the *cis*-methyl derivatives compared with the *trans*-methyl derivatives may occur as a result of two factors: (1) the difference in stereochemistry causing a difference in symmetry, bond angles, etc., and (2) the trans influence of the carbonyl ligand in the cis isomer upon the phosphine or phosphite ligand. No unique explanation is available to account for the inversion of the magnitude of J_{PW} for the *trans*-methyl phosphites; the value for $P(OC_6H_5)_3$ may be abnormally low or $P(OCH_3)_3$ may be abnormally high. Without a larger series of phosphites it is imprudent to speculate.

Erratum

In a previous paper[1] we reported carbon-13 chemical shift data for a series of organotungsten compounds; $\eta^5\text{-}C_5H_5W(CO)_2LSn(CH_3)_3$ where L = $P(CH_3)_3$, $P(CH_3)_2C_6H_5$, $P(C_6H_5)_2CH_3$, $P(OCH_3)_3$, and $P(OC_6H_5)_3$. The $\delta(CO)$ reported are incorrect.[19] The correct values, relative to tetramethylsilane, are 223.0, 223.2, 223.3, 220.6, and 220.5, respectively.

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Registry No. $\eta^5\text{-}C_5H_5W(CO)_2P(CH_3)_3Pb(CH_3)_3$, 57156-63-5; $\eta^5\text{-}C_5H_5W(CO)_2P(CH_3)_2C_6H_5Pb(CH_3)_3$, 57156-64-6; $\eta^5\text{-}C_5H_5W(CO)_2P(C_6H_5)_2CH_3Pb(CH_3)_3$, 57156-65-7; $\eta^5\text{-}C_5H_5W(CO)_2P(C_6H_5)_3Pb(CH_3)_3$, 57156-66-8; $\eta^5\text{-}C_5H_5W(CO)_2P(OCH_3)_3Pb(CH_3)_3$, 57156-67-9; $\eta^5\text{-}C_5H_5W(CO)_2P(OC_6H_5)_3Pb(CH_3)_3$, 57156-68-0; $\eta^5\text{-}C_5H_5W(CO)_2P(C_6H_5)_2CH_3Ge(CH_3)_3$, 57156-73-7; $\eta^5\text{-}C_5H_5W(CO)_2[P(CH_3)_3]CH_3$-*cis*, 57156-69-1; $\eta^5\text{-}C_5H_5W(CO)_2[P(CH_3)_3]CH_3$-*trans*, 57194-79-3; $\eta^5\text{-}C_5H_5W(CO)_2[P(CH_3)_2C_6H_5]CH_3$-*cis*, 57156-70-4; $\eta^5\text{-}C_5H_5W(CO)_2[P(CH_3)_2C_6H_5]CH_3$-*trans*, 57194-80-6; $\eta^5\text{-}C_5H_5W(CO)_2[P(C_6H_5)_2CH_3]CH_3$-*cis*, 57156-71-5; $\eta^5\text{-}C_5H_5W(CO)_2[P(C_6H_5)_2CH_3]CH_3$-*trans*, 57194-81-7; $\eta^5\text{-}C_5H_5W(CO)_2[P(C_6H_5)_3]CH_3$-*cis*, 57194-82-8; $\eta^5\text{-}C_5H_5W(CO)_2[P(C_6H_5)_3]\text{-}H_3$-*trans*, 57236-51-8; $\eta^5\text{-}C_5H_5W(CO)_2[P(OCH_3)_3]CH_3$-*cis*, 57194-83-9; $\eta^5\text{-}C_5H_5W(CO)_2[P(OCH_3)_3]CH_3$-*trans*, 57194-84-0; $\eta^5\text{-}C_5H_5W(CO)_2[P(OC_6H_5)_3]CH_3$-*cis*, 57156-72-6; $\eta^5\text{-}C_5H_5W(CO)_2[P(OC_6H_5)_3]CH_3$-*trans*, 57194-85-1; $(\eta^5\text{-}C_5H_5)W(CO)_2[P(CH_3)_3]I$, 37449-00-6; $(\eta^5\text{-}C_5H_5)W(CO)_2[P(CH_3)_2(C_6H_5)]I$, 37449-01-7; $(\eta^5\text{-}C_5H_5)W(CO)_2[P(C_6H_5)_2CH_3]I$, 37474-46-7; $(\eta^5\text{-}C_5H_5)W(CO)_2[P(C_6H_5)_3]I$, 37474-48-9; $(\eta^5\text{-}C_5H_5)W(CO)_2[P(OCH_3)_3]I$, 33269-47-5; $(\eta^5\text{-}C_5H_5)W(CO)_2[P(OC_6H_5)_3]I$, 57156-74-8; $P(CH_3)_3$, 594-09-2; $P(C_6H_5)_3$, 603-35-0; $P(OCH_3)_3$, 121-45-9; $P(OC_6H_5)_3$, 101-02-0; $\eta^5\text{-}C_5H_5W(CO)_2[P(CH_3)_3]Sn(CH_3)_3$, 37583-10-1; $\eta^5\text{-}C_5H_5W(CO)_2[P(CH_3)_2C_6H_5]Sn(CH_3)_3$, 37583-11-2; $\eta^5\text{-}C_5H_5W(CO)_2[P(C_6H_5)_2CH_3]Sn(CH_3)_3$, 37583-13-4; $\eta^5\text{-}C_5H_5W(CO)_2[P(OCH_3)_3]Sn(CH_3)_3$, 37583-14-5; $\eta^5\text{-}C_5H_5W(CO)_2[P(OC_6H_5)_3]\text{-}Sn(CH_3)_3$, 37583-15-6.

