Title
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Publication Date
1982-04-01

LBL-14339
Preprint

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

Materials & Molecular Research Division

Submitted to the Journal of the American Chemical Society

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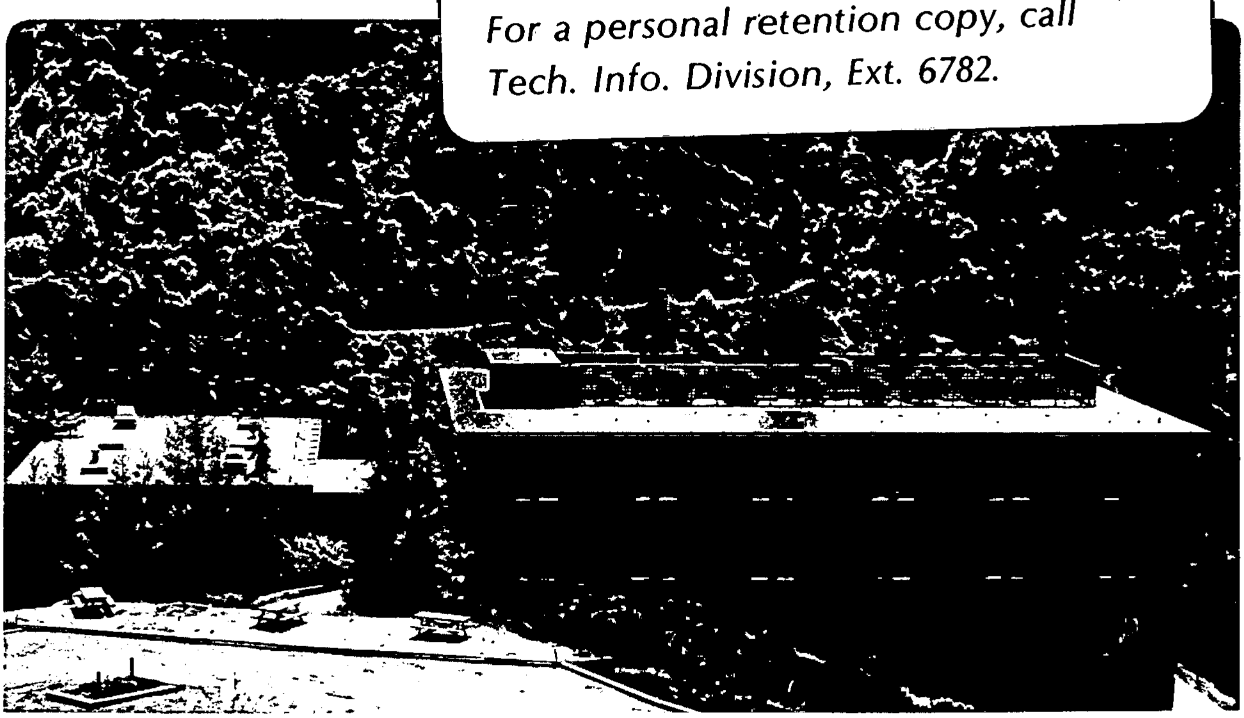
April 1982



Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

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Terminal vs. Bridge Bonding of Methylene to Metal Systems. $A\ell_2CH_2$ as a Model System.

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Abstract

The metal dimer-methylene system M_2CH_2 is the simplest which can in principle display both terminal M-M-CH_2 and bridging M$\overset{CH_2}{\diagup\!\!-\!\!\diagdown}$M geometrical structures. Having previously studied the terminal Aℓ-CH, Aℓ-CH_2, and Aℓ-CH_3 metal-organic fragment species, the $A\ell_2CH_2$ system was chosen to allow a competition between the terminal and bridged structures. Nonempirical molecular electronic structure theory was used, with double zeta (DZ) and DZ + polarization basis sets in conjunction with both self-consistent-field (SCF) and configuration interaction (CI) methods. Among structures considered, the bridging arrangement, with the Aℓ$\overset{C}{\diagup\!\!-\!\!\diagdown}$Aℓ and CH_2 planes perpendicular to each other, lies lowest energetically. For this structure the Aℓ-Aℓ distance is 3.61 Å, the Aℓ-C distance 2.00 Å, and the methylene bond angle 105.5°. The completely planar structure, found by twisting the methylene group by 90°, is predicted to lie 31 kcal higher, but has a much shorter Aℓ-Aℓ distance, 3.03 Å. The terminal structure lies 46 kcal above the absolute minimum on the energy

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. This manuscript was printed from originals provided by the authors.

surface and has $r_e(A\ell-A\ell) = 2.87$ Å, $r_e(A\ell-C) = 1.81$ Å, and a methylene bond angle of 112.2°. All of the above structures are closed-shell singlets in their lowest electronic states, but the energies of several triplet species are also discussed. The Aℓ-C bond energy for the terminal structure is 81 kcal, in good agreement with that predicted (77 kcal) earlier by comparable methods for $A\ell CH_2$. However, for the bridging $A\ell_2CH_2$, the $A\ell_2\cdots CH_2$ dissociation energy is much larger, 127 kcal. Vibrational frequencies for the bridging and terminal $A\ell_2CH_2$ species are presented and discussed.

