(23) M. L. H. Green, M. Ishaq, and R. N. Whitely, *J. Chem. Soc. A*, 1508 (1967).
(24) A. Greco, M. Green, and F. G. A. Stone, *J. Chem. Soc. A*, 3476 (1971).
(25) T. G. Appleton, H. C. Clark, R. C. Poller, and R. J. Puddephatt, *J. Organomet. Chem.*, **39**, C 13 (1972).
(26) B. E. Mann, *Adv. Organomet. Chem.*, **12**, 135 (1974).
(27) H. C. Clark and W. S. Tsang, *J. Am. Chem. Soc.*, **89**, 533 (1967).
(28) P. M. Treichel, E. Pitcher, and F. G. A. Stone, *Inorg. Chem.*, **1**, 511 (1962).
(29) J. B. Wilford and F. G. A. Stone, *Inorg. Chem.*, **4**, 93 (1965).
(30) T. Blackmore, M. I. Bruce, F. G. A. Stone, R. E. Davis, and A. Garza, *Chem. Commun.*, 852 (1971).
(31) T. Blackmore, M. I. Bruce, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 106 (1974).
(32) J. L. Davidson, M. Green, F. G. A. Stone, and A. Welch, *J. Chem. Soc., Chem. Commun.*, 286 (1975).
(33) M. Cooke, M. Green, and T. A. Kuc, *J. Chem. Soc. A*, 1200 (1971).
(34) J. Clemens, M. Green, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 375 (1973).
(35) R. E. Bichler, M. R. Booth, and H. C. Clark, *J. Organomet. Chem.*, **24**, 145 (1970).
(36) J. Clemens, M. Green, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 93 (1974).
(37) Preliminary communication: J. P. Williams and A. Wojcicki, *Inorg. Chim. Acta*, **15**, L19 (1975).
(38) B. L. Booth and R. G. Hargreaves, *J. Chem. Soc. A*, 308 (1970).
(39) R. B. King and M. N. Ackermann, *Inorg. Chem.*, **13**, 637 (1974).
(40) F. Hague, J. Miller, P. L. Pauson, and J. B. Pd. Tripathi, *J. Chem. Soc. C*, 743 (1971).
(41) F. Calderazzo, E. A. C. Lucken, and D. F. Williams, *J. Chem. Soc. A*, 154 (1967).
(42) P. V. Petrovskii, E. I. Fedin, L. A. Fedorov, A. G. Ginzburg, V. N. Setkina, and D. N. Kursanov, *Dokl. Akad. Nauk, SSSR*, **210**, 425 (1973).
(43) E. O. Fischer and W. Fellman, *J. Organomet. Chem.*, **1**, 191 (1963).
(44) W. P. Giering, S. Raghu, M. Rosenblum, A. Cutler, D. Ehntholt, and R. W. Fish, *J. Am. Chem. Soc.*, **94**, 8251 (1972).
(45) H. C. Clark, D. G. Ibbott, N. C. Payne, and A. Shaver, *J. Am. Chem. Soc.*, **97**, 3555 (1975).
(46) H. Gilman and L. A. Gist, Jr., *J. Org. Chem.*, **22**, 250 (1957).
(47) M. L. Maddox, S. L. Stafford, and H. D. Kaesz, *Adv. Organomet. Chem.*, **3**, 1 (1965).
(48) This implies that no precoordination is occurring of the attacking electrophile to the metal.[45] Addition from the same side of the ring as the metal has been observed for nickel; see, for example, D. W. McBride, E. Dudek, and F. G. A. Stone, *J. Chem. Soc.*, 1752 (1964).
(49) J. L. Davidson, M. Green, F. G. A. Stone, and A. J. Welch, *J. Chem. Soc., Dalton Trans.*, 2044 (1976).
(50) A. Wojcicki, *Adv. Organomet. Chem.*, **11**, 87 (1973).
(51) R. P. Hughes and J. Powell, *J. Organomet. Chem.*, **30**, C45 (1971).
(52) C. S. Kraihanzel and M. L. Losee, *J. Am. Chem. Soc.*, **90**, 4701 (1968).

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Cyclopentadienylnitrosylmanganese Derivatives with Terminal and Carbon-Bridging Thiocarbonyl Groups[1]

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Received May 16, 1977 AIC703470

Reaction of $[RC_5H_4Mn(CO)(CS)(NO)]^+PF_6^-$ (R = H, CH_3) with KI gives the iodomanganese derivatives $RC_5H_4Mn(CS)(NO)I$. The reactions of these complexes with *trans*-perfluoro(1-methylpropenylate)silver, trifluoromethylthiosilver, and zinc dust yield $RC_5H_4Mn(CS)(NO)(\eta^1\text{-}C_4F_7)$, $RC_5H_4Mn(CS)(NO)SCF_3$, and $[RC_5H_4Mn(CS)(NO)]_2$ (cis and trans mixture), respectively. The reactions of several of the new complexes with Ph_3P are also described and discussed.

