4.15–4.20 ppm). Second, cis–trans ozonide ratios obtained from adding the complexing agent to the cold (<−150 °C) reaction mixture after ozonolysis with pure ozone was complete were, within experimental error, the same as those obtained using ozone complexed with the same agent, as seen in Table II. Thus, the complexing agent affects the reaction course after the primary ozonide is produced, not before. Third, in several cases ozonide yields were determined and were shown to be the same with complexed and uncomplexed ozone.

We conclude from these results that complexation of the carbonyl oxide zwitterions occurs as the primary ozonide decomposes in the presence of the complexing agent and this prevents or slows down equilibration of syn and anti zwitterions or, perhaps, causes one to be favored over the other to some extent. The following pertinent observations support this conclusion.

Table I reveals that the differences in cis–trans ozonide ratios obtained with complexed and uncomplexed ozone in Freon-12 at −150 °C are important only with the cis olefin. The same is true in isopentane except for toluene, *o*-xylene, and hexaethylbenzene as complexing agents. This is understandable in view of the fact that cis primary ozonides are much less stable than their trans isomers.[8] We were unable to observe the primary ozonide of *cis*-1,2-diisopropylethylene at −130 °C, whereas that of the trans olefin is stable up to at least −78 °C. At the decomposition temperature of the trans primary ozonide, very little complexation of carbonyl oxide zwitterions would be expected.

Table I further shows that in Freon-12 at −78 °C (no complex) the cis–trans ozonide ratios for both isomers of 1,2-diisopropylethylene were identical, within experimental error (ca. 50:50). Even at −150 °C (no complex) the ratios were close to each other. In contrast, in isopentane there was some difference in the cis–trans ozonide ratios from the isomeric olefins even at −78 °C and a large difference at −150 °C. This is indicative that equilibration of syn and anti zwitterions is promoted by increases in temperature and in the polarity of the solvent.

Ozonations with complexed ozone (Table I) and ozonations in which the primary ozonide was allowed to decompose in the presence of the complexing agent (Table II) resulted in large differences in cis–trans ozonide ratios between the cis and trans olefins even in Freon-12. The differences were greater in the less polar isopentane. The logical conclusion is that the complexing agent binds and stabilizes the syn and anti zwitterions, thereby preventing or impeding equilibration. The carbonyl oxide zwitterion is isoelectronic with ozone and should similarly form complexes. Although some recent calculations indicate that both ozone and carbonyl oxides are singlet diradicals in the ground state,[11] it is unreasonable to assume from this that they cannot react as dipoles in the presence of suitable organic substrates. Their chemical properties strongly support this viewpoint.[5,12]

Fliszar and Carles[13] have previously suggested the possibility of complexation of zwitterions, in their case with benzene at 25 °C. However, our results indicate that complexation does not occur at so high a temperature.

The fact that three of the complexing agents (toluene, *o*-xylene, and hexaethylbenzene) caused different cis–trans ozonide ratios with *trans*-diisopropylethylene in isopentane, in comparison to ozonations in the absence of a complexing agent (Tables I and II), is intriguing. The significance of this is under study. Also, the possibility of stabilizing, and characterizing for the first time, a zwitterion through complexation is being investigated.

Although this and other recent work (ref 14, 15) strongly support the syn–anti zwitterion variation of the Criegee mechanism as the only route to ozonides during ozonolysis, it also seems clear that no simple set of rules (ref 5, 6) will handle all stereochemical findings.

**Acknowledgment.** The authors are grateful to the Robert A. Welch Foundation for the financial support which made this research possible. We also thank the Council for International Exchange of Scholars for a Fulbright-Hays travel grant for A. Rustaiyan who was on leave from the National University of Iran.

