

excitation. Several authors have noted the similarity between the geometry of coordinated olefins and the geometry adopted by olefins in their lowest electronically excited state.^{31,32}

As can be seen, the relationship between olefin binding energy shifts and metal-olefin interactions is complex. The important factors which determine the ionization energy of the coordinated olefin π orbital are summarized in Table IV. The three columns show how each contributing factor affects the olefin π ionization energy if the π -donation and π^* -acceptance interactions are considered individually. For instance, π -donation has a stabilizing effect on the olefin π orbital as a result of overlap stabilization and the buildup of positive charge on the olefin, but a destabilizing effect due to a decrease in C=C bond order. The π^* -acceptance has strictly a destabilizing effect on the olefin π orbital. The π^* -acceptance results in an accumulation of negative charge on the olefin and also reduces the C=C bond order. The overall shift in olefin π ionization energy upon coordination is determined by both the relative dominance of the π -donation/ π^* -acceptance interactions and the relative magnitudes of each contributing factor.

The small charge redistribution upon ethylene coordination in $\text{MeCpMn}(\text{CO})_2(\text{C}_2\text{H}_4)$ indicates that, in this system, the π -donation and π^* -acceptance interactions are approximately of equal importance, resulting in no significant overall charge transfer between the metal and olefin. The observed 0.40 eV destabilization of the ethylene π orbital in $\text{MeCpMn}(\text{CO})_2(\text{C}_2\text{H}_4)$ from free ethylene results from the combined reduction in C=C bond order of both π -donation and π^* -acceptance, which more than compensates for the small metal-olefin overlap stabilization. In this

compound one cannot conclude that the decrease in olefin ionization energy implies a buildup of electron density on the olefin resulting from a dominant π^* -acceptance interaction.

The $\text{MeCpMn}(\text{CO})_2(\text{C}_3\text{H}_6)$ and $\text{Me}_3\text{CpMn}(\text{CO})_2(\text{C}_2\text{H}_4)$ compounds provide convenient perturbations which help illustrate the usefulness of Table IV. In $\text{MeCpMn}(\text{CO})_2(\text{C}_3\text{H}_6)$ the coordinated propylene π orbital has been destabilized by only 0.10 eV relative to free propylene. This molecule has the largest energy separation between the filled metal levels and the olefin π^* level, and therefore has the least amount of π^* -acceptance. In addition, the enhanced π -donation of propylene, due to its electron-donating methyl group, makes propylene an overall stronger donor than acceptor ligand in this system. In this case the donor and acceptor charge-transfer mechanisms do not cancel, but instead, furnish a stabilizing influence which reduces the overall destabilization of the propylene upon coordination. The $\text{Me}_3\text{CpMn}(\text{CO})_2(\text{C}_2\text{H}_4)$ complex presents a perturbation in the opposite direction. The five ring methyl groups destabilize the ring e_1'' orbital and supply an increased amount of electron density to the metal.¹⁶ This decreases the energy separation between the metal levels and the C_2H_4 π^* orbital which enhances olefin π^* -acceptance, and diminishes olefin π -donation to the more electron rich metal. The charge-transfer contribution now furnishes a further destabilization which helps to shift the C_2H_4 π orbital to lower ionization energy by 0.85 eV in $\text{Me}_3\text{CpMn}(\text{CO})_2(\text{C}_2\text{H}_4)$.

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The Valence Electronic Structure of Bridging Methylene: UV Photoelectron Spectroscopy of μ -Methylene- bis(dicarbonyl(η^5 -cyclopentadienyl)manganese)

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Abstract: The He I photoelectron spectrum of $\mu\text{-CH}_2\text{-}[(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)\text{Mn}(\text{CO})_2]_2$ in the ionization energy range below 11 eV is reported and compared with the ionizations of $(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)\text{Mn}(\text{CO})_3$ and $(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)\text{Mn}(\text{CO})_2(\text{C}_2\text{H}_4)$. Excellent agreement is found between the observed ionizations and the predictions of parameter-free molecular orbital calculations. The valence orbitals of the $\mu\text{-CH}_2$ group appear to have near ideal matching with the frontier orbitals of the $(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)\text{Mn}(\text{CO})_2$ fragments to produce the bonding and stability of this cyclopropane analogue. An effective charge transfer from the metals to the methylene occurs in this interaction which results in a high negative charge on the methylene carbon and formation of a net metal-metal bond. The bonding of the bridging methylene in this complex is also compared with the bonding of a terminal methylene with the analogous $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2$ species. It is concluded that the formation of the metal-metal bond is an important factor in the greater stability of the bridging system.

