but the product is comparatively less stable than the others, and thus defied final purification.
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Organometallic Anions Containing Isocyanide Ligands. IV. Synthesis and Reaction Chemistry of Methyl Isocyanide Derivatives of the Manganese Pentacarbonyl Anion

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Evidence is presented for the syntheses of the anions $Mn(CO)_{5-x}(CNCH_3)_x^-$, $x = 1-3$. Their infrared spectra indicate an increased amount of π back-bonding to the isocyanide ligands. The anions are valuable reagents and the new isocyanide-containing compounds $Mn(CO)_4(CNCH_3)R$, where $R = CH_2CN$, $(C_6H_5)_3Ge$, $(CH_3)_3Sn$, $(C_6H_5)_3Sn$, $(C_6H_5)_3Pb$, H, I, and HgI, $[Mn(CO)_4(CNCH_3)]_2Hg$, $Mn(CO)_3(CNCH_3)_2R$, where $R = CH_2CN$, $(C_6H_5)_3Ge$, $(C_6H_5)_3Sn$, $(C_6H_5)_3Pb$, and I, $[Mn(CO)_3(CNCH_3)_2]_2Hg$, and $Mn(CO)_2(CNCH_3)_3R$, where $R = CH_2CN$, $(C_6H_5)_3Sn$, $(C_6H_5)_3Pb$, and I, have been prepared. The stability and patterns of reactivity of the anions are discussed. The structures of the new molecules are deduced. Several of the new molecules show evidence of long-range coupling of the heteronuclei $^{117,119}Sn$, ^{199}Hg, and ^{207}Pb to the methyl groups on the isocyanide ligands.

Introduction

We have recently initiated a program to investigate the synthesis of anionic organometallic complexes, which contain isocyanide ligands.[2] Since isocyanide ligands have been shown to engage effectively in metal to ligand π back-bonding[3] and since this mechanism is very important in the stabilization of low-valent transition metal complexes,[4] it seemed plausible that these ligands would yield viable systems. In this paper, we report results of our investigations of methyl isocyanide derivatives of the manganese pentacarbonyl anion. As organometallic anions have generally proven to be valuable reagents for the syntheses of new compounds,[5] we have investigated the reaction chemistry of these anions through their ability to effect halide displacements. Their value as reagents has been demonstrated through their use in the synthesis of several new organometallic compounds which contain isocyanide ligands.

Experimental Section

General Data. All reactions were performed in an argon atmosphere. The solvents tetrahydrofuran, hexane, and toluene were dried by refluxing over sodium–benzophenone and distilling under argon just prior to use. The chemicals $Mn(CO)_5Br$, $CH_2(CN)Cl$, $(C_6H_5)_3GeBr$, $(CH_3)_3SnCl$, $(C_6H_5)_3SnCl$, and $(C_6H_5)_6Pb_2$ were obtained commercially. $(C_6H_5)_3PbI$ was prepared by a known method.[6] $Mn(CO)_3(CNCH_3)_2Br$ and $Mn(CO)_2(CNCH_3)_3Br$ were prepared in this laboratory by Mr. Thomas P. Lawrence according to the method of Treichel.[7] $Mn(CO)_4(CNCH_3)Br$ was prepared as described below. Methyl isocyanide was prepared by an established procedure.[8]

$Mn(CO)_4(CNCH_3)Br$. Unlike Treichel,[7] we have found it quite convenient to prepare $Mn(CO)_4(CNCH_3)Br$ by the direct reaction of $Mn(CO)_5Br$ and $CNCH_3$. A typical preparation went as follows. A 2.0-g (7.28-mmol) amount of $Mn(CO)_5Br$ was dissolved in approximately 100 ml of THF. A 0.35-ml (6.5-mmol) amount of $CNCH_3$ was added via syringe. After stirring of the mixture 4 days at room temperature, the solvent was removed in vacuo. The residue was chromatographed over Florisil with benzene. A small amount of $Mn(CO)_5Br$ eluted first. A large orange band eluted next. This band was collected and the solvent was removed in vacuo. This gave 1.05 g of $Mn(CO)_4(CNCH_3)Br$ as flaky crystals. An infrared spectrum showed it to be pure; yield 50%.

Preparation of Anions and Their Reactions. In Table I are listed important physical properties of the compounds that have been prepared, in addition to the methods of purification, typical yields, and microanalytical data. Here will be listed other pertinent synthetic information.

$Mn(CO)_4CNCH_3$ Anion. Solutions containing approximately 1 mmol of $Mn(CO)_4(CNCH_3)Br$ in 50 ml of THF were stirred with 1% Na(Hg) at 0° for 20 min. Filtration of these solutions produced clear light yellow solutions containing the anion $Mn(CO)_4CNCH_3^-$.

Reactions of $Mn(CO)_4(CNCH_3)^-$ with Alkyl and Aryl Group 4 Halides and HgI_2. The THF solutions of the anion were cooled to −78° and stoichiometrically appropriate amounts of a given halide were added. These solutions were stirred approximately 15 min at −78° and then allowed to warm slowly to room temperature. Upon reaching room temperature, they were usually stirred an additional 15 min. The solvent was then removed in vacuo, and the compounds were isolated as reported in Table I. Final purifications were obtained by recrystallization from hexane or toluene–hexane solvent mixtures.