Introduction

Within the last decade, considerable attention has been given to the study of metal complexes containing coordinated thiocarbonyl.[3a] In contrast with metal carbonyls, the preparation of metal thiocarbonyl complexes requires the utilization of indirect synthetic routes since the free ligand is extremely labile. Despite the obvious resemblance between the coordinated carbonyl and thiocarbonyl ligands, their chemical properties differ substantially, and this can be attributed in part to the considerably greater polarity of the latter ligand. The carbon atom of a coordinated thiocarbonyl is significantly more electrophilic than that of a carbonyl ligand as evident by its higher susceptibility toward an attack by nucleophiles.[3] Furthermore, the nucleophilic character of the sulfur atom of a coordinated thiocarbonyl is evident from its facile reaction with electrophiles.[4] This specific feature suggests that the preparation of η^1-alkyl derivatives of metal thiocarbonyl complexes by synthetic routes involving strong nucleophiles is not likely to be straightforward. In fact, metal thiocarbonyl complexes of this type have not yet been reported.

In the majority of the currently known metal thiocarbonyl complexes, the coordinated thiocarbonyl behaves as a carbon-bonded terminal ligand. Recently, Dombek and Angelici reported[5] the preparation of some novel derivatives of tungsten which contain end-to-end bridging thiocarbonyl ligands. Carbon-bridging thiocarbonyl ligands were first proposed for the binuclear manganese complexes $[RC_5H_4Mn(CS)(NO)]_2$ (R = H, CH_3)[1] and have recently been confirmed by the x-ray crystal-structure analysis of *cis*-$[C_5H_5Fe(CS)(CO)]_2$.[6]

The present paper provides further details concerning the preparation of the above cited carbon-bridged thiocarbonyl derivatives of manganese and describes the syntheses and chemical properties of some novel mononuclear cyclopentadienylmanganese thiocarbonyl complexes.

Experimental Section

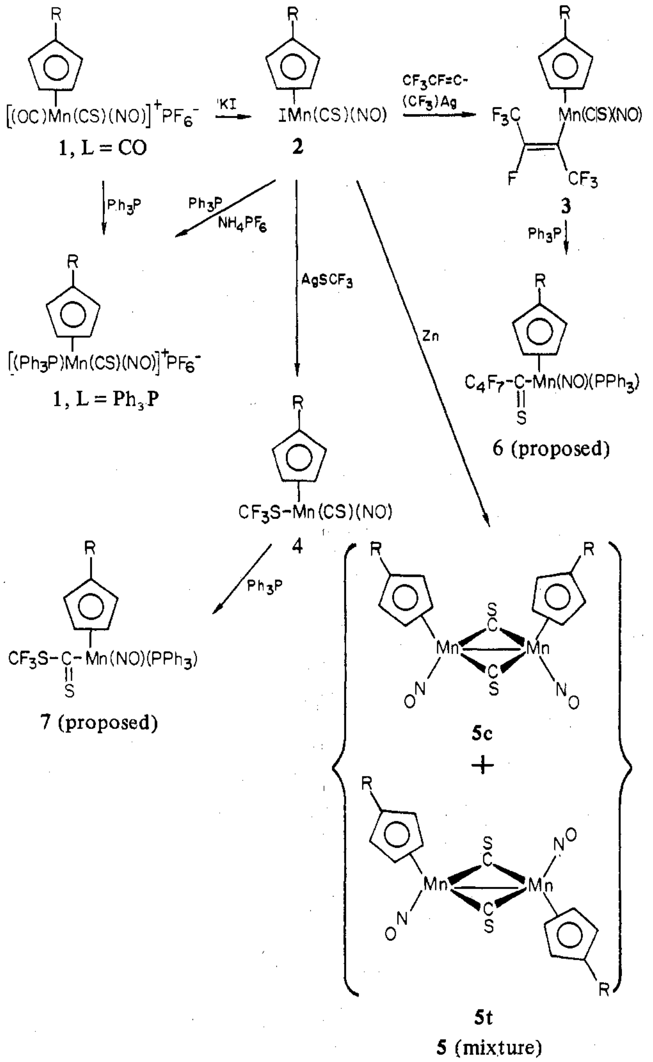
Microanalyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. Infrared spectra were recorded on a Perkin-Elmer 225 grating spectrometer and calibrated against the 1601- and 1944-cm^{-1} bands of polystyrene film. Proton NMR spectra were recorded on a Jeol JHM-MH-100 spectrometer using TMS as an internal reference.