Introduction

The first mononuclear transition metal methylene complex, $Cp_2TaCH_3CH_2$, was synthesized[1] (and its crystal structure 1 simultaneously reported[2]) by Schrock in 1975. However, during the intervening six years, only one other terminally bonded neutral methylene complex, the $Cp_2Zr(PPh_2Me)CH_2$ molecule 2 of Schwartz and Gell,[3] has been reported. In addition, a single cationic methylene complex 3, $Cp[Ph_2PCH_2CH_2PPh_2]FeCH_2^+$, was characterized in 1980 by Brookhart, Tucker, Flood, and Jensen.[4] A simpler cationic carbene $CpFe(CO)_2CH_2^+$ was quite likely generated as a transient by Jolly and Petit[5] as early as 1966 and reported to react with several olefins to yield cyclopropanes. However, compound 4 has resisted spectroscopic characterization thus far, although the sulfide $CpFe(CO)_2CH_2SCH_3$ has been developed[6] as a stable precursor to 4.

The very first transition metal methylene complex reported in the literature was not a terminal structure at all but rather 5, the bridged molecule $[CpMn(CO)_2]_2CH_2$ of Herrmann, Reiter, and Biersack.[7] These authors simultaneously reported the analogous complex in which one of the cyclopentadienyl hydrogens is replaced by a methyl group, but for our purposes this is essentially the same molecule as 5. Since 1975, quite a number of additional neutral bridging CH_2 organometallics have been synthesized. Among these, the rhodium complex[8] 6 is analogous to 5, with the two additional valence electrons of the Rh atoms relative to Mn allowing (in the sense of the 18 electron rule[9]) the displacement of two CO groups.

Moreover, the cobalt complex completely analogous to 6 has very recently been synthesized by Theopold and Bergman,[10] along with the heterobinuclear Co-Rh μ-methylene complex.

The simplest (constructed exclusively from Fe, CO, and CH_2 components) and most elegant bridging transition metal methylene complex synthesized to date is 7, the $Fe_2(CO)_8CH_2$ molecule.[11] In solution, only terminal IR vibrational frequencies are observed, suggesting that the structure therein is 7b. However, under other circumstances, the structure 7a with two bridging carbonyls cannot be unambiguously excluded. Nevertheless, the Mössbauer spectrum shows the two iron atoms to be equivalent, clearly indicating a bridging, rather than terminal, CH_2 group.

A number of more complicated bridging methylene complexes, involving two[12-17] or three[18-21] metal atoms, have been synthesized. Of the binuclear compounds 8 ($R=CH_3$)[12] is of particular relevance to the present study, since one of the two metal atoms which the CH_2 bridges is an aluminum. Among the trinuclear methylene complexes, the $Os_3(CO)_{11}CH_2$ molecule[20] 9 is impressive in its simplicity in the same sense that Petit's $Fe_2(CO)_8CH_2$ is thus far unique. Shapley and co-workers[20] have found that upon pyrolysis, it is possible to remove from 9 a single CO ligand, yielding the coordinately unsaturated $Os_3(CO)_{10}CH_2$. In general, of course, unsaturated species such as this osmium trium are expected to be quite reactive, and may ultimately serve as models for heterogeneous catalysis.[15]

The weight of the evidence[1-20] would appear to suggest that bridging transition metal methylene complexes are going to be far more prevalent than the analogous terminally bound species. In fact, to date there are less than a handful of examples of a terminal methylene occurring within a binuclear M_2 or trinuclear M_3 organometallic complex.[21] The goal of the present theoretical study, then, is to ask why the bridging methylene is apparently favored over the terminal structure. The approach taken here is to adopt a simple binuclear model which allows both bridging and terminal geometries and carry out detailed theoretical comparisons between the two.

The Theoretical Model

Our previous theoretical study[22] of $A\ell CH$, $A\ell CH_2$, and $A\ell CH_3$ has provided a fairly complete picture of the possible varieties of aluminum-carbon terminal bonds. Superficially, one might expect each of these to reflect the maximum $A\ell$-C bond order possible, namely triple ($A\ell \equiv CH$), double ($A\ell \equiv CH_2$), and single ($:A\ell - CH_3$) bonds. In fact, the electronic ground state of each of these species displays a predominantly single bond. There is some suggestion of multiple bond character in going from $A\ell CH_3$ to $A\ell CH$, namely an increase in the predicted dissociation energy from 68 to 88 kcal and decrease in the $A\ell$-C bond distance by 0.039 Å. But the overall picture for each of the three model species is that of an $A\ell$-C single bond.

Given these theoretical predictions[22] for $A\ell CH$, $A\ell CH_2$, and $A\ell CH_3$, we have a standard of comparison by which to judge the $A\ell_2$-CH_2 system, which is the subject of the present paper.

That is, now that a reasonable understanding of the isolated $A\ell$-C terminal bond is at hand, one can compare this both with the terminal M-M-CH_2 results (as noted in the Introduction, very few such molecules have yet been synthesized) and with those for the bridging $M\overset{CH_2}{\diagup\!\!-\!\!\diagdown}M$. One possible criticism of this model is that the metal used (aluminum) is not a transition metal and hence the theoretical predictions might be inappropriate for organotransition metal chemistry. We recall here that one of the known metal methylene complexes, namely **8**, does involve an aluminum atom, and its structure appears to be qualitatively the same as those involving only transition metal atoms. More generally we inclined to the position[23] that main group metals (such as aluminum) are not as different from transition metals as is popularly assumed.