Since the first identification of a CH_2 moiety stabilized as a bridging group between two metal centers,² such compounds have been increasingly recognized for their importance in organometallic chemistry. The metal-methylene unit may be an intermediate

in olefin metathesis reactions, and it recently has been implicated as significant in certain Fischer-Tropsch type reactions.³⁻⁵ A growing number of μ -alkylidene complexes have been synthesized in recent years and an understanding of the stabilities and reactivities of these species is beginning to unfold.^{6,7} This paper

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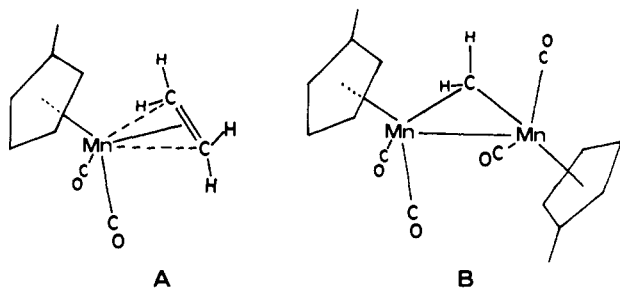


Figure 1. Perspective views of $(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)\text{Mn}(\text{CO})_2(\text{C}_2\text{H}_4)$ (A) and $\mu\text{-CH}_2\text{-}[(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)\text{Mn}(\text{CO})_2]_2$ (B).

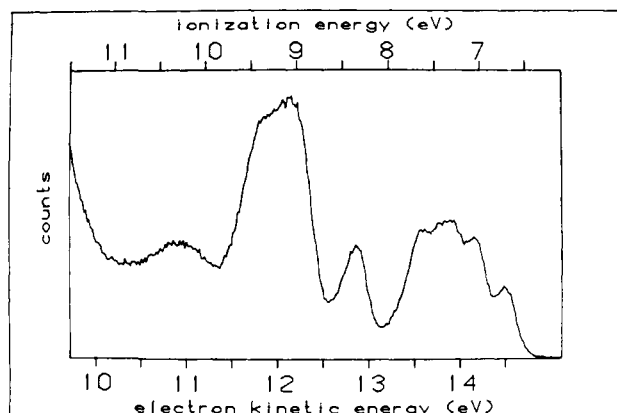


Figure 2. The $11 \rightarrow 6\text{eV}$ He I photoelectron spectrum of $\mu\text{-CH}_2\text{-}[(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)\text{Mn}(\text{CO})_2]$.

reports the first He I valence photoelectron spectrum of a bridging methylene complex.⁸ The valence ionizations provide a direct experimental probe into the valence orbitals and interactions in these complexes.

It should be noted that an understanding of the ionization features and orbital interactions in $\mu\text{-CH}_2\text{-}[\text{MeCpMn}(\text{CO})_2]_2$ ($\text{MeCp} = \eta^5\text{-C}_5\text{H}_4\text{CH}_3$) is greatly facilitated by our previous detailed examinations of $\text{MeCpMn}(\text{CO})_3$ ⁹ and $\text{MeCpMn}(\text{CO})_2(\text{C}_2\text{H}_4)$.¹⁰ The olefin and bridging methylene complexes (Figure 1) are intermediate members of a series of three-member ring molecules from cyclopropane to trinuclear metal clusters. The $\mu\text{-CH}_2\text{-}[\text{MeCpMn}(\text{CO})_2]_2$ complex may be visualized as following from the $\text{MeCpMn}(\text{CO})_2(\text{C}_2\text{H}_4)$ complex by replacing one CH_2 of the olefin by a $\text{MeCpMn}(\text{CO})_2$ unit. However, as will be seen in the following discussion, the bonding descriptions for the olefin and methylene complexes are considerably different.

Experimental Section

The title compound was prepared by a previously reported method.² The He I photoelectron spectrum was recorded on a McPherson ESCA 36 electron spectrometer with modifications as described in an earlier

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(8) After submitting this manuscript two other photoelectron studies of bridging methylene complexes have come to our attention. One is the He I and Ne I spectra of $\mu\text{-CH}_2\text{-Fe}_2(\text{CO})_8$ (T. P. Fehlner, personal communication). The assignment and interpretation of the ionizations of this complex are closely similar to those in the present paper. The second study concerns the He I and He II spectra of $\mu\text{-CH}_2\text{-}[(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2]_2$. (Granozzi, G.; Tondello, E.; Casarin, M.; Ajo, D. *Inorg. Chim. Acta* **1981**, *48*, 73.) We agree with the general assignment of the valence ionizations. However, our paper disagrees with their conclusion, based on their modified CNDO calculations, that there is no metal-metal bond. We also must mention that Granozzi et al. acknowledge one of us (W.A.H.) for assistance in providing the sample. In fact, we were never aware of this other work until the note appeared in print.