The solvents used during the course of this investigation were dried by conventional procedures as appropriate (e.g., tetrahydrofuran and diglyme were dried by boiling with $LiAlH_4$ and Na(spheres), respectively) and freshly distilled under nitrogen. Reactions and other manipulations involving organometallic solids and their solutions were carried out routinely under an atmosphere of dry nitrogen.

The cationic manganese complexes $[RC_5H_4Mn(CO)(CS)(NO)]^+PF_6^-$ (**1**, R = H, CH_3)[7] and the reagents trifluoromethylthiosilver[8] and perfluoro-1-methylpropenylsilver[9] were prepared according to published procedures.

Preparation of $RC_5H_4Mn(CS)(NO)I$ (2, R = H, CH_3). 2, R = H. A mixture of $[C_5H_5Mn(CO)(CS)(NO)]^+PF_6^-$ (6.0 g, 16.3 mmol) and KI (5.0 g, 30.1 mmol) was stirred in tetrahydrofuran (~180 mL) at ambient temperature for a period of 3 h. The solution was then filtered and the filtrate was dried under reduced pressure (25 °C (20 mm)). The crude green product was dissolved in a minimum amount of dichloromethane (~10 mL) and the solution obtained was diluted with pentane (~200 mL). The resulting solution was filtered and the clear green filtrate was cooled to −78 °C for ~5 h to afford, after separation, 2.0 g (38% yield) of the deep green crystalline product $C_5H_5Mn(CS)(NO)I$, mp 87–89 °C. The analytically pure sample of this compound was obtained by recrystallizations from pentane followed by sublimation at 50 °C (10^{-2} mm). Anal. Calcd for

Scheme I



$C_6H_5NOSIMn$: C, 22.45; H, 1.57; N, 4.36; S, 9.99; mol wt, 321. Found: C, 22.63; H, 1.72; N, 4.62; S, 9.86; mol wt, 321 (mass spectrum). ^{1}H NMR ($CDCl_3$) spectrum, τ 4.3 (s).

2, R = CH_3. This complex was prepared from $[CH_3C_5H_4Mn(CO)(CS)(NO)]^+PF_6^-$ and excess of KI by essentially the same procedure described above for the preparation of **2**, R = H. The green crystalline product $CH_3C_5H_4Mn(CS)(NO)I$, mp 43–45 °C, was obtained in 46% yield. Anal. Calcd for $C_7H_7NOSIMn$: C, 25.09; H, 2.10; S, 9.57; mol wt, 335. Found: C, 25.11; H, 2.07; S, 9.83; mol wt, 335 (mass spectrum).

Preparation of $RC_5H_4Mn(CS)(NO)(\eta^1\text{-}C_4F_7)$ [3, R = H, CH_3]. 3, R = H. A solution of $C_5H_5Mn(CS)(NO)I$ (0.4 g, 1.24 mmol) and *trans*-perfluoro(1-methylpropenylate)silver, $CF_3CF{=}C(CF_3)Ag$ (0.5 g, 1.73 mmol), was stirred in dichloromethane (~50 mL) at ambient temperature in the dark for a period of 20 h. The reaction mixture was filtered, the filtrate was taken to dryness under reduced pressure (25 °C (20 mm)), and the gray solid obtained was then sublimed at 60 °C (0.05 mm) to afford the dark violet crystalline product $C_5H_5Mn(CS)(NO)(\eta^1\text{-}C_4F_7)$, mp 80–81 °C, in 24% yield (0.112 g). Anal. Calcd for $C_{10}H_5NOSF_7Mn$: C, 32.02; H, 1.34; mol wt, 375. Found: C, 32.05; H, 1.36; mol wt, 375 (mass spectrum).

3, R = CH_3. This complex was prepared from $CH_3C_5H_4Mn(CS)(NO)I$ and *trans*-perfluoro(1-methylpropenylate)silver by essentially the same procedure described above for **3**, R = H. The dark brown oily product $CH_3C_5H_4Mn(CS)(NO)(\eta^1\text{-}C_4F_7)$ was obtained in ~20% yield and purified by sublimation onto a cold finger (−78 °C) at 60 °C (0.05 mm). Anal. Calcd for $C_{11}H_7NOSF_7Mn$: C, 34.22; H, 1.81; mol wt, 389. Found: C, 34.12; H, 178; mol wt, 389 (mass spectrum).

