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π-Cyclopentadienylmanganese Thiocarbonyl and Carbon Disulfide Complexes[1]

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The reactions of the *cis*-cyclooctene complex $CpMn(CO)_2(C_8H_{14})$ ($Cp = \pi\text{-}C_5H_5$) with CS_2, alone and in the presence of PPh_3, have been investigated. The former reaction is extremely complex, with small amounts of $CpMn(CO)_2CS$, $CpMn(CO)_3$, and various unidentified CO- and/or CS_2-containing species being produced. However, in the presence of a stoichiometric amount of PPh_3, the reaction is remarkably simple—$CpMn(CO)_2CS$ is formed in essentially quantitative yield and the only other products are PPh_3S and C_8H_{14}. Spectroscopic and kinetic data for this reaction suggest the formation of $CpMn(CO)_2(\pi\text{-}CS_2)$ (the first π-CS_2 complex of manganese) prior to formation of the thiocarbonyl. The related π-methylcyclopentadienylmanganese complexes $(\pi\text{-}MeC_5H_4)Mn(CO)_2CS$ and $(\pi\text{-}MeC_5H_4)Mn(CO)_2(\pi\text{-}CS_2)$ have been identified spectroscopically. In addition, the di- and trithiocarbonyl complexes $CpMn(CO)(CS)_2$ and $CpMn(CS)_3$ have been synthesized by the reactions of $CpMn(CO)(CS)(C_8H_{14})$ and $CpMn(CS)_2(C_8H_{14})$, respectively, with CS_2 in the presence of PPh_3 as the sulfur acceptor. A few derivatives of $CpMn(CO)_2CS$ have also been prepared, *viz.*, $CpMn(CO)(CS)PPh_3$, $CpMn(CO)(CS)[P(OMe)_3]$, $CpMn(CS)(diphos)$, and $[CpMn(CO)(CS)]_2(diphos)$ ($diphos = Ph_2PCH_2CH_2PPh_2$).

Introduction

In recent years, there has been growing interest in the synthesis of transition metal thiocarbonyl complexes containing terminal CS groups bonded to the metal atoms.[2] X-Ray data for *trans*-$Rh(CS)(PPh_3)_2Cl$[3] and $[Ir(CO)_2(CS)(PPh_3)_2]PF_6\cdot Me_2CO$[4] indicate that the CS groups are attached to the metal atoms (M) in much the same manner as are the CO groups in the carbonyl analogs, *i.e.*, with linear M-C-S linkages. Moreover, it is believed[5] that CS groups should be bonded more strongly to transition metal atoms than are CO groups. However, despite this, there are relatively few thiocarbonyls known and even then only for the group VIII metals iron,[6,7] ruthenium,[8,9] cobalt,[10] rhodium,[11-13] and iridium.[14-17] We have been attempting to extend the range of known thiocarbonyls and now report[18] the syntheses and some of the physical and chemical properties of the first manganese thiocarbonyls $CpMn(CO)_{3-n}(CS)_n$ ($Cp = \pi\text{-}C_5H_5$; $n = 1\text{-}3$). The di- and trithiocarbonyls are of particular importance because they are the first examples of thiocarbonyls having more than one CS group attached to the same metal atom.

Experimental Section

The π-cyclopentadienylmanganese complexes $CpMn(CO)_3$ and $(\pi\text{-}MeC_5H_4)Mn(CO)_3$ were generous gifts from Ethyl Corp., New York, N. Y. Other chemicals were obtained from the sources indicated: CS_2 (Fisher Scientific Co.), C_8H_{14} and $P(OMe)_3$ (Aldrich Chemicals Co. Inc.), $Ph_2PCH_2CH_2PPh_2$ (diphos) (Strem Chemicals Ltd.). The literature methods were used to prepare $CpMn(CO)_2(C_8H_{14})$[19] and $(\pi\text{-}MeC_5H_4)Mn(CO)_2(C_8H_{14})$.[20]

Elemental analyses and molecular weight determinations (vp osmometry) were performed by Schwarzkopf Microanalytical Laboratory Inc., Woodside, N. Y. Melting points were taken on a Gallenkamp melting point apparatus and are uncorrected. Infrared spectra were recorded as described previously.[21] A Hewlett-Packard Model 5720 chromatograph was used for the vpc analyses. Mass spectra were recorded at ~50° on an AEI Model MS902 spectrometer operating at 70 eV. The ^1H nmr spectra were taken on a Varian A-60 spectrometer; τ values are relative to tetramethylsilane (τ 10.0).

All operations were performed routinely under a nitrogen atmosphere. Large-scale photochemical reactions (200–2000 ml) were carried out in a Pyrex vessel fitted with a water-cooled quartz finger. The uv source (450-W Hanovia high-pressure mercury lamp, No. 679A) was located inside the finger. A quartz vessel placed in a Rayonet circular photochemical reactor (equipped with up to 16 low-pressure mercury lamps emitting at 253.7 nm) was used for small-scale reactions (30–80 ml).

The ir spectra in the CO and CS stretching regions[22] of the new complexes prepared in this work are given in Table I.

Reactions of $CpMn(CO)_2(C_8H_{14})$ with CS_2. A. In the Absence of PPh_3. A solution of $CpMn(CO)_2(C_8H_{14})$ (2.5 g, 8.7 mmol) in CS_2 (500 ml) was maintained at reflux temperature (~45°) for 54 hr. Considerable decomposition was observed. The reaction mixture was filtered and the volume of the dark green filtrate was then reduced to a minimum on a vacuum line. The solution remaining was chromatographed on a deaerated alumina column using a 1:1 benzene-*n*-hexane mixture as eluent. The presence of four species—light yellow (II), yellow (III), green (IV), and purple (V)—was noted on the column. The solvent was evaporated from the front-running light yellow fraction and the resulting solid was redissolved in a minimum of *n*-hexane. Yellow crystals of II, $CpMn(CO)_2CS$, were obtained following removal of the solvent under a slow stream of nitrogen (yield 45 mg, 6%; mp

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[1] Taken in part from the Ph.D. thesis of A. E. F., McGill University, 1972. Presented in part at the 161st National Meeting of the American Chemical Society, Los Angeles, Calif., April 1971.