References and Notes

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Organometallic Anions Containing Isocyanide Ligands. III. Synthesis and Reaction Chemistry of Methyl Isocyanide Derivatives of the Cyclopentadienylmolybdenum Tricarbonyl Anion

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The syntheses of the anions $(\eta^5\text{-}C_5H_5)Mo(CO_{3-x}(CNCH_3)_x$, $x = 1, 2$, have been accomplished by sodium amalgam reduction of the molecules $(\eta^5\text{-}C_5H_5)Mo(CO)_{3-x}(CNCH_3)_xCl$, $x = 1, 2$. Infrared spectra demonstrate the existence of extensive π back-bonding between the metal atom and the isocyanide ligands. The anions are valuable reagents. Through a series of halide displacement reactions, the new isocyanide-containing complexes $(\eta^5\text{-}C_5H_5)Mo(CO)_2CNCH_3R$, where R = CH_2CN, $Ge(CH_3)_3$, $Sn(CH_3)_3$, $Pb(C_6H_5)_3$, and HgI, and $(\eta^5\text{-}C_5H_5)Mo(CO)(CNCH_3)_2R$, where R = $Ge(C_6H_5)_3$, $Sn(CH_3)_3$, and $Pb(C_6H_5)_3$, have been synthesized. The dimolybdenum complexes $[(\eta^5\text{-}C_5H_5)Mo(CO)_2(CNCH_3)]_2Hg$ and $[(\eta^5\text{-}C_5H_5)Mo(CO)(CNCH_3)_2]_2Hg$ were also made. Long-range coupling of the heteronuclei ^{207}Pb and ^{189}Hg is observed to the methyl groups on the isocyanide ligands in these new complexes.

Introduction

As a great variety of reports continue to appear, it is becoming increasingly evident that isocyanide molecules may yet prove to be one of the most versatile and useful classes of ligand known to inorganic chemistry. While readily complexing and stabilizing metal atoms in positive oxidation states,[2] a variety of low-valent metal complexes are also known.[3] The physical behavior of these ligands in many ways resembles that of the ubiquitous carbon monoxide ligand.[4] The reason for this great versatility undoubtedly lies in its adaptable two-part bonding

Table I

Compd	Color	Mp, °C	Method of purification (solvent used)	Yield, %	Exptl (calcd) analyses, %				
					C	H	N	Hg	I
$(\eta^5\text{-}C_5H_5)Mo(CO)_2(CNCH_3)Cl$	Red	105–108.5	C[a] (benzene)	75	36.76 (36.82)	2.79 (2.75)	4.76 (4.77)		
$(\eta^5\text{-}C_5H_5)Mo(CO)(CNCH_3)_2Cl$	Red	91–98	C (benzene–THF)	44	45.86 (45.98)	4.27 (4.29)	7.94[c] (7.94)		
$(\eta^5\text{-}C_5H_5)Mo(CNCH_3)_4{}^+Cl^-$	Orange	170–171	C (ethanol or acetone)	6	39.38 (39.36)	4.87 (5.36)	13.96[d] (14.12)		
$(\eta^5\text{-}C_5H_5)Mo(CO)_2(CNCH_3)CH_2CN$	Yellow	78–80	C (benzene–THF)	49	44.21 (44.31)	3.52 (3.38)	9.32 (9.40)		
$(\eta^5\text{-}C_5H_5)Mo(CO)_2(CNCH_3)Ge(CH_3)_3$	Pink	137.5–139.5	E[b] (hexane)	39	38.70 (38.35)	4.72 (4.56)	3.58 (3.73)		
$(\eta^5C_5H_5)Mo(CO)_2(CNCH_3)Sn(CH_3)_3$	Off-white	112–113.5	E (hexane)	46	33.99 (34.16)	4.15 (4.06)	3.31 (3.32)		
$(\eta^5\text{-}C_5H_5)Mo(CO)_2(CNCH_3)Pb(C_6H_5)_3$	Yellow	152.5 dec	E (toluene)	71	47.55 (46.55)	3.67 (3.33)	2.00 (2.01)		
$(\eta^5\text{-}C_5H_5)Mo(CO)_2(CNCH_3)HgI$	Orange	107.5–109	C (benzene)	61	19.28 (18.46)	1.55 (1.37)	2.43 (2.39)	35.0 (34.3)	20.93 (21.67)
$[(\eta^5\text{-}C_5H_5)Mo(CO)_2(CNCH_3)]_2Hg$	Orange	164–166	C (benzene)	51	30.75 (30.16)	2.51 (2.25)	3.86 (3.91)		
$(\eta^5\text{-}C_5H_5)Mo(CO)(CNCH_3)_2Ge(C_6H_5)_3$	Yellow-brown	131–133	E (toluene–hexane)	40	58.10 (58.48)	4.72 (4.56)	4.68 (4.87)		
$(\eta^5\text{-}C_5H_5)Mo(CO)(CNCH_3)_2Sn(CH_3)_3$	Yellow	95–96.5	E (hexane)	71	35.89 (35.90)	4.78 (4.63)	6.43 (6.44)		
$(\eta^5\text{-}C_5H_5)Mo(CO)(CNCH_3)_2Pb(C_6H_5)_3$	Yellow	129–137	E (benzene)	37	49.28 (50.06)	4.00 (4.00)	3.55[c] (3.71)		
$[(\eta^5\text{-}C_5H_5)Mo(CO)(CNCH_3)_2]_2Hg$	Yellow	65–72	C (benzene–THF)	30	31.54 (32.33)	3.16 (2.98)	7.18 (7.54)	26.5 (27.10)	