Preparation of $RC_5H_4Mn(CS)(NO)SCF_3$ (4, R = H, CH_3). 4, R = H. A mixture of $C_5H_5Mn(CS)(NO)I$ (0.4 g, 1.24 mmol) and $AgSCF_3$ (0.26 g, 1.24 mmol) was stirred in dichloromethane (~50 mL) at ambient temperature in the dark for a period of 25 h. The reaction mixture was filtered, the filtrate was dried under reduced pressure (25 °C (25 mm)), and the brown oily product obtained was then extracted with several portions (~40 mL each) of hexane until the washings obtained were colorless. The hexane washings were combined, the total volume was reduced to ~70 mL, and the solution was then cooled to −78 °C for several hours to afford the deep brown waxy product $C_5H_5Mn(CS)(NO)SCF_3$ in ~50% yield (0.163 g). The analytically pure sample of this complex was obtained by chromatography on a silica-gel column, using hexane–benzene mixture (1:2 v/v) to elute the desired product. Anal. Calcd for $C_7H_5NOSF_3Mn$: C, 31.95; H, 1.97; mol wt, 263. Found: C, 31.8; H, 1.98; mol wt, 260 (osmometric in benzene).

4, R = CH_3. This dark brown waxy complex was prepared in ~22% yield from $CH_3C_5H_4Mn(CS)(NO)I$ and $AgSCF_3$ by essentially the same procedure described above for **4**, R = H. Anal. Calcd for $C_8H_7NOSF_3Mn$: C, 34.69; H, 2.55, mol wt, 277. Found: C, 34.52; H, 2.51; mol wt, 265 (osmometric in benzene).

Preparation of $[RC_5H_4Mn(CS)(NO)]_2$ (5, R = H, CH_3). 5, R = H. A solution of $C_5H_5Mn(CS)(NO)I$ (1.0 g, 3.1 mmol) in dry diglyme (~50 mL) was stirred with zinc powder (~2.0 g) at 80 °C for a period of 1 h. After cooling to ambient temperature, the reaction mixture was treated with dichloromethane (~220 mL), hexane (~100 mL), and water (~100 mL) and then the excess zinc was filtered off. The filtrate obtained consisted of two phases: diglyme–water and dichloromethane–hexane product, which were separated using a separatory funnel. The brown solution containing the product was washed several times with cold water (4 × 40 mL) in order to remove traces of diglyme and dried over anhydrous $MgSO_4$, and then the solvent was removed under reduced pressure (25 °C (20 mm)) to afford a solid brown crude product. Deep brown crystals of the product $[C_5H_5Mn(CS)(NO)]_2$, mp >200 °C dec, were obtained in 38% yield (0.228 g) by crystallization from a dichloromethane–hexane mixture (~1:6, v/v) at −78 °C. The analytically pure sample of this complex was obtained by recrystallization from a CS_2 solution at −78 °C. Anal. Calcd for $C_{12}H_{10}N_2O_2S_2Mn_2$: C, 37.13; H, 2.60; S, 16.52; mol wt, 388. Found: C, 37.29; H, 2.95; S, 16.26; mol wt, 388 (mass spectrum). The ^{1}H NMR spectrum of this complex, taken in several solvents, shows the following singlets (τ): $CDCl_3$, 4.83; CD_2Cl_2, 4.85; CS_2, 4.93 and 4.95 (intensity ratio, ~3:1); benzene, 5.28 and 5.47 (intensity ratio, ~3:1).

5, R = CH_3. This complex was prepared from $CH_3C_5H_4Mn(CS)(NO)I$ and excess of zinc dust by essentially the same procedure described above for **5**, R = H. The brown crystalline product $[CH_3C_5H_4Mn(CS)(NO)]_2$, mp 119–121 °C, was obtained in 20% yield. Anal. Calcd for $C_{14}H_{14}N_2O_2S_2Mn_2$: C, 40.39; H, 3.40; S, 15.4; mol wt, 416. Found: C, 39.66; H, 3.29; S, 16.6; mol wt, 416 (mass spectrum).

Results and Discussion

Recently, we have reported the preparation of the cationic thiocarbonyl-containing manganese complexes $[RC_5H_4Mn(CS)(NO)L]^+X^-$ [**1**, L = CO; R = H, CH_3; X = SbF_6, PF_6][7] and some of their reactions with Lewis bases to give the carbonyl-substituted derivatives **1**, L = Ph_3P, Ph_3As, and Ph_3Sb. We report here some interesting reactions of **1**, L = CO, with certain inorganic anions. Treatment of this complex with excess KI, in tetrahydrofuran solution at ambient temperature, gave a moderate yield of the carbonyl-free iodo derivative $RC_5H_4Mn(CS)(NO)I$ [**2**, R = H, CH_3]. Attempts to effect a similar reaction with either chloride or bromide ion were apparently unsuccessful. In contrast with iodide, the anions NCX^- [X = S, O] attack the coordinated thiocarbonyl in **1**, L = CO, to afford the cyanomanganese derivatives $RC_5H_4Mn(CO)(NO)CN$ [R = H, CH_3] in low yields (< 5%).[10] These conversions are similar to those already reported[11] between $[C_5H_5Fe(CO)_2CS]^+$ and NCX^-.