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[22] *Warning!* Silicon lubricant dissolves readily in most organic solvents and its ir spectrum exhibits a strong, sharp band at 1256 cm^{-1} (in CS_2 solution) which can easily be mistaken for a thiocarbonyl absorption. Great care must therefore be taken when greasing the joints of reaction vessels so that excess grease does not contaminate the reaction mixtures.

Table I. Characteristic Ir-Active CO and CS stretching Absorptions of the New π-Cyclopentadienylmanganese, π-CS_2, and Thiocarbonyl Complexes (cm^{-1})

Complex	ν(CO)	ν(CS)	Medium
$CpMn(CO)_2(\pi\text{-}CS_2)$	2012 s, 1962 s	1235 s,[a] ~640 m[b]	CS_2
$\pi\text{-}MeC_5H_4Mn(CO)_2(\pi\text{-}CS_2)$	2009 s, 1959 s	1229 s[a]	CS_2
$CpMn(CO)_2CS$[c]	2006 s, 1954 s	1266 s	CS_2
	2010 s, 1959 s	1271 s	Nujol
$\pi\text{-}MeC_5H_4Mn(CO)_2CS$	2004 s, 1952 s	1262 s	CS_2
$CpMn(CO)(CS)(C_8H_{14})$	1951 s	1242 s	CS_2
$CpMn(CO)(CS)PPh_3$[d]	1925 s	1231 s	CS_2
	1939 s, 1929 s	1236 s	*n*-Hexane
	1913 s	1217 s	Nujol
$CpMn(CO)(CS)P(OMe)_3$	1934 s	1238 s	CS_2
$[CpMn(CO)(CS)]_2$(diphos)	1920 s	1226 s	CS_2
	1922 s, 1903 sh	1230 s	Nujol
CpMn(CS)(diphos)		1208 s	CS_2
		1211 s	Nujol
$CpMn(CO)(CS)_2$[e]	1991 s	1305 s, 1235 vs	CS_2
	1996 s	1308 s, 1240 s	Nujol
$CpMn(CS)_2(C_8H_{14})$		1289 s, 1217 vs	CS_2
$CpMn(CS)_3$		1338 m, 1240 vs	CS_2

[a] Out-of-ring ν(C=S) mode. [b] In-ring ν(C–S) mode. [c] Raman data (Kr^+ laser, 647.1-nm excitation; solid-state sample in a capillary tube): ν(CO) 1986, 1956 cm^{-1}. [d] Raman (solid-state sample, see footnote *c*): ν(CO) 1913 cm^{-1}. The appearance of two C–O stretching absorptions for this monocarbonyl complex in *n*-hexane solution is attributed to conformational isomerism due to restricted rotation of the phenyl groups within the PPh_3 ligand [*cf.* D. A. Brown, H. J. Lyons, and A. R. Manning, *Inorg. Chim. Acta*, 4, 428 (1970)]. [e] Raman (solid-state sample, see footnote *c*): ν(CO) 1978 cm^{-1}.

52–53°). *Anal.* Calcd for $C_8H_5O_2SMn$: C, 43.6; H, 2.3; S, 14.6. Found: C, 43.1; H, 2.6; S, 14.7. Molecular weight: calcd, 220; found, 211 (osmometry), 220 (mass spectrum). ^{1}H nmr: τ 5.18 (CS_2 solution). The complex is air stable in the solid state but decomposes slowly in solution.

The product contained in the second yellow fraction, III, was $CpMn(CO)_3$ (yield ~5%). This complex was identified by comparison of its ir and mass spectra with the spectra of an authentic sample. The green species IV, was too unstable to be isolated. The purple complex, V, was obtained in too small a quantity to be analyzed.

The first step in the above reaction is the formation of $CpMn(CO)_2(\pi\text{-}CS_2)$ (I). Complex I was obtained alone when the reaction was carried out for a 2×10^{-3} *M* solution of $CpMn(CO)_2(C_8H_{14})$ in CS_2 for 4 days at 40°. The π-CS_2 complex, which could not be isolated in the solid state, was identified by its ir spectrum and by its instantaneous *in situ* reaction with PPh_3 to give $CpMn(CO)_2CS$ and PPh_3S.

The related π-methylcyclopentadienyl derivatives $(\pi\text{-}MeC_5H_4)Mn(CO)_2CS$ and $(\pi\text{-}MeC_5H_4)Mn(CO)_2(\pi\text{-}CS_2)$ were prepared on a spectroscopic scale as above from the reaction of $(\pi\text{-}MeC_5H_4)Mn(CO)_2(C_8H_{14})$ with CS_2.

B. In the Presence of PPh_3. One liter of a CS_2 solution containing $CpMn(CO)_2(C_8H_{14})$ (14.3 g, 50 mmol) and PPh_3 (13.1 g, 50 mmol) was refluxed for 27 hr. After solvent removal on a vacuum line, the crude reaction product was washed repeatedly with 50-ml portions of *n*-pentane until the washings were colorless. All the washings were collected. The white, crystalline solid remaining was identified as PPh_3S by ir spectroscopy and vpc analysis by comparison with data obtained for the known compound. Removal of *n*-pentane from the combined colored washings afforded a yellow residue from which pure $CpMn(CO)_2CS$ was obtained in high yield (9.35 g, 85%) by vacuum sublimation (0.01 mm (25°)).[23] Because the complex sublimes so readily at room temperature, some losses could not be avoided during the successive solvent removals on the vacuum line.

Preparation of $CpMn(CO)(CS)(C_8H_{14})$. A mixture of $CpMn(CO)_2CS$ (220 mg, 1 mmol) and C_8H_{14} (4 ml, ~30 mmol) in *n*-hexane (200 ml) was irradiated with a 450-W Hanovia uv source for 20 min. Extensive decomposition was observed. The reaction mixture was filtered and then the solvent was evaporated from the filtrate under vacuum. A yellow, air-sensitive oil was obtained from which unreacted $CpMn(CO)_2CS$ was removed by sublimation (0.01 mm (25°)). The crude, oily product remaining was used as $CpMn(CO)(CS)(C_8H_{14})$ for subsequent syntheses without any additional purification (estimated yield ~25%). For a higher purity product, the oil was first dried *in vacuo* for 24 hr when a black soild was obtained. Then, pure $CpMn(CO)(CS)(C_8H_{14})$ was sublimed (0.01 mm (50°)) from this black solid as small, air-sensitive, yellow crystals (yield 20 mg, 6%; dec pt ~55°). *Anal.* Calcd for $C_{15}H_{19}OSMn$: C, 59.6; H, 6.3; S, 10.6. Found: C, 57.7; H, 6.0; S, 10.3. Molecular weight: calcd, 302; found, 302 (mass spectrum).

