 4.78; N, 8.98%.

c) L = pyr. Obtained as yellow crystals from dichloromethane/hexane in 77% yield after reacting in pyridine for 24 hr at 25°C. mp. 174-176°C.

Found: C, 58.87; H, 4.25; N, 8.85. $C_{38}H_{33}N_5OF_6PMn$ calcd: C, 58.80; H, 4.29; N, 9.03%.

d) L = o-$MeC_6H_4NH_2$. Obtained as yellow needles from dichloromethane/hexane in 71% yield after reacting in o-toluidine at 50°C for 24 hr. mp. 150°C.

Found: C, 59.84; H, 4.73; N, 8.68. $C_{40}H_{37}N_5OF_6PMn$ calcd: C, 59.78; H, 4.64; N, 8.72%.

e) L = CNC_6H_4Me. To a solution of $Mn(CO)(CNC_6H_4Me)_4Br$ (0.25 g, 0.42 mmol) in 30 ml THF was added a solution of $AgPF_6$ (0.15 g, 0.60 mmol) and MeC_6H_4NC (∿10 ml) in 20 ml THF. The solution was stirred at 25° for ∿2 hr, solvent evaporated, and the residue extracted with dichloromethane. The solvent was removed and 0.25 g of product was crystallized from acetone/ether (77% yield). mp. 85-86°C.

Found: C, 60.77; H, 4.60; N, 7.93. $C_{41}H_{35}N_5OPF_6Mn$ calcd: C, 60.52; H, 4.34; N, 8.61%.

Results and Discussion

A rapid reaction occurs between $AgPF_6$ and $Mn(CO)L_4X$ or MnL_5X compounds (L = several isocyanides; X = Cl, Br) in tetrahydrofuran to give AgX and, respectively, $[Mn(CO)L_5]PF_6$ or $[MnL_6]PF_6$ in good yield:

$$Mn(CO)L_4X + AgPF_6 \longrightarrow [Mn(CO)L_5]PF_6 + AgX$$

$$MnL_5X + AgPF_6 \longrightarrow [MnL_6]PF_6 + AgX$$

Presumably these products arise from a reaction involving initial halide abstraction. The intermediate species could then decompose to provide a source of isocyanide which in turn would be scavenged to give the resulting metal complexes. The presence of excess isocyanide improves the yield in this reaction; apparently the process of adding the additional ligand group must be a fas process in contrast to the rate of decomposition of the intermediate species.

The intermediate in this reaction is likely to be the solvated species, $[Mn(CO)L_4(solv)]^+$ or $[MnL_5solv]^+$ (solv = tetrahydrofuran). Attempts at isolation of such species were unsuccessful, however; they must be quite unstable with respect to formation of the eventual reaction products. The same behavior was observed using acetonitrile, also a weakly basic solvent. Instability of complexes containing these ligands is not particularly surprising; much data on other systems seem to suggest that acetonitrile and ethers are weakly bonded and easily displaced [10].

Because the reaction intermediate quickly adds excess isocyanide, it seemed likely that similar reactions with other ligands would be successful. This type of reaction would specifically generate mixed ligand complexes which are often difficult to obtain by other routes. Such reactions were successful in a number of instances:

$$MnL_5X + L' + AgPF_6 \rightarrow [MnL_5L']PF_6 + AgX$$

$(L = CNPh, CNC_6H_4Cl; L' = pyr, CNMe)$

$$Mn(CO)L_4X + L' + AgPF_6 \rightarrow [Mn(CO)L_4L']PF_6 + AgX$$

$(L = CNC_6H_4Me; L' = py, CNMe, CNBu^t, o\text{-}H_2NC_6H_4Me)$

The reactions of $Mn(CO)L_4X$ were stereospecific; the starting material having CO and in trans positions, were converted to trans $[Mn(CO)L_4L']^+$ complexes. The stereospecificity of this type of reaction had been noted earlier [2].

Characterization of the new complexes was accomplished in the usual manner, using analytical and spectroscopic data. The presence of CO and CNR ligands was easily defined by infrared data. Nmr data was useful in identifying the coordinated amines, and also was used to show the equivalence of isocyanides in $[Mn(CO)L_4L']^+$, required for assignment of the trans configuration.

It may be noted that these reactions with $AgPF_6$ were attempted hoping to accomplish a one-electron oxidation of these complexes. Previous electrochemical studies [4,8] on $Mn(CNPh)_5X$ compounds had shown a one electron oxidation at ∿0.3 v vs. SCE; these oxidations are chemically reversible, and very close to electrochemically reversible ($E_{p,a}-E_{p,c}$ ∿0.060 v). The low $E_{1/2}$ value for this process indicated that oxidation could be accomplished with mild oxidizing agents such as $AgPF_6$, which was chosen here for convenience. The fact that halide abstraction occurred, rather than oxidation probably is a result of the relative rates of these two processes, a faster rate of halide abstraction taking precedence.