The new green iodomanganese derivatives **2**, R = H, CH_3, are air stable in the solid state as well as in solution. This feature is of considerable interest, since it contrasts with the failure to synthesize the related carbonyl derivative $C_5H_5Mn(CO)(NO)I$ by the analogous reaction between $[C_5H_5Mn(CO)_2NO]^+PF_6^-$ and KI[10] or by the direct iodination

Table I. Selected Infrared Spectral Data of Some New Cyclopentadienylmanganese Thiocarbonyl Nitrosyl Derivatives

	Infrared spectrum,[a] cm^{-1}			
Complex	ν(NO)	ν(CS)	ν(CF)	Other
$C_5H_5Mn(CS)(NO)I$ (**2**, R = H)	1786 (vs)	1285 (vs)		
$CH_3C_5H_4Mn(CS)(NO)I$ (**2**, R = CH_3)	1780 (vs)	1291 (vs)		
$C_5H_5Mn(CS)(NO)(\eta^1\text{-}C_4F_7)$ (**3**, R = H)	1790 (vs)	1308 (vs)	1224 (s), 1185 (s), 1134 (s)	ν(C=C) 1625 (w)
$CH_3C_5H_4Mn(CS)(NO)(\eta^1\text{-}C_4F_7)$ (**3**, R = CH_3)	1791 (vs)	1302 (vs)	1222 (s), 1190 (s), 1135 (s)	ν(C=C) 1624 (w)
$C_5H_5Mn(CS)(NO)SCF_3$ (**4**, R = H)	1783 (vs)	1298 (vs)	1084 (vs and broad)	
$CH_3C_5H_4Mn(CS)(NO)SCF_3$ (**4**, R = CH_3)	1779 (vs)	1295 (vs)	1080 (vs and broad)	
$[C_5H_5Mn(CS)(NO)]_2$ (**5**, R = H)	1750 (m)	1150 (sh)		
	1718 (vs)	1118 (vs)		
$[CH_3C_5H_4Mn(CS)(NO)]_2$ (**5**, R = CH_3)	1742 (m)	1141 (sh)		
	1707 (vs)	1123 (vs)		

[a] For KBr pellets of the complexes, except in the instances of **3**, R = CH_3, and **4**, R = H and CH_3, where the spectra are those of the neat liquids.

of the dimer $[C_5H_5Mn(CO)(NO)]_2$.[12] Evidently, both of the attempted syntheses of the carbonyl analogue of **2** resulted in the formation of carbonyl- and nitrosyl-free decomposition products of an unknown nature. The facile preparation of **2** and the failure to obtain its carbonyl analogue suggest that in the system under consideration a strong stabilizing effect is being exerted by the presence of the coordinated thiocarbonyl. The x-ray crystal structure of **2**, R = CH_3,[13] reveals a significantly longer Mn–C(S) [1.776 (8) Å] than Mn–N(O) [1.642 (11) Å] bond distance. It should, therefore, be of interest to compare this feature with known structural data on certain carbonyl and nitrosyl complexes.

Significantly shorter (ca. 0.06–0.12 Å) M–C(S) compared with M–C(O) bond distances were found in numerous thiocarbonylcarbonyl-containing complexes such as *trans*-$W(CO)_4(CS)(CNC_6H_{11})$,[14] $[Ir(PPh_3)_2(CO)_2(CS)]^+PF_6^-$,[15] and $(C_6H_5COOMe)Cr(CO)_2CS$.[16] Insofar as nitrosylcarbonyl-containing complexes are concerned, the M–N(O) bonds are generally found to be ~0.07 Å shorter than the M–C(O) bonds. The foregoing considerations would have suggested the bond distance relationship: M–C(S) $\lesssim$ M–N(O) in nitrosylthiocarbonyl-containing complexes. Evidently, this expected relationship is totally inconsistent with the significantly longer (~0.13 Å) Mn–C(S) than Mn–N(O) bond distance found in **2**, R = CH_3, and this might suggest that in the complex under consideration the coordinated thiocarbonyl exhibits a reduced π acidity and/or enhanced σ basicity character.