Theoretical Approach

Although the $A\ell_2CH_2$ system is significantly larger than the organoaluminum structures investigated earlier, it was considered important to approach certain aspects of this metal dimer system at a higher level of theory than employed previously.[22] Specifically, the optimization of the geometries of certain species was carried out with polarization basis functions (i.e., d functions on the carbon and aluminum atoms and p functions on the hydrogens) and the prediction of vibrational frequencies was carried out similarly.

All geometrical structures were initially determined at the double zeta (DZ) basis set, self-consistent-field (SCF) level of theory. The precise basis used was, in strict consistency with earlier work on $A\ell CH_n$ (n=1-3), the standard Dunning-Hay[24] DZ basis, designated Aℓ(11s 7p/6s 4p), C(9s 5p/4s 2p), H(4s/2s). Certain molecular structures were subsequently reoptimized at the double zeta plus polarization (DZ+P) SCF level and the polarization function orbital exponents chosen were $\alpha_d(C) = 0.75$, $\alpha_d(A\ ) = 0.6$, and $\alpha_p(H) = 1.0$, as in the previous study.[22] All geometrical structures were optimized using closed- and open-shell SCF analytic gradient techniques.[25,26] Subsequently, quadratic force constants in terms of cartesian coordinates were evaluated as central differences of analytic forces and subjected to standard harmonic vibrational analyses.[27]

Given the stationary point geometries determined at the SCF level of theory, relative energies of the various species were examined using correlated wave functions.[28] In the configuration interaction (CI) procedure, the eleven lowest occupied SCF molecular orbitals (Aℓ 1s,2s,2p;C 1s) describe core electrons and are accordingly constrained to be doubly occupied in all configurations. Furthermore, the eleven highest-lying virtual SCF orbitals are also localized in the core regions (using a DZ or DZ+P basis set of the type employed here) and were therefore deleted from the CI procedure. With these restrictions, the CI wave functions included all Hartree-Fock interacting[29] single and double excitations relative to the appropriate SCF reference configuration. Since all stationary points have C_{2v} symmetry, the number of configurations is not excessive, the maximum being 13,955 for the terminal-bonded $^3A_2$ state of $A\ell_2CH_2$. The correlated wave functions were obtained via the graphical unitary group approach.[30]

Diatomic Aluminum

Before embarking on our discussion of $A\ell_2CH_2$, it is appropriate to give some attention to the naked aluminum dimer. In addition, since there is some experimental data available for $A\ell_2$, it may be possible to obtain some insight into the reliability of the theoretical methods adopted here.

The definitive work of Dupuis and Liu[32] on the isoelectronic B_2 molecule, together with the experimental background[31] on $A\ell_2$, give us a clear idea of the expected low-lying electronic states of the latter. The observed electronic transition (T_e = 17,270 cm^{-1}) for $A\ell_2$ is X $^3\Sigma_g^-$ - A $^3\Sigma_u^-$, and these two states arise from the electron configurations

$$^3\Sigma_g^- \quad 1\sigma_g^2\ 1\sigma_u^2\ 2\sigma_g^2\ 2\sigma_u^2\ 1\pi_u^4\ 3\sigma_g^2\ 1\pi_g^4\ 3\sigma_u^2\ 4\sigma_g^2\ 4\sigma_u^2\ 2\pi_u^2 \qquad (1)$$

$$^3\Sigma_u^- \quad \ldots\ldots\ 4\sigma_g^2\ 4\sigma_u\ 2\pi_u^2\ 5\sigma_g \qquad (2)$$

The equilibrium bond distances are known to be r_e = 2.466 Å and r_e = 2.560 Å, respectively and the ground state dissociation energy is ∿ 1.6 eV,[31] suggesting a single bond between the two aluminum atoms. However, there are other candidates for the $A\ell_2$ ground state. Following previous work[32-34] on B_2, one appreciates (in light of Hund's rules) that the $^5\Sigma_u^-$ state,

$^5\Sigma_u^-$ ..... $4\sigma_g^2\ 4\sigma_u\ 2\pi_u^2\ 5\sigma_g$ (3)

arising from the same electron configuration as the $^3\Sigma_u^-$ state, will surely lie energetically below the latter electronic state. Furthermore, the work of Sabelli[35] brought to our attention a low-lying $^3\Pi_u$ state, arising from the electron configuration

$^3\Pi_u$ ..... $4\sigma_g^2\ 4\sigma_u^2\ 2\pi_u\ 5\sigma_g$ (4)

Initially the three candidates (1), (3), and (4) for the ground state of Al_2 were examined at the DZ SCF level of theory. The ordering of electronic states is $^3\Pi_u$ (r_e = 2.912 Å), followed by $^3\Sigma_g^-$ (r_e = 2.661 Å), followed by $^5\Sigma_u^-$ (r_e = 2.372 Å). The same ordering of states was found at the DZ+P SCF level of theory, with the predicted bond distances being 2.815 Å ($^3\Pi_u$), 2.592 Å ($^3\Sigma_g^-$), and 2.349 Å ($^5\Sigma_u^-$). The results appear to establish conclusively that within the Hartree-Fock approximation, the $^3\Pi_u$ state of Al_2 is predicted to be the electronic ground state. However, the MCSCF results of Sabelli[35] (and our own subsequent CI studies) reverse this ordering and find the $^3\Sigma_g^-$ state to be the ground state, consistent with the simplest interpretation of the experimental data.[31]