Efforts to prepare the complex on a larger scale by using more concentrated solutions of the starting materials resulted in even more extensive decomposition. Moreover, the black decomposition product coated the wall of the reaction vessel so thickly that transmission of uv light was impossible and the reaction was terminated at an early stage.

The complex is thermally unstable in solution. For instance, after 3 hr in methylcyclohexane solution at 70°, it decomposed to $CpMn(CO)_2CS$, $CpMn(CO)_3$, and a brown precipitate.

Preparation of $CpMn(CO)(CS)PPh_3$. A mixture of freshly prepared, crude, "oily" $CpMn(CO)(CS)(C_8H_{14})$ and excess PPh_3 (130 mg, 0.5 mmol) in *n*-hexane (100 ml) was refluxed for 1 hr. The solvent was then removed on a vacuum line affording a dark orange residue. The excess PPh_3 was sublimed off (0.001 mm (50°)) and the solid remaining was dissolved in a minimum of CS_2. After filtration, addition of *n*-hexane to the filtrate followed by removal of the solvent under a slow stream of nitrogen gave orange crystals of $CpMn(CO)(CS)PPh_3$ [yield ~15%, based on the amount of $CpMn(CO)_2CS$ used for the synthesis of the crude $CpMn(CO)(CS)(C_8H_{14})$; dec pt ~180°]. *Anal.* Calcd for $C_{25}H_{20}OPSMn$: C, 66.1; H, 4.4; S, 7.0. Found: C, 66.0; H, 4.5; S, 6.3.

The related complex $CpMn(CO)(CS)[P(OMe)_3]$ was prepared in a similar manner on a spectroscopic scale from crude $CpMn(CO)(CS)(C_8H_{14})$ and $P(OMe)_3$. The complex was identified by the similarity of its ir spectrum to that of $CpMn(CO)(CS)PPh_3$.

Preparations of $[CpMn(CO)(CS)]_2$(diphos) and CpMn(CS)(diphos). A mixture of freshly prepared, crude, "oily" $CpMn(CO)(CS)(C_8H_{14})$ and diphos (200 mg, 0.5 mmol) in *n*-hexane (100 ml) was maintained at reflux for 1 hr. The solution was filtered hot. The solvent was then removed from the filtrate on a vacuum line. The orange residue was dissolved in a minimum of CS_2 and the solution was chromatographed on a silica gel preparative tlc plate using a 1:1 benzene-*n*-hexane mixture as eluent. The required complexes, corresponding to the yellow and orange bands on the plate, respectively, were extracted from the silica gel with acetone. The solvent was removed and the materials were redissolved in CS_2. The resulting solutions were then filtered to remove the small amounts of silica gel still remaining. After the volumes of the CS_2 solutions were reduced to a minimum, *n*-hexane was added causing the precipitation of the desired products: (i) $[CpMn(CO)(CS)]_2$(diphos) (yield ~5%; dec pt 212–214°) and (ii) CpMn(CS)(diphos) (yield ~5%; dec pt ~140°).

Anal. Calcd for $C_{40}H_{34}O_2S_2P_2Mn_2$ (i): C, 61.4; H, 4.3; S, 8.2; P, 7.9. Found: C, 62.0; H, 4.9; S, 7.9; P, 8.0. Molecular weight: calcd, 782; found, 751 (osmometry). Calcd for $C_{32}H_{29}SP_2Mn$ (ii): C, 68.3; H, 5.2; S, 5.7; P, 11.0. Found: C, 67.8; H, 5.8; S, 5.9; P, 11.2. Molecular weight: calcd, 562; found, 634 (osmometry).

Preparation of $CpMn(CO)(CS)_2$. A CS_2 solution (100 ml) con-

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(23) More complete details of this synthesis will be published shortly: I. S. Butler, N. J. Coville, and A. E. Fenster, *Inorg. Syn.*, in press.

taining freshly prepared, crude, "oily" $CpMn(CO)(CS)(C_8H_{14})$ and PPh_3 (130 mg, 0.5 mmol) was heated at reflux temperature for 12 hr. The desired thiocarbonyl product (yield ~20%, mp 71-72°) was isolated and purified by a procedure similar to that described for the analogous preparation of $CpMn(CO)_2CS$. *Anal.* Calcd for $C_8H_5OS_2Mn$: C, 40.7; H, 2.1; S, 27.1. Found: C, 41.0; H, 2.5; S, 27.8. Molecular weight: calcd, 236; found, 236 (mass spectrum). ^1H nmr: τ 5.18 (CS_2 solution).

Preparations of $CpMn(CS)_2(C_8H_{14})$ and $CpMn(CS)_3$. A mixture of $CpMn(CO)(CS)_2$ (20 mg, ~0.1 mmol) and C_8H_{14} (1.5 ml, ~10 mmol) in *n*-hexane (40 ml) was irradiated (Rayonet reactor, four 243.7-nm uv lamps) for 1 hr. Extensive decomposition was observed. Filtration of the reaction mixture, followed by evaporation of the solvent under vacuum, afforded a yellow oil containing $CpMn(CS)_2(C_8H_{14})$ and unreacted $CpMn(CO)(CS)_2$ and C_8H_{14}. The olefin complex is extremely air sensitive and further purification could not be achieved without more decomposition. The yellow oil was dissolved in CS_2 (10 ml) containing PPh_3 (20 mg). The resulting mixture was heated at reflux temperature for 5 hr. After evaporation of the solvent, minute quantities of $CpMn(CS)_3$ (identified by its ir spectrum in the CS stretching region) together with a little unreacted $CpMn(CO)(CS)_2$ were removed from the residue by vacuum sublimation (0.01 mm (25°)).