The facile loss of halide ion from electron-rich complexes such as MnL_5X may well be a consequence of electron rich metal character. This would seem to make sense: the halide-metal bond might be weakened by the charge buildup at the metal. Loss of halide ion also conveys a dimunition of electron density at a metal center; qualitatively this seems to be a reasonable direction to go. Clearly, more careful studies on the rates of these reactions are needed to establish and fully define this situation; this work is underway.

For the series of trans-$[Mn(CO)(CNC_6H_4Me)_4L]PF_6$ compounds studied, a correlation of ν(CO) with the donor ability of L was noted, with ν(CO) values varying over 60 cm^{-1}. The large range of ν(CO) values results as the bonding to the single carbonyl adjusts to donation of electron density to the metal by the ligand trans to it. It is interesting to note that the isocyanide stretching frequency remains almost unchanged in this series. Electrochemical data also reflect the characteristics of L (Table II). The complex $[Mn(CO)(CNC_6H_4Me)_5]PF_6$ has the highest $E_{1/2}$ value, 1.21 v. The $E_{1/2}$ value for the o-toluidine complex is 1.04 v, reflecting the better donor ability of the amine compared to the isocyanide. The other complexes lie in the intermediate range.

The similar relationship which defines both infrared and $E_{1/2}$ values for this series can be seen in Figure I. There is a very good linear correlation between these sets of data.[10].The regression line, $E_{1/2} = b_0 + b_1(\nu(CO))$, has y-intercept $b_0 = -4.00$ v, slope $b_1 = 0.00261$ v-cm^{-1}, standard deviation of

