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MANGANESE(I) ISOCYANIDE COMPLEXES

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SUMMARY

The reaction of methyl isocyanide (L) and $MnBr(CO)_5$ in tetrahydrofuran gives several products, depending on the reaction conditions, including: $MnBr(CO)_3L_2$ (room temperature, 48 h), $MnBr(CO)_2L_3$ (reflux, 6 h), and a mixture of $MnBr(CO)_2L_3$, $MnBr(CO)L_4$, and $[Mn(CO)L_5]Br$ (reflux, 24 h). The monosubstituted product $MnBr(CO)_4L$ was obtained from $Mn_2Br_2(CO)_8$ and L, and other ionic species, $[Mn(CO)_{6-x}L_x]^+$ ($x=1$–4), were obtained from $MnBr(CO)_{5-x}L_x$, $AlCl_3$, and CO. The reactions of $MnX(CO)_5$ (X = Cl, Br, I) and CNC_6H_5 in tetrahydrofuran were reinvestigated. The product distribution was dependent on reaction time and on the ratio of reactants. The compound previously reported as $MnBr(CNC_6H_5)_5$ was shown to be a mixture of $[Mn(CO)(CNC_6H_5)_5]Br$ and $[Mn(CNC_6H_5)_6]Br$, and the new complex $MnCl(CNC_6H_5)_5$ was characterized. Chemical oxidation of $[Mn(CO)L_5]PF_6$ yielded $[Mn(CO)L_5](PF_6)_2$. Electrochemical oxidations of various cationic species were recorded. The difficulty of oxidation ($E_{\frac{1}{2}}$) increased with increasing carbonyl substitution (*i.e.*, decreasing values of x) in the series $[Mn(CO)_{6-x}L_x]PF_6$, presumably a result of the higher net positive charge on the metal due to removal of electron density to the CO ligands. Oxidation of the phenyl isocyanide complexes $[Mn(CO)_{6-x}(CNC_6H_5)_x]PF_6$ ($x=5,6$) was more difficult than was oxidation of the corresponding methyl isocyanide species.

INTRODUCTION

Three previous papers describe reactions of manganese carbonyl halides with isocyanides. Hieber and Schropp[1] reported the formation of $MnCl(CO)_3(CNC_6H_4OCH_3)_2$ as the single product, obtained in a nearly quantitative yield, in the reaction of chloropentacarbonylmanganese and *p*-methoxyphenyl isocyanide in ethanol at 70°. Shortly thereafter, there was a reference to a monosubstituted complex, $MnBr(CO)_4(CNC_2H_5)$, by Angelici and Basolo[2]. A more detailed study of the reactions of phenyl isocyanide and halopentacarbonylmanganese compounds (chloride, bromide, and iodide) was later reported by Joshi, Pauson, and Stubbs[3]. These authors reported that bromopentacarbonylmanganese and phenyl isocyanide give the $MnBr(CO)_3(CNC_6H_5)_2$ in refluxing ethanol, $MnBr(CO)_2(CNC_6H_5)_3$ when the reaction is carried out in diglyme at 100°, and a mixture of $MnBr(CO)(CNC_6H_5)_4$ and $MnBr(CNC_6H_5)_5$ when the reaction was carried out in refluxing tetrahydrofuran.

TABLE 1

INFRARED AND PROTON MAGNETIC RESONANCE DATA

Compound	*Infrared spectral data (cm^{-1})*			NMR
	ν(C≡N)^a	ν(CO)^a	*Other*^{b}	τ(*intensity*)^c
$MnBr(CO)_4(CNCH_3)$	2226 m	2105 m, 2033 vs, 1980 s (br)	1650 vw, 710 vw, 650 m, 620 s, 545 vw, 495 w	6.43 (s)
$MnBr(CO)_3(CNCH_3)_2$	2220 m, 2202 m	2048 vs, 1997 s, 1949 s	1415 w, 1400 vw, 715 vw, 665 m, 635 m, 615 m, 545 vw, 485 vw	6.32
$MnBr(CO)_2(CNCH_3)_3$	2212 m, 2182 (sh) 2166 vs	1993 s, 1913 s	1410 m, 710 w, 655 m, 630 m, 605 m, 510 vw	6.36 (s), 6.40 (s, o) (approx. 1/2)
$MnBr(CO)(CNCH_3)_4$	2142 vs (br)	1881 s (br)	1415 m, 715 vw, 630 m, 615 m, 510 m	6.40
$MnBr(CO)_2(CNCH_3)_2$-$[P(C_6H_5)_3]$	2192 s, 2168 s	1973 vs, 1900 vs	1435 m, 1410 w, 1090 w, 745 m, 720 vw, 695 m, 655 m, 635 m, 600 m, 520 s, 495 w	2.33, 2.63 (15); 6.58 (3); 6.98 (3); all b
$MnBr(CO)_3(CNCH_3)$-$[P(C_6H_5)_3]$	2202 s	2037 vs, 1978 vs, 1932 vs	1895 w, 1480 w, 1435 m, 1415 w, 1090 w, 745 m, 735 w, 695 m, 660 m, 630 m, 610 m, 540 w, 520 m, 510 m, 495 w	2.40 m (15), 6.98 (3) d, J 2 Hz
$[Mn(CO)(CNCH_3)_5]PF_6$	2226 w, 2180 (sh), 2156 vs	1956 s	1415 m, 875 (sh), 830 s [νPF)] 710 w, 630 m, 600 w, 550 w, 510 vw	6.43 (s), 6.47 (s, o) (approx. 1/4)
$[Mn(CO)_3(CNCH_3)_3]PF_6$	2245 m, 2220 (sh), 2202 s	2090 m, 2020 vs (br)	1415 m, 875 (sh), 830 vs [ν(PF)]. 715 vw, 625 m, 615 m, 550 m, 520 w	6.42 (s)
$[Mn(CO)_5(CNCH_3)]PF_6$	2264 m	2158 m, 2075 vs (br)	1415 w, 875 (sh), 830 vs [ν(PF)] 715 w, 645 (sh), 625 s, 550 m	6.20 t approx. 1/1/1, J 2.5 Hz
$[Mn(CO)_4(CNCH_3)_2]PF_6$	2249 m (br), 2221 (sh)	2125 m, 2064 (sh), 2051 vs, 2036 (sh)	1415 w, 875 (sh), 850 (sh), 830 vs, [ν(PF)], 715 vw, 645 m, 625 s, 550 m	6.31 t approx. 1/1/1, J 2.3 Hz
$[Mn(CO)_2(CNCH_3)_4]PF_6$	2177 vs (br)	1985 vs	1415 m, 875 (sh), 850 (sh), 830 vs [ν(PF)], 635 m, 580 m, 550 m, 475 vw	6.53 (s)
$[Mn(CNCH_3)_6](PF_6)_2$	2220 s		1415 w, 875 (sh), 830 vs [ν(PF)], 715 vs, 550 m	
$[Mn(CO)(CNCH_3)_5](PF_6)_2$	2238 s	2050 m	1415 w, 940 vw, 875 (sh), 830 vs [ν(PF)], 715 vw, 550 m, 530 w	