Kinetic Measurements. Kinetic data for the reactions of $CpMn(CO)_2(C_8H_{14})$ with CS_2 and PPh_3, with PPh_3 in methylcyclohexane solution, and with CS_2 alone were obtained by monitoring the rate of decrease of the ir-active CO stretching absorption of $CpMn(CO)_2(C_8H_{14})$ at ~1890 cm^{-1}. Pseudo-first-order conditions were employed in all cases, the substrate concentration being kept at about 2×10^{-3} *M*. Carbon disulfide and methylcyclohexane solutions of the complex and, where appropriate, varying concentrations of PPh_3 were prepared in aluminum foil wrapped reaction vessels fitted with neoprene serum caps and thermostated in a constant-temperature (±0.1°) oil bath. Samples were withdrawn with a syringe at regular intervals and their ir spectra were scanned in the CO stretching region. Linear first-order plots of ln $(A - A_\infty)$, where A is the absorbance at time t and A_∞ is the absorbance at infinite time, *vs.* t were obtained. The reactions went to completion and the plots were linear to at least 85% completion. The rate constants for identical runs were reproducible to within ±6%. All the rate constants were calculated using a least-squares computer program.

Results and Discussion

Reactions of $CpMn(CO)_2(C_8H_{14})$ with CS_2. A. In the Absence of PPh_3. The reaction of $CpMn(CO)_2(C_8H_{14})$ with CS_2 alone is extremely complex; the number and nature of the products formed depend critically upon the actual experimental conditions employed. For instance, when a 2×10^{-3} *M* CS_2 solution of $CpMn(CO)_2(C_8H_{14})$ is heated at 40° for about 4 days, the color of the solution changes gradually from yellow to orange. Concurrently, the two strong ir-active CO absorptions of the olefin complex at 1956 and 1893 cm^{-1} are replaced by a new set of bands at 2012, 1962, and 1235 cm^{-1} attributable to a complex I. This complex appears particularly unstable in the absence of CS_2 and all efforts to isolate it in the solid state failed. When a more concentrated solution of the olefin complex in CS_2 (1.5×10^{-2} *M*) is maintained at reflux temperature (~45°) for about 2 days, a different series of color changes takes place. The solution turns red within a few hours, then dark purple, and finally dark green. Infrared spectra taken during the reaction indicate that complex I is formed initially but then disappears as the reaction proceeds further. The complexity of the reaction is underscored by thin-layer chromatography which shows that there are at least four species present at the end of the reaction. The colors of these species on the tlc plate are light yellow (II), yellow (III), green (IV), and purple (V). Filtration of the solution at the end of the reaction reveals a large amount of a gummy, black deposit. This decomposition product is insoluble in all common solvents and its ir spectrum does not exhibit any noticeable absorption in the 4000-400-cm^{-1} region. Only species II, III, and V could be isolated by column chromatography of the filtrate; the green band corresponding to IV fades away as it travels down the column.

The front-running light yellow band affords air-stable, yellow crystals of complex II. Elemental analysis, molecular weight determinations (vp osmometry and mass spectrum), and an interpretation of the mass spectral fragmentation pathways indicate that II is $CpMn(CO)_2CS$, the first known thiocarbonyl complex of manganese. As expected, its ir spectrum in CS_2 solution exhibits two strong CO bands (at 2006 and 1954 cm^{-1}) and a strong CS stretching absorption (at 1266 cm^{-1}).[24]

The second, yellow product III is $CpMn(CO)_3$, easily identifiable by its ir spectrum in CS_2 solution [ν(CO) 2022 and 1938 cm^{-1}]. Both $CpMn(CO)_2CS$ and $CpMn(CO)_3$ are obtained in very low yield (~5% based on the amount of the original *cis*-cyclooctene complex). The purple species V is produced in even more minute quantities and only spectroscopic data could be obtained for it. In CS_2 solution, this complex exhibits two strong ir-active CO absorptions at 2009 and 1959 cm^{-1} together with medium-intense shoulders at 1940 and 1925 cm^{-1}. The fragmentation pattern observed in its mass spectrum suggests the presence of four CO groups. Since the starting material $CpMn(CO)_2(C_8H_{14})$ has only two CO groups, these data hint that complex V could possibly be a dimer.

At any given time, the ratio of the amount of complex I to that of the other species formed during the reaction at 40° and under reflux condition depends upon the initial concentration of $CpMn(CO)_2(C_8H_{14})$ in CS_2 solution. For example, at 40°, when the initial concentration of the olefin complex in CS_2 solution is 2×10^{-3} *M*, complex I is produced with little apparent decomposition and the ir spectrum of the reaction mixture after about 4 days indicates that this complex is the only carbonyl-containing species formed in any significant amount. However, when the initial concentration of olefin complex is increased tenfold, the reaction proceeds in a similar manner to the reaction under reflux conditions.

When the dilute solution of I in CS_2 is left to stand at 40°, the complex decomposes slowly. However, an ir spectrum taken after 3 weeks indicates that only an insignificant amount of $CpMn(CO)_2CS$ has been produced by comparison with the amount formed in the reaction under reflux conditions. Moreover, the appearance of two new bands at 2038 and 1260 cm^{-1} suggests that another carbonyl-thiocarbonyl complex (VI) is formed instead.

A complex VII, characterized so far only by its ir absorptions in CS_2 solution at 2022 (s), 1967 (s), 1932 (s), 1878 (s), and 1195 (m) cm^{-1}, is formed and disappears in step with complex I during the reaction under reflux conditions. Minute quantities of complex VII are obtained by terminating the reaction when the intensities of the absorptions associated with the complex are at a maximum compared to the other absorptions in the spectrum. Removal of CS_2 affords a mixture of purple, green, and yellow materials. Washing this mixture with *n*-pentane gives a green solution which almost instantly turns yellow. The ir spectrum of this yellow solution shows that it contains $CpMn(CO)_2CS$ and $CpMn(CO)_3$ as well as some unreacted $CpMn(CO)_2(C_8H_{14})$. The solid residue, which is insoluble in *n*-pentane, dissolves readily in benzene. Filtration and subsequent removal of the benzene solvent yields the purple-black solid VII. When a CS_2 solution of complex VII is left to stand for several hours at

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[24] The range of the ν(CS) modes of known thiocarbonyls is 1381-1193 cm^{-1} (see ref 2).

room temperature, the color changes gradually from purple to orange. At the same time its CO absorptions are replaced by new ones characteristic of complex I.