A more disturbing aspect of the Al_2 results is the large differences between the SCF and experimental bond distances for the $^3\Sigma_g^-$ ground state of Al_2. Specifically, the DZ SCF bond distance is 0.195 Å longer than experiment and even the DZ+P SCF bond distance is 0.126 Å longer. Such errors are certainly much larger than is normally observed at these levels of theory.[36] For example, for thioformaldehyde ($H_2C=S$) the DZ basis set strictly analogous to the present one yields a bond distance[37] of 1.637 Å, in reasonable agreement with experiment,[38] 1.611 Å. Therefore it was decided to further pursue the $A\ell_2$ bond distance at higher levels of theory. DZ CI yielded a $^3\Sigma_g^-$ distance of 2.602 Å, a decrease of 0.059 Å compared with the analogous SCF result, but still much larger than experiment. Better agreement with experiment is obtained at the DZ+P CI level, where the theoretical prediction of 2.509 Å is now 0.043 Å too long. Finally, appendage of the Davidson correction[39] for the effect of higher excitations yields $r_e(A\ell\text{-}A\ell)$ = 2.496 Å, a bond distance only 0.030 longer than experiment.

It is clear that both polarization functions and explicit treatment of electron correlation are required to make a satisfactory theoretical prediction of the bond distance for ground state $A\ell_2$. In this regard it may be noted that correlation effects reduce the Aℓ-Aℓ distance by about 0.1 Å, whereas for normal closed-shell molecules the typical result[40] is an increase in bond distances by a few hundredths of an angstrom. However this result may be explained in light of the systematic studies of Chandler and McLean[41] on homonuclear diatomics of the first and second row. There it is seen that for molecules with a large number of valence orbitals unoccupied (or partially occupied) in the Hartree-Fock configuration, CI decreases the predicted SCF bond distances. More specifically, a molecule such as $A\ell_2$ has one half-filled bonding orbital (the

$2\pi_u$ orbital) and another bonding orbital ($5\sigma_g$) not occupied at all, and the promotion of antibonding electrons (in the $4\sigma_u$ orbital) into these bonding orbitals increases the bond order and decreases the bond distance. In the same spirit, one should be forewarned that the Aℓ-Aℓ SCF bond distances predicted for $A\ell_2CH_2$ might also be somewhat longer than the true (as yet unknown) bond distances.

Terminally Bound Methylene Structures

Structures of the general type $A\ell\text{-}A\ell\text{-}CH_2$ correspond in a qualitative sense to the previously studied $A\ell\text{-}CH_2$ molecule.[22] Perhaps the simplest intuitive way to think about the electronic structures of $A\ell_2CH_2$ is in terms of the molecular orbitals of the $A\ell_2$ and CH_2 fragments. The triplet ground state of methylene arises from the electron configuration

$$^3B_1 \qquad 1a_1^2\ 2a_1^2\ 1b_2^2\ 3a_1\ 1b_1 \tag{5}$$

while the first excited state, lying only about 9 kcal higher,[43] emanates from

$$^1A_1 \qquad 1a_1^2\ 2a_1^2\ 1b_2^2\ 3a_1^2 \tag{6}$$

Since the terminally bonded $A\ell_2CH_2$ structures are expected to have C_{2v} symmetry, the next step is to resolve the $A\ell_2$ ground state electron configuration (1) into C_{2v} symmetry. When this resolution[42] is carried out in a manner consistent with the C_{2v} symmetry operations implicit in the nuclear arrangement Aℓ-Aℓ-CH_2, one obtains

$$^3A_2 \qquad 1a_1^2\ 2a_1^2\ 3a_1^2\ 4a_1^2\ 1b_1^2\ 1b_2^2\ 5a_1^2\ 2b_1^2\ 2b_2^2\ 6a_1^2\ 7a_1^2\ 8a_1^2\ 3b_1\ 2b_2 \qquad (7)$$

That is, the term symbol $^3\Sigma_g^-$ for the full $D_{\infty h}$ symmetry becomes $^3A_2$ for the C_{2v} subgroup specified above.

Perhaps the simplest merger of the ground states (5) and (7) of CH_2 and $A\ell_2$ is to keep the fragment unpaired spins parallel, yielding an electronic quintet state (S=2). With the core electrons included implicitly, the quintet electron configuration is

$$^5B_2 \qquad \ldots\ldots\ 8a_1^2\ 9a_1^2\ 3b_2^2\ 10a_1^2\ 11a_1\ 3b_1\ 4b_1\ 4b_2 \qquad (8)$$

However, if one assumes that the $A\ell_2$ and CH_2 bonds are not disrupted by this merger of fragments, then the Aℓ-C linkage has no bonding character. Indeed, quantitative SCF studies of the quintet state show that it is not a serious contender for the ground state of terminally bound $A\ell_2CH_2$. In like manner, as long as the $11a_1$ orbital of $A\ell_2CH_2$ (which in this picture is the nonbonding $3a_1$ orbital of the CH_2 fragment) remains singly occupied, one does not deduce the ground state electron configuration.