[a] C = chromatography on Al_2O_3·6%H_2O. [b] E = solvent extraction. [c] Crystallizes as a 2:1 complex–toluene adduct. [d] Crystallizes as dihydrate.

scheme which employs both ligand to metal σ donation and metal to ligand π back-bonding. In an early study, Cotton[5] pointed out the importance of the π-back-bonding component in low-valent complexes while more recently Fenske[6] has shown that it also makes a substantial contribution in typical cationic complexes. In an effort to exploit this capability and to demonstrate further the utility of these ligands we have set about to prepare a series of organometallic anions that contain isocyanide ligands. Naturally, the stability of these anions would be strongly dependent on efficient π back-bonding of the isocyanide ligands. Although a few species of this general type have been reported previously,[7-9] they are, in general, exceedingly rare. Recognizing that organometallic anions are standard intermediates in organometallic syntheses,[10] we have also investigated the synthetic usefulness of the anions. We report, here, results of our investigations of the mono- and disubstituted methyl isocyanide derivatives of cyclopentadienylmolybdenum tricarbonyl anion. A preliminary report on this work has already appeared.[11]

Experimental Section

General Data. All reactions were performed in an argon atomosphere. $(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl$[12] and methyl isocyanide[13] were made by established procedures. $CH_2(CN)Cl$, $(CH_3)_3GeBr$, $(C_6H_5)_3GeBr$, $(CH_3)_3SnCl$, and $[(C_6H_5)_3Pb]_2$ were obtained commercially. $(C_6H_5)_3PbI$ was made from $[(C_6H_5)_3Pb]_2$.[14] THF, toluene, and hexane solvents were dried by refluxing over sodium–benzophenone and distilled under argon shortly before use.

Measurements. ^1H 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 by a syringe. Infrared spectra were recorded on a Perkin-Elmer 467 infrared spectrophotometer and were calibrated with polystyrene. Infrared samples of the anions were taken in 0.1-mm cavity cells and were prepared in a glovebag. A strip of Teflon tape placed between the plastic cap and the cell made the sample airtight. Melting points were obtained under an argon atomosphere in sealed capillaries using a Thomas-Hoover capillary melting point apparatus. The reported values stand uncorrected. Elemental microanalyses were performed by Midwest Microanalytical Laboratory, Indianapolis, Ind.

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.

$(\eta^5\text{-}C_5H_5)Mo(CO)_2CNCH_3Cl$. A 1:1 mixture of $(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl$ and $CNCH_3$ in THF solvent was stirred 8 hr at room temperature. The purified compound was crystallized from a toluene–hexane solution at −20° overnight.

$(\eta^5\text{-}C_5H_5)Mo(CO)(CHCH_3)_2Cl$ and $(\eta^5\text{-}C_5H_5)Mo(CHCH_3)_4{}^+Cl^-$. A 1:2 $(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl$–$CNCH_3$ mixture was stirred approximately 20 hr in refluxing THF. After removal of solvent, the red $(\eta^5\text{-}C_5H_5)Mo(CO)(CNCH_3)_2Cl$ was taken up with C_6H_6–THF solvent and chromatographed. Solvent was removed from the eluted complex which was then dissolved in a minimum of toluene. Stirring will induce crystallization. Solvent cocrystallizes in a ratio of two molecules of complex per molecule of solvent.

A yellow residue in the reaction flask can be purified and was determined to be $(\eta^5\text{-}C_5H_5)Mo(CNCH_3)_4{}^+Cl^-$ which crystallized as a dihydrate.

$(\eta^5\text{-}C_5H_5)Mo(CO)_2CNCH_3$ Anion. Solutions containing approximately 1 mmol of $(\eta^5\text{-}C_5H_5)Mo(CO)_2CNCH_3Cl$ in 50 ml of THF were stirred with 1% Na(Hg) at room temperature approximately 30 min. Filtration gave clear light yellow solutions that contain the anion $(\eta^5\text{-}C_5H_5)Mo(CO)_2CNCH_3{}^-$.