The isolation of $Mn(CO)_4(CNCH_3)HgI$ required special care. The reaction solutions of this compound were evaporated in vacuo. The residue was taken up with benzene plus a small amount of THF and filtered over a short column of $Al_2O_3 \cdot 6\%H_2O$ to remove impurities. A large yellow band eluted. The solvent was removed from the eluent and the residue was dissolved in approximately 3 ml of toluene. Then, 50 ml of pentane was added to the toluene solution. Flaky yellow crystals of pure $Mn(CO)_4(CNCH_3)HgI$ formed slowly at room temperature. After ∼15 min, the yellow mother liquor was removed and the crystals were washed with pentane and dried in vacuo. Difficulty can arise if the final crystallization is pursued too far. We found that the chromatography causes partial decomposition of the mercury complex to $Mn(CO)_4(CNCH_3)I$, and thus the eluent contains some of this compound. However, this complex is much more soluble than $Mn(CO)_4(CNCH_3)HgI$ and therefore can be removed by the fractional crystallization.

$Mn(CO)_4(CNCH_3)I$. Excess concentrated HCl was added to a THF solution of $IHgMn(CO)_4(CNCH_3)$. Hg metal precipitated and the solution became more yellow. The product, $Mn(CO)_4(CNCH_3)I$, was chromatographed over $Al_2O_3 \cdot 6\%H_2O$ and crystallized from toluene–hexane at −20°.

$Mn(CO)_4(CNCH_3)H$. At −78°, 0.095 ml of degassed acetic acid was added to a THF solution of $Mn(CO)_4CNCH_3^-$ that had been prepared from 0.32 g of $Mn(CO)_4(CNCH_3)Br$ (vide supra). After 5 min at −78°, the solution was allowed to warm to room temperature. During this time the solutions became lighter yellow. Stirring was continued $^1/_2$ hr at room temperature after which the solvent was removed in vacuo. The residue was extracted with hexane and filtered. An infrared spectrum at this time showed an absorption pattern typical of complexes of the form $RMn(CO)_4(CNCH_3)$. Vacuum evaporation of the hexane caused the solution to become orange. Infrared spectra indicated decomposition was occurring. However, a ^1H NMR spectrum of the residue still showed a prominent metal–hydride resonance at −7.15 ppm.[9]

$Mn(CO)_3(CNCH_3)_2$ Anion. At −15°, solutions containing 1 mmol

Table I

Compd	Color	Mp, °C	Method of purification (solvent used)	Yield, %	Exptl (calcd) analyses, %				
					C	H	N	Hg	I
$Mn(CO)_4(CNCH_3)CH_2CN$	Yellow	50.5–52.5	E^a (toluene–hexane)	35	38.44 (38.73)	2.15 (2.03)	11.01 (11.29)		
$Mn(CO)_4(CNCH_3)Ge(C_6H_5)_3$	Yellow	132–134	E (toluene–hexane)	37	56.05 (56.31)	3.59 (3.54)	2.57 (2.74)		
$Mn(CO)_4(CNCH_3)Sn(CH_3)_3$	White	~25	E (pentane)	56	29.21 (29.00)	3.44 (3.25)	3.58 (3.76)		
$Mn(CO)_4(CNCH_3)Sn(C_6H_5)_3$	White	144–145.5	E (toluene–hexane)	64	51.56 (51.66)	3.30 (3.25)	2.82 (2.51)		
$Mn(CO)_4(CNCH_3)Pb(C_6H_5)_3$	Pale yellow	148.5–150	E^b (benzene–hexane)	47	44.81 (44.59)	2.85 (2.81)	2.07 (2.17)		
$Mn(CO)_4(CNCH_3)HgI$	Pale yellow	93–95	E^b (benzene–THF)	17	13.45 (13.46)	0.64 (0.56)		38.0 (37.5)	23.41 (23.70)
$Mn(CO)_4(CNCH_3)]_2Hg$	Yellow	169.5–170	C^c (benzene)	37	23.20 (23.37)	0.99 (0.98)	4.47 (4.54)		
$Mn(CO)_4(CNCH_3)I$	Orange	101–102	C (benzene)	18	21.70 (21.52)	0.93 (0.90)	4.16 (4.18)		38.11 (37.89)
$Mn(CO)_3(CNCH_3)_2CH_2CN$	Yellow	73–77	E (toluene)	50	41.12 (41.40)	3.18 (3.09)	15.90 (16.09)		
$Mn(CO)_3(CNCH_3)_2Ge(C_6H_5)_3$	Golden	192–193	E (toluene)	46	56.89 (57.20)	4.08 (4.03)	5.22 (5.34)		
$Mn(CO)_3(CNCH_3)_2Sn(C_6H_5)_3$	Golden	179–180.5	E (toluene)	47	52.56 (52.58)	3.66 (3.71)	4.81 (4.91)		
$Mn(CO)_3(CNCH_3)_2Pb(C_6H_5)_3$	Brown	171.5–172.5	E (toluene)	62	44.21 (45.53)	3.26 (3.21)	3.94 (4.25)		
$[Mn(CO)_3(CNCH_3)_2]_2Hg$	Yellow	174–175.5	C (benzene)	30	26.33 (26.16)	1.97 (1.88)	8.22 (8.72)		
$Mn(CO)_3(CNCH_3)_2I$	Orange	129.5–132.5	C (benzene)	46	24.23 (24.16)	1.71 (1.74)	8.10 (8.05)		35.29 (36.47)
$Mn(CO)_2(CNCH_3)_3CH_2CN$	Golden	129–130.5	E (toluene–hexane)	47	43.33 (43.81)	4.02 (4.04)	18.85 (20.44)		
$Mn(CO)_2(CNCH_3)_3Sn(C_6H_5)_3$	Golden	85–87	E (toluene–hexane)	28	56.30 $(56.22)^d$	4.48 (4.48)	6.55 (6.67)		
$Mn(CO)_2(CNCH_3)_3Pb(C_6H_5)_3$	Light brown	95–100.5	E (toluene)	46	48.78 $(49.30)^d$	3.97 (3.93)	5.66 (5.85)		
$Mn(CO)_2(CNCH_3)_3I$	Orange	169.5–172	C (benzene–THF)	30	26.29 (26.62)	2.48 (2.51)			35.40 (35.15)