$[Mn(CO)(CNC_6H_5)_5]PF_6$	2192 w, 2136 (sh), 2111 vs	1991 s	1590 w, 1480 w, 840 m [ν(PF)], 740 w, 675 w, 620 m, 590 w, 545 w, 520 w	2.44
$[Mn(CO)(CNC_6H_5)_5]Br$	2112 s	1997 m		
$[Mn(CNC_6H_5)_6]PF_6$	2088 vs		1590 m, 1480 m, 840 m [ν(PF)], 780 w, 745 m, 715 w, 680 m, 615 m, 590 m, 545 w, 510 w	2.43
$MnBr(CO)(CNC_6H_5)_4$	2089 vs	1908 m		
$[Mn(CNC_6H_5)_6]Br$	2088 vs			
$MnCl(CO)(CNC_6H_5)_4$	2091 vs	1906 s	1590 w, 1480 m, 780 w, 750 m, 720 w, 680 w, 625 m, 540 w, 515 m	2.61
$MnCl(CNC_6H_5)_5$	2070 vs		1590 m, 1480 w, 780 vw, 745 m, 715 w, 680 w, 590 w, 515 w	2.62 (s)
$[Mn(CNC_6H_5)_6]Cl$	2088 vs			
$MnI(CO)_2(CNC_6H_5)_2$	2171 m, 2143 s	2037 vs, 1995 s, 1944 s	1590 w, 1480 m, 750 m, 715 w, 680 w, 650 m, 625 m, 605 m, 550 vw, 520 w, 500 vw, 480 w	2.54
$MnI(CO)_3(CNC_6H_5)_3$	2165 m, 2126 m, 2080 s	1982 s, 1964 (sh)	1590 w, 1480 w, 740 m, 675 w, 635 w, 615 w, 600 w	2.56 (s), 2.70 (s), (2/1)
$[Mn(CNC_6H_5)_6]I$	2088 vs			
$MnI(CO)(CNC_6H_5)_4$	2082 vs	1905 m		

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[a] High resolution data, Perkin–Elmer 421, using chloroform for uncharged species, dichloromethane for monocations, and acetonitrile for dications. [b] Low resolution, Beckman IR-10, using Nujol mulls. [c] $CDCl_3$ was used as solvent for uncharged species; acetone-d_6 was used for ionic compounds; b = broad, o = overlapping, (s) = singlet, d = doublet, t = triplet, m = multiplet.

In refluxing tetrahydrofuran, iodo- and chloropentacarbonylmanganese and phenyl isocyanide were reported to give $MnI(CO)(CNC_6H_5)_4$ and $[Mn(CNC_6H_5)_6]Cl$, respectively, as the only products.

We undertook a study of the reaction of bromopentacarbonylmanganese and methyl isocyanide for several reasons. First, it appeared that the number and variety of new isocyanide carbonyl complexes of manganese could be substantially extended. In particular we hoped to characterize manganese isocyanide carbonyl cations, which had not previously been described; the obvious precursors to such complexes are the $MnX(CO)_{5-x}(CNCH_3)_x$ species. In addition we hoped to elaborate on the chemistry of various cationic and neutral species. Indeed, very little has yet been done in this area; only the reaction of $[Mn(CNC_6H_5)_6]I$ and sodium cyclopentadienide, giving $C_5H_5Mn(CNC_6H_5)_3$[4], has been reported. It may be noted that we have been involved in the study of reactions of various cationic isocyanide complexes recently[5,6]. Finally, we hoped that methyl isocyanide might exhibit a behavior somewhat different from that observed for phenyl (or other aryl) isocyanides. There have been numerous comments on the lower ability of alkyl isocyanides to accept electron density from a low-valent metal, in comparison to aryl isocyanides[7]. These comments are based entirely on infrared spectral evidence; substantive differences in chemical behavior between alkyl and aryl isocyanide–metal complexes have not been observed yet and would be most significant.

In the course of this work, we decided that a reinvestigation of the phenyl isocyanide/halopentacarbonylmanganese reaction was desirable. We have done this also, and find striking differences between our work and the published report[3].

EXPERIMENTAL

Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville,

TABLE 2

CONDUCTIVITY DATA

Compound	*A* ($cm^2 \cdot mol^{-1} \cdot ohm^{-1}$)	
	CH_2Cl_2[a]	CH_3CN[b]
$MnBr(CO)_3(CNCH_3)_2$	0	
$MnBr(CO)_2(CNCH_3)_3$	3	
$MnBr(CO)(CNCH_3)_4$	4	
$[Mn(CO)(CNCH_3)_5]Br$	60	
$[Mn(CO)(CNCH_3)_5]PF_6$		142
$[Mn(CNCH_3)_6]PF_6$		145
$[Mn(CNCH_3)_6](PF_6)_2$		335
$[Mn(CO)(CNCH_3)_5](PF_6)_2$		336
$[Mn(CO)(CNC_6H_5)_5]PF_6$	66	
$[Mn(CNC_6H_5)_6]PF_6$		136
$[Mn(CNC_6H_5)_6]Cl$	65	
$MnCl(CNC_6H_5)_5$	4	

[a] CH_2Cl_2 solution (approx 5×10^{-4} *M*). Value reported[20] for a 1/1 electrolyte in dichloromethane is 78.
[b] CH_3CN solution (approx 5×10^{-4} *M*). Values reported[21] for 1/1 and 2/1 electrolytes in acetonitrile are 135–155 and 250–310, respectively.