A possible deficiency of the above picture is that it ignores the presence of the low-lying $5\sigma_g$ orbital of $A\ell_2$. Although the $5\sigma_g$ orbital is unoccupied in the $^3\Sigma_g^-$ ground state, it does become occupied for the earlier discussed $^3\Sigma_u^-$ and $^5\Sigma_u^-$ states (2) and (3) of $A\ell_2$. The presence of this additional a_1 orbital ($\sigma_g \rightarrow a_1$ in C_{2v}) suggests a greater occupation of a_1 orbitals than would be deduced simply on the basis of the electron configurations for $^3B_1$ CH_2 and $^3\Sigma_g^-$ $A\ell_2$. Alternately, one of the low-lying electronic states of $A\ell_2CH_2$ may be envisioned as arising from the merger of ground state $A\ell_2$ (7) and singlet methylene (6):

$$^3A_2 \qquad \ldots\ldots\ 8a_1^2\ 9a_1^2\ 3b_2^2\ 10a_1^2\ 11a_1^2\ 3b_1\ 4b_2 \qquad (9)$$

Theoretical exploration of a number of other possible electronic states of $A\ell$-$A\ell$-CH_2 also showed the $^3A_1$ state

$$^3A_1 \qquad \ldots\ldots\ 8a_1^2\ 9a_1^2\ 3b_2^2\ 10a_1^2\ 11a_1^2\ 3b_1\ 4b_1 \qquad (10)$$

to be quite low-lying energetically.

The presence of the $^3A_1$ state (10) as an energetically viable species suggested rather directly the existence of the closed-shell singlet state

$$^1A_1 \qquad \ldots\ldots\ 8a_1^2\ 9a_1^2\ 3b_2^2\ 10a_1^2\ 11a_1^2\ 3b_1^2 \qquad (11)$$

which turns out to be the ground electronic state for terminally bound $A\ell_2CH_2$. Although this anticipates results not yet presented, in light of the qualitative discussion thus far, it is appropriate to discuss the electronic structure of (11) now. Table I shows orbital energies for the closed-shell singlet state of $A\ell$-$A\ell$-CH_2 along with a simplified description of each valence orbital.

Table I indicates that the "bonding" canonical molecular orbitals are not necessarily the highest occupied MO's. Specifically, the $9a_1$ and $10a_1$ orbitals, more than 0.2 hartree (= 5.4 eV) below the Fermi level, have considerable $A\ell_2$-CH_2 bonding character. Moreover, the higher lying $11a_1$ orbital is primarily the $A\ell_2$ $3s\sigma_u$ orbital. However, the HOMO, the $3b_1$ orbital, is a bonding orbital mixing the $A\ell_2$ π orbital with the CH_2 out-of-plane 2p orbital. Note of course that the orbital designations in Table I are only qualitative. For example, while the $10a_1$ orbital is labeled $A\ell_2$ $3s\sigma_u$ + CH_2 $3a_1$, in fact the aluminum 3s population on the end $A\ell$ atom is much greater than that on the central atom. This general remark notwithstanding, it is clear that the $5\sigma_g$ orbital ($3p\sigma_g$) of $A\ell_2$ is <u>not</u> strongly populated. More quantitatively, the total $A\ell$ 3p populations on the end and central $A\ell$ atoms are 0.69 and 1.20 Mulliken electrons, respectively, and most of this occurs in the above mentioned $3b_1$ π-bonding orbital.

With the above qualitative discussion in mind, we present in Figure 2 the predicted DZ SCF geometrical structures for the three low-lying electronic states of terminally bound $A\ell_2CH_2$. This figure shows clearly that the $A\ell$-C bond distance for the closed-shell singlet ground state corresponds to that of a true double bond. The predicted $r_e(A\ell{=}C)$ = 1.814 Å is much less than the 2.013 Å obtained[22] at the same level of theory for the prototype Aℓ-C single bond in $A\ell CH_3$. Moreover the predicted 1.814 Å agrees well with the 1.802 Å found[22] for the first excited electronic state of $A\ell CH_2$, and the latter state was shown to display a double bond, albeit ∿ 21 kcal above the $A\ell CH_2$ ground state, which is singly-bonded. Thus a primary difference between $A\ell_2CH_2$ and the previously studied $A\ell CH_2$ is that the Aℓ=C double bonded species is the ground state of the former, but an excited state of the latter. Although one hesitates to draw general conclusions, the thought that a naked metal dimer is more suitable for forming a π-bond to methylene than is a single metal atom is intriguing.

Figure 2 also shows that the two excited triplet states of $A\ell_2CH_2$ do not display Aℓ=C double bonds. Indeed the $^3A_2$ and $^3A_1$ r_e(Aℓ-C) distances of 1.960 Å and 1.974 Å fall nicely between the "short single bond" of the $A\ell CH_2$ ground state (1.938 Å) and the prototype 2.013 Å predicted for $A\ell CH_3$. This supports the notion that the $3b_1$ molecular orbital (doubly-occupied in the closed-shell ground state) is a π-bonding Aℓ-C orbital, while the $4b_1$ and $4b_2$ orbitals (singly occupied for the two excited triplets) are nonbonding in this regard.