^{a} E = solvent extraction. ^{b} Extracted and filtered over a 6-in. column of $Al_2O_3 \cdot 6\%H_2O$. ^{c} C = chromatography over $Al_2O_3 \cdot 6\%H_2O$. ^{d} Crystallizes as a 2:1 complex–toluene adduct.

of $Mn(CO)_3(CNCH_3)_2Br$ in approximately 50 ml of THF were reduced with 1% Na(Hg). After 30 min, the solutions were filtered and gave clear yellow solutions (which slowly developed a brown tinge) that contain the anion $Mn(CO)_3(CNCH_3)_2^-$.

Reactions of $Mn(CO)_3(CNCH_3)_2^-$ with Alkyl and Aryl Group 4 Halides and HgI_2. To the filtered THF solutions of the anion at $-78°$ were added stoichiometrically appropriate amounts of the given halides. The solutions were stirred at $-78°$ approximately 15 min and then allowed to warm slowly to room temperature. After about 15 min of stirring, the solvent was removed in vacuo. The compounds were isolated as indicated in Table I. Final purification was obtained by crystallization from toluene–hexane solvent mixtures.

$Mn(CO)_3(CNCH_3)_2I$. A 1-mmol amount of $Mn(CO)_3(CNCH_3)_2^-$ was allowed to react with 1 mmol of HgI_2 in 50 ml of THF at $-78°$. After warming of the mixture to room temperature and stirring for 10–15 min, an ir spectrum showed an absorption pattern characteristic of the molecules $Mn(CO)_3(CNCH_3)_2R$. Over a period of hours new absorptions appeared in the spectra while the original absorptions slowly disappeared. After 21 hr, the original absorptions were completely absent and were replaced by the new absorptions, which displayed a pattern characteristic of $Mn(CO)_3(CNCH_3)_2X.^7$ Also during this time, finely divided mercury metal appeared on the walls of the flask. Finally, the solvent was removed in vacuo and the residue was worked up (Table I). Recrystallization from toluene–hexane at $-20°$ gave orange crystals that have been identified as $Mn(CO)_3(CNCH_3)_2I$.

$Mn(CO)_2(CNCH_3)_3$ **Anion.** At -15 to $-20°$, solutions containing 1 mmol of $Mn(CO)_2(CNCH_3)_3Br$ in approximately 50 ml of THF were reduced with 1% Na(Hg) for about 30 min. The solutions were filtered cold and then maintained at $-78°$. However, the initially dark yellow solutions readily developed a brown tinge.

Reactions of $Mn(CO)_2(CNCH_3)_3^-$ with Alkyl and Aryl Group 4 Halides. Freshly prepared solutions of the anion $Mn(CO)_2(CNCH_3)_3^-$ were allowed to react at $-78°$ with stoichiometrically appropriate

amounts of the halides $(C_6H_5)_3SnCl$, $(C_6H_5)_3PbI$, and $CH_2(CN)Cl$. After being stirred for 15 min, at $-78°$, the solutions were allowed to warm to room temperature. Finally, after 10–15 min of stirring at room temperature, the solvent was removed in vacuo and the compounds were isolated as indicated in Table I. Final purifications were obtained by recrystallization from toluene–hexane solvent mixtures at $-20°$.

$Mn(CO)_2(CNCH_3)_3I$. To 1 mmol of $Mn(CO)_2(CNCH_3)_3^-$ in THF at $-78°$ was added 1 mmol of HgI_2. Upon addition, the solution turned black. The solution was stirred 15 min at $-78°$ and then 15 min at room temperature. At this time an infrared spectrum showed an ir pattern characteristic of the compounds $Mn(CO)_2(CNCH_3)_3X.^7$ The solvent was removed in vacuo. Work-up (Table I) followed by recrystallization from toluene–hexane gave pure $Mn(CO)_2(CNCH_3)_3I$.