Reactions of $(\eta^5\text{-}C_5H_5)Mo(CO)_2(CNCH_3)^-$ 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. The solutions were stirred approximately 15 min at −78° and then allowed to warm slowly to room temperature. They were then stirred an additional 15 min at room temperature. Solvent was removed in vacuo and the compounds were isolated as indicated in Table I. All compounds were finally purified by crystallization from hexane or toluene–hexane solvent mixtures.

$(\eta^5\text{-}C_5H_5)Mo(CO)_2CNCH_3H$. A 2–3-fold excess of degassed acetic acid was added to a THF solution of the anion at −78°. After warming to room temperature, the solvent was removed in vacuo. Hexane extraction, followed by filtration and cooling to −78° gave a deposit of light brown crystals. The solvent was decanted and the crystals dried at low temperature, in vacuo. However, when warmed to room temperature, they melted. ^1H NMR and ir spectra indicated that these melted crystals were predominantly $(\eta^5\text{-}C_5H_5)Mo(CO)_2(CNCH_3)H$.

Decomposition of $(\eta^5\text{-}C_5H_5)Mo(CO)_2CNCH_3H$. The oil obtained above was heated to 50–60° for approximately 1 hr in vacuo. When cooled, the residue was chromatographed over $Al_2O_3 \cdot 6\% H_2O$ with benzene. A red band eluted. The benzene was removed in vacuo and the residue dissolved in toluene. From this solution, crystals formed when cooled to −20° overnight. ^1H NMR spectra indicated these crystals to be a mixture of $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_5CNCH_3$ and $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ in approximately a 3:1 concentration ratio.

$(\eta^5\text{-}C_5H_5)Mo(CO)(CNCH_3)_2$ Anion and $[(\eta^5\text{-}C_5H_5)Mo(CO)(CNCH_3)_2]_2Hg$. Solutions containing approximately 1 mmol of $(\eta^5\text{-}C_5H_5)Mo(CO)(CNCH_3)_2Cl$ in 50 ml of THF were stirred with 1% Na(Hg) at room temperature. The red color of the halide complex slowly disappeared. After approximately 15 min, the solutions assumed a yellow-orange color (mixed with gray Na(Hg) dispersion). Further stirring (approximately 30 min) caused disappearance of the yellow-orange color and left only a finely divided gray Na(Hg) dispersion. Filtration at this stage produced clear yellow solutions that contain the anion $(\eta^5\text{-}C_5H_5)Mo(CO)(CNCH_3)_2^-$.

If the solution is removed from the Na(Hg) at the yellow-orange intermediate stage, one can chromatographically isolate the compound $[(\eta^5\text{-}C_5H_5)MoCO(CNCH_3)_2]Hg$, although a substantial amount of product is lost through decomposition on the column. The compound does not crystallize but can be precipitated as a powder by flooding concentrated solutions with pentane. Decantation or filtration permits isolation of this powder.

Reactions of $(\eta^5\text{-}C_5H_5)Mo(CO)(CNCH_3)_2^-$ with Alkyl and Aryl Group 4 Halides and HgI_2. These reactions were performed very similarly to those with $(\eta^5\text{-}C_5H_5)Mo(CO)_2CNCH_3$ anion.

Results

The synthesis of these anions first required the preparation of suitable precursors from which the anions could be generated. The molecules we found most useful for this purpose were the mono- and disubstituted methyl isocyanide derivatives of $(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl$.

Reaction of $CNCH_3$ with $(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl$. Isocyanide derivatives of $(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl$ are conveniently prepared by thermal reactions of the free ligand with the metal complex in THF. A 1:1 stoichiometric mixture reacts at room temperature to give good yields of the monosubstituted derivative $(\eta^5\text{-}C_5H_5)Mo(CO)_2(CNCH_3)Cl$. Refluxing a 2:1 ligand–complex mixture gives good yields of the disubstituted derivative $(\eta^5\text{-}C_5H_5)Mo(CO)(CNCH_3)_2Cl$. Under the latter conditions one also observes the formation of a small amount of yellow precipitate. This has been identified as $(\eta^5\text{-}C_5H_5)Mo(CNCH_3)_4{}^+Cl^-$. The yield of this product can be substantially improved through reactions at higher temperatures (e.g., refluxing toluene). An analogous cationic complex has been obtained by the reaction of $(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl$ with *tert*-butyl isocyanide.[15] At no time did we obtain evidence for formation of the compound $(\eta^5\text{-}C_5H_5)Mo(CNCH_3)_3Cl$.

Cyclopentadienylmolybdenum Dicarbonyl Methyl Isocyanide Anion. Red THF solutions of $(\eta^5\text{-}C_5H_5)Mo(CO)_2(CNCH_3)Cl$ readily react with Na(Hg) at room temperature to give upon filtration clear light yellow solutions which contain the anion $(\eta^5\text{-}C_5H_5)Mo(CO)_2(CNCH_3)$, I. This is supported by the infrared spectrum, which shows three absorptions in the CO and CN stretching region. These have been greatly shifted to lower energy when compared with those of the starting complex, Figure 1. The ^1H NMR spectrum in THF-d_8 shows two resonances which appear at 4.95 (5) and 2.90 (3) ppm and may be assigned to the cyclopentadienyl and *N*-methyl protons, respectively.