The replacement of a hydrogen atom in the π-cyclopentadienyl ring of $CpMn(CO)_2(C_8H_{14})$ by a methyl group does not appear to bring about any significant change in reactivity. The *cis*-cyclooctene complex $(\pi\text{-}MeC_5H_4)Mn(CO)_2(C_8H_{14})$ does react with CS_2 to produce the following species (among others): $(\pi\text{-}MeC_5H_4)Mn(CO)_2CS$ and $(\pi\text{-}MeC_5H_4)Mn(CO)_3$. It is also worth mentioning here that small amounts of $CpMn(CO)_2CS$ are formed by uv irradiation of a CS_2 solution of $CpMn(CO)_3$.

B. In the Presence of PPh_3. It has been demonstrated that the presence of PPh_3 is essential to the formation in good yield of the thiocarbonyl complexes *trans*-$MCl(CS)(PPh_3)_2$ (M = Rh, Ir).[12,14] Therefore, we felt that it would be worthwhile repeating the reaction of $CpMn(CO)_2(C_8H_{14})$ with CS_2 in the presence of PPh_3. Indeed, $CpMn(CO)_2CS$ is produced in essentially quantitative yield regardless of the concentration of the olefin complex and the reaction temperature. At reflux temperature, the reaction reaches completion after only about 1 day. Moreover, in sharp contrast to the identical reaction in the absence of PPh_3, there is no appreciable decomposition and no other carbonyl-containing products are formed. The only side products present in any significant amount in the reaction mixture are PPh_3S and C_8H_{14} (identified by ir spectroscopy and vpc analysis). The stoichiometry of the reaction may be written, therefore, as

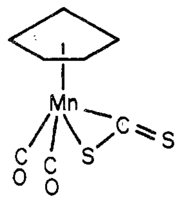
$$CpMn(CO)_2(C_8H_{14}) + PPh_3 + CS_2 \rightarrow CpMn(CO)_2CS + PPh_3S + C_8H_{14} \qquad (1)$$

C. Mechanisms. Owing to the apparent relative simplicity of reaction 1, the mechanism of this reaction will be discussed first. Neither PPh_3 nor C_8H_{14} reacts thermally with CS_2, even after 24 hr at reflux temperature. This suggests that one step in the reaction must be the formation of a reactive intermediate complex from which sulfur can be abstracted by PPh_3 to give PPh_3S and $CpMn(CO)_2CS$. The most reasonable stoichiometry for the sulfur-containing intermediate is $CpMn(CO)_2(CS_2)$ bearing in mind the presumed dissociation of C_8H_{14} from $CpMn(CO)_2(C_8H_{14})$ to form $CpMn(CO)_2$.[20] That reaction 1 proceeds *via* the fast abstraction of a sulfur atom from a CS_2-containing intermediate and that this intermediate is complex I, formed during the reaction of $CpMn(CO)_2(C_8H_{14})$ with CS_2 in the absence of PPh_3, is supported by the following experimental evidence.

(1) Addition of PPh_3 to a solution of I [prepared by maintaining a 2×10^{-3} *M* solution of $CpMn(CO)_2(C_8H_{14})$ in CS_2 at 40° for 4 days] results in the *instanteous* formation of $CpMn(CO)_2CS$ and PPh_3S.

(2) Monitoring reaction 1 by ir spectroscopy when it is carried out at 40° for a 2×10^{-3} *M* solution of $CpMn(CO)_2(C_8H_{14})$ and *less* than a stoichiometric amount of PPh_3 shows that $CpMn(CO)_2CS$ is formed only provided that there is still some unreacted PPh_3 left in solution. After all the PPh_3 has been converted into PPh_3S, the ir absorptions characteristic of $CpMn(CO)_2CS$ stop increasing in intensity and the bands associated with complex I appear and continue to grow until further reactions take place.

The ir data for $CpMn(CO)_2(CS_2)$ (I) leave little doubt that it is the first example of a π-CS_2 complex of manganese. In CS_2 solution, there are two strong CO absorptions at 2012 and 1962 cm^{-1} and strong and medium-intense absorptions at 1235 and 640 cm^{-1} which may be assigned to the out-of-ring $\nu(C{=}S)$ and in-ring $\nu(C{-}S)$ modes, respectively.[25] The formulation of $CpMn(CO)_2(CS_2)$ as a π-CS_2 complex is particularly reasonable when one remembers that the syntheses of the group VIII metal thiocarbonyls also appear to involve the formation of π-CS_2 complexes.[2] The proposed structure for I is shown below. The manganese atom is formally heptacoordinated and in the +3 oxidation state. Such a π-cyclopentadienylmanganese(III) species is not without precedent because $CpMn(CO)_2(SiPh_3)H$,[26] $CpMn(CO)_2(SiCl_3)H$,[27] and $CpMn(CO)_2(SiCl_3)(SnCl_3)$[28] have been synthesized recently. An X-ray structure determination of $CpMn(CO)_2(SiPh_3)H$[26] suggests the presence of a hydrogen bridge between manganese and silicon thereby forming a three-membered ring similar to that proposed here for $CpMn(CO)_2(\pi\text{-}CS_2)$.