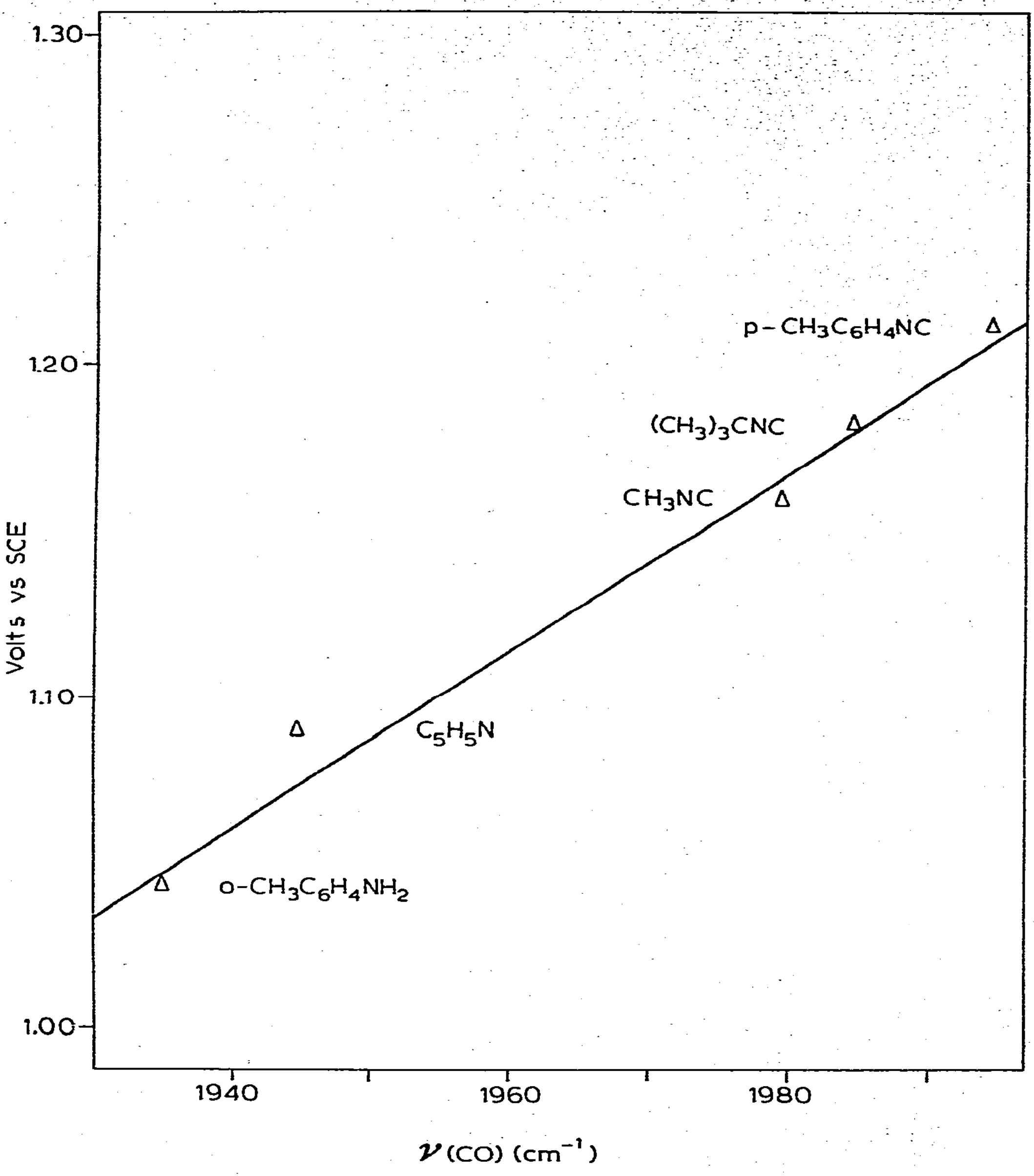

Fig. I. Plot of ν(CO) vs. $E_{1/2}$ for the Complexes $[Mn(p\text{-}CH_3C_6H_4NC)_4(CO)(L)]PF_6$.

the slope s = 0.000180, and a correlation coefficient r = 0.991. It may be noted that McCleverty and coworkers [11] had previously noted correlations of $E_{1/2}$ with the A_1 carbonyl absorption mode of complexes of the type $M(CO)_{6-n}(CNR)_n$ (M = Cr, Mo, W; n = 1-3). Also, Fenske and Sarapu [3] noted a similar correlation of carbonyl force constants, k(CO) and stretching frequencies, ν(CO), with $E_{1/2}$ values for the complexes $Mn(CO)_{5-x}(CH_3NC)_xBr$ (x = 0-4) and $Mn(CO)_{6-x}(CH_3NC)_x^+$ (x = 1-6).

The $E_{1/2}$ value for the complex $[Mn(CNPh)_5(CNMe)]PF_6$, 0.93 v, when compared to the value for the complex $[Mn(C_6H_5NC)_6]PF_6$, 1.01 v [1], presents further evidence of the significantly poorer π-acceptor ability of alkyl vs. aryl isocyanides. Likewise, the $E_{1/2}$ value of the complex $[Mn(CNC_6H_4Me)_5(py)]PF_6$, 0.62 v, when compared to that of the complex $[Mn(CNC_6H_4Me)_6]PF_6$, 0.93 v [1], shows the even poorer π-acceptor ability of the pyridine ligand. A comparison of these $E_{1/2}$ differences, 0.31 v, and the differences between the complexes $[Mn(p\text{-}CH_3C_6H_4NC)_4(CO)(pyr)]PF_6$ and $[Mn(p\text{-}CH_3C_6H_4NC)_5(CO)]PF_6$, 0.12 v, presents an insight into flexibility of the carbonyl to serve as a π acceptor and moderate the effect of ligand substitution.

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References

1 P. M. Treichel, G. E. Dirreen, and H. J. Mueh, J. Organometal. Chem., 44 (1972) 339.

2 P. M. Treichel, H. J. Mueh, and B. E. Bursten, J. Organometal. Chem., 110 (1976) C49.

3 A. C. Sarapu and R. F. Fenske, Inorg. Chem., 14 (1975) 247.

4 Communication on this work: P. M. Treichel, K. P. Wagner, and H. J. Mueh, J. Organometal. Chem., **86** (1975) C13.

5 R. Appel, R. Kleinstuck, and K-D. Zeihn, Angew. Chem. Int. Ed. Engl., **10** (1971) 132.

6 R. E. Schuster, J. E. Scott, and J. Casanova, Org. Syn., **46** (1966) 75.

7 E. W. Abel and G. Wilkinson, J. Chem. Soc., (1959) 1501.

8 H. J. Mueh, Ph.D. Thesis, Univ. of Wisconsin, Madison (1976); P. M. Treichel and H. J. Mueh, manuscript in preparation.

9 R. S. Nicholson, Anal. Chem., **37** (1965) 1351.

10 J. Shorter, *Correlation Analyses in Organic Chemistry: An Introduction to Linear Free Energy Relationships*, Clarendon Press, Oxford (1973) Appendix 1.

11 J. A. Connor, E. M. Jones, G. K. McEwen, M. K. Lloyd, and J. A. McCleverty, J. Chem. Soc. Dalton, (1972) 1246.