The Aℓ-Aℓ equilibrium separations for the three terminally bonded structures are also of interest. By comparison with the comparably predicted DZ SCF distance of 2.662 Å for $A\ell_2$ in its $^3\Sigma_g^-$ ground state, all three $A\ell_2CH_2$ distances are longer. Since the ground state of $A\ell_2$ is thought to represent a single bond, logic would suggest that the $^1A_1$ ground state (2.868 Å) and $^3A_2$ excited state (2.823 Å) represent somewhat weaker Aℓ-Aℓ single bonds. However, the Aℓ-Aℓ distance for the $^3A_1$ state (3.296 Å) is so much longer that some different category must be devised to describe it. We will return to the question of the length of a "normal" single bond between aluminum atoms during the discussion of the bridge-bonded $A\ell_2CH_2$.

The structure of the methylene fragments in the three $A\ell_2CH_2$ are remarkably similar, with CH distances 1.083 Å ($^1A_1$), 1.083 Å ($^3A_2$), 1.085 Å ($^3A_1$) and methylene bond angles of 112.2°, 112.0°, and 111.3°. Previously we have shown[22,44] that for $MnCH_2$ and $A\ell CH_2$, the methylene bond angles of the various electronic states may be correlated by a simple Walsh-like argument[45] with the population of the methylene lone pair orbital, designated $3a_1$ for the isolated CH_2. The gist of the argument is that a doubly-occupied $3a_1$ orbital [as in singlet methylene, electron configuration (6)] gives a CH_2 bond angle of ∿ 102°, while a singly-occupied orbital [as in triplet methylene, electron configuration (5)] yields a CH_2 bond angle of ∿ 133°. In like manner for $A\ell_2CH_2$, by projecting out carbon and hydrogen atom a_1 populations (and subtracting off the 4.0 such electrons due to the CH_2 $1a_1$ and $2a_1$ orbitals), the correlation

$^1A_1$ $3a_1^{1.50}$	$^3A_2$ $3a_1^{1.63}$	$^3A_1$ $3a_1^{1.65}$
112.2°	112.0°	111.3°

is found. That is, the magnitude of the methylene bond angle is inversely related to the CH_2 fragment $3a_1$ orbital population. However, the three bond angles are so nearly the same that this correlation may be fortuitous. Nevertheless, these CH_2 bond angles are intermediate between the known bond angles of isolated singlet and triplet methylene; and in a similar manner the $3a_1$ fragment populations lie between the integer values of 2 and 1 inherent in the Hartree-Fock descriptions of $^1A_1$ and $^3B_1$ methylene. In this more general sense, the correlation is certainly seen to be an effective one.

Bridge Bonded Methylene Structures

The chemically intuitive way to put together an $A\ell_2CH_2$ bridge species is to allow the carbon atom to be roughly tetrahedrally bound to its four neighbors, as illustrated explicitly in structures 5 and 6 of Figure 1. For this C_{2v} arrangement, the $^3\Sigma_g^-$ ground electron configuration (1) of $A\ell_2$ resolves as

$$^3B_2 \qquad 1a_1^2\ 1b_1^2\ 2a_1^2\ 2b_1^2\ 1b_2^2\ 3a_1^2\ 4a_1^2\ 1a_2^2\ 3b_1^2\ 4b_1^2\ 5a_1^2\ 5b_1^2\ 2b_2\ 6a_1 \qquad (12)$$

As was illustrated in more detail for the terminally bound isomer, one can merge (12) with the triplet CH_2 configuration (5) to yield a quintet state

$$^5A_2 \qquad \ldots\ 6a_1^2\ 7a_1^2\ 2b_2^2\ 5b_1^2\ 8a_1\ 6b_1\ 3b_2\ 9a_1 \qquad (13)$$

with a formal bond order of zero between the $A\ell_2$ and CH_2 fragments.

Starting from the no bond structure (13) a first bond can be constructed by pairing up the $3a_1$ lone pair orbital of CH_2 [designated $8a_1$ in (13)] with the a_1 component of the $2\pi_u$ bonding orbital of $A\ell_2$ [designated $9a_1$ in (13)]. The resulting triplet state

$$^3A_2 \qquad \ldots\ldots\ 6a_1^2\ 7a_1^2\ 2b_2^2\ 5b_1^2\ 8a_1^2\ 6b_1\ 3b_2 \qquad (14)$$

has been subjected to the DZ SCF level of theory and determined unlikely to be a candidate for the ground state. The true ground state is eventually reached, relative to (14), by removing an electron from the $3b_2$ orbital and placing it in the $6b_1$ orbital, thus creating the closed-shell singlet state

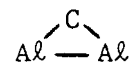
$$^1A_1 \qquad \ldots\ldots\ 6a_1^2\ 7a_1^2\ 2b_2^2\ 5b_1^2\ 8a_1^2\ 6b_1^2 \qquad (15)$$

