(CO)$_4$msc]$_2$ in cyclohexane (1.6 mM, the cell temperature ca. 50 °C), depicted in Figure 2. The solution initially exhibited a strong ν(C=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 ν(C=O) of *anti*-[Mn(CO)$_3$msc]$_2$.[1] The 1550-cm^{-1} band that appeared transiently is reasonably associated with monomeric Mn(CO)$_4$msc involving chelating msc, because in some Pd(II) and Pt(II) complexes the ν(C=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)$_4$msc]$_2$ first dissociates into two monomeric Mn(CO)$_4$msc, followed by the release of carbon monoxide to dimerize, giving *anti*-[Mn(CO)$_3$msc]$_2$ with the inversion of configuration in cyclohexane. Such a labile property of [Mn(CO)$_4$msc]$_2$ in solution has led us to an erroneous conclusion that monomeric Mn(CO)$_4$msc has been isolated, on the basis of molecular weight determination.[1]

The existence of monomeric Mn(CO)$_4$msc is also supported by the time-dependent infrared spectra of Mn(CO)$_5$msc in cyclohexane (2.8 mM); the ν(C=O) band of Mn(CO)$_5$msc (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)$_4$msc]$_2$. Finally, the latter band remained, and no band due to [Mn(CO)$_4$msc]$_2$ has been found in the course of the formation of [Mn(CO)$_3$msc]$_2$. A more concentrated cyclohexane solution of Mn(CO)$_5$msc (35 mM), however, exhibited the ν(C=O) band of [Mn(CO)$_4$msc]$_2$ at 1661 cm^{-1} as well as that of Mn(CO)$_4$msc at 1550 cm^{-1} in the pathway to form [Mn(CO)$_3$msc]$_2$ from Mn(CO)$_5$msc. Thus, dimeric [Mn(CO)$_4$msc]$_2$ can exist in concentrated solutions. This does not contradict the fact that dimeric [Mn(CO)$_4$msc]$_2$ was isolated in the solid-state thermolysis of Mn(CO)$_5$msc.

Registry No. I, 65995-83-7; II, 54751-26-7; Mn(CO)$_5$msc, 54751-19-8.

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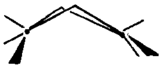
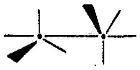
Nonbridged Structures of Dicobalt Octacarbonyl

Sir:

Recent experiments have verified the coexistence of three isomers of Co$_2$(CO)$_8$ in solution[2-4] and in frozen matrices.[5] The crystal structure of Co$_2$(CO)$_8$ indicates that the solid-state isomer, **1**, has two bridging carbonyls.[6] On the basis of vibrational 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.



1



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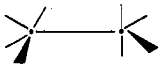
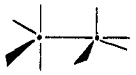


3

Isomers **2** and **3** together represent a substantial portion of the Co$_2$(CO)$_8$ in solution or in the gas phase. From the matrix isolation[5] and solution[3] results, it appears that about 30% of the Co$_2$(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)$_4$EX$_3$ the stable structure is one in which the EX$_3$ group occupies an axial position,[7] why are the structural forms of (CO)$_4$CoCo(CO)$_4$ with axial and radial sitings of the (CO)$_4$Co– 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.



4

Evaluation of the variable-temperature ^{13}C NMR data for trigonal-bipyramidal (CO)$_4$CoEX$_3$ complexes reveals that the free energy barrier to rearrangement is strongly dependent upon the size of EX$_3$.[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 EX$_3$ in the radial site of the trigonal bipyramid is greater than with EX$_3$ in the axial site. Isomers **2** and **3** of Co$_2$(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 EX$_3$.