Measurements. ^{1}H NMR spectra were recorded on either a Varian T-60 or a Jeolco MH-100 NMR spectrometer. Solvents for the samples were either degassed in vacuo or deaerated by bubbling argon through them 5–10 min before use. The solvents were then added to the solid samples under argon in serum cap adaptable NMR tubes via syringe. Coupling constants were verified through measurements at both 60 and 100 MHz. Infrared spectra were recorded on a Perkin-Elmer 467 infrared spectrophotometer and were calibrated with polystyrene. Infrared samples were taken in 0.1-mm cavity cells. The samples of the anions were prepared in a glovebag and were made airtight by placing a small strip of Teflon tape between the plastic cap and the cell. Melting points were obtained in sealed capillaries under an argon atmosphere using a Thomas-Hoover capillary melting point apparatus. The reported values stand uncorrected. Elemental analyses were performed by Midwest Microlaboratory, Indianapolis, Ind., and Baron Consulting, Orange, Conn.

Results

$Mn(CO)_4(CNCH_3)$ **Anion.** Reduction of $Mn(CO)_4(CNCH_3)Br$ with Na(Hg) at room temperature or $0°$ readily

Table II

Compd	Infrared (CO and CN region), cm^{-1}	^{1}H NMR, ppm (TMS)
$Mn(CO)_4(CNCH_3)^-$ (I)	2118 m, 1935 s, 1863 s, sh, 1837 vs, 1786 s^a	j
$Mn(CO)_4(CNCH_3)CH_2CN$ (II)	2220 m, 2205 w, 2090 s, 2013 vs, 1975 vs^b	2.00 (NCH$_3$); 0.64 (CH$_2$)^c
$Mn(CO)_4(CNCH_3)Ge(C_6H_5)_3$ (III)	2195 m, 2063 s, 1994 s, 1982 vs, 1973 vs^b	7.0–7.9 (C$_6$H$_5$); 1.55 (NCH$_3$)^d
$Mn(CO)_4(CNCH_3)Sn(CH_3)_3$ (IV)	2180 m, 2050 s, 1980 s, 1969 vs^b	1.83 (NCH$_3$); 0.48 (SnCH$_3$);^{c} $J(^{117,119}Sn\text{–}NCH_3) = 7.5$ Hz; $J(^{117,119}Sn\text{–}CH_3) = 45$ Hz
$Mn(CO)_4(CNCH_3)Sn(C_6H_5)_3$ (V)	2192 m, 2060 s, 1992 s, 1980 vs, 1977 vs, sh^b	7.2–7.7 (C$_6$H$_5$); 3.20 (NCH$_3$);^{d} $J(^{117,119}Sn\text{–}NCH_3) = 8.5$ Hz
$Mn(CO)_4(CNCH_3)Pb(C_6H_5)_3$ (VI)	2195 m, 2060 s, 1994 s, 1984 vs, 1973 vs^b	7.1–7.7 (C$_6$H$_5$); 3.17 (NCH$_3$);^{d} $J(^{207}Pb\text{–}NCH_3) = 18$ Hz
$Mn(CO)_4(CNCH_3)HgI$ (VII)	2195 m, 2066 s, 2008 vs, 1992 vs, 1980 s^b	1.70 (NCH$_3$)^c
$[Mn(CO)_4(CNCH_3)]_2Hg$ (VIII)	2165 m, 2048 m, 2020 vs, 1975 s, 1968 vs, 1964 vs, sh, 1955 s, 1945 s^b	1.90 (NCH$_3$)^c $J(^{199}Hg\text{–}NCH_3) = 14$ Hz
$Mn(CO)_4(CNCH_3)H$ (IX)	2200 m, 2078 m, 2000 s, 1989 s, 1976 s^e	1.64 (NCH$_3$); –7.15 (Mn–H)^c
$Mn(CO)_4(CNCH_3)I$ (X)	2218 m, 2100 s, 2040 vs, 2035 vs, 1980 vs^b	1.67 (NCH$_3$)^c
$Mn(CO)_3(CNCH_3)_2^-$ (XI)	2118 m, 1935 s, 1865 s, 1839 s^a	j
$Mn(CO)_3(CNCH_3)_2CH_2CN$ (XII)	2215 m, 2190 m, 2033 s, 1972 s, 1898 s^b	2.16 (NCH$_3$); 0.87 (CH$_2$)^c
$Mn(CO)_3(CNCH_3)_2Ge(C_6H_5)_3$ (XIII)	2190 m, 2167 m, 2012 s, 1950 s, 1940 s, sh^f	7.2–7.6 (C$_6$H$_5$); 3.02 (NCH$_3$)^d
$Mn(C))_3(CNCH_3)_2Sn(C_6H_5)_3$ (XIV)	2190 m, 2160 m, 2016 s, 1956 s, 1950 s^b	7.2–7.6 (C$_6$H$_5$); 3.02 (NCH$_3$);^{d} $J(^{117,119}Sn\text{–}NCH_3) = 11$ Hz
$Mn(CO)_3(CNCH_3)_2Pb(C_6H_5)_3$ (XV)	2191 m, 2160 m, 2016 s, 1961 s, 1949 s^b	7.1–7.7 (C$_6$H$_5$); 3.12 (NCH$_3$);^{d} $J(^{207}Pb\text{–}NCH_3) = 22$ Hz
$[Mn(CO)_3(CNCH_3)_2]_2Hg$ (XVI)	2156 m, 2025 vw, 1980 m, 1962 s, 1913 s, br^g	2.18 (NCH$_3$); $J(^{199}Hg\text{–}NCH_3) = 15$ Hz
$Mn(CO)_3(CNCH_3)_2I$ (XVII)	2218 m, 2198 m, 2040 s, 1987 s, 1940 s^f	1.70 (NCH$_3$)^c
$Mn(CO)_2(CNCH_3)_3^-$	See text	j
$Mn(CO)_2(CNCH_3)_3CH_2CN$ (XVIII)	2205 w, 2185 m, sh, 2165 s, sh, 2150 vs, 1965 vs, 1902 vs^f	2.38 (NCH$_3$ (1)^h); 2.22 (NCH$_3$ (2)^h); 1.00 (CH$_2$)^{c,i}
$Mn(CO)_2(CNCH_3)_3Sn(C_6H_5)_3$ (XIX)	2175 w, 2135 m, sh, 2118 s, 1964 vs, 1924 vs^b	7.0–7.7 (C$_6$H$_5$); 3.03 (NCH$_3$ (2)^h); 2.98 (NCH$_3$ (1)^h)^d
$Mn(CO)_2(CNCH_3)_3Pb(C_6H_5)$ (XX)	2177 w, 2141 m, sh, 2126 s, 1969 vs, 1926 vs^b	7.1–7.7 (C$_6$H$_5$); 3.12 (NCH$_3$ (2)^h); 3.09 (NCH$_3$ (1)^h);^{d} $J(^{207}Pb\text{–}NCH_3) = 22$ Hz
$Mn(CO)_2(CNCH_3)_3I$ (XXI)	2213 w, 2189 m, sh, 2163 s, 1980 vs, 1909 vs^a	2.15 (NCH$_3$ (1)^h); 2.12 (NCH$_3$ (2)^h)^c