I

Angelici and Loewen[20] have investigated the kinetics and mechanism of reaction 2 in methylcyclohexane solution at

$$CpMn(CO)_2(olefin) + L \rightarrow CpMn(CO)_2L + olefin \qquad (2)$$

50-95° in which various olefins (including *cis*-cyclooctene) are replaced by monodentate ligands (L) such as PPh_3. They proposed that the reactions proceed by an SN1 dissociative mechanism involving the slow loss of olefin in the rate-determining step to form the intermediate $CpMn(CO)_2$, followed by rapid entry of L. In an attempt to ascertain the role of *cis*-cyclooctene in the formation of $CpMn(CO)_2CS$ from $CpMn(CO)_2(C_8H_{14})$, kinetic data were obtained at 40° for reactions 1, 2 (olefin = C_8H_{14}; L = PPh_3), and 3. The ob-

$$CpMn(CO)_2(C_8H_{14}) + CS_2 \rightarrow CpMn(CO)_2(\pi\text{-}CS_2) + C_8H_{14} \qquad (3)$$

served pseudo-first-order rate constants (k_{obsd}) for the reactions are given in Table II. The data indicate that when the concentration of $CpMn(CO)_2(C_8H_{14})$ is 2×10^{-3} *M*, the rates for reactions 1 and 3 at 40° are experimentally identical;[29] moreover, the rate for reaction 1 is independent of $[PPh_3]$. The observed rates for reactions 1 and 3 are also essentially the same as that for reaction 2. The small discrepancy is within the range noted by Angelici and Loewen[20] for reaction 2 when the nature of either the solvent or the entering ligand is changed.

On the basis of the kinetic results, it seems likely that the same rate-determining step is operative in all three reactions, *viz.*, the slow dissociation of *cis*-cyclooctene from $CpMn(CO)_2(C_8H_{14})$ to produce the $CpMn(CO)_2$ intermediate. This suggestion receives some support from the results obtained

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[25] The ranges of the out-of-ring $\nu(C{=}S)$ and in-ring $\nu C{-}S)$ modes of known π-CS_2 complexes are 1235-955 and 653-632 cm^{-1}, respectively (see ref 2).

[26] M. J. Bennett and W. Brooks, *Chem. Eng. News*, 48, 75 (June 8, 1970).

[27] W. Jetz and W. A. G. Graham, *Inorg. Chem.*, 10, 4 (1971).

[28] W. Jetz and W. A. G. Graham, *Inorg. Chem.*, 10, 1647 (1971).

[29] It should be emphasized that these results are valid only when the reaction of $CpMn(CO)_2(C_8H_{14})$ with CS_2 affords the π-CS_2 complex as the only carbonyl-containing species. At higher temperatures or with an increased concentration of the olefin complex, when the reaction yields $CpMn(CO)_2CS$, $CpMn(CO)_3$, and other products, the rate for reaction 3 is approximately half that for reaction 1.

Table II. Pseudo-First-Order Rate Constants for the Reactions at 40° of $CpMn(CO)_2(C_8H_{14})$ with CS_2 and PPh_3, with PPh_3 in Methylcyclohexane, and with CS_2 Alone

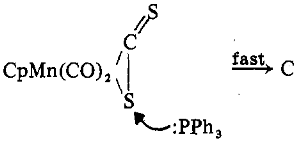
Reaction	No.	$[PPh_3]$,[a] M	$10^5 k_{obsd}$, sec^{-1}
$CpMn(CO)_2(C_8H_{14}) + PPh_3 \xrightarrow{CS_2} CpMn(CO)_2CS + PPh_3S + C_8H_{14}$	1	0.02	7.4
		0.05	7.9
		0.1	7.6
$CpMn(CO)_2(C_8H_{14}) + PPh_3 \xrightarrow{\text{methylcyclohexane}} CpMn(CO)_2(PPh_3) + C_8H_{14}$	2	0.02	6.4[b]
$CpMn(CO)_2(C_8H_{14}) \xrightarrow{CS_2} CpMn(CO)_2(\pi\text{-}CS_2) + C_8H_{14}$	3		7.8[b]

[a] $[CpMn(CO)_2(C_8H_{14})] = 2 \times 10^{-3}$ *M*. [b] Average of several identical runs; reproducibility ±6%.

for the reaction of the norbornadiene derivative $CpMn(CO)_2(nor\text{-}C_7H_8)$ with CS_2 and PPh_3 under reflux conditions. The reaction again leads to $CpMn(CO)_2CS$ but extremely slowly. This observation is in accord with Angelici and Loewen's results for reaction 2 which indicate that the rate of dissociation of *nor*-C_7H_8 is appreciably slower than that for C_8H_{14}.

The results discussed above suggest that the overall mechanism for the formation of $CpMn(CO)_2CS$ from $CpMn(CO)_2$(olefin), CS_2, and PPh_3 is as shown in eq 4. The sulfur-abstraction step is considered to be similar to that proposed by Yagupsky and Wilkinson[14] for the formation of rhodium and iridium thiocarbonyls from π-CS_2 species.

$$CpMn(CO)_2(\text{olefin}) \xrightarrow[\text{slow}]{-\text{olefin}} CpMn(CO)_2 \xrightarrow[\text{fast}]{+CS_2}$$

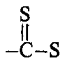


$$\xrightarrow{\text{fast}} CpMn(CO)_2CS + PPh_3S \qquad (4)$$

Owing to its complexity, the mechanism of the reaction of $CpMn(CO)_2(C_8H_{14})$ with CS_2 alone is more difficult to assess, particularly as some of the complexes formed could not be identified. Nevertheless, it is possible to make a few comments. The amount of $CpMn(CO)_2CS$, $CpMn(CO)_3$, black decomposition product, and other carbonyl-containing species present in the reaction mixture at any given time relative to the amount of $CpMn(CO)_2(\pi\text{-}CS_2)$ (complex I) appears to be dependent on the concentration of $CpMn(CO)_2(C_8H_{14})$ and the temperature. This suggests that in the absence of PPh_3 the reaction of $CpMn(CO)_2(C_8H_{14})$ with CS_2 leads to the formation of the products mentioned above *via* the thermal decomposition of $CpMn(CO)_2(\pi\text{-}CS_2)$. In partial support of this hypothesis is the fact that $RhCl(PPh_3)_2(CS_2)(\pi\text{-}CS_2)$ decomposes thermally in chloroform solution to give *trans*-$RhCl(CS)(PPh_3)_2$.[30] It should also be noted that the approximate rate for the thermal decomposition process leading to $CpMn(CO)_2CS$ is half that for the reaction in the presence of PPh_3 but under otherwise identical experimental conditions. A similar rate decrease is observed for the thermal decomposition of $CpMn(CO)_2(C_8H_{14})$ in methylcyclohexane solution [to give $CpMn(CO)_3$ and a brown precipitate] when compared to the reaction with PPh_3 affording $CpMn(CO)_2PPh_3$.