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**Philip S. Bailey,* A. Rustaiyan, T. M. Ferrell**
*Department of Chemistry, The University of Texas at Austin*
*Austin, Texas 78712*

*Received October 9, 1975*

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## Cyclopentadienylnitrosylthiocarbonylmanganese Dimer. A Novel Complex Believed to Contain Carbon-Bridging Thiocarbonyl Groups

*Sir:*

Since the preparation of the first metal thiocarbonyl complexes *trans*-$RhX(CS)(PPh_3)_2$ and $RhX_3(CS)(PPh_3)_2$ (X = Cl, Br) by Baird and Wilkinson,[1] relatively few such compounds have been synthesized and studied.[2] In contrast with metal carbonyls, less than a handful of complexes with more than one thiocarbonyl group have been characterized, and so far complexes with carbon-bridging thiocarbonyl groups of the type M–C(S)–M′ (M = M′ or M ≠ M′) have not yet been reported. Recently, Dombek and Angelici have reported[3] the preparation of DPE (ethylenebis(diphenylphosphine)) complexes of tungsten with end-to-end bridging thiocarbonyl ligand of the type MC═SM′, such as $W(CO)(DPE)_2CSW(CO)_5$ and $[(DPE)_2(CO)WCSAgSCW(CO)(DPE)_2]BF_4$. Noteworthy are the infrared spectra of these complexes which show ν(CS) lower than that found in their precursor $W(CO)(CS)(DPE)_2$ (1161 cm$^{-1}$). The lowering of ν(CS) provides strong support to the assigned end-to-end bridging character of the thiocarbonyl ligand in these complexes.

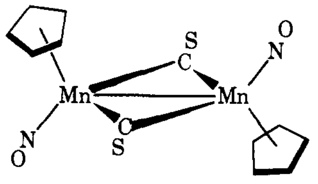
Recently, we have reported[4] the synthesis of the cationic manganese-thiocarbonyl complex $[CpMn(CO)(CS)(NO)]^+$ (I) (Cp, henceforth stands for cyclopentadienyl) and some of its reactions with several Lewis bases. We now wish to communicate the synthesis of the first known complex with carbon-bridging thiocarbonyl ligands.

The thiocarbonyl iodide complex CpMn(CS)(NO)I (II),[5] mp 88–89 °C, prepared in 38% yield by the treatment of I with excess KI in tetrahydrofuran at ambient temperature, reacts with zinc dust in diglyme solution at 80 °C to afford a deep brown complex of the composition $[CpMn(CS)(NO)]_2$ (III), mp >200 °C dec, in ~20% yield. (Anal. Calcd for $C_{12}H_{10}N_2O_2S_2Mn_2$: C, 37.13; H, 2.60; N, 7.22; S, 16.52; mol wt, 388. Found: C, 37.29; H, 2.95; N, 7.08; S, 16.26; mol wt, 388 (mass spectral)). The infrared spectrum (KBr pellet) of III shows two sets of nitrosyl and thiocarbonyl stretching frequencies ($\nu$(NO) 1750 (m) and 1718 (vs) $cm^{-1}$; $\nu$(CS) 1150 (sh) and 1118 (vs) $cm^{-1}$). The infrared spectrum of this complex, taken in solution (e.g., $CS_2$, $CH_2Cl_2$, cyclohexane, etc.), displays similar bands of about the same intensity as those noted above. The proton NMR spectrum of III, taken in several solvents, shows the following singlets ($\tau$): $CDCl_3$, 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). The main metallic ions in the mass spectrum (80 eV, inlet temperature 165 °C and chamber temperature 200 °C) of III include (relative abundances of ions are given in parentheses): $[Cp_2Mn_2(CS)_2(NO)_2]^+$ (41), $[Cp_2Mn_2(CS)_2(NO)]^+$ (10), $[Cp_2Mn_2(CS)_2]^+$ (69), $[CpMn_2(CS)_2(NO)]^+$ (11), $[Cp_2Mn_2(CS)]^+$ (18), $[CpMn_2(CS)_2]^+$ (77), $[CpMn(CS)_2(NO)]^+$ (35), $[CpMn_2(CS)]^+$ (8), $[CpMn(CS)_2]^+$ (9), $[Mn_2(CS)_2]^+$ (8), $[CpMn(CS)(NO)]^+$ (8), $[Cp_2Mn]^+$ (49), $[CpMn(CS)]^+$ (27), $[CpMn]^+$ (74); $[Mn_2]^+$ (7), $[Mn(CS)]^+$ (5), and $[Mn]^+$ (100).