Reactions of this anion with the molecules $CH_2(CN)Cl$, $(CH_3)_3GeBr$, $(CH_3)_3SnCl$, and $(C_6H_5)_3PbI$ have led via halide displacements to the substituted neutral molecules $(\eta^5\text{-}C_5H_5)Mo(CO)_2CNCH_3R$, R = CH_2CN, $(CH_3)_3Ge$, $(CH_3)_3Sn$, and $(C_6H_5)_3Pb$, II–V. Reaction with HgI_2 in a 1:1 stoichiometric ratio leads to the formation of $(\eta^5\text{-}C_5H_5)Mo(CO)_2(CNCH_3)HgI$, VI, while mixing in a 2:1 ratio gives the disubstituted compound $[(\eta^5\text{-}C_5H_5)Mo(CO)_2CNCH_3]_2Hg$, VII. Table II lists the infrared and ^1H NMR spectra of these compounds. These spectra indicate that each of compounds II–V exist in solution as a mixture of cis and trans isomers similar to that which has been established for the analogous series of phosphine-substituted complexes.[16] Examination of the infrared spectra of freshly prepared solutions of compound V shows that it crystallizes as the trans isomers[17] but comes to equilibrium with the cis isomer in a matter of minutes. The ^1H NMR spectra of freshly prepared solutions show a large cyclopentadienyl resonance at a slightly higher field value of a small singlet. Over a period of minutes the small singlet increases in intensity while the large resonance simultaneously decreases. The relative shift positions of these resonances are similar to those observed by Faller[16] for the phosphine complexes; namely, the cyclopentadienyl resonance at the higher field value invariably belongs to the trans isomer. Assuming this is a characteristic feature of all complexes of this type, we used this observation to assign the resonances to the cis and trans isomers in each of compounds II–V. Interestingly, there are located small side bands arounds each of the *N*-methyl resonances of compounds V and VII, as well as the cyclopentadienyl resonance of the trans isomer of compound V. Their shift position is insensitive to the magnetic field strength and their relative intensities are consistent with their assignment as splittings of the main resonances due to coupling to the heteronuclei ^{207}Pb and ^{199}Hg, both of which have nuclear spin values of $^1/_2$.

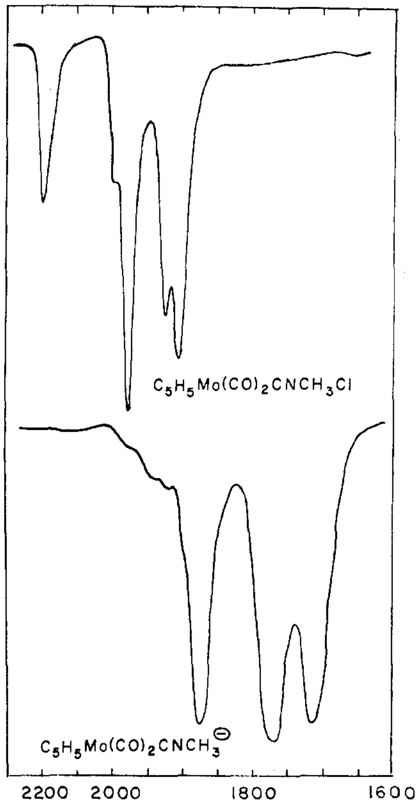

Figure 1. Infrared spectra of $(\eta^5\text{-}C_5H_5)Mo(CO)_2(CNCH_3)Cl$ (upper spectrum) and $(\eta^5\text{-}C_5H_5)Mo(CO)_2CNCH_3$ anion. Spectra were taken in THF solvent.

We have not been able to isolate any stable alkyl- or arylsilicon derivatives through reactions with either of these anions; however, it is well-known that silicon–metal complexes often cannot be made by this route.[18] Protonation with acetic acid leads to formation of the hydride $(\eta^5\text{-}C_5H_5)Mo(CO)_2(CNCH_3)H$, VIII, which shows the characteristic metal-hydride resonance[12] at −5.05 ppm. This complex is thermally unstable and decomposes at room temperature over a period of hours, or more rapidly when heated. The principal decomposition products have been identified as $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_5CNCH_3$[19] and $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ which