^{a} In THF. ^{b} In C$_6$H$_{12}$. ^{c} In C$_6$H$_6$. ^{d} In acetone-d_6. ^{e} In hexane. ^{f} In C$_6$D$_6$. ^{g} In CH$_2$Cl$_2$. ^{h} Relative intensity. ^{i} Broad. ^{j} Not measured.

affords the anion Mn(CO)4CNCH3⁻, I. The anion is stable at these temperatures when kept under an inert atmosphere. The anionic character of the complex is supported by the infrared spectrum. As shown in Figure 1, the absorptions of the anion (spectrum B) have been substantially shifted to lower energy when compared with those of the neutral starting complex (spectrum A). This shift reflects the increased amount of π back-bonding that occurs between the metal atom and the ligands and is a characteristic feature of organometallic anions.[5]

This anion readily reacts through halide displacement with the compounds CH2(CN)Cl, (C6H5)3GeBr, (CH3)3SnCl, (C6H5)3SnCl, (C6H5)3PbI, and HgI2 and the corresponding compounds Mn(CO)4(CNCH3)R, R = CH2CN, (C6H5)3Ge, (CH3)3Sn, (C6H5)3Sn, (C6H5)3Pb, and HgI, II–VII, have been prepared. In addition, the disubstituted mercury compound [Mn(CO)4(CNCH3)]2Hg, VIII, was obtained. Reaction with acetic acid gave Mn(CO)4(CNCH3)H, IX. All of these compounds, except the hydride, IX, are stable molecules which are easily isolated and purified.

The infrared and ¹H NMR spectra of the compounds are presented in Table II. The presence of three or four carbonyl absorptions in the region 1900–2100 cm⁻¹ in compounds II–VII and IX indicates that in each of these molecules the isocyanide ligand and the substituent lie in cis-related positions. The trans stereochemistry would allow only two infrared carbonyl absorptions. The ¹H NMR spectra of the molecules are as expected, except for the observation of long-range coupling of the heteroatoms ¹¹⁷,¹¹⁹Sn, ²⁰⁷Pb, and ¹⁹⁹Hg to the methyl groups on the isocyanide ligands in compounds IV–VI and VIII. Similar coupling was observed in an analogous series of molybdenum compounds.[2a] The infrared spectrum of

compound VIII shows seven carbonyl absorptions, and unless intramolecular ligand rearrangement is rapid on the ¹H NMR time scale, the structure of this molecule is A in which the
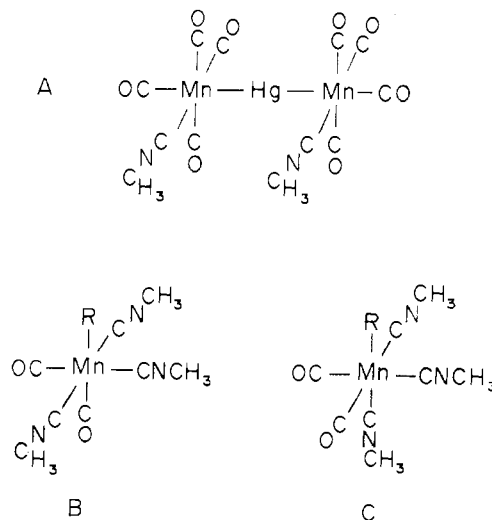
isocyanide ligands on each manganese atom are cis positioned with respect to the mercury atom.