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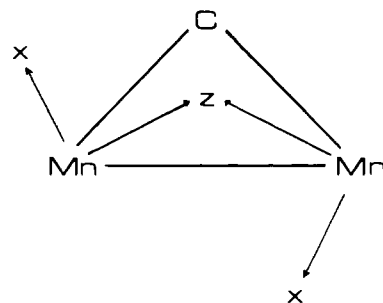


Figure 3. Local coordinate axes for the molecular orbital calculations.

paper.⁹ A temperature of 80 °C was required to maintain a convenient sample vapor pressure for data collection. The displayed spectrum is corrected for the analyzer transmission function. The results of parameter-free Fenske-Hall molecular orbital calculations are also reported. The atomic coordinates and basis functions for the $\text{CpMn}(\text{CO})_2$ fragments were the same as those used in previous work,^{9,11,12} and the fragments and other atomic positions were oriented according to the crystal structure of the complex.¹³

Results and Assignment

The 11-6 eV photoelectron spectrum of $\mu\text{-CH}_2\text{-}[\text{MeCpMn}(\text{CO})_2]_2$ is shown in Figure 2. It is helpful to compare this spectrum with our previous spectra of a variety of $\text{MeCpMn}(\text{CO})_2(\text{ligand})$ compounds.^{9,11,12} The most intense ionization band centered at ~ 9.2 eV exhibits the familiar band-shape and ionization energy of the cyclopentadienyl e_1'' ionization observed in a large number of cyclopentadienyl-containing compounds. We have studied this ionization in detail and have attributed its characteristic bandshape to a ground state structural distortion in the coordinated cyclopentadienyl ring.⁹ The lowest energy, broad ionization band in the 6.5-8.0 eV region contains at least four resolvable peaks. This envelope falls in a region where ionization from orbitals which are high in metal d character typically occur in $\text{MeCpMn}(\text{CO})_2(\text{ligand})$ compounds. Ionizations from M-M bonding orbitals may also fall in this region.¹⁴

This leaves the peaks at 10.23 and 8.34 eV as specific to this complex. The peak at 10.23 eV is similar in position to the ethylene π ionization of $\text{MeCpMn}(\text{CO})_2(\text{C}_2\text{H}_4)$.¹⁰ It is also similarly low in intensity and very broad. A broad ionization band is caused by a long unresolved vibrational progression, and this indicates appreciable bonding character in the orbital. We therefore assign this ionization as primarily associated with the $2e^-$ donor orbital of the methylene which is significantly bonding to the Mn-Mn dimer. A peak in the region of 8.34 eV has not been previously observed in any other $\text{CpMn}(\text{CO})_2(\text{ligand})$ complexes. We interpret this ionization as being associated primarily with the methylene ligand. One might attempt to ascribe this ionization to a single metal-metal bond. However, the position of this ionization is not consistent with the ionizations of similar dimers like $\text{Mn}_2(\text{CO})_{10}$.^{14a} Additional evidence for assignment comes from the following consideration of the orbital interactions in this complex.

Molecular Orbital Analysis

Before considering the results of the calculations on the μ -methylene complex, one must remember the nature of the frontier orbitals and bonding capabilities of the $\text{CpMn}(\text{CO})_2$ fragments, as discussed in detail in earlier papers.^{10,15} Briefly, the fragment has an empty low-lying d_{z^2} type orbital ($3a'$) directed toward its

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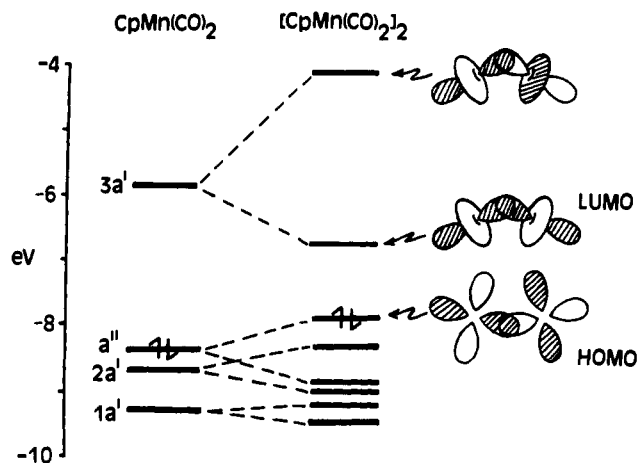