Tenn., Schwarzkopf Microanalytical Laboratory, Woodside, N.Y., or Meade Microanalytical Laboratory, Amherst, Mass. Molecular weights were determined from mass spectral data, obtained on an AEI-902 mass spectrometer or by vapor pressure osmometry in chloroform (0.02–0.07 m) on a Mechrolab Model 301A osmometer. Infrared spectra were recorded on Beckman IR-10 and Perkin–Elmer 421 spectrophotometers. Proton NMR spectra were recorded on Varian A-60 and T-60 spectrometers. Infrared and proton NMR data are given in Table 1.

Conductivity measurements (Table 2) were determined at 24.5° using a Beckman conductivity bridge, Model RC-18A, in dry acetonitrile or dichloromethane. Melting points were taken on a Kofler micro hot-stage or in a Thomas-Hoover capillary melting point apparatus and are uncorrected. All reactions were performed in a nitrogen atmosphere.

Electrochemical measurements were made with a three electrode configuration, using a stationary platinum bead working electrode, platinum spiral counter electrode, and saturated calomel (KCl) reference electrode. Voltage and current functions were controlled by conventional operational amplifier circuitry, but no compensation for resistive potential drop between the working electrode and Luggin capillary was included. The cyclic voltammetry experiments were controlled with a variable frequency triangle wave generator and displayed on an X–Y recorder or oscilloscope. Dry acetonitrile was employed as the solvent and tetraethylammonium perchlorate (0.1 M) as the base electrolyte. Solutions were 5×10^{-3} M in substrate. These data are presented in Table 3.

TABLE 3

VOLTAMMETRIC DATA

Compound	$\frac{1}{2}[E_{p,c}+E_{p,a}]^{a}$	*Process*
$[Mn(CNCH_3)_6]PF_6$	0.38	$+1\rightarrow+2$
	1.54	$+2\rightarrow+3$
$[Mn(CNC_6H_4OCH_3)_6]PF_6$	0.69	$+1\rightarrow+2$
	1.55	$+2\rightarrow+3$
$[Mn(CNC_6H_4CH_3)_6]PF_6$	0.76	$+1\rightarrow+2$
	1.69	$+2\rightarrow+3$
$[Mn(CNC_6H_5)_6]PF_6$	0.83	$+1\rightarrow+2$
	1.77	$+2\rightarrow+3$
$[Mn(CNC_6H_4Cl)_6]PF_6$	0.89	$+1\rightarrow+2$
	1.79	$+2\rightarrow+3$
$[Mn(CO)(CNCH_3)_5]PF_6$	0.79	$+1\rightarrow+2$
	1.99	$+2\rightarrow+3$
$[Mn(CO)(CNC_6H_5)_5]PF_6$	1.11	$+1\rightarrow+2$
	2.15^{c}	$+2\rightarrow+3$
$[Mn(CO)_2(CNCH_3)_4]PF_6$	1.12	$+1\rightarrow+2$
$[Mn(CO)_3(CNCH_3)_3]PF_6$	1.65	$+1\rightarrow+2$
$[Mn(CO)_4(CNCH_3)_2]PF_6$	2.14^{b}	$+1\rightarrow+2$
$[Mn(CO)_5(CNCH_3)]PF_6$	2.65^{c}	$+1\rightarrow+2$

[a] Cathodic and anodic peak potentials in volts *vs.* saturated calomel electrode (aq. KCl). Solutions in CH_3CN (5×10^{-3} M) with $[Et_4N][ClO_4]$ (0.1 M) as base electrolyte. The electrode reactions appear reversible for the first oxidation, except as noted. (Difference in peak potentials is 0.06 V for a one-electron reversible system.) [b] $E_{p,c}$ not well defined. [c] Value of $E_{p,c}$; $E_{p,a}$ not defined.

Tetrahydrofuran was dried by distillation from lithium aluminum hydride. Acetonitrile was dried by refluxing over calcium hydride, distillation onto phosphorus pentoxide, and distillation from phosphorus pentoxide. Dichloromethane was dried by reflux and distillation from phosphorus pentoxide. These solvents were also deaerated by purging with nitrogen for conductivity studies and for cyclic voltammetry.

Methyl isocyanide[8], phenyl isocyanide[9], bromopentacarbonylmanganese[10,11], manganese(II) iodide[12], and bromotetracarbonyl(triphenylphosphine)manganese[2] were prepared by published methods.

Chloropentacarbonylmanganese[11] was prepared by the addition of acetic acid and carbon tetrachloride to $NaMn(CO)_5$ in tetrahydrofuran solution in a manner analogous to the preparation of π-$C_5H_5Mo(CO)_3Cl$[13]. It was recrystallized from dichloromethane/heptane. Iodopentacarbonylmanganese[10,11] was prepared from $NaMn(CO)_5$ and iodine in tetrahydrofuran and was recrystallized from dichloromethane/heptane.

Hexakis(methylisocyanide)manganese(I) hexafluorophosphate was obtained by metathesis from hexakis(methylisocyanide)manganese(I) iodide[14] and ammonium hexafluorophosphate in ethanol and was recrystallized from dichloromethane/ether. Bromotricarbonylbis(triphenylphosphine)manganese[11,15] was prepared by refluxing bromopentacarbonylmanganese and triphenylphosphine in chloroform overnight and was crystallized from chloroform/hexane. Dibromooctacarbonyldimanganese[11] was prepared by refluxing bromopentacarbonylmanganese in n-heptane or in benzene for 2 h.