The observation of coupling of the mercury atom to the methyl group on the isocyanide ligands indicates that intermolecular rearrangements are slow on the ¹H NMR time scale. Interestingly, we find that treatment of compound VII with excess HCl causes elimination of mercury and formation of the compound Mn(CO)4(CNCH3)I, X, in good yield. This reaction has been observed previously for similar compounds.[10]
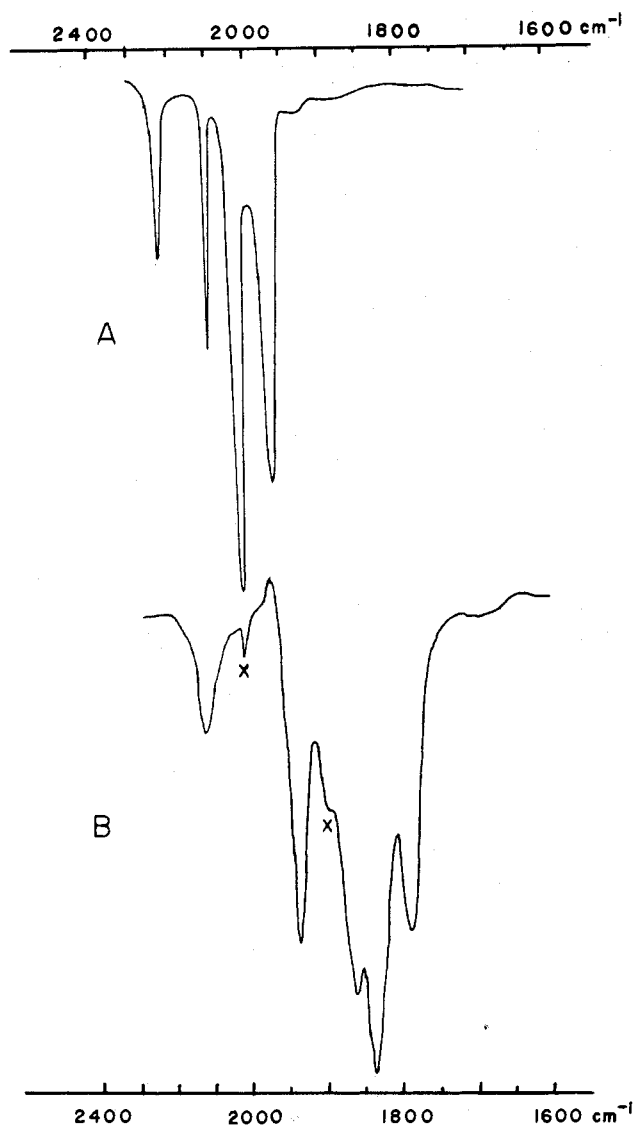
Figure 1. Infrared spectra: (A) Mn(CO)$_4$(CNCH$_3$)Br. (B) Mn(CO)$_4$(CNCH$_3$) anion. Both were taken in tetrahydrofuran solvent. Absorptions labeled X are trace impurities.

Mn(CO)$_3$(CNCH$_3$)$_2$ Anion. The reduction of Mn(CO)$_3$(CNCH$_3$)$_2$Br with Na(Hg) at −15° gives good yields of the anion Mn(CO)$_3$(CNCH$_3$)$_2^-$, XI, whereas reduction at room temperature gives little or none of this anion.[17] Once it is made, however, the anion can be warmed to room temperature and will survive in significant amounts for several hours. Evidence of decomposition is revealed as the solutions slowly begin to turn brown. The anionic nature of the complex is indicated by the infrared spectrum which shows absorptions at 2118 (CN), 1936 (CO), 1864 (CO), and 1839 (CO) cm^{-1}. This is very similar to the spectrum of anion I except that this anion shows only three CO absorptions while anion I shows four.

In reactions with the molecules CH$_2$(CN)Cl, (C$_6$H$_5$)$_3$GeBr, (C$_6$H$_5$)$_3$SnCl, (C$_6$H$_5$)$_3$PbI, and HgI$_2$ the compounds Mn(CO)$_3$(CNCH$_3$)$_2$R, R = CH$_2$(CN), (C$_6$H$_5$)$_3$Ge, (C$_6$H$_5$)$_3$Sn, and (C$_6$H$_5$)$_3$Pb, XII–XV, and [Mn(CO)$_3$(CNCH$_3$)$_2$]$_2$Hg, XVI, have been prepared in good yields (cf. Table I). The infrared and ^{1}H NMR spectra are listed in Table II. Compounds XII–XV show three strong carbonyl absorptions. This intensity pattern has been recognized as characteristic of the *fac* structure[11] in which all three carbonyl ligands are mutually cis related to one another. The ^{1}H NMR spectra support this structural type as a single *N*-methyl resonance

is observed for each complex. Once again coupling of the heteroatoms ^{117,119}Sn, ^{207}Pb, and ^{199}Hg is observed to the methyl groups on the isocyanide ligands.

