

Correspondence

Thermolysis of Selenocarbamate(pentacarbonyl)manganese(I), $\text{Mn}(\text{CO})_5\text{SeC}(\text{O})\text{NMe}_2$, in Solid State and in Solution

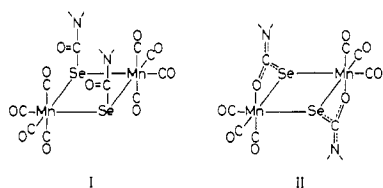
Sir:

The authors previously reported that $\text{Mn}(\text{CO})_5\text{msc}$ ($\text{msc} = \text{SeC}(\text{O})\text{NMe}_2$) on heating in the solid state under dry nitrogen evolves one molecule of carbon monoxide to give $\text{Mn}(\text{CO})_4\text{msc}$ with the chelating msc ligand, followed by the release of another carbon monoxide yielding dimeric $[\text{Mn}(\text{CO})_3\text{msc}]_2$.¹ However, our recent reexamination on the thermolysis has revealed that the first product is dimeric $[\text{Mn}(\text{CO})_4\text{msc}]_2$ contaminated with a small amount of $[\text{Mn}(\text{CO})_3\text{msc}]_2$, but not monomeric $\text{Mn}(\text{CO})_4\text{msc}$, as confirmed by infrared and mass spectra. This correspondence describes the thermolysis of $\text{Mn}(\text{CO})_5\text{msc}$ under carbon monoxide to give analytically and spectroscopically pure $[\text{Mn}(\text{CO})_4\text{msc}]_2$. It is also reported that monomeric $\text{Mn}(\text{CO})_4\text{msc}$ can still be an unstable intermediate in the thermolysis of $\text{Mn}(\text{CO})_5\text{msc}$ giving $[\text{Mn}(\text{CO})_3\text{msc}]_2$ in solution.

When solid $\text{Mn}(\text{CO})_5\text{msc}$ (10 mg) was heated in a Shimadzu SC-20 differential scanning calorimeter (DSC) under flowing carbon monoxide ($30 \text{ cm}^3/\text{min}$), two endothermic peaks were observed, as shown in Figure 1, which is the thermogram obtained by heating the DSC cell to 126°C , followed by holding it at this temperature, because of decomposition of the product above 130°C . The first peak around 95°C can be associated with release of one molecule of carbon monoxide from $\text{Mn}(\text{CO})_5\text{msc}$ to afford dimeric $[\text{Mn}(\text{CO})_4\text{msc}]_2$, which was confirmed by the mass spectrum and elemental analysis. Observed parent peak, 636 (calcd 636). Anal. Calcd for $\text{C}_{14}\text{H}_{12}\text{Mn}_2\text{N}_2\text{O}_{10}\text{Se}_2$: C, 26.43; H, 1.91; N, 4.40. Found: C, 26.32; H, 1.89; N, 4.43.

The second peak around 125°C results from a loss of another carbon monoxide, giving $[\text{Mn}(\text{CO})_3\text{msc}]_2$ contaminated with a small amount of $[\text{Mn}(\text{CO})_4\text{msc}]_2$, as suggested by the infrared spectrum of the thermolysis product, which showed a weak $\nu(\text{C}=\text{O})$ band at the same wavenumber as $[\text{Mn}(\text{CO})_4\text{msc}]_2$ (1660 cm^{-1} in Nujol mulls) in addition to an absorption at 1582 cm^{-1} assignable to $\nu(\text{C}=\text{O})$ of $[\text{Mn}(\text{CO})_3\text{msc}]_2$.¹ Not only analytically but also spectroscopically pure $[\text{Mn}(\text{CO})_3\text{msc}]_2$ can be obtained by the thermolysis of $\text{Mn}(\text{CO})_5\text{msc}$ under flowing nitrogen as reported previously.¹

The $[\text{Mn}(\text{CO})_4\text{msc}]_2$ complex immediately after dissolving in cyclohexane exhibited seven infrared-active $\nu(\text{C}=\text{O})$ bands ($2076, 2021, 2010, 1995, 1954, 1935, \text{ and } 1916 \text{ cm}^{-1}$), of which the 2021 - and 2010-cm^{-1} bands coalesced in the solid-state spectrum and the six absorptions ($2071, 2017, 1994, 1958, 1946, \text{ and } 1923 \text{ cm}^{-1}$) were observed. The complex is therefore confirmed to adopt a syn configuration (I) in the solid state



and in cyclohexane; the presence of bridging selenium is suggested from the appearance of the MnSe^+ fragment in the

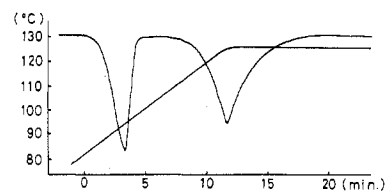


Figure 1. DSC curve for $\text{Mn}(\text{CO})_5\text{msc}$ under carbon monoxide.