Preparation of $MnBr(CO)_4(CNCH_3)$

A sample of $Mn_2Br_2(CO)_8$ (0.60 g, 1.2 mmol) was dissolved in 50 ml of tetrahydrofuran. Methyl isocyanide (0.12 ml, 2.2 mmol) was added and the solution was stirred at room temperature for 3 h. The solvent was removed on a rotary evaporator and the residue was chromatographed on Florisil using a 1/1 chloroform/benzene solvent mixture. Evaporation of solvent from the major band gave 0.40 g (63%) of $MnBr(CO)_4(CNCH_3)$ as orange crystals, which were recrystallized from chloroform-pentane. The crystals darken at 99–105° and decompose above 140°. [Found: C, 24.81; H, 0.98; N, 4.80; mol wt. (mass spec.) 289. $C_6H_3BrMnNO_4$ calcd.: C, 25.0; H, 1.05; N, 4.87%; mol.wt., 289 (^{81}Br).]

Preparation of $MnBr(CO)_3(CNCH_3)_2$

Bromopentacarbonylmanganese (2.75 g, 10 mmol) was dissolved in 50 ml of tetrahydrofuran. Methyl isocyanide (1.1 ml, 20 mmol) was added and the solution was stirred at room temperature for 48 h. Solvent was removed and the residue recrystallized from dichloromethane/hexane giving 2.45 g (81%) of yellow-orange needles, m.p. 123–124°. (Found: C, 28.29; H, 2.18; N, 9.50; mol.wt., 314. $C_7H_6BrMnN_2O_3$ calcd.: C, 27.9; H, 2.00; N, 9.31%; mol.wt., 301.)

Preparation of $MnBr(CO)_2(CNCH_3)_3$

Methyl isocyanide (2.6 ml, 45 mmol) was added to $MnBr(CO)_5$ (2.75 g, 10 mmol) in 75 ml of tetrahydrofuran and the mixture was refluxed. A precipitate began to form after about 2 h. After 6 h the reaction was allowed to cool and the yellow product was filtered. Addition of petroleum ether to the filtrate resulted in precipitation of additional yellow solid. The combined precipitate (2.9 g, 85%) was recrystallized from dichloromethane/hexane, m.p. 151–153°. (Found: C, 30.23; H, 3.38; N, 13.14; mol.wt., 328. $C_8H_9BrMnN_3O_2$ calcd.: C, 30.6; H, 2.87; N, 13.4%; mol.wt., 314.)

The same product results from the reaction of $MnBr(CO)_3[P(C_6H_5)_3]_2$ with methyl isocyanide in refluxing chloroform or tetrahydrofuran.

Preparation of $MnBr(CO)(CNCH_3)_4$

A sample of $MnBr(CO)_5$ (5.5 g, 20 mmol) was refluxed with methyl isocyanide (4.1 g, 100 mmol) in 200 ml of tetrahydrofuran for 24 h. A pale yellow precipitate formed which appeared to consist of at least two products. Initial crystallization from dichloromethane/hexane resulted in 1.0 g (15%) of a bright yellow product, $MnBr(CO)(CNCH_3)_4$, m.p., 176–178°. (Found: C, 33.24; H, 3.88; N, 17.17; mol.wt., 339. $C_9H_{12}BrMnN_4O$ calcd.: C, 33.0; H, 3.67; N, 17.1%; mol.wt., 327.)

The next two fractions from crystallization were mixtures, but the fourth resulted in 1.3 g (18%) of a white crystalline product, $[Mn(CO)(CNCH_3)_5]Br$, m.p. 201–203° dec. This was dissolved in hot water and treated with excess aqueous ammonium hexafluorophosphate. The product, $[Mn(CO)(CNCH_3)_5]PF_6$, which precipitated immediately, was recrystallized from dichloromethane/ether, m.p. 215°. (Found: C, 30.20; H, 3.37; N, 16.29; O, 3.89. $C_{11}H_{15}F_6MnN_5OP$ calcd.: C, 30.5; H, 3.46; N, 16.2; O, 3.70%.)

Addition of petroleum ether to the tetrahydrofuran filtrate from the initial reaction gave $MnBr(CO)_2(CNCH_3)_3$ (2.5 g, 40%).

Reaction of $MnBr(CO)_3[P(C_6H_5)_3]_2$ with methyl isocyanide

A mixture of $MnBr(CO)_3[P(C_6H_5)_3]_2$ (1.5 g, 2 mmol) and methyl isocyanide, (0.36 ml, 6 mmol) in 50 ml tetrahydrofuran was stirred at room temperature for 4 h. Tetrahydrofuran was removed and the residue dissolved in dichloromethane. Careful addition of hexane and cooling precipitated 0.8 g (75%) of orange crystals, $MnBr(CO)_2(CNCH_3)_2[P(C_6H_5)_3]$, which were recrystallized from chloroform/hexane. Free triphenylphosphine was isolated upon complete evaporation of the filtrate. The product undergoes a slight color change at 95° and melts with decomposition at 142–143°. (Found: C, 51.31; H, 3.66; N, 5.21; mol.wt., 562. $C_{24}H_{21}BrMnN_2O_2P$ calcd.: C, 53.9; H, 3.96; N, 5.23%; mol.wt., 535.)

The same product results from the reaction between $MnBr(CO)_3(CNCH_3)_2$ with triphenylphosphine in refluxing tetrahydrofuran.