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)$_4$L complexes has always been found to be less than 90°. When the ligand L is SiF$_3$, SiCl$_3$, SiH$_3$, or GeH$_3$, the angle is on the order of 85° or less.[12] In the D_{3d} structure of Co$_2$(CO)$_6$[P(C$_4$H$_9$)$_3$]$_2$, the angle is 88°.[10] It may be anticipated that

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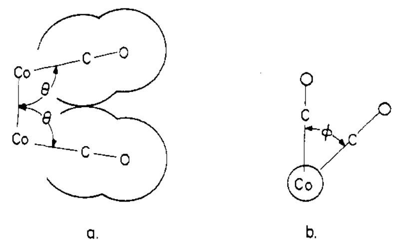


Figure 1. Illustration of (a) van der Waals contact angle θ and (b) dihedral angle φ between carbonyl groups on different metal centers in $Co_2(CO)_8$.

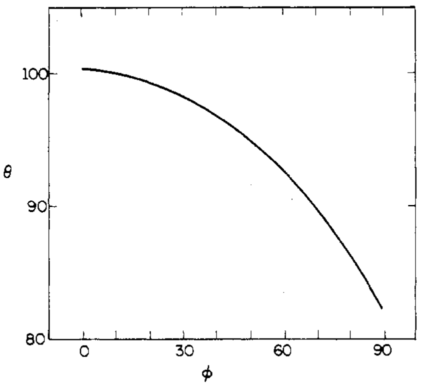
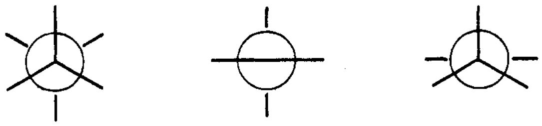


Figure 2. Variation in van der Waals contact angle θ with dihedral angle φ for CO groups on opposite metal centers in $Co_2(CO)_8$.



2 **3** **4**

Figure 3. Newman diagrams for three nonbridged isomers of $Co_2(CO)_8$.

the stability of a particular isomer will be influenced by nonbonded repulsions between the carbonyls if contact occurs at angles θ much greater than 90°. On this basis, isomers **2** and **3** are reasonable structures for $Co_2(CO)_8$. Newman diagrams for structures **2**, **3**, and **4** are shown in Figure 3. The angle θ equals 60° for isomer **2** and 90° for isomer **3**. Isomer **4** requires a dihedral angle φ of 30° or less and is not favored on the basis of steric interactions. Likewise, many otherwise plausible isomers[2,3,5] have dihedral angles of 45° or less.

The comparative stabilities of isomeric structures such as **2** and **3** are the result of a complex interplay of steric and electronic factors. Isomer **2** would appear to be less favorable than **3** on the basis of steric factors alone, since the calculated contact angle for **2** is larger than the expected Co–Co–CO angle. This factor must be offset by a corresponding electronic contribution to the stability of **2**. Molecular orbital calculations for structures **2** and **3** of $Co_2(CO)_8$, employing the parameter-free Fenske–Hall model,[13] reveals that the metal–metal interaction is stronger in **2**, because of more effective hybridization of the axial orbital of the $Co(CO)_4$ group. Only one absorption ascribable to the σ–σ^* transition of the metal–metal bond electrons is seen in $Co_2(CO)_8$ under conditions where both isomers are present.[14] Apparently the increased steric interactions in **2** just compensate for the expected greater metal–metal bond strength. There is substantial evidence that steric effects of ligands in substituted derivatives of $Mn_2(CO)_{10}$ are important in affecting the metal–metal bond strength, as reflected in the position of the σ–σ^* transition and in the energetics of metal–metal bond rupture.[15]

Our analysis for $Co_2(CO)_8$ suggests that electronic structural considerations cannot be completely ignored. Electronic energy terms may determine the minimum energy conformations of local portions of a multinuclear molecule, as well as the degree of interaction between these fragments. The relative energies of alternative structures of an entire molecule are, in the general case, the result of both electronic and steric contributions. The model described here should prove useful in assessing the steric contribution to the relative stabilities of alternative isomeric forms of polynuclear metal complexes.

Registry No. $Co_2(CO)_8$, 15226-74-1.

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