Table II

Compd	Infrared (CO and CN region), cm^{-1}	^1H NMR, (TMS)	Trans:cis ratio
$(\eta^5\text{-}C_5H_5)Mo(CO)_2(CNCH_3)^-$ (I)	1875 s, 1765 s, 1710 s[a]	4.95 (C_5H_5); 2.90 (CH_3)[a]	
$(\eta^5\text{-}C_5H_5)Mo(CO)_2(CNCH_3)CH_2CN$ (II)	2205 w, 2163 m, 1980 w, 1970 s, 1913 m, 1908 s[c]	5.30 (C_5H_5); 5.13 (C_5H_5);[b] 3.60 (CH_3);[b] 3.57 (CH_3); 1.23 (CH_2);[b] 1.15 (CH_2)	0.6
$(\eta^5\text{-}C_5H_5)Mo(CO)_2(CNCH_3)Ge(CH_3)_3$ (III)	2142 m, 1950 m, 1937 m, 1890 m, 1898 s[c]	5.04 (C_5H_5); 4.98 (C_5H_5);[b] 3.49 (NCH_3);[b] 3.44 ($N\text{-}CH_3$); 0.52 ($GeCH_3$);[b] 0.46 ($GeCH_3$)[d]	3.7
$(\eta^5\text{-}C_5H_5)Mo(CO)_2(CNCH_3Sn(CH_3)_3$ (IV)	2139 m, 2110 sh, 1947 m, 1927 m, 1883 m, 1871 s[c]	4.99 (C_5H_5); 4.93 (C_5H_5);[b] 3.47 (NCH_3);[b] 3.38 (NCH_3); 0.32 ($SnCH_3$);[b] 0.27 ($SnCH_3$);[d] $J(^{117,119}Sn\text{-}CH_3) \cong 45$ Hz	4.6
$(\eta^5\text{-}C_5H_5)Mo(CO)_2(CNCH_3)Pb(C_6H_5)_3$ (V)	2125 m, 1959 s, 1945 sh, 1899 s, 1890 sh[c]	7.40 (C_6H_5); 5.40 (C_5H_5); 5.17 (C_5H_5)[b] 3.73 (CH_3);[b] 3.05 (CH_3);[e] $J(^{207}Pb\text{-}NCH_3{}^{trans}) = 8$ Hz; $J(^{207}Pb\text{-}NCH_3{}^{cis}) = 26$ Hz; $J(^{207}Pb\text{-}C_5H_5{}^{trans}) = 5$ Hz	2.0
$(\eta^5\text{-}C_5H_5)Mo(CO)_2(CNCH_3)HgI$ (VI)	2175 m, 1954 m, 1885 s[f]	4.51 (C_5H_5); 2.16 (CH_3)[g]	
$[(\eta^5\text{-}C_5H_5)Mo(CO)_2(CNCH_3)]_2Hg$ (VII)	2135 m, 1960 m, 1935 w, 1887 s[f]	5.00 (C_5H_5); 1.67 (NCH_3);[g] $J(^{199}Hg\text{-}NCH_3) = 11$ Hz	
$(\eta^5\text{-}C_5H_5)Mo(CO)_2(CNCH_3)H$ (VIII)	2136 m, 1963 s, 1900 vs[c]	4.85 (C_5H_5); 2.17 (CH_3); −5.05(Mo-H)[g]	
$(\eta^5\text{-}C_5H_5)Mo(CO)(CNCH_3)_2^-$ (IX)	1855 s, 1745 s, 1690 s[a]	5.07 (C_5H_5); 2.95 (CH_3)[a]	
$[(\eta^5\text{-}C_5H_5)Mo(CO)(CNCH_3)_2]_2Hg$ (X)	2100 s, 1805 s[f]	5.12 (C_5H_5); 2.88 (CH_3);[g] $J(^{199}Hg\text{-}NCH_3) = 12$ Hz	
$(\eta^5\text{-}C_5H_5)Mo(CO)(CNCH_3)_2Ge(C_6H_5)_3$ (XI)	2090 m, 1873 s[c]	7.1–7.8 (C_6H_5); 5.27 (C_5H_5); 2.95 (CH_3); 2.28 (CH_3)[h]	
$(\eta^5\text{-}C_5H_5)Mo(CO)(CNCH_3)_2Sn(CH_3)_3$ (XII)	2113 m, 2022 w, 1897 w,[i] 1872 s[c]	4.83 (C_5H_5); 2.67 (NCH_3); 2.43 (NCH_3); 0.58 ($SnCH_3$);[g] $J(Sn\text{-}CH_3) = 42$ Hz	
$(\eta^5\text{-}C_5H_5)Mo(CO)(CNCH_3)_2Pb(C_6H_5)_3$ (XIII)	2120 m, 2080 m, 1902 s,[i] 1882 m[c]	7.1–7.6 (C_6H_5); 5.17 (C_5H_5);[i] 5.03 (C_5H_5); 3.62 (CH_3);[k] 2.97 (CH_3);[l] 2.93 (CH_3)[e,i]; $J(^{207}Pb\text{-}NCH_3{}^{trans}) = 6$ Hz; $J(^{207}Pb\text{-}NCH_3{}^{cis}) = 30$ Hz; $J(^{207}Pb\text{-}C_5H_5{}^{cis}) = 6$ Hz	0.15[n]
$(\eta^5\text{-}C_5H_5)Mo(CO)_2(CNCH_3)Cl$	2190 m, 1995 m, 1975 vs, 1920 s, 1900 s[a]	5.03 (C_5H_5); 4.93 (C_5H_5);[b] 2.48 (CH_3)[b]	0.2
$(\eta\text{-}C_5H_5)Mo(CO)(CNCH_3)_2Cl$	2168 s, 2142 s, 1894 s, 1866 m[a]	5.15 (C_5H_5);[i] 5.07 (C_5H_5); 2.65 (CH_3); 2.60 (CH_3); 2.48 (CH_3)[i]	2[n]
$(\eta^5\text{-}C_5H_5)Mo(CNCH_3)_4{}^+Cl^-$	2193 w, 2134 s[o]	5.17 (C_5H_5); 3.70 (CH_3)[e]	