It was thought originally[18a] that the liberated olefin might play the role of sulfur acceptor in the reaction of $CpMn(CO)_2(C_8H_{14})$ with CS_2 in the absence of PPh_3. Moreover, in doing so it would be converted into cyclooctene episulfide, $C_8H_{14}S$. However, further investigation has failed to give any evidence for the formation of the known episulfide $C_8H_{14}S$.[31]

The purple complex VII is formed and disappears in step with $CpMn(CO)_2(\pi\text{-}CS_2)$ in the reaction in the absence of PPh_3 provided that either the concentration of $CpMn(CO)_2(C_8H_{14})$ or the reaction temperature is high enough. Once isolated, complex VII can be converted to $CpMn(CO)_2(\pi\text{-}CS_2)$ by addition of CS_2. Consequently, VII could possibly be the dimeric form of $CpMn(CO)_2(\pi\text{-}CS_2)$ containing two



$$-\overset{\overset{\displaystyle S}{\|}}{C}-S$$

bridges. Similar structures containing CS_2 bridges have been proposed for materials formed during the reaction of $IrCl(PPh_3)_3$ with CS_2 in the absence of PPh_3.[14]

Thiocarbonyl Derivatives of $CpMn(CO)_2CS$. The synthetic route to $CpMn(CO)_2CS$ suggested that the preparation of an olefin derivative of the complex might be the first step leading to the di- and trithiocarbonyl derivatives, $CpMn(CO)(CS)_2$ and $CpMn(CS)_3$. The monothiocarbonyl complex appears to be relatively inert toward CO and, for that matter, thermal replacement of the CS ligand. For instance, when an *n*-hexane solution of $CpMn(CO)_2CS$ is maintained under a $C^{18}O$ atmosphere for about 1 week at 40°, there are no apparent changes in the ir spectrum. Similarly, no reaction occurs when an *n*-hexane solution of the thiocarbonyl complex and excess C_8H_{14} is refluxed for 48 hr. However, the thiocarbonyl complex does undergo photochemical *carbonyl* replacement. Ultraviolet irradiation of an *n*-hexane solution of $CpMn(CO)_2CS$ and excess C_8H_{14} proceeds with extensive decomposition and yields the air-sensitive complex $CpMn(CO)(CS)(C_8H_{14})$ as an impure oil. This oil can be used as $CpMn(CO)(CS)(C_8H_{14})$ for most practical purposes. Further purification results in additional decomposition and a reasonably pure sample of the product is obtained in only ~5% yield. Since there is no evidence for the formation of $CpMn(CO)_2(C_8H_{14})$ in this reaction, it appears that under the photochemical conditions employed one of the CO groups in $CpMn(CO)_2CS$ is lost preferentially to the CS group. This observation is supported by the results obtained for the photochemical reactions of $CpMn(CO)_2CS$ with various monodentate and bidentate ligands.[32,33]

It is of interest that $CpMn(CO)_2CS$ does not react thermally

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(30) M. C. Baird and G. Wilkinson, *J. Chem. Soc. A*, 865 (1967).

(31) D. J. Pettitt and G. K. J. Helmkamp, *J. Org. Chem.*, 28, 2932 (1963).

(32) N. J. Coville and I. S. Butler, *J. Organometal. Chem.*, in press.

(33) N. J. Coville and I. S. Butler, to be submitted for publication.

with $NaNO_2$ and HCl as does $CpMn(CO)_3$,[34] and so efforts to obtain $[CpMn(CO)(CS)(NO)]^+$, the thiocarbonyl analog of $[CpMn(CO)_2(NO)]^+$, failed. A possible explanation for this is that CS requires a larger share of the electrons available for back-bonding than does CO. The resultant lowering of the electron density on the manganese atom would thus destabilize a cationic state with respect to a neutral one.

The reaction of $CpMn(CO)(CS)(C_8H_{14})$ with CS_2 in the presence of PPh_3 proceeds very similarly to that described for the synthesis of $CpMn(CO)_2CS$. The dithiocarbonyl complex $CpMn(CO)(CS)_2$ is produced without apparent decomposition and the only side products present in the reaction mixture are C_8H_{14} and PPh_3S. The most likely mechanism (eq 5) for the reaction is similar to that discussed earlier for

$$CpMn(CO)(CS)(C_8H_{14}) \xrightarrow[\text{slow}]{-C_8H_{14}} CpMn(CO)(CS) \xrightarrow[\text{fast}]{+CS_2}$$

$$CpMn(CO)(CS)(\pi\text{-}CS_2) \xrightarrow[+PPh_3]{\text{fast}} CpMn(CO)(CS)_2 + PPh_3S \qquad (5)$$

the reaction affording the monothiocarbonyl complex. That the first step in the reaction is the slow dissociation of the olefin to give the reactive 16-electron intermediate CpMn(CO)(CS) is supported by kinetic data obtained previously for the reaction of $CpMn(CO)(CS)(C_8H_{14})$ with PPh_3.[35] In contrast to the reactions leading to $CpMn(CO)_2CS$ [and $(\pi\text{-}MeC_5H_4)Mn(CO)_2CS$], there is no ir evidence for the formation of a π-CS_2 species.

The olefin thiocarbonyl complex reacts readily in *n*-hexane solution with PPh_3 and $P(OMe)_3$ to give $CpMn(CO)(CS)(PPh_3)$ and $CpMn(CO)(CS)[P(OMe)_3]$, respectively. These complexes and $CpMn(CO)(CS)(C_8H_{14})$ presumably have pseudotetrahedral structures, and so enantiomeric pairs are possible.