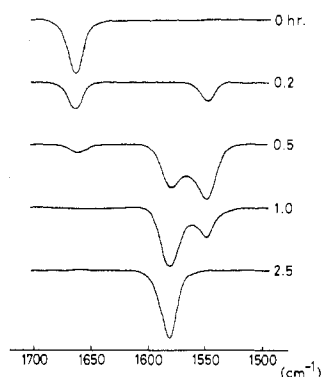


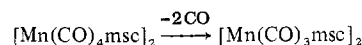
Figure 2. Time-dependent infrared spectra ($\nu(\text{C}=\text{O})$ region) of $[\text{Mn}(\text{CO})_4\text{msc}]_2$ in cyclohexane (3.2 mM).

Table I. The Mass Spectrum of $[\text{Mn}(\text{CO})_4\text{msc}]_2$ ($\text{msc} = \text{SeC}(\text{O})\text{NMe}_2$)

m/e	Rel intens	Assignment
636	9	$[\text{P}]^+{}^a$
524	40	$[\text{P} - 4\text{CO}]^+$
496	7	$[\text{P} - 5\text{CO}]^+$
468	27	$[\text{P} - 6\text{CO}]^+$
440	9	$[\text{P} - 7\text{CO}]^+$
412	88	$[\text{P} - 8\text{CO}]^+$
261	17	$[\text{Mn}_2\text{msc}]^+$
206	100	$[\text{Mn}(\text{msc})]^+$
134	32	$[\text{MnSe}]^+$

^a $[\text{P}] \equiv [\text{Mn}(\text{CO})_4\text{msc}]_2^+$.

mass spectrum (Table I) and the position of the $\nu(\text{C}=\text{O})$ band (ca. 1660 cm^{-1} in Nujol mulls and in cyclohexane) which shows unequivocally that the carbonyl group is in fact not coordinated to the manganese atom, in contrast to $\text{Mn}(\text{CO})_4\text{msc}$ and $[\text{Mn}(\text{CO})_3\text{msc}]_2$ described below. On the other hand, $[\text{Mn}(\text{CO})_3\text{msc}]_2$ displayed three $\nu(\text{C}=\text{O})$ bands both in cyclohexane ($2015, 1940, \text{ and } 1918 \text{ cm}^{-1}$) and in Nujol mulls ($1992, 1908, \text{ and } 1892 \text{ cm}^{-1}$), which predict an anti configuration (II) of the complex. Thus, the reaction



involves the inversion of configuration with respect to the orientation of the msc ligand.

Although monomeric $\text{Mn}(\text{CO})_4\text{msc}$ has not been identified in the solid-state thermolysis of $\text{Mn}(\text{CO})_5\text{msc}$, its existence was confirmed by time-dependent infrared spectra of $[\text{Mn}$

(CO)₄msc]₂ in cyclohexane (1.6 mM, the cell temperature ca. 50 °C), depicted in Figure 2. The solution initially exhibited a strong $\nu(\text{C}=\text{O})$ band at 1661 cm⁻¹, whose intensity decreased with time. After a few minutes, there appeared a new band at 1550 cm⁻¹, which was intensified with time at the expense of the 1661-cm⁻¹ band. Another new band began to occur at 1582 cm⁻¹ after about 20 min. The 1550-cm⁻¹ band attained to a maximum intensity in about 30 min, followed by its weakening as the 1582-cm⁻¹ band was intensified. Finally, there remained only the 1582-cm⁻¹ band, whose wavenumber coincides with that of $\nu(\text{C}=\text{O})$ of *anti*-[Mn(CO)₃msc]₂.¹ The 1550-cm⁻¹ band that appeared transiently is reasonably associated with monomeric Mn(CO)₄msc involving chelating msc, because in some Pd(II) and Pt(II) complexes the $\nu(\text{C}=\text{O})$ band of chelating msc was reported to occur around 1540 cm⁻¹.² Thus, the result of time-dependent spectra indicates that *syn*-[Mn(CO)₄msc]₂ first dissociates into two monomeric Mn(CO)₄msc, followed by the release of carbon monoxide to dimerize, giving *anti*-[Mn(CO)₃msc]₂ with the inversion of configuration in cyclohexane. Such a labile property of [Mn(CO)₄msc]₂ in solution has led us to an erroneous conclusion that monomeric Mn(CO)₄msc has been isolated, on the basis of molecular weight determination.¹