The valence orbital energies for this $^1A_1$ ground state of bridged-bonded $A\ell_2CH_2$ are seen in Table I, which also gives a brief description of each molecular orbital. There it is apparent that the two Aℓ-C bonds are spread out amongst the four highest occupied SCF molecular orbitals. Of course, a transformation to localized orbitals would probably result in the isolation of two well-defined Aℓ-C bonding orbitals. In addition, the aluminum 3p orbitals are much less involved in the Hartree-Fock electronic structure of the bridged structure than for the above-discussed terminal $A\ell_2CH_2$ geometry. Specifically, the Aℓ 3p populations (necessarily equal for this C_{2v} structure) are only 0.52 Mulliken electrons. The bonding is thus primarily between the Aℓ 3s ($Aℓ_2$ $3s\sigma_g$ and $3s\sigma_u$) orbitals and the $3a_1$ and $1b_1$ orbitals of the CH_2 fragment. As Table II shows there is a Mulliken charge of +0.64 on each Aℓ atom, yield formally a CH_2 fragment with a negative charge of 1.29. Without having to believe these numbers literally, it is apparent that there is a significant transfer of electron density from $Aℓ_2$ to CH_2 when the tetrahedrally bridged structure is formed.

Since the bridge bonded $^1A_1$ state represents the lowest minimum on the regions of the $Aℓ_2CH_2$ potential energy hypersurface studied here, this geometrical structure was determined at both the DZ SCF and DZ+P SCF levels of theory. The good agreement between the two structures seen in Figure 3 gives us reasonable hope that in the cases here where only DZ SCF theory was employed the results are comparably reliable. One notes in particular that the Aℓ-Aℓ separation decreases by only 0.004 Å when polarization functions are added to the basis. Recall in contrast that for the naked $Aℓ_2$ dimer, the same extension of the basis decreased the Aℓ-Aℓ distance by 0.068 Å. This result confirms the view that the electronic structure of naked metal clusters can be far more difficult to describe than that of analogous metal system with a few ligands attached. Notoriously ill-behaved in this regard are the Cr_2 and Mo_2 dimers,[46] whereas systems such as $Mo_2(O_2CH)_4$ seem fairly "normal" with respection to their electronic structure.[47] Also worthy of some mention is the fact that the methylene bond angle decreases by only 0.7° with the addition of polarization functions to the basis. For the isolated CH_2 fragment it is well known[48] that the addition of d functions on the carbon atom decreases the HCH bond angle by ∿ 4°. Thus it would appear that the DZ basis set does a better job in predicting the structure of $A\ell_2CH_2$ than would be anticipated from analogous results for the $A\ell_2$ and CH_2 fragments.

It is quite clear that the bridge-bonded closed-shell singlet structure in Figure 3 contains two Aℓ-C single bonds. The DZ SCF Aℓ-C distance is 2.002 Å, quite similar to the 2.013 Å predicted at the same level of theory for the prototype single bond in $A\ell$-CH_3. The slightly shorter DZ+P SCF distance of 1.980 Å is likewise only a bit longer than the value 1.957 Å determined by electron diffraction experiments[49] for the saturated $A\ell(CH_3)_3$ molecule. Thus the two Aℓ-C bonds in the ground state bridge-bonded species are conventional single bonds.

The most unexpected feature of the μ methylene structures is the relatively long Aℓ-Aℓ bond. Specifically the DZ+P SCF prediction r_e = 3.610 Å is more than one angstrom longer than for the ground state of $A\ell_2$. Thus we are forced to re-examine the question "what is an Aℓ-Aℓ single bond?" In this regard it is helpful to note that the Aℓ-Aℓ distance in $A\ell_2(CH_3)_6$, which has the diborane structure,[50] is 2.60 Å, a value not too much longer than that (2.47 Å) found experimentally for the $^3\Sigma_g^-$ ground state of $A\ell_2$. Furthermore, similar Aℓ-Aℓ distances are found for several other carbon-bridged aluminum dimers.[50] Thus one concludes that a typical Aℓ-Aℓ single bond distance is ∿ 2.5 Å, and consequently that the Aℓ-Aℓ bond in bridging $A\ell_2CH_2$ is of bond order considerably less than unity.

The above established long Aℓ-Aℓ separation cannot be rationalized as a mechanism for avoiding a "tight"  ring structure. In fact the Aℓ-C-Aℓ bond angles, although not shown in Figure 3, are 128.5° (DZ SCF) and 131.5° (DZ+P SCF), significantly larger than would be expected from a model of tetrahedral carbon. For what might appear to be a plausible explanation of this long Aℓ-Aℓ bond, the reader is directed back to electron configuration (13), the no-bond quintet structure which arises when triplet methylene and $^3\Sigma_g^-$ ground state are brought together in a bridging C_{2v} arrangement. Recall that the first Aℓ-C bond was then constructed by pairing up the $8a_1$ and $9a_1$ orbitals in (13), and the second Aℓ-C bond somehow came into being when the $6b_1$ orbital was doubly occupied. Note that the singly-occupied $6b_1$ orbital in (13) is the carbon 2p orbital perpendicular to the HCH plane in the isolated triplet methylene fragment. This $1b_1$ orbital of methylene is called the methylene p orbital in Hoffmann's papers.[51] So, it must be asked "How did the $6b_1$ orbital become an Aℓ-C bonding orbital?" This question might in turn be answered by inquiring with which unoccupied orbitals of the $A\ell_2$ fragment can the methylene p (or $1b_1$) orbital interact. The unequivocal answer to the latter question is the $7b_1$ orbital of $A\ell_2CH_2$, the b_1 component (in C_{2v} symmetry) of the $2\pi_g$ antibonding orbital of $A\ell_2$.