The reaction of Mn(CO)$_3$(CNCH$_3$)$_2^-$ with 1 equiv of HgI$_2$ leads to the production of Mn(CO)$_3$(CNCH$_3$)$_2$I, XVII, and a deposit of mercury metal. However, infrared spectra of the reaction solutions show that an intermediate is initially formed and that this is eventually converted into XVII. In view of the substitutional character of this anion and the stoichiometric mixing ratio of the reagents, it seems probable that this intermediate is Mn(CO)$_3$(CNCH$_3$)$_2$HgI. It, then, decomposes to give XVII with elimination of mercury metal.

Mn(CO)$_2$(CNCH$_3$)$_3$ Anion. Treatment of THF solutions of Mn(CO)$_2$(CNCH$_3$)$_3$Br with Na(Hg) at −15 to −20° produces solutions that have been very effective for the syntheses of new compounds. If the reduction is carried out at room temperature, the substitution products that are obtained from the solutions prepared at low temperatures cannot be obtained. If the solutions prepared at low temperatures are warmed to room temperature, they rapidly decompose. The synthetic capabilities (vide infra) of the reduced solutions prepared at low temperatures suggest the presence of the anion Mn(CO)$_2$(CNCH$_3$)$_3^-$. Spectroscopic verification is scant. Infrared spectra (in THF) of samples prepared from cold solutions and run immediately after preparation showed absorptions at 2050 (sh), 1870 (sh), 1815, and 1725 cm^{-1}. These absorptions rapidly (minutes) disappeared as repeated spectra were run. Other absorptions initially present in the spectra occurred at 2115, 1940, 1890, and 1860 cm^{-1}. These absorptions grew within the first few minutes of spectral observation and then eventually disappeared themselves. However, they were long-lived compared to those of the first reported set of absorptions. The low-energy position of the first reported set suggests that the species, which is present, is highly reduced and may be Mn(CO)$_2$(CNCH$_3$)$_3^-$. The strongest evidence for the existence of Mn(CO)$_2$(CNCH$_3$)$_3$ anion comes from the reaction chemistry. If the reduced solutions are generated (−20°), filtered, and maintained (−78°) cold and used shortly after preparation, they are useful for chemical syntheses. In reactions with the compounds CH$_2$(CN)Cl, (C$_6$H$_5$)$_3$SnCl, and (C$_6$H$_5$)$_3$PbI, the new compounds Mn(CO)$_2$(CNCH$_3$)$_3$R, R = CH$_2$(CN), (C$_6$H$_5$)$_3$Sn, and (C$_6$H$_5$)$_3$Pb, XVIII–XX, have been prepared. These compounds are stable at ambient temperature and can be readily manipulated and isolated. As expected, their infrared spectra show three isocyanide absorptions and only two carbonyl absorptions. The ^{1}H NMR spectra show two *N*-methyl resonances occuring in a 2:1 intensity ratio. Either of structures B or C are consistent with these observations.[12]

Coupling of ^{207}Pb to the methyl groups on the isocyanide ligands was observed in compound XX.

Reactions with 1 equiv of HgI$_2$ led to formation of orange Mn(CO)$_2$(CNCH$_3$)$_3$I, XXI, and the production of black reaction solutions. The black color is probably due to finely divided mercury metal and the reaction most likely goes through the intermediate Mn(CO)$_2$(CNCH$_3$)$_3$HgI in a sequence similar to that observed for the reaction between Mn(CO)$_3$(CNCH$_3$)$_2^-$ and HgI$_2$.

Discussion

Treatment of each of the halides Mn(CO)$_{5-x}$(CNCH$_3$)$_x$Br, x = 1–3, with sodium amalgam leads to the production of reduced species whose infrared spectra and reaction chemistry are consistent with their formulation as the anions Mn(CO)$_{5-x}$(CNCH$_3$)$_x^-$, x = 1–3. The parent anion Mn(CO)$_5^-$ has been known for some time although it is generally prepared from Mn$_2$(CO)$_{10}$.[13] A variety of monosubstituted phosphine anions[14] Mn(CO)$_4$PR$_3^-$, R = C$_6$H$_5$, OC$_6$H$_5$, and N(CH$_3$)$_2$, and disubstituted phosphine anions[15] Mn(CO)$_3$(PR$_3$)$_2^-$, R =

C_6H_5, OC_6H_5, and c-C_6H_{11}, are known. The latter anions were prepared by sodium amalgam reduction of the corresponding bromides. Evidence has also been presented for the trisubstituted phosphite anion[16] $Mn(CO)_2(P(OMe)_3)_3^-$.