Reaction of $MnBr(CO)_4[P(C_6H_5)_3]$ with methyl isocyanide

A sample of $MnBr(CO)_4[P(C_6H_5)_3]$ (1.02 g, 2 mmol) and methyl isocyanide (0.22 ml, 4 mmol) was stirred at room temperature in 50 ml of tetrahydrofuran for 6 h. No further change in infrared spectrum of the reaction mixture was observed after 4 h. The solvent was evaporated and the residue recrystallized from dichloromethane/hexane. Orange crystals of $MnBr(CO)_3(CNCH_3)[P(C_6H_5)_3]$, m.p. 145–147°, were obtained and further recrystallized from chloroform/hexane; (0.6 g, 60% yield). (Found: C, 52.59; H, 3.55; N, 2.58; mol.wt., 528. $C_{23}H_{18}BrMnNO_3P$ calcd.: C, 53.0; H, 3.47; N, 2.68%; mol.wt., 522.)

Preparation of $[Mn(CO)_3(CNCH_3)_3]PF_6$ and similar cationic complexes

A mixture of $MnBr(CO)_2(CNCH_3)_3$ (1.0 g, 3 mmol) and anhydrous aluminum chloride (1.2 g, 9 mmol) was suspended in 40 ml of benzene. Carbon monoxide was bubbled slowly through the mixture for 1 h. A red-orange oil separated and the benzene layer was decanted. The oil was taken up in ice water and a saturated solution of ammonium hexafluorophosphate added. A white precipitate separated immediately and was recrystallized from acetone/ether giving 0.5 g (40%) of $[Mn(CO)_3(CNCH_3)_3]PF_6$, m.p. 175–177°. (Found: C, 26.48; H, 2.06; N, 9.97. $C_9H_9F_6MnN_3O_3P$ calcd.: C, 26.5; H, 2.23; N, 10.3%.)

Attempts were made to add triphenylphosphine and acetonitrile to $MnBr(CO)_2(CNCH_3)_3$ by a similar method. In each case the only product isolated was the above compound, $[Mn(CO)_3(CNCH_3)_3]PF_6$.

The preparations of other cationic complexes were carried out in an entirely analogous manner.

$[Mn(CO)_5(CNCH_3)]PF_6$ was prepared from $MnBr(CO)_4(CNCH_3)$, $AlCl_3$, and CO followed by metathetical reaction with ammonium hexafluorophosphate. Yield 60%; m.p. 192–194°. (Found: C, 22.67; H, 0.82; N, 3.56. $C_7H_3F_6MnNO_5P$ calcd.: C, 22.1; H, 0.80; N, 3.69%.)

$[Mn(CO)_4(CNCH_3)_2]PF_6$ was prepared from $MnBr(CO)_3(CNCH_3)_2$, $AlCl_3$, and CO, followed by conversion to the hexafluorophosphate salt. Yield 80%; m.p. 141–142°. (Found: C, 24.45; H, 1.41; N, 7.01. $C_8H_6F_6MnN_2O_4P$ calcd.: C, 24.4; H, 1.53; N, 7.12%.)

$[Mn(CO)_2(CNCH_3)_4]PF_6$ was prepared from $MnBr(CO)(CNCH_3)_4$, $AlCl_3$, and CO, followed by conversion to the hexafluorophosphate salt. Yield 60%; m.p. 215–216°. (Found: C, 28.59; H, 2.97; N, 13.14. $C_{10}H_{12}F_6MnN_4O_2P$: C, 28.6; H, 2.86; N, 13.3%.)

Preparation of $[Mn(CNCH_3)_6](PF_6)_2$

Solid $[Mn(CNCH_3)_6]PF_6$ (1.8 g, 4 mmol) was dissolved in 40 ml of glacial acetic acid. Concentrated nitric acid (≈1 ml) was added and the solution immediately changed to a pink color. The mixture was stirred for 30 min and excess ammonium hexafluorophosphate in water was added. The pink precipitate (1.6 g, 66%) was collected and recrystallized from acetonitrile/ether. The complex decomposes without melting above 145°. (Found: C, 24.69; H, 3.16; N, 14.38. $C_{12}H_{18}F_{12}MnN_6P_2$: C, 24.4; H, 3.07; N, 14.2%.)

Preparation of $[Mn(CO)(CNCH_3)_5](PF_6)_2$

A sample of $[Mn(CO)(CNCH_3)_5]Br$ (0.73 g, 2 mmol) was dissolved in 40 ml of water. Concentrated nitric acid was added dropwise until the precipitate which initially formed dissolved to a yellow solution. Excess ammonium hexafluorophosphate in water was added and the tan colored precipitate (0.9 g, 80%) was collected and recrystallized from acetone/ether. The salt decomposes without melting above 100°. (Found: C, 22.48; H, 2.69; N, 12.09. $C_{11}H_{15}F_{12}MnN_5OP_2$ calcd.: C, 22.9; H, 2.62; N, 12.1%.)

Several attempts to oxidize $[Mn(CO)_2(CNCH_3)_4]PF_6$ were made using various oxidizing agents. All resulted in either decomposition or recovery of starting material.

Reaction of $MnBr(CO)_5$ with phenyl isocyanide

A mixture of $MnBr(CO)_5$ (2.75 g, 10 mmol) and phenyl isocyanide (5.15 g, 50 mmol) was refluxed in 100 ml of tetrahydrofuran for 6 h. The solvent was removed and the residue washed thoroughly with benzene leaving 0.4 g of yellow solid. Recrystallization from dichloromethane/ether gave what appeared to be a mixture of two products. The mixture was dissolved in acetone and a saturated solution of ammonium hexafluorophosphate in acetone was added. The resulting yellow precipitate was fractionally recrystallized from acetone/ether. White crystals of $[Mn(CO)(CNC_6H_5)_5]PF_6$ (0.20 g, 2%) were initially precipitated, m.p. 196–198° (decomp.). (Found: C, 58.35; H, 3.38; N, 9.23; O, 2.17. $C_{36}H_{25}F_6MnN_5OP$ calcd.: C, 58.16; H, 3.39; N, 9.41; O, 2.15%.)

The second product, yellow crystalline $[Mn(CNC_6H_5)_6]PF_6$ (0.15 g, 2%), was characterized by its infrared spectrum. Its spectrum is identical to the compound made by metathesis from the iodide salt reported by Sacco[16]. The salt decomposes without melting at 260–270°.