Figure 4. Valence molecular orbital diagram of the $[(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2]_2$ fragment.

vacant coordination site that is suitable for forming a dative bond with an electron donor ligand. The three occupied orbitals of the d^6 metal fragment are $1a'$, $2a'$, and a'' (see previous paper in this series). The $1a'$ and a'' are suitable for π -donation toward the vacant site, with the a'' most effective because it is the least stable and directed for best overlap. The orientation of the $\text{CpMn}(\text{CO})_2$ fragments in the bridging methylene complex is shown in Figure 3. It is interesting that the vacant site of each $\text{CpMn}(\text{CO})_2$ fragment is directed near the center of the Mn–C–Mn triangle, and the a'' orbitals are essentially in the plane of this triangle.

The orbitals which are obtained for the dinuclear fragment, that is $[\text{CpMn}(\text{CO})_2]_2$ in the absence of the CH_2 group, are shown in Figure 4. The frontier orbitals of each $\text{CpMn}(\text{CO})_2$ portion simply combine into the corresponding bonding and antibonding combinations. The strongest combination is naturally between the d_{z^2} -type $3a'$ orbitals, which are each directed toward the same region. The LUMO is the symmetric combination of these orbitals. Of the filled metal levels, the strongest interaction is between the a'' orbitals. The HOMO is the antisymmetric (antibonding) combination of these orbitals. The net bond order between the metals is zero since the bonding and antibonding combinations are filled in pairs.

As in the bonding of carbenes with metals,¹⁶ the methylene group in the coordination sphere of the metal can be envisioned as having a filled orbital (a_1) that acts as a σ donor to the metal. It then also has an empty $p\pi$ orbital (b_1) that can accept π -electron density from the metal. The interaction of these orbitals with those of the dinuclear $[\text{CpMn}(\text{CO})_2]_2$ fragment is shown in Figure 5. The LUMO of the dinuclear fragment has the correct symmetry, is relatively low in energy, and has a nearly ideal spatial distribution for accepting electron density from the donor orbital of the methylene group. Similarly, the HOMO of the dinuclear fragment is well-situated for donating electron density into the empty $p\pi$ orbital of the methylene group.

Figure 5 and the calculated methylene carbon charge in Table I show $\mu\text{-CH}_2$ to be an overall better acceptor than donor in this system. It is important to note that these calculations place the originally empty $p\pi$ orbital of CH_2 slightly below the filled metal levels. Because of this ordering the donation into this $p\pi$ orbital should effectively be described as a charge transfer from the HOMO of the dinuclear fragment to the methylene group. This results in the high negative charge on the methylene carbon.^{7a} Also, the HOMO of the dinuclear fragment is antibonding between the metals, and removal of density from this orbital now leaves a net metal–metal bond. The electron donation from the methylene group is not as great as its electron acceptance because of the stability of the methylene donor orbital. Although the molecular orbital resulting from methylene σ donation remains

