related technetium and rhenium (2½) complexes.[17]

One feature of the above data which merits some comment is the origin of the low energy absorption (λ_{max} 780, ϵ 2600 l. mol^{-1} cm^{-1}) apparently characteristic of the $[Mo_2(O_2CCF_3)_4]^-$ moiety. The absorption contrasts markedly with the lowest known absorption of $[Mo_2(O_2CCF_3)_4]$ (λ_{max} 430 nm, ϵ 130 l. mol^{-1} cm^{-1}) which is assigned[16] to the forbidden $\delta \rightarrow \pi^*$ or $\pi \rightarrow \delta^*$ transition of the metal center. If, as suggested above, the additional electron is accommodated in the δ^* orbital, possible electronic rearrangements which could give rise to the low energy absorption include (i) a $\delta^* \rightarrow \pi^*$ transition on the metal center and (ii) a $\delta^* \rightarrow$ carboxylato-π^* transition. Of these two possibilities the latter is favored since its metal ligand charge-transfer character is more consistent with the rather considerable intensity observed for this low energy absorption and a small $\delta^* \rightarrow \pi^*$ promotion energy is inconsistent with the interpretation that dimeric Mo(1½) and Mo(2½) species have similar *g* values.

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Complexation of Carbonyl Oxide Zwitterions[1]

Sir:

In earlier papers[2-4] π (or charge transfer) complexes of ozone were described for the first time. Among the complexing agents employed were 1-mesityl-1-phenylethylene, toluene, mesitylene, and hexaethylbenzene. It was also shown that the cis-trans ozonide ratios obtained from ozonation of *cis*- and *trans*-1,2-diisopropylethylene with complexed ozone differed from those obtained with "free" ozone.[4]

We wish now to report evidence which indicates that these differences in results obtained with complexed and uncomplexed ozone are due to complexation of Criegee carbonyl oxide zwitterions with the complexing agent rather than to different mechanisms of ozone attack and/or ozonolysis with complexed and "free" ozone. Accordingly, these results further strengthen and support the concept that stereospecificity of ozonide formation results from the preferential manner in which syn or anti zwitterions are produced from cis or trans olefins during ozonolysis.[5,6]

Table I. Cis/Trans Ozonide Ratios from Ozonation of *cis*- and *trans*-1,2-Diisopropylethylenes with Ozone Complexes

		Freon-12		Isopentane	
Temp, °C	Complex agent	Cis isomer	Trans isomer	Cis isomer	Trans isomer
−78	None	50:50	49:51	54:46	49:51
−150	None	55:45	51:49	67:33	58:42
−150	Toluene	[a]	[a]	74:26	62:38
−150	*o*-Xylene	61:39	48:52	76:24	65:35
−150	Isodurene	61:39	51:49	75:25	57:43
−150	HEB	[b]	[b]	75:25	65:35
−150	MPE	64:36	50:50	78:22	54:46

[a] Complex is stable in Freon-12 only at lower temperatures. [b] The complexing agent is too insoluble in Freon-12 to use in the usual concentration. [c] HEB = hexaethylbenzene. [d] MPE = 1-mesityl-1-phenylethane.

Table II. Comparison of Normal and Inverse[a] Ozonation with Complexing Agents

DIPE[b] isomer	Solvent	Complex	Cis/trans normal	ozonide ratios inverse
Cis	Freon-12	*o*-Xylene	61:39	60:40
Cis	Freon-12	Isodurene	61:39	58:42
Cis	Freon-12	MPE[c]	64:36	62:38
Cis	Isopentane	*o*-Xylene	76:24	75:25
Cis	Isopentane	Isodurene	75:25	74:26
Cis	Isopentane	MPE[c]	78:22	77:23
Trans	Freon-12	*o*-Xylene	48:52	47:53
Trans	Freon-12	Isodurene	51:49	49:51
Trans	Isopentane	Toluene	62:38	64:36
Trans	Isopentane	*o*-Xylene	65:35	65:35
Trans	Isopentane	Isodurene	57:43	55:45
Trans	Isopentane	HEB[d]	65:35	65:35
Trans	Isopentane	MPE[c]	54:46	53:47

[a] Inverse ozonation refers to ozonation with "free" ozone followed by addition of the complexing agent before warm-up. [b] DIPE = 1,2-diisopropylethylene. [c] MPE = 1-mesityl-1-phenylethane. [d] HEB = hexaethylbenzene.

Table I shows cis-trans ozonide ratios obtained by ozonizing *cis*- and *trans*-1,2-diisopropylethylene with "free" and with complexed ozone, using several different complexing agents and two different solvents.[7] The differences observed between complexed and uncomplexed ozone and between the two solvents are real. Most of the values are averages of several runs which varied by no more than ±1%.

The values do differ in some cases from those reported earlier,[4] but this was due to undeveloped technique in the preliminary work, particularly in regard to the nature of the warm-up. We have found, like Murray and Hagen,[9] that a fast warm-up gives scattered results which differ greatly from those obtained using a slow warm-up, at least with the trans olefin. The results in Tables I and II were from a very slow warm-up, from −150 °C to room temperature in the Dewar flask over a period of 24 or more h.

That the differences in cis-trans ozonide ratios observed between complexed and "free" ozone are not due to different mechanisms of ozone attack was established in three ways. First, the primary ozonide of *trans*-1,2-diisopropylethylene was observed by NMR using either "free" or complexed (*o*-xylene) ozone.[10] The characteristic ring proton doublet was present in equal intensity in both cases (δ

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.

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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)