The infrared spectra of the isocyanide-substituted anions indicate a high degree of π back-bonding between the metal atom and the carbonyl ligands.[5] The isocyanide CN absorption in anion I occurs at 2118 cm^{-1} and is shifted approximately 100 cm^{-1} to lower wavenumbers than the position, 2226 cm^{-1}, observed in the starting bromide.[7] This shift indicates that the isocyanide ligand is also involved in a substantial increase in π back-bonding. In this complex, the isocyanide CN absorption has not been shifted to lower energy nearly as much as was observed for the anions $(\eta^5$-$C_5H_5)Mo(CO)_{3-x}$-$(CNCH_3)_x$, $x = 1$, 2.[2a] This is easily rationalized. In the present case the isocyanide ligand is competing with four carbonyl ligands in π back-bonding, whereas in the case of the molybdenum compounds there were only one or two carbonyl ligands engaged in π back-bonding. The share of π back-bonding available to the isocyanide ligand in anion I is thus markedly smaller than in the molybdenum anions.

The stability of these anions appears to be directly related to the number of isocyanide ligands bonded to the metal atom. Of the three anions, only the monosubstituted anion can be prepared in good yield and is stable at room temperature. The di- and trisubstituted anions can be prepared in useful amounts only at lower temperatures (e.g., -15 to 20°). When warmed to room temperature, the disubstituted anion will survive in significant amounts for several hours, but the trisubstituted anion rapidly decomposes. On this basis, this series of anions can thus be arranged in order of decreasing stability

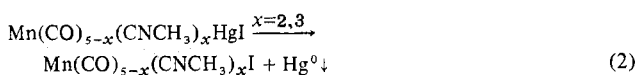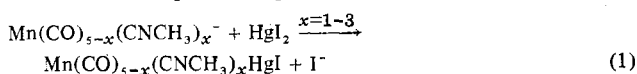$$Mn(CO)_4(CNCH_3)^- > Mn(CO)_3(CNCH_3)_2^- > Mn(CO)_2(CNCH_3)_3^-$$
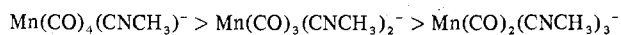
No attempt was made to prepare the tetrasubstituted anion $Mn(CO)(CNCH_3)_4^-$.

All three anions readily react through halide displacement and a variety of new complexes have been prepared (vide supra).

Reactions of anions I and XI with HgI_2 in a 2:1 molar ratio produce the disubstituted mercury compounds VIII and XVI, respectively. The observation of seven carbonyl absorptions and a single N-methyl resonance in the ^1H NMR spectra indicates that the structure is A in which the isocyanide ligands on each manganese atom are cis positioned to the mercury substituent (vide supra). The spectra of compound XVI are consistent with a structure in which the three carbonyl ligands on each manganese atom have a *fac* arrangement. Efforts were made to prepare the compound $[Mn(CO)_2(CNCH_3)_3]_2Hg$ from $Mn(CO)_2(CNCH_3)_3^-$ and HgI_2. Reactions produced dark yellow solutions which slowly deposited mercury when warmed to room temperature. The desired compound was not isolated.

The reactions of the anions with 1 equiv of HgI_2 produced $Mn(CO)_4(CNCH_3)HgI$, VII, $Mn(CO)_3(CNCH_3)_2I$, XVII, and $Mn(CO)_2(CNCH_3)_3I$, XXI. The latter two compounds were formed in the presence of a deposit of mercury metal. The reaction sequence (eq 1 and 2) evidently involves initial

$$Mn(CO)_{5-x}(CNCH_3)_x^- + HgI_2 \xrightarrow{x=1-3}$$
$$Mn(CO)_{5-x}(CNCH_3)_xHgI + I^- \qquad (1)$$

$$Mn(CO)_{5-x}(CNCH_3)_xHgI \xrightarrow{x=2,3}$$
$$Mn(CO)_{5-x}(CNCH_3)_xI + Hg^0\downarrow \qquad (2)$$

formation of the complexes $Mn(CO)_{5-x}(CNCH_3)_xHgI$, $x = 1-3$, followed by the spontaneous elimination of Hg^0 and

formation of the iodide complexes XVII and XXI, eq 2, $x = 2$, 3. Spectral evidence for an intermediate was obtained in the reaction with the disubstituted anion. Complex VII did not spontaneously expel Hg^0 (or did so very slowly at room temperature). However, this could be induced by treatment with HCl and led to formation of the corresponding iodide, X. The ease of mercury elimination seems to reflect the overall reducing potential of the $Mn(CO)_{5-x}(CNCH_3)_x$ fragment. By this criterion the order of reducing ability then increases in the order

$$Mn(CO)_4CNCH_3 < Mn(CO)_3(CNCH_3)_2 < Mn(CO)_2(CNCH_3)_3$$
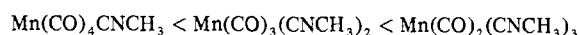
The results of this work clearly demonstrate the ability of isocyanide molecules to function as ligands in anionic complexes. However, there is obviously a limit to the degree of substitution which can be achieved, at least, in the cases of alkyl isocyanides. For a variety of reactions these anions have proven to be valuable reagents, and a number of new and stable complexes have been prepared. It seems most likely that a large variety of anionic organometallic complexes could be prepared and that they will, in general, be synthetically useful.

References and Notes

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