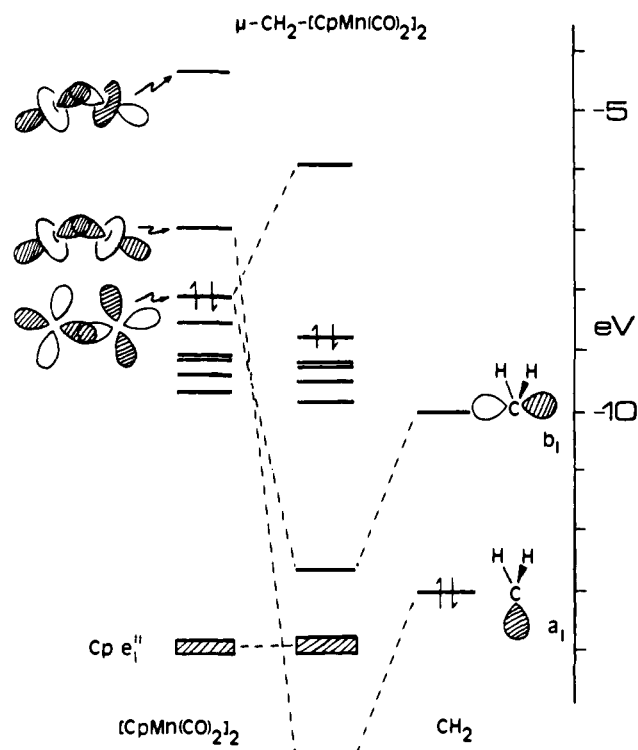


Figure 5. Molecular orbital diagram of $\mu\text{-CH}_2\text{-}[(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2]_2$. The highest occupied orbital is indicated by an electron pair in each case. For the metal-coordinated methylene, the electrons contributed by the methylene are paired in the a_1 orbital for purposes of the discussion.

Table I. Mulliken Populations and Atomic Charges

| | $\mu\text{-CH}_2\text{-}$ $[\text{CpMn}(\text{CO})_2]_2$ | $\text{CpMn}(\text{CO})_2(\text{CH}_2)$ |
|--|---|---|
| methylene carbon atomic charge | -0.526 | -0.529 |
| methylene a_1 population | 1.367 | 1.279 |
| methylene b_1 population | 1.025 | 1.022 |
| total metal d-methylene carbon overlap population | 0.418 | 0.385 |
| total overlap population between the frontier orbitals of the $\text{CpMn}(\text{CO})_2$ fragments | 0.170 | |

primarily methylene in character, this donation does serve to strengthen the metal–metal bond since it is placing density in the LUMO of the dinuclear fragment, which is bonding between the two metals. Thus both interactions tend to produce a net metal–metal bond. The bonding in the Mn–C–Mn triangle may be viewed as a 6-electron, three-center description similar to cyclopropane. This description is similar to that discussed for $\mu\text{-CH}_2\text{-Os}_3(\text{CO})_{10}(\mu\text{-H})_2$.^{7a}

The discussion given above is roughly analogous to that provided by Hofmann in his extended Hückel study of $\mu\text{-CH}_2\text{-}[\text{CpRh}(\text{CO})_2]_2$.¹⁷ Extended Hückel calculations on these systems give qualitatively similar results although there is more mixing in the molecular orbitals, making it difficult to separate the individual interactions. There is also considerable uncertainty in the eigenvalues and the relative placement of some of the orbitals, particularly the placement of the methylene orbitals relative to the metal orbitals. This latter point is an important question for the parameter-free calculations. The molecular orbital calculations used here have been very successful in the past in correlating with ionizations of $\text{CpMn}(\text{CO})_2(\text{ligand})$ complexes.^{11,12} Comparison of Figure 5 with the spectrum in Figure 2 shows that the calculations also account well for the important ionization features of

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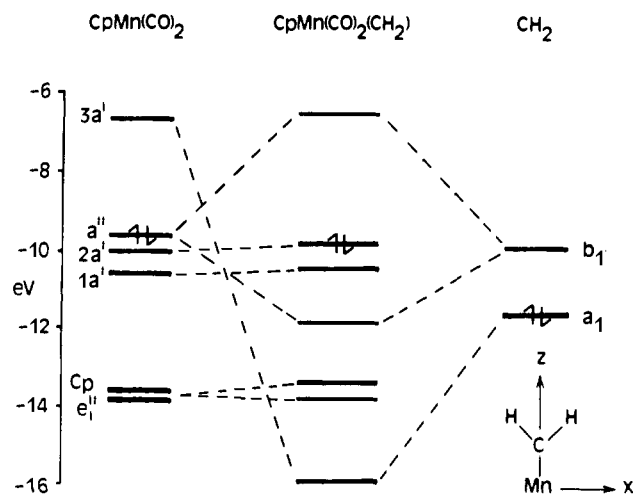


Figure 6. Calculated orbital interactions in $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2(\text{CH}_2)$. The highest occupied orbital is indicated by an electron pair in each case. For the metal-coordinated methylene, the electrons contributed by the methylene are paired in the a_1 orbital for purposes of the discussion.

this bridging methylene complex. Both figures indicate a group of closely spaced levels (mostly metal d) separated from a single level (mostly methylene $\pi\pi^*$). The characteristic cyclopentadienyl e_1'' band comes next and is followed by a final low intensity band observed at 10.23 eV. As mentioned earlier, the width of this final band indicates appreciable bonding character, and the molecular orbital analysis indicates that this orbital is totally bonding in the Mn–C–Mn triangle. The band at 8.34 eV is associated with an orbital that has a node at the C atom and between the two metal atoms in the Mn–C–Mn triangle, and this band is considerably sharper.