Some of the chemical properties of **2**, which have been examined during the course of the current study, will be discussed next. The reaction of **2** with Ph_3P in boiling benzene, followed by treatment of the product mixture with $NH_4^+PF_6^-$, gave a low yield (~10%) of **1**, R = H, CH_3; L = Ph_3P. Attempts to improve the yield of **1**, L = Ph_3P, by performing the above cited reaction in the presence of the silver salts $Ag^+PF_6^-$ or $Ag^+BF_4^-$ invariably led to an extensive decomposition of the starting iodomanganese complex. Incidentally, extensive decomposition of **2** was also encountered in the presence of the silver salts and the absence of the phosphine. In the absence of any ν(CS) bands in the infrared spectra of the decomposition products of these reactions, it might be suggested that the decomposition of **2** in the presence of Ag^+ proceeds via labile end-to-end bridged (Mn–CS–Ag^+) intermediates. In contrast with the labilization effects prompted by the presence of ionic silver, the covalent *trans*-perfluoro(1-methylpropenylate)- and trifluoromethylthiosilver reagents reacted with **2** to afford the nitrosylthiocarbonylmanganese derivatives **3** and **4**, respectively. These new air-sensitive derivatives were characterized by their elemental compositions and infrared spectra (Table I). Of particular note in the spectra of these complexes are the intense nitrosyl and thiocarbonyl stretching frequencies which differ by little, if any, from the respective frequencies in the spectra of **2**, R = H, CH_3. Characteristic bands due to the presence of the fluorocarbon moieties $CF_3CF{=}C(CF_3)$ [in **3**] and SCF_3 [in **4**] are unmistakably similar to those found in the infrared spectra of related derivatives of such ligands.[18,19] The syntheses of **3**, the first known example of a thiocarbonyl-containing η^1-alkyl complex, and **4** cannot be considered trivial in view of the high susceptibility toward an attack by nucleophiles of the electrophilic carbon atom of coordinated thiocarbonyl. In this context, it is pertinent to mention that a concerted effort was made to synthesize simple η^1-alkyl (e.g., Me, *n*-Bu, etc.) and -aryl (e.g., Ph) derivatives by reacting their lithium salts with **2** under various conditions. Invariably, these attempted syntheses led to the extensive decomposition of the starting manganese complexes **2**, R = H, CH_3, rather than to the desired derivatives.

The formation of $[C_5H_5Mn(CO)(NO)]_2$ by the reactions of $[C_5H_5Mn(CO)_2(NO)]^+PF_6^-$ with either $NaBH_4$[12] or Et_3N[20] suggested similar synthetic routes to $[C_5H_5Mn(CS)(NO)]_2$ (**5**, R = H) starting with the readily available complex $[C_5H_5Mn(CO)(CS)(NO)]^+PF_6^-$ [**1**, R = H; L = CO].[7] Evidently, the attempted synthesis of **5** by the indicated procedures only resulted in the extensive decomposition of the starting manganese complex; in the instance of the reaction with $NaBH_4$ the formation of significant amounts of H_2S was clearly apparent. An alternative approach to the synthesis of **5** based on the deiodination of **2** using activated metal dust led, ultimately, to the preparation of the desired dimer. The reaction of **2** with zinc dust in dry diglyme solution at 80 °C gave dimer **5** in a maximum yield of 38%. Selected spectroscopic data on the new dimers **5**, R = H, CH_3, are given in the Experimental Section as well as in Table I. The dimeric nature of **5** is evident from the presence of the molecular ion peaks in the mass spectra. The character of the nitrosyl groups in **5** is indicated from the ν(NO) frequencies which are well within the region assigned to linear terminal NO;[21] bands due to bridging NO, normally expected in the 1500–1600-cm^{-1} region,[21] are totally absent from the infrared spectra (solid or solution) of **5**, R = H, CH_3. By contrast, the abnormally low ν(CS) frequencies in **5** are similar to those found in the infrared spectra of the recently reported cis and trans isomers of $[C_5H_5Fe(CS)(CO)]_2$;[6] in the cis isomer, the presence of the CS groups in the bridging positions was confirmed by an x-ray structure analysis. Incidentally, the ν(CS) frequencies in **5** are ~87% of the frequency of the terminal CS in **2**. This frequency relationship is quite similar to that found between bridging and terminal carbonyl and nitrosyl frequencies [e.g., the bridging ligands in $[C_5H_5Fe(CO)_2]_2$[22] and $[C_5H_5Cr(NO)_2]_2$[12] as compared with the respective ligands of terminal character in $C_5H_5Fe(CO)_2I$[23] and $C_5H_5Cr(NO)_2I$[12]]. The ν(NO) and ν(CS), two of each, found in the infrared spectrum of **5**, coupled with the two singlets observed in the proton NMR spectra of the complex (R = H) in both CS_2 and benzene, are consistent with the presence of a mixture of cis