The benzene solution from the initial washing was evaporated and the residue recrystallized from dichloromethane/hexane yielding orange crystals of $MnBr(CO)(CNC_6H_5)_4$[3] (5.2 g, 90%).

The same reaction using a 6/1 isocyanide/manganese ratio after 6 h reflux gave 4% $[Mn(CNC_6H_5)_6]Br$ and none of the carbonyl salt. When an 8/1 ratio of reactants was used, and the solution refluxed for 40 h the compound $[Mn(CNC_6H_5)_6]Br$ was obtained in 64% yield, along with a small amount (not measured) of $MnBr(CO)(CNC_6H_5)_4$.

Reaction of $MnCl(CO)_5$ with phenyl isocyanide

Phenyl isocyanide (2.58 g, 25 mmol) was added to $MnCl(CO)_5$ (1.15 g, 5 mmol) in 25 ml of tetrahydrofuran and the mixture refluxed for 4 h. The solution was allowed to cool to room temperature and an orange precipitate was filtered and washed with tetrahydrofuran. The solid was recrystallized from dichloromethane/heptane to give orange crystals of $MnCl(CO)(CNC_6H_5)_4$ (0.8 g, 30%); m.p. 163–164° (decomp.). (Found: C, 65.69; H, 3.96; Cl, 6.70; N, 10.37; O, 2.97; mol.wt., 534. $C_{29}H_{20}ClMnN_4O$ calcd.: C, 65.61; H, 3.80; Cl, 6.68; N, 10.55; O, 3.01%; mol.wt., 530.9.)

The tetrahydrofuran solution was evaporated and the residue recrystallized from dichloromethane/heptane yielding orange crystals of $MnCl(CNC_6H_5)_5$ (0.9 g, 30%); mp. 155–156° (decomp.). (Found: C, 69.40; H, 4.20; Cl, 5.80; N, 11.52; mol.wt., 549. $C_{35}H_{25}ClMnN_5$ calcd.: C, 69.37; H, 4.16; Cl, 5.85; N, 11.56%; mol.wt., 606.)

Reflux of a similar mixture for three days gave only $[Mn(CNC_6H_5)_6]Cl$ (11%) contaminated with a grey-green product which was not investigated further.

Reaction of $MnI(CO)_5$ with phenyl isocyanide

A mixture of $MnI(CO)_5$ (0.5 g, 1.5 mmol) and phenyl isocyanide (0.75 g, 7.5 mmol) in 30 ml of tetrahydrofuran was refluxed for 3 h. Evaporation of solvent gave an oil. The oil was dissolved in chloroform and was chromatographed on alumina. Two poorly resolved bands were seen. Elution and evaporation of solvent from the first band resulted in an oily solid which was rechromatographed on alumina in benzene. Solvent was removed and the solid dissolved in acetone. Careful addition of water and cooling gave orange crystals, $MnI(CO)_3(CNC_6H_5)_2$ (0.35 g, 50%); m.p. 101–102°. (Found: C, 43.31; H, 2.09; I, 26.80; N, 5.86; O, 10.10; mol.wt., 455. $C_{17}H_{10}IMnN_2O_3$ calcd.: C, 43.25; H, 2.14; I, 26.88; N, 5.93; O, 10.17%; mol. wt., 472.)

Careful recrystallization of the second band, also from acetone/water, yielded orange crystals, $MnI(CO)_2(CNC_6H_5)_3$ (0.12 g, 15%); m.p. 122–123°. (Found: C, 50.47; H, 2.98; I, 23.00; N, 7.87; O. 5.80; mol.wt., 497. $C_{23}H_{15}IMnN_3O_2$ calcd.: C, 50.48; H, 2.76; I, 23.19; N, 7.68; O, 5.85%; mol.wt., 547.)

Prolonged reflux (4 days) of a similar mixture resulted in an 8% yield of $[Mn(CNC_6H_5)_6]I$[16], 30% $MnI(CO)(CNC_6H_5)_4$[3], and decomposition products.

RESULTS AND DISCUSSION

Several products may be obtained from the reaction of bromopentacarbonylmanganese and methyl isocyanide in tetrahydrofuran, depending on the conditions employed. When stoichiometric quantities of the reactants are mixed at room temperature and allowed to stand over 48 hours, the disubstituted complex $MnBr(CO)_3L_2$ ($L = CH_3NC$), is the only product obtained. If bromopentacarbonylmanganese and an excess of the isocyanide are allowed to react in refluxing tetrahydrofuran, a yellow precipitate is observed. Initially this precipitate appears to be the trisubstituted complex $MnBr(CO)_2L_3$; the yield of this complex is maximized by running the reaction for about six hours. For longer periods at reflux, there is a further conversion to two additional products, $MnBr(CO)L_4$ and $[Mn(CO)L_5]Br$, obtained with $MnBr(CO)_2L_3$. The three species are separated on the basis of different solubilities.

No monosubstituted derivative $MnBr(CO)_4L$ was isolated in the direct halopentacarbonylmanganese/$CNCH_3$ reaction, even using mild conditions and choosing a favorable stoichiometry. However this species could be obtained from methyl isocyanide and $Mn_2Br_2(CO)_8$, the isocyanide replacing the bridging halide groups in a facile reaction.

The methyl isocyanide/$MnBr(CO)_5$ system thus appears to involve a sequence of replacement reactions, first of four carbonyls and finally of a bromide ion, from the coordination sphere of manganese.

$$MnBr(CO)_5 \rightarrow [MnBr(CO)_4L] \rightarrow MnBr(CO)_3L_2 \rightarrow MnBr(CO)_2L_3 \\ \rightarrow MnBr(CO)L_4 \rightarrow [Mn(CO)L_5]Br$$

Interestingly, there is no evidence that $[MnL_6]Br$ forms. This is in contrast to reactions with phenyl isocyanide, described below.