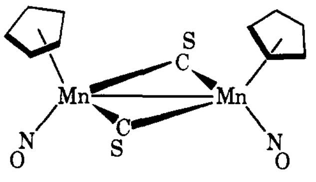
The dimeric structure of III is evident from its mass spectrum which shows high abundance of bimetallic ions. This feature is of interest, since it might suggest a strong bonding interaction between the two halves of the molecular ion. In fact, the energy required to cleave the molecular ion in half has been estimated from the difference between the ionization potential of the molecular ion (6.77 eV)[6] and the appearance potential of the half molecular ion (11.04 eV)[6] to be 100 kcal/mol. The formation of the half molecular ion by CS loss from $[CpMn(CS)_2(NO)]^+$, rather than by the above process, has been ruled unlikely, since nitrosyl cleavage from ions in the mass spectra of III and II[6] precedes that of thiocarbonyl, suggesting that the latter ligand forms considerably stronger bonds with the metal atom. The ionic bond dissociation energy of III, which is about fivefold greater than $D(Mn^+{-}Mn)$ in $Mn_2(CO)_{10}$[7], when taken in the context of the high abundance of $[Mn(CS)]_2$-containing ions and the presence of $[CpMn(CS)_2(NO)]^+$ in the mass spectrum of III, may suggest the existence of a thiocarbonyl-bridged structure in the complex.

The character of the nitrosyl groups in III is indicated from the $\nu$(NO) frequencies which are well within the region assigned to terminal NO; bands due to bridging NO, normally expected in the 1500–1600-$cm^{-1}$ region, are totally absent from the infrared spectrum (solid or solution) of III. By contrast, the abnormally low $\nu$(CS) frequencies, the lowest found to-date,[2] are ~ 87% of the frequency of the terminal thiocarbonyl in II.[5] This frequency relationship is similar to that found between bridging and terminal carbonyl and nitrosyl frequencies (e.g., the bridging ligands in $[CpFe(CO)_2]_2$[8] and $[CpCr(NO)_2]_2$[9] as compared with the respective ligands of terminal character in $CpFe(CO)_2I$[10] and $CpCr(NO)_2I$[9]) and, therefore, supports having carbon-bridging thiocarbonyl groups in III.

The $\nu$(NO) and $\nu$(CS), two of each, found in the infrared spectrum of III, coupled with the two singlets observed in the proton NMR spectra of the complex in both $CS_2$ and benzene, suggest the presence of a mixture consisting of cis (IIIC) and trans (IIIT) isomers. The singlet in the proton NMR spectrum, in both $CDCl_3$ 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 $\nu$(NO) and $\nu$(CS) in each set and the proton resonance appearing at higher field have tentatively been assigned to the more polar cis isomer IIIC and this by analogy with similar assignments made in the isoelectronic series $[CpML_2]_2$,[11] where M = Cr, Mn, and Fe and L = CO and NO.



IIIT



IIIC

The spectral data of III, reported herein, were obtained at ambient temperature (~30 °C) on the same sample of the complex whose approximate composition, according to the above assignments, consisted of about 25% IIIC and 75% IIIT. The interconversion of the isomers at ambient temperature has been ruled out, since in the infrared spectra of III, 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. The isomeric composition of this complex can be altered by fractional crystallization at low temperature (−78 °C) due to the somewhat higher solubility of the trans isomer in common, polar, and nonpolar organic solvents. However, so far, all attempts to effect the total separation of the isomers of III have been unsucessful. Recently, the methylcyclopentadienyl analogue $[CH_3C_5H_4Mn(CS)(NO)]_2$,[12] mp 119–120 °C, has been prepared in 18% yield by the same procedure described earlier for III. In this case, repeated fractional crystallization from pentane at −78°C has subsequently led to the isolation of trace amounts of the pure (~99%) trans isomer (infrared (KBr pellet) $\nu$(NO), 1707; $\nu$(CS), 1123 $cm^{-1}$).

**Acknowledgments.** This work was supported, in part, by the School of Chemistry and the Research Council of Rutgers University, New Brunswick, N.J.

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**Avi Efraty,* Ruza Arneri, M. H. A. Huang**
*Rutgers University, School of Chemistry*
*New Brunswick, New Jersey 08903*

*Received June 2, 1975*