[a] In THF; [b] Trans isomer (see text); [c] In C_6H_{12}; [d] In $CDCl_3$; [e] In acetone-d_6; [f] In CH_2Cl_2; [g] In C_6H_6; [h] In C_6D_6; [i] Due to second isomer, probably having trans positioned $CNCH_3$ groups; [j] In acetone-d_6; [k] Probably $CNCH_3$ ligand trans to Pb atom[m]; [l] Probably $CNCH_3$ ligand cis to Pb atom[m]; [m] Cis and trans ligand assignments were made by comparison with similar shift positions and couplings observed for compound V; [n] In this case trans refers to the isomer having oppositely positioned isocyanide ligands; [o] In acetone.

occur in approximately a 3:1 ratio.

Cyclopentadienylmolybdenum Carbonylbis(methyl isocyanide) Anion. Na(Hg) reduction of $(\eta^5\text{-}C_5H_5)Mo(CO)(CNCH_3)_2Cl$ begins with a slow disappearance of the red color. After approximately 15 min, the solution has assumed a distinct yellow-orange color. Further stirring, causes the disappearance of this color leaving a finely divided gray Na(Hg) dispersion. Filtration at this stage gives clear light yellow solutions containing the anion $(\eta^5\text{-}C_5H_5)Mo(CO)(CNCH_3)_2^-$, IX. The infrared spectrum of this anion is similar to that of the monosubstituted anion and shows absorptions at 1855, 1745, and 1690 cm^{-1}. The ^1H NMR spectrum in THF-d_8 shows absorptions at 5.07 (5) and 2.95 (6) ppm which may be assigned to the cyclopentadienyl protons and two chemically equivalent *N*-methyl groups.

If, however, one stops the reaction at this intermediate yellow-orange stage by removing the solution from the Na(Hg), one can chromatographically isolate and precipitate a yellow-orange powder that we have identified as $[(\eta^5\text{-}C_5H_5)Mo(CO)(CNCH_3)_2]_2Hg$, X. This compound is isolated in good yields and is ultimately converted into the anion since solutions of the anion show no spectroscopic evidence for the presence of compound X. The conversion of the halide into compound X appears to go in very high yield, perhaps quantitatively. A considerable amount was lost through decomposition during its isolation.

This anion is a useful synthetic intermediate and reactions with the appropriate halide compounds have led to good yields of the complexes $(\eta^5\text{-}C_5H_5)Mo(CO)(CNCH_3)_2R$, R = $Ge(C_6H_5)_3$, $Sn(CH_3)_3$, and $Pb(C_6H_5)_3$, XI–XIII. Table II lists the ir and ^1H NMR spectra of these compounds. ^1H NMR spectra indicate that each of these compounds exists predominantly as the cis isomer (i.e., the isomer which has adjacently positioned and chemically inequivalent isocyanide ligands) although in some cases evidence for a low concentration of the trans isomer was obtained. Once again, coupling of the heteronuclei ^{199}Hg and ^{207}Pb was observed to the *N*-methyl groups of compounds X and XII, as well as to the cyclopentadienyl protons of compound XIII. No silicon–metal complexes could be obtained and even inspection of freshly reacted solutions of the anion with acetic acid gave no evidence for the metal hydride complex. ^1H NMR spectra of the latter reaction solutions indicated the presence of several other compounds that we have not completely characterized.

Discussion

Reduction of the metal–halide complexes proceeds smoothly in each case, eq 1 and 2.

$$CpMo(CO)_2(CNCH_3)Cl \xrightarrow[THF]{Na(Hg)} CpMo(CO)_2CNCH_3^- \tag{1}$$

$$CpMo(CO)(CNCH_3)_2Cl \xrightarrow[THF]{Na(Hg)} [CpMo(CO)(CNCH_3)_2]_2Hg \xrightarrow{Na(Hg)} CpMo(CO)(CNCH_3)_2^{-\ 20} \tag{2}$$

However, the reduction of $CpMo(CO)(CNCH_3)_2Cl$ is considerably slower and appears to go through the intermediate disubstituted mercury compound, X, before conversion into the anion. The formation of compound X is not straightforward and is obviously the result of a sequence of reactions. Mercury complexes have been observed before in sodium amalgam reduction reactions.[21] Although it seems reasonable that reduction of the monosubstituted complex may also proceed via such a mercury intermediate, none was observed.

Both anions I and IX are stable at room temperature under an inert atmosphere. They were not isolated as solids, but generated, spectroscopically investigated, and allowed to react in THF solutions. A variety of similarly structured phosphine anions have been known for some time.[22]

The infrared spectra of the anions provides strong support for their anionic character and also the degree to which the isocyanide ligands are engaged in π back-bonding to the molybdenum atoms. This is demonstrated by the large shift to lower energy of the CO and CN stretching vibrations.[23] The spectrum of anion I, Figure 1, shows three ligand absorptions. Assuming that carbon monoxide is a more effective π-back-bonding ligand than methyl isocyanide, the two absorptions at lowest energy, 1718 and 1775 cm^{-1}, can be assigned to the symmetrically and antisymmetrically coupled stretching vibrations of the two carbon monoxide ligands. The absorption at 1877 cm^{-1} must then be assigned to the CN stretching vibration of the isocyanide ligand. The large shift of this absorption to lower energy[24] indicates that the isocyanide ligand is also extensively engaged in π back-bonding to the molybdenum atom. Similar assignments can be made for the disubstituted anion. The large shift in the absorptions of this anion also indicates a large degree of π back-bonding to the isocyanide ligands.