The relative intensities of the ionization bands are also consistent with the charge transfer from the metals to the methylene. For instance, in the photoelectron spectrum of $\text{MeCpMn}(\text{CO})_3$ the ionization band area in the metal region relative to that in the MeCp region is 0.93 to 1. These bands represent six metal electrons to four MeCp electrons. From the orbital analysis of $\mu\text{-CH}_2\text{-}[\text{CpMn}(\text{CO})_2]_2$ there are five metal electrons to four MeCp electrons per $\text{CpMn}(\text{CO})_2$ fragment. If ionization cross-sections do not change we should then see a ratio of 0.77 to 1 for the area of the first band (overlapping metal ionizations) to the area of the MeCp band. The ratio determined from the spectrum in Figure 2 is 0.73 to 1, which supports loss of one filled orbital of predominantly metal character in dimer formation.

Bridging vs. Terminal Methylene Bonding

Carbene ligands normally occupy terminal positions in their bonding to metal complexes. In fact, several terminal metal–carbene complexes of the form $\text{CpMn}(\text{CO})_2(\text{carbene})$ are known.¹⁸ The preparation of the title compound also suggests the terminal metal–methylene complex, $\text{MeCpMn}(\text{CO})_2\text{CH}_2$, as a probable

intermediate.⁷ This is because the bridged dimer is obtained from the reaction of $\text{MeCpMn}(\text{CO})_2(\text{THF})$ with CH_2N_2 , and there is no reason to suspect the presence of $[\text{MeCpMn}(\text{CO})_2]_2$. Interconversion between bridging and terminal positions may be important in mechanisms of catalytic hydrocarbon formation at surfaces⁵ and in other reactions. It is therefore appropriate to examine those factors that favor the bridging dimer geometry over the terminal-bonded monomer geometry for this particular methylene complex. This comparison is somewhat related to the recent discussions of bridging vs. terminal bonding in metal dimers.¹⁹

The results of Fenske–Hall calculations on a model $\text{CpMn}(\text{CO})_2(\text{CH}_2)$ complex are presented in Figure 6 and Table I. A typical Mn–C distance of 1.90 Å from the structures of other $\text{CpMn}(\text{CO})_2(\text{CR}_2)$ compounds was used,¹⁸ and the H–C–H angle was set at 120°. The plane of the CH_2 group was oriented perpendicular to the plane of the MeCp ring, as is found in the structures of other carbene complexes.¹⁵ The molecular orbital diagram of $\text{CpMn}(\text{CO})_2(\text{CH}_2)$ in Figure 6 has many similarities to that of $\mu\text{-CH}_2\text{-}[\text{CpMn}(\text{CO})_2]_2$ in Figure 5. The methylene a_1 donor interacts with the $3a'$ LUMO of $\text{CpMn}(\text{CO})_2$, while the vacant methylene $\pi\pi^*$ accepts density from the $\text{CpMn}(\text{CO})_2$ a'' HOMO. The data in Table I show the methylene group to be in remarkably similar environments in the terminal $\text{CpMn}(\text{CO})_2(\text{CH}_2)$ and bridging $\mu\text{-CH}_2\text{-}[\text{CpMn}(\text{CO})_2]_2$ compounds. The calculated charge on the methylene carbon atom is essentially identical in these compounds. The Mulliken populations of the methylene donor and acceptor orbitals change negligibly in going from terminal to bridging configurations. The orbital eigenvalues show some expected shifts for the unoptimized geometry in the model calculations, but the relative ordering of the orbitals is the same in both the mononuclear and dinuclear metal complexes. The overall methylene bonding interaction appears to show no significant preference for either conformation.

Obviously, a significant difference between the two bonding modes is the formation of a Mn–Mn bond in the dimer, which is made possible by the charge transfer to the low-lying $\pi\pi^*$ orbital of the methylene group. The formation of the metal–metal bond is illustrated by the overlap population between the frontier orbitals ($1a'$, $2a'$, a'' , and $3a'$) of the two $\text{CpMn}(\text{CO})_2$ fragments shown in Table I. The increased stability gained by the additional metal–metal bond formation is apparently a driving force for formation of the dimer complex. In situations where changes in the metal–metal bond interaction are not so severe, there should be a less pronounced preference for the bridging vs. terminal methylene coordination.

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