The products obtained were characterized by analyses. The final product in this sequence, $[Mn(CO)L_5]Br$ was converted to the PF_6^- salt and this was shown to have a conductivity value in acetonitrile appropriate for a 1/1 electrolyte. PMR data were generally not useful in establishing a geometry for these complexes; the methyl resonances are relatively broad singlets, and chemical shift differences are small when they are observed. However infrared data were somewhat more helpful in establishing structures. For example, the complex $MnBr(CO)L_4$ has single $\nu(CN)$ (2142 cm^{-1}) and $\nu(CO)$ (1881 cm^{-1}) absorptions, which can be accounted for by assuming that one isomer having C_{4v} symmetry is present. The species, $MnBr(CO)_3L_2$, has two $\nu(CN)$ absorptions suggesting the isocyanides are *cis*; a *fac* geometry seems most likely here, analogous to some other disubstituted complexes[15]. Infrared data for $MnBr(CO)_2L_3$ [three $\nu(CN)$ and two $\nu(CO)$ absorptions] and PMR data for this complex (2 resonances, approx. intensity 2/1) are consistent with a structure in which the three isocyanides substitute in positions *cis* to the bromine.

The sequential substitution of equatorial carbonyl groups (*cis* to Br) is inferred from these data. This reaction is analogous to that observed between $MnX(CO)_5$ and trimethyl phosphite[17].

Few monodentate ligands other than isocyanides are known to substitute more than two or three carbonyls in reactions of $MnX(CO)_5$ complexes. The extent of phosphine substitution in these reactions is generally two[15]; phosphites often will replace three carbonyls. Four carbonyls in $Mn(CH_3)(CO)_5$ are replaced by trimethyl phosphite ligands using forcing conditions; however, the analogous reaction with $MnBr(CO)_5$ gives $MnBr(CO)_2[P(OCH_3)_3]_3$[17].

We have prepared other cationic complexes $[Mn(CO)_{6-n}L_n]PF_6$. A standard method[18], from the isocyanide substituted halocarbonyl, aluminum chloride, and carbon monoxide is quite appropriate; the resulting tetrahaloaluminate salt is then converted to the hexafluorophosphate salt by a metathesis reaction.

$$MnBr(CO)_{5-n}L_n + CO + AlCl_3 \rightarrow [Mn(CO)_{6-n}L_n]AlX_4 \xrightarrow{NH_4PF_6} [Mn(CO)_{6-n}L_n]PF_6$$

$$n = 1, 2, 3, 4$$

It might be observed that use of methyl isocyanide in place of carbon monoxide in this reaction in hopes of obtaining $[Mn(CO)_{5-n}L_{n+1}]AlX_4$ is not possible as the isocyanide is destroyed by the aluminum halide.

We also isolated two triphenylphosphine complexes, $MnBr(CO)_3[P(C_6H_5)_3]L$ and $MnBr(CO)_2[P(C_6H_5)_3]L_2$, from reactions of $MnBr(CO)_4[P(C_6H_5)_3]$ and $MnBr(CO)_3[P(C_6H_5)_2]_2$, respectively, with methyl isocyanide. In order to avoid displacement of phosphines by methyl isocyanide it was necessary to run the reaction at room temperature. The product $MnBr(CO)_2[P(C_6H_5)_3]L_2$ may also be obtained from $MnBr(CO)_3L_2$ and triphenylphosphine.

There were several qualitative differences between our work on methyl isocyanide/$MnBr(CO)_5$ reactions, and the analogous reactions described by Joshi *et al.*[3], with phenyl isocyanide. Two differences in particular warrant mention. The first concerns rates of the reactions, apparently slower for the methyl isocyanide reactions than was reported for phenyl isocyanide. More important perhaps was the difference in the final products reported, $[Mn(CO)(CNCH_3)_5]Br$ in the former reaction and $MnBr(CNC_6H_5)_5$ in the latter. However, there was some reason to suspect that the complex $MnBr(CNC_6H_5)_5$ had been incorrectly formulated. The characterization of this species, based primarily on analytical data, is not conclusive, and the reported white color for this complex is definitely suspect as is the infrared spectrum with bands at 2101 and 2012 cm^{-1}. The latter, if assigned to $\nu(CN)$, is unrealistically low.

Because of these points, we felt it best to reevaluate the reactions of phenyl isocyanide and the various $MnX(CO)_5$ species, particularly the bromide; we looked only at the tetrahydrofuran reactions for comparison purposes, and chose conditions identical to those reported [for $MnBr(CO)_5$, 6 h reflux]. In our hands the reaction rate appeared somewhat slower; we isolated and identified three products, none of which corresponded to the formulation as reported. The major product was $MnBr(CO)(CNC_6H_5)_4$ (90%) separated by virtue of its solubility in the solvent. [Note that this product had been obtained in lower yield in the earlier work[3]; also that the reaction with methyl isocyanide under similar conditions gave $MnBr(CO)_2L_3$.] The tetrahydrofuran insoluble fraction proved to be a mixture of two ionic products; after metathesis to give the hexafluorophosphate salts they were separated by fractional crystallization and identified as $[Mn(CO)(CNC_6H_5)_5]PF_6$ and $[Mn(CNC_6H_5)_6]PF_6$, the latter a known compound.

The identification of $[Mn(CO)(CNC_6H_5)_5]PF_6$ was conclusive, from analyses (including oxygen analysis) and conductivity data. This complex must certainly have arisen from $[Mn(CO)(CNC_6H_5)_5]Br$ present in the original product mixture. The infrared spectra (CH_2Cl_2) bears this out; $[Mn(CO)(CNC_6H_5)_5]PF_6$ has major absorptions at 2111 [ν(CN)] and 1991 [ν(CO)], whereas $[Mn(CO)(CNC_6H_5)_5]Br$ has absorptions at 2112 and 1997 cm^{-1}. {The latter measurements were made on the mixture of this complex and $[Mn(CNC_6H_5)_6]Br$ in the same solvent. The higher frequency peak appears as a shoulder on the 2088 cm^{-1} absorption from the latter compound.} The spectrum of this product mixture, under anything but optimum resolution, appears quite like that reported for the supposed $MnBr(CNC_6H_5)_5$. The infrared of the latter, in 1,2-dichloroethane, reportedly consists of two absorptions at 2101 vs and 2012 m cm^{-1}. The higher frequency band is a composite of the 2112 and 2088 cm^{-1} absorptions for $[Mn(CO)(CNC_6H_5)_5]Br$ and $[Mn(CNC_6H_5)_6]Br$, respectively.