Both anions have proven to be valuable reagents for the synthesis of new compounds. They readily displace halide ion from a variety of alkyl and aryl halide compounds of the group 4 elements. The presence of the coordinated isocyanide ligand in these products shows that the ligand has survived the reducing environment of the anion and has come through the entire reaction sequence intact. Compounds II–V exist in solution as a mixture of cis and trans isomers that are slowly interconverting on the NMR time scale. Preliminary investigations showed that they are dynamically active in a very similar degree to their phosphine-substituted analogs.[16] Detailed investigations of the isomerizations were not carried out. The disubstituted complexes XI–XIII exist predominantly as cis isomers having adjacently positioned isocyanide ligands. The observation of separate methyl resonances for the isocyanide ligands at room temperature indicates that the rearrangement of these molecules is also dynamically slow. This is unlike the disubstituted phosphine derivatives which rapidly rearrange at room temperature and are slowed only by cooling to −62°.[25] Another interesting feature of the ^1H NMR spectra of these compounds is the observation on long-range coupling of the heteronuclei ^{207}Pb and ^{199}Hg to the cyclopentadienyl protons and methyl groups on the isocyanide ligands. Coupling of phosphorus to cyclopentadienyl protons has been observed before in similar complexes.[16,26] The long-range coupling to the methyl groups is curious. It seems likely, however, that its spatial position is sufficiently remote so as to preclude any sort of through-space interaction.

Protonation of anion I leads to formation of the hydride, VIII, which has a limited stability at room temperature. Protonation of anion IX gave no evidence for formation of the corresponding metal hydride. Since the unsubstituted hydride, $(\eta^5\text{-}C_5H_5)Mo(CO)_3H$, is relatively stable at room temperature, the pattern of stability

$$(\eta^5\text{-}C_5H_5)Mo(CO)_3H > (\eta^5\text{-}C_5H_5)Mo(CO)_2(CNCH_3)H > (\eta^5\text{-}C_5H_5)Mo(CO)(CNCH_3)_2H$$

suggests that as the number of isocyanide ligands in the complex increases the overall stability of the metal hydride complex decreases.

The reaction of these anions with alkyl halides, in general, has not been straightforward. The infrared spectra of complexes that have been isolated show absorptions which could be attributed to acyl or iminoacyl functional groups. Further investigations of these complexes are being made. Only in reactions with $CH_2(CN)Cl$ have the direct substitution products been isolated.[27] A basic difference between a normal alkyl group (e.g., CH_3) and the CH_2CN grouping is that the latter is resistant toward the well-known insertion rearrangement.[28] It thus appears likely that in reactions with normal alkyl halides a sequence of reactions occurs which includes an insertion rearrangement. In the case of reaction with $CH_2(CN)Cl$, this sequence is aborted upon alkylation of the metal since the CH_2CN function will not insert.

This work further demonstrates the ability of isocyanide molecules to function as ligands in unusually low-valent complexes. It is also obvious that these ligands do extensively engage in π back-bonding to metal atoms. This ability undoubtedly contributes to the versatility of these ligands. The anions, themselves, are useful reagents and have led to the syntheses of a number of new complexes. As is shown in the following paper,[29] the usefulness of isocyanide ligands and other isocyanide containing anions is more general than implied by the single system presented, here. It seems likely that similar systems will pervade much of the transition metal block of elements and that these anions will provide a general means for the synthesis of new compounds.

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Registry No. I, 56665-40-8; *cis*-II, 57195-42-3; *trans*-II, 57195-43-4; *cis*-III, 57195-36-5; *trans*-III, 57195-37-6; *cis*-IV, 57195-38-7; *trans*-IV, 56698-73-8; *cis*-V, 57195-39-8; *trans*-V, 57195-40-1; VI, 57173-91-8; VII, 57173-90-7; VIII, 56665-43-1; IX, 57173-96-3; X, 57173-94-1; *cis*-XI, 57173-93-0; *cis*-XII, 57173-92-9; *cis*-XIII, 57195-41-2; *trans*-XIII, 57173-95-2; *cis*-$(\eta^5\text{-}C_5H_5)Mo(CO)_2(CNCH_3)Cl$, 57195-45-6; *trans*-$(\eta^5\text{-}C_5H_5)Mo(CO)_2(CNCH_3)Cl$, 57195-44-5; $(\eta^5\text{-}C_5H_5)Mo(CO)(CNCH_3)_2Cl$, 57173-89-4; $(\eta^5\text{-}C_5H_5)Mo(CNCH_3)_4{}^+Cl^-$, 57173-88-3; $(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl$, 12128-23-3.

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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