When $CpMn(CO)(CS)(C_8H_{14})$ is treated thermally with diphos in *n*-hexane solution, both the bridged complex $[CpMn(CO)(CS)]_2$(diphos) and the chelated complex CpMn(CS)(diphos) are readily produced. The formation of CpMn(CS)(diphos) is remarkable in view of the fact that *thermal* replacement of a CO group in $CpMn(CO)_3$ or in one of its derivatives is extremely rare. By comparison, the thermal reaction of $CpMn(CO)_2(C_8H_{14})$ with diphos affords the bridged species $[CpMn(CO)_2]_2$(diphos) exclusively.[36] The facile thermal replacement of the CO group in $CpMn(CO)(CS)(C_8H_{14})$ by diphos may be interpreted in terms of the better π-acceptor character of CS compared to that of CO. Such a situation would result in a weakening of the Mn-CO bond in the thiocarbonyl compared to those in $CpMn(CO)_2(C_8H_{14})$, as is observed. However, CpMn(CS)(diphos) certainly must also be stabilized by the "chelate effect" of diphos.

The photochemically induced substitution of CO in CpMn(CO)(CS) by C_8H_{14} proceeds with extensive decomposition, even in the presence of a large excess of olefin. When eventually prepared, $CpMn(CS)_2(C_8H_{14})$ is obtained only in minute quantities and could be identified only by its ir spectrum [ν(CS) 1289 (s), 1217 (vs) cm^{-1} in CS_2 solution] and its subsequent reaction with CS_2.

When a CS_2 solution of $CpMn(CS)_2(C_8H_{14})$ and PPh_3 is refluxed for 5 hr, the ir spectra of the reaction mixture exhibit changes in the CS stretching region consistent with the formation of the trithiocarbonyl complex $CpMn(CS)_3$. The decrease in intensity of the two strong absorptions of $CpMn(CS)_2(C_8H_{14})$ at 1289 and 1217 cm^{-1} is accompanied by the concomitant appearance of two new CS stretching absorptions at 1338 (m) and 1240 (vs) cm^{-1}. As is the case for the syntheses of $CpMn(CO)_2CS$ and $CpMn(CO)(CS)_2$, the reaction also involves the formation of PPh_3S and presumably proceeds *via* the π-CS_2 intermediate $CpMn(CS)_2(\pi\text{-}CS_2)$. Owing to the low-yield syntheses of its precursors, $CpMn(CS)_3$ could be obtained only in minute quantities and so was identified solely by its ir spectrum. In addition to the two bands expected in the CS stretching region, there is also an out-of-plane C-H deformation mode at ~825 cm^{-1} characteristic of the Cp moiety. The synthesis of the trithiocarbonyl $CpMn(CS)_3$ completes the series of $CpMn(CO)_{3-n}(CS)_n$ (n = 0-3) complexes sought in this work. All the complexes are presumably isostructural with $CpMn(CO)_3$. The CO and CS stretching regions of the ir spectra of the complete series are compared in Figure 1.

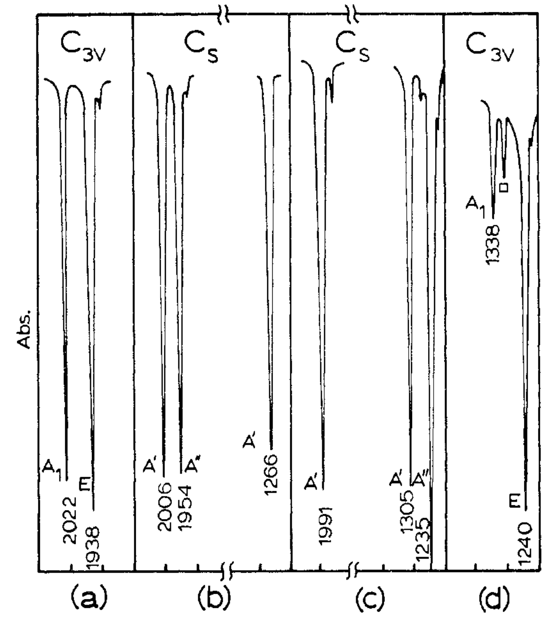

Figure 1. Infrared spectra (cm^{-1}) in the CO and/or CS stretching regions of (a) $CpMn(CO)_3$, (b) $CpMn(CO)_2CS$, (c) $CpMn(CO)(CS)_2$, and (d) $CpMn(CS)_3$ (in CS_2 solution). The band assignments are based on the local symmetries of the $Mn(CO)_{3-n}(CS)_n$ (n = 0-3) moieties. The band labeled □ in spectrum (d) is attributed to a small amount of $CpMn(CO)(CS)_2$ present as an impurity.

Conclusion

It is evident from the work described in this paper that thiocarbonyl complexes are more accessible than was heretofore realized. The displacement of an olefin by CS_2 in the presence of PPh_3 as a sulfur acceptor may prove to be a general synthetic route to these complexes. We are currently studying a number of these reactions with the hope of further extending the known range of thiocarbonyl complexes.

Acknowledgments. This work was supported by a grant from the National Research Council of Canada. A postgraduate scholarship to A. E. F. from the Canada Council is gratefully acknowledged.

Registry No. $CpMn(CO)_2(C_8H_{14})$, 49716-47-4; $(\pi\text{-}MeC_5H_4)Mn(CO)_2(C_8H_{14})$, 49716-48-5; CS_2, 75-15-0; PPh_3, 603-35-0; $P(OMe)_3$, 121-45-9; $CpMn(CO)_2(\pi\text{-}CS_2)$, 49716-49-6; $(\pi\text{-}MeC_5H_4)Mn(CO)_2(\pi\text{-}CS_2)$, 49716-50-9; $CpMn(CO)_2CS$, 31741-76-1; $(\pi\text{-}MeC_5H_4)Mn(CO)_2CS$, 49716-52-1; $CpMn(CO)(CS)(C_8H_{14})$, 49716-53-2; $CpMn(CO)(CS)PPh_3$, 49716-54-3; $CpMn(CO)(CS)P(OMe)_3$, 49716-55-4; $[CpMn(CO)(CS)]_2$(diphos), 50297-91-1; CpMn(CS)(diphos), 49716-56-5; $CpMn(CO)(CS)_2$, 49716-57-6; $CpMn(CS)_3$, 49716-58-7; $CpMn(CS)_2(C_8H_{14})$, 49846-31-3.

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(35) I. S. Butler and A. E. Fenster, *Inorg. Chim. Acta*, 7, 79 (1973).

(36) A. E. Fenster and I. S. Butler, unpublished results.