(**5c**) and trans (**5t**) isomers. The singlet found in the proton NMR spectra of **5**, R = H, taken in $CDCl_3$ and CD_2Cl_2, could be due to either coincidental equivalence or separation too small to be observed in the chemical shifts of the cyclopentadienyl protons of the trans and cis isomers. The higher ν(CS) and ν(NO) frequencies found in the infrared spectra of **5**, R = H, CH_3, and the resonance appearing at higher field in the proton NMR spectrum of **5**, R = H, have now been assigned to the trans isomer. This revised assignment[24] has been made in light of the recently reported data on the cis and trans isomers of $[C_5H_5Fe(CS)(CO)]_2$, of which the molecular geometry of the former isomer has been confirmed unambiguously.[6]

Despite the successful syntheses of **5**, R = H, CH_3, the first known examples of complexes with carbon-bridging thiocarbonyl groups,[1] the study of their physical and chemical properties was made difficult by the relatively small amounts (0.2 g or less) available following a rather tedious preparation. Considerable efforts to improve the yields of **5**, R = H, CH_3, and/or the scaling-up of the syntheses met with little success. Attempts to separate the cis and trans isomers of **5** using conventional chromatography techniques were unsuccessful, especially since the majority of the samples evidently decomposed on the column. In one instance, the repeated fractional crystallization of **5**, R = CH_3, from pentane at −78 °C did subsequently lead to the isolation of trace amounts of the pure (~99%) cis isomer [infrared (KBr pellet) ν(NO) 1707, ν(CS) 1123 cm^{-1}; mp 118–120 °C]. The interconversion of the isomers of **5**, R = H, CH_3, at ambient temperature has been ruled out, since in the infrared spectra, taken in various organic solvents as well as mixed solvents of different polarity, the intensity ratio of the nitrosyl and thiocarbonyl stretches remains essentially unchanged. These findings, however, do not rule out a slow cis $\rightleftharpoons$ trans isomerization at an elevated temperature as was reported for the analogous thiocarbonyl-bridged iron system.[6]

The feasibility of the intramolecular insertion of the coordinated thiocarbonyl into the $Mn-C_4F_7$ bond in **3** and the $Mn-SCF_3$ bond in **4** was also examined briefly during the course of the current study. The reactions of Ph_3P with **3** (for 30 min) and **4** (for 20 h) carried out in refluxing cyclohexane resulted in the total disappearance of the starting complexes and the formation of new products of the proposed compositions, $RC_5H_4Mn(NO)(PPh_3)C(S)C_4F_7$ [**6**, R = H, CH_3] and $RC_5H_4Mn(NO)(PPh_3)C(S)SCF_3$ [**7**, R = H, CH_3], respectively. The full characterization of the new waxy products was hampered due to purification difficulties. The tentative structural assignments have been based primarily on some infrared data, in particular the very strong bands shifted to lower energies at 1734 (**6**, R = H), 1735 (**6**, R = CH_3), 1741 (**7**, R = H), and 1739 cm^{-1} (**7**, R = CH_3) and the absence of bands in the 1280–1310-cm^{-1} region characteristic of terminal coordinated thiocarbonyl in complexes such as **2**, **3**, and **4**. Strong and broad bands due to the fluorocarbon moieties, observed in the infrared spectra of these complexes in the region below 1230 cm^{-1}, made it rather difficult to assign unambiguously the thioacyl (>C═S) stretches which are normally expected at 1100–1200 cm^{-1}. Further studies on related intramolecular insertion of coordinated thiocarbonyl are currently in progress and will be reported in due course.

Acknowledgment. The authors are indebted to Mr. D. Liebman and Dr. M. H. A. Huang for their assistance. This research program was supported in part by the School of Chemistry and the Research Council of Rutgers University. The research work described in this paper was performed at Rutgers College.