The existence of monomeric Mn(CO)₄msc is also supported by the time-dependent infrared spectra of Mn(CO)₅msc in cyclohexane (2.8 mM); the $\nu(\text{C}=\text{O})$ band of Mn(CO)₅msc (1620 cm⁻¹) initially observed became gradually weak with intensifying of the 1550-cm⁻¹ band, which was followed by the occurrence of the 1582-cm⁻¹ band as in the spectra of [Mn(CO)₄msc]₂. Finally, the latter band remained, and no band due to [Mn(CO)₄msc]₂ has been found in the course of the formation of [Mn(CO)₃msc]₂. A more concentrated cyclohexane solution of Mn(CO)₅msc (35 mM), however, exhibited the $\nu(\text{C}=\text{O})$ band of [Mn(CO)₄msc]₂ at 1661 cm⁻¹ as well as that of Mn(CO)₄msc at 1550 cm⁻¹ in the pathway to form [Mn(CO)₃msc]₂ from Mn(CO)₅msc. Thus, dimeric [Mn(CO)₄msc]₂ can exist in concentrated solutions. This does not contradict the fact that dimeric [Mn(CO)₄msc]₂ was isolated in the solid-state thermolysis of Mn(CO)₅msc.

Registry No. I, 65995-83-7; II, 54751-26-7; Mn(CO)₅msc, 54751-19-8.

References and Notes

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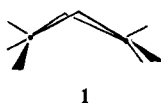
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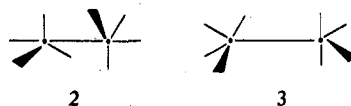
Nonbridged Structures of Dicobalt Octacarbonyl

Sir:

Recent experiments have verified the coexistence of three isomers of Co₂(CO)₈ in solution²⁻⁴ and in frozen matrices.⁵ The crystal structure of Co₂(CO)₈ indicates that the solid-state isomer, **1**, has two bridging carbonyls.⁶ On the basis of vi-



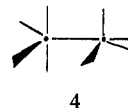
brational data, a second isomer has been assigned a *D*_{3d} symmetry, **2**;² the third isomer has been assigned a *D*_{2d} symmetry structure, **3**.⁵ In isomers **2** and **3** the idealized



coordination geometry about each cobalt atom is trigonal bipyramidal. In **2** the Co-Co bond is in an axial coordination site of each trigonal bipyramid, while in **3** it is in a radial coordination site.

Isomers **2** and **3** together represent a substantial portion of the Co₂(CO)₈ in solution or in the gas phase. From the matrix isolation⁵ and solution³ results, it appears that about 30% of the Co₂(CO)₈ possesses structure **3** at room temperature and that this form dominates at higher temperatures.

The main influences in determining the relative stabilities of structures **2** and **3** are not immediately clear. Given that these forms are comparatively stable, why should structure **4**, in which the Co(CO)₄ group on one cobalt is sited in an



axial position and on the other in a radial position, not also be stable? Furthermore, since in compounds of the form Co(CO)₄EX₃ the stable structure is one in which the EX₃ group occupies an axial position,⁷ why are the structural forms of (CO)₄CoCo(CO)₄ with axial and radial sitings of the (CO)₄Co- groups of comparable stability? Johnson has proposed a model for the structures of polynuclear binary carbonyls based only on simple packing arguments and the sizes of the metal atoms.⁸ We show in this contribution that the relative stabilities of structures **2** and **3** can be explained in terms of steric interactions between the CO groups bound to the metal centers and consideration of metal-metal bond energies.

Evaluation of the variable-temperature ¹³C NMR data for trigonal-bipyramidal (CO)₄CoEX₃ complexes reveals that the free energy barrier to rearrangement is strongly dependent upon the size of EX₃.⁷ An important characteristic of our model for the steric interactions in these complexes is consideration of the actual geometrical rearrangements of all the atoms involved in alternative structures. For instance, we find the repulsive interaction between the CO groups and EX₃ in the radial site of the trigonal bipyramid is greater than with EX₃ in the axial site. Isomers **2** and **3** of Co₂(CO)₈ present a similar situation. An important difference is that the Co(CO)₄ portion of the molecule is bound to another Co(CO)₄ unit rather than EX₃.

The quantitative aspect of the analysis involves determination of the van der Waals contact angle, θ (Figure 1), the angle between the Co-CO and Co-Co vectors at which the van der Waals radii of the carbonyls are in contact.⁹ The van der Waals contact angle, θ , is dependent on the dihedral angle, ϕ , between the two Co-CO vectors viewed down Co-Co axis (Figure 1b). The computed values of the contact angles for selected dihedral angles are illustrated in Figure 2. The contact angle increases rapidly as the dihedral angle decreases from 90 and 60°.

In the absence of appreciable steric effects, the angle between the Co-CO vector and the Co-L vector in Co(CO)₄L complexes has always been found to be less than 90°. When the ligand L is SiF₃, SiCl₃, SiH₃, or GeH₃, the angle is on the order of 85° or less.¹² In the *D*_{3d} structure of Co₂(C-O)₆[P(C₄H₉)₃]₂, the angle is 88°. ¹⁰ It may be anticipated that