When the reaction of $MnBr(CO)_5$ and phenyl isocyanide was carried out for a longer time (40 h reflux), the only isolable product was $[Mn(CNC_6H_5)_6]Br$ (64%). It is noted that the end product of this reaction is $[Mn(CNC_6H_5)_6]Br$ whereas in the reaction with methyl isocyanide the product is $[Mn(CO)(CNCH_3)_5]Br$.

In our hands, the reactions of phenyl isocyanide and $MnX(CO)_5$ were appreciably slower than reported earlier[3]. However, we feel that it would be inappropriate to elaborate on any differences since in neither our work nor the earlier work was an attempt made to define the system sufficiently rigorous criteria to justify any kinetic measurements.

The reaction of phenyl isocyanide and $MnI(CO)_5$ (3 h reflux) gave $MnI(CO)_3(CNC_6H_5)_2$ (50%) and $MnI(CO)_2(CNC_6H_5)_3$ (15%). This contrasts with the report[3] that the only product was $MnI(CO)(CNC_6H_5)_4$. Prolonged reflux (4 days) did eventually give the latter species (30%) and in addition the ionic complex $[Mn(CNC_6H_5)_6]I$ (8%).

The reaction of phenyl isocyanide and $MnCl(CO)_5$ had been reported to give only $[Mn(CNC_6H_5)_6]Cl$; we found (using similar conditions to those reported) $MnCl(CO)(CNC_6H_5)_4$ (30%) and a new species $MnCl(CNC_6H_5)_5$ (30%). Prolonged reflux (3 days) gave much decomposition and a small yield of $[Mn(CNC_6H_5)_6]Cl$.

The complex $MnCl(CNC_6H_5)_5$ is a yellow crystalline substance. It is quite different from the complex $MnBr(CNC_6H_5)_5$, incorrectly reported[3]. In the infrared spectrum a single broad ν(CN) absorption at 2070 cm^{-1} was noted.

The one-electron oxidation of hexakis(isocyanide)manganese(I) complexes is a well known process[7]. In addition, several other multiply substituted manganese carbonyl complexes are reported to be oxidized. Hence, we felt that at least several of the isocyanide substituted complexes described here might also be oxidized to isolable species. Indeed this proved to be the case; $[Mn(CO)L_5]PF_6$ could be converted to the complex $[Mn(CO)L_5](PF_6)_2$ by nitric acid oxidation.

Oxidation causes a shift of approximately 100 cm^{-1} of the value of ν(CO) and an 80 cm^{-1} shift of $\nu(CN)$ values in this compound. This shift is expected, of course; because of the higher positive charge on the metal there should be greater σ donation to the metal and less π electron delocalization back to the ligands.

Analogous chemical oxidations of the other cationic species were not accomplished. Nitric acid appeared not to be a strong enough oxidizing agent to convert $[Mn(CO)_2L_4]PF_6$ to $[Mn(CO)_2L_4](PF_6)_2$, and stronger oxidizing agents such as hydrogen peroxide and sodium peroxydisulfate led to degradation of the complex.

We were able to obtain useful information on these oxidations from cyclic voltammetry experiments, however[19]. Table 3 presents data from these experiments. One sees that the oxidation of $[MnL_6]PF_6$ is a relatively easy process to accomplish; $E_{\frac{1}{2}}$ has a low value, *vs.* SCE. With subsequent substitution of carbon monoxide for methyl isocyanide, however, the relative difficulty of oxidation increases. The change of $E_{\frac{1}{2}}$ is regular, increasing by about 0.4 V at each substitution.

Interestingly, a second oxidation wave is observed at high potential for $[MnL_6]PF_6$ and $[Mn(CO)L_5]PF_6$. We believe this corresponds to a second oxidation to give a complex bearing a +3 charge, though no chemical evidence supports this idea.

We also note the substantial differences in $E_{\frac{1}{2}}$ values for the analogous phenyl and methyl isocyanide complexes. It is rather more difficult to oxidize the phenyl isocyanide complexes. As we have commented earlier[19] there seems to be a substantial difference between alkyl and aryl isocyanide complexes.

The differences in ease of oxidation, for both the $[Mn(CO)_{6-x}L_x](PF_6)$ series and for analogous phenyl and methyl isocyanide complexes, can most easily be rationalized in terms of electron withdrawing capability of the ligand*. For ligands which are better electron acceptors, there will be a higher effective positive charge at the metal and it will then be harder to remove an electron. Obviously carbon monoxide is a better acceptor than are any of the isocyanides. Phenyl isocyanide has been suggested to be a better electron acceptor than are alkyl isocyanides on the basis of infrared spectral studies[7]. With the current resurgence of isocyanide chemistry this feature is now commonly mentioned in discussions of spectral data.

If we assume that this oxidation potential difference is going to be a general phenomenon among isocyanide complexes, which seems reasonable, then these data have obvious important implications to the chemistry of the isocyanides. The oxidation potential of a complex is, after all, a chemical property of considerable importance. Up until now chemists working with isocyanides as ligands in metal complexes might have anticipated little difference in chemical behavior as a function of the isocyanide chosen. Obviously this assumption will have to be reexamined.

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* It is important to remember that while this argument seems logical and reasonable, it will be difficult to make any quantitative comparisons. The value of $E_{\frac{1}{2}}$ is, after all, a measure of an energy difference between oxidized and reduced species, whereas this bonding argument is directed only to the reduced species. Still, for a qualitative argument this seems reasonably sound.

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