Registry No. **1** (R = H)(L = CO), 64057-02-9; **1** (R = CH_3)(L = CO), 64057-03-0; **1** (R = H)(L = PPh_3), 64056-99-1; **1** (R = CH_3)(L = PPh_3), 64057-01-8; **2** (R = H)(L = CO), 58450-74-1; **2** (R = CH_3)(L = CO), 64057-05-2; **3** (R = H), 64057-07-4; **3** (R = CH_3), 64057-08-5; **4** (R = H), 64057-04-1; **4** (R = CH_3), 64057-06-3; **5** (R = H), 64090-73-9; **5** (R = CH_3), 64090-74-0; *cis*-**5** (R = H), 58450-72-9; *cis*-**5** (R = CH_3), 64090-72-8; *trans*-**5** (R = H), 58501-18-1; *trans*-**5** (R = CH_3), 58450-73-0; **6** (R = H), 64056-96-8; **6** (R = CH_3), 64056-92-4; **7** (R = H), 64056-93-5; **7** (R = CH_3), 64056-94-6; $CF_3CF{=}C(CF_3)Ag$, 24703-63-7; $AgSCF_3$, 811-68-7.

References and Notes

(1) Preliminary communication; A. Efraty, R. Arneri, and M. H. A. Huang, *J. Am. Chem. Soc.*, **98**, 639 (1976).
(2) (a) The Weizmann Institute of Science; (b) Rutgers.
(3) (a) I. S. Butler and A. E. Fenster, *J. Organomet. Chem.*, **66**, 161 (1974); (b) L. Busetto and A. Palazzi, *Inorg. Chim. Acta*, **19**, 233 (1976), and pertinent references therein.
(4) B. D. Dombek and R. J. Angelici, *J. Am. Chem. Soc.*, **97**, 1261 (1975).
(5) B. D. Dombek and R. J. Angelici, *J. Am. Chem. Soc.*, **96**, 7568 (1974).
(6) J. W. Dunker, J. S. Finer, J. Clardy, and R. J. Angelici, *J. Organomet. Chem.*, **114**, C49 (1976).
(7) A. Efraty, R. Arneri, and J. Sikora, *J. Organomet. Chem.*, **91**, 65 (1975).
(8) H. J. Emeleus and D. E. MacDuffie, *J. Chem. Soc.*, 2597 (1961).
(9) W. T. Miller, R. H. Snider, and R. J. Hummel, *J. Am. Chem. Soc.*, **91**, 6532 (1969).
(10) A. Efraty, R. Arneri, and W. A. Ruda, unpublished results.
(11) L. Busetto, M. Graziani, and R. Belluco, *Inorg. Chem.*, **10**, 78 (1971).
(12) R. B. King and M. B. Bisnette, *Inorg. Chem.*, **3**, 791 (1964).
(13) J. A. Potenza, A. Efraty, and R. J. Johnson; investigation in progress (current refinement values; R_F = 0.057 and R_{wF} = 0.073).
(14) S. S. Woodard, R. A. Jacobson, and R. J. Angelici, *J. Organomet. Chem.*, **117**, C75 (1976).
(15) J. S. Field and P. J. Wheatley, *J. Chem. Soc., Dalton Trans.*, 2269 (1972).
(16) J. Y. Saillard, G. LeBorgne, and D. Grandjean, *J. Organomet. Chem.*, **94**, 409 (1975).
(17) B. A. Bertram, J. H. Enemark, and J. A. Ibers, *Inorg. Chem.*, **8**, 1288 (1969).
(18) R. B. King and W. C. Zipperer, *Inorg. Chem.*, **11**, 2119 (1972), and pertinent references therein concerning frequencies of $CF_3CF{=}C(CF_3)$-metal containing complexes.
(19) R. B. King and N. Welcman, *Inorg. Chem.*, **8**, 2540 (1969), and pertinent references therein concerning frequencies of CF_3S-metal containing complexes.
(20) T. A. James and J. A. McCleverty, *J. Chem. Soc. A*, 850 (1970).
(21) B. L. Haymore and J. A. Ibers, *Inorg. Chem.*, **14**, 3060 (1975), and pertinent references therein.
(22) R. B. King and F. G. A. Stone, *Inorg. Synth.*, **7**, 110 (1963).
(23) T. S. Piper, F. A. Cotton, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **1**, 165 (1955).
(24) In the absence of structure information, the earlier assignment[1] was made by analogy with the spectral data interpretation of the isoelectronic series $[C_5H_5ML_2]_2$, where M = Cr, Mn, and Fe and L = CO and NO [R. M. Kirchner, T. J. Marks, J. S. Kristoff, and J. A. Ibers, *J. Am. Chem. Soc.*, **95**, 6602 (1973), and pertinent references therein]. The revised assignment, based on the analogy with the cis and trans isomers of $[C_5H_5Fe(CS)(CO)]_2$, is consistent only with respect to ν(CS) and $\tau(C_5H_5)$. By contrast, the relationship cis ν(CO) > trans ν(CO) found for the iron isomers differs from that of cis ν(NO) < trans ν(NO) for the manganese isomers.