The above argument suggests that the second Aℓ-C bond in bridging $A\ell_2CH_2$ might be formed by the interaction between the methylene p orbital and the antibonding $2\pi_g$ or $2\pi^*$ orbital of $A\ell_2$. Thus the total wave function would take on an additional amount of $A\ell$-$A\ell$ antibonding character with the attachment of the CH_2 bridge to $A\ell_2$. This in turn might explain the unusually long $A\ell$-$A\ell$ bond distance. If one pursues this oversimplified argument to the extreme and hypothesizes that the $6b_1$ orbital is 50% $A\ell_2$ π^* in character, then the overall complex would have an $A\ell$-$A\ell$ bond of order one-half. However, reference to the earlier discussions of the orbitals of the bridged closed-shell singlet shows that this view is not supported by the population analysis or, for that matter, by inspection of the wave function itself. The net positive charge (+1.29) on the $A\ell_2$ fragment mitigates against any significant population of its π^* antibonding orbital. The $A\ell_2$ π^* character is found to reside rather in the LUMO $7b_1$ orbital.

Given the electronic population analyses of Tables I and II, the long $A\ell$-$A\ell$ bond in bridging $A\ell_2CH_2$ is seen to be due to the decrease in aluminum 3p character relative to the isolated diatomic $A\ell_2$. Configuration (1) shows that for $A\ell_2$ each atom contributes one $2p\pi$ electron to the single bond. However, in $A\ell_2CH_2$, the $A\ell$ 3p population is reduced to 0.52 Mulliken electrons. Thus the carbene complex has lost significant bonding character relative to $A\ell_2$, and this results in a longer $A\ell$-$A\ell$ distance. The terminal $A\ell_2CH_2$ structure, in contrast, has about the same total aluminum 3p population. However, the $A\ell$-$A\ell$ distance in the terminal $A\ell_2CH_2$ is also increased (but to a much smaller degree) relative to naked $A\ell_2$. This is because for the terminal structure, the distribution of the (substantial) Aℓ 3p populations is quite unsymmetrical. That is, a significant fraction of the Aℓ 3p character is used to create bonding character between the adjacent Aℓ and C atoms. In summary, the Mulliken 3p populations suggests a 50% Aℓ-Aℓ bond for bridging $A\ell_2CH_2$, a 70% Aℓ-Aℓ bond for terminal $A\ell_2CH_2$, and a 100% bond for naked $A\ell_2$.

The structure of the CH_2 fragment within the tetrahedrally bridged $A\ell_2CH_2$ is much closer to that of isolated singlet methylene[52] [DZ SCF r_e(CH) = 1.103 Å, θ_e(HCH) = 106.6°] than were the previously discussed terminal $A\ell_2CH_2$ structures. Following our earlier line of reasoning, the CH_2 lone pair $3a_1$ population within the tetrahedral bridge is $3a_1^{1.68}$, or 0.18 Mulliken electrons greater than that found for the terminal closed-shell singlet structure. Thus the correlation of methylene bond angle with $3a_1$ population is seen to be of some value. However, were this correlation more quantitative, one would expect the CH_2 $3a_1$ population within tetrahedrally bridged $A\ell_2CH_2$ to be much closer to the value 2.0 inherent in the Hartree-Fock description of isolated singlet methylene.

The bridged structure in which all five atoms lie in a planar C_{2v} arrangement was also examined in some detail, and the DZ SCF theoretical structure is illustrated in Figure 2. The latter structure is stikingly different from the tetrahedrally bridged $A\ell_2CH_2$, which has an Aℓ-Aℓ distance 0.575 Å longer. In fact the Aℓ-Aℓ distance for the planar bridge is 3.031 Å, short enough to be labeled a weak single bond. To attempt to explain this large difference in Aℓ-Aℓ bond differences, one may again resort to considering the electron configuration of the $A\ell_2$ $^3\Sigma_g^-$ ground state, but this time in a third C_{2v} subgroup, which again retains the labeling of the molecular orbitals of the CH_2 fragment in (5) and (6):

$$^3B_1 \quad 1a_1^2\ 1b_2^2\ 2a_1^2\ 2b_2^2\ 1b_1^2\ 3a_1^2\ 4a_1^2\ 1a_2^2\ 3b_2^2\ 4b_2^2\ 5a_1^2\ 5b_2^2\ 2b_1\ 6a_1 \tag{16}$$

Comparison with electron configuration (5) for triplet CH_2 shows that the two $A\ell$-C bonds are trivially constructed by pairing up the $2b_1$ or $A\ell_2$ π orbital with the $1b_1$ or p orbital of CH_2 on the one hand; and the second component of the π orbital ($6a_1$) with the methylene $3a_1$ or lone pair orbital on the other hand. Since this introduces no $A\ell_2$ π^* antibonding character whatever into the wave function, one might not expect the dramatic increase in the $A\ell$-$A\ell$ distance that characterized the tetrahedrally-bridged closed-shell singlet state. However, there is still for the planar structure a significant increase relative to the $^3\Sigma_g^-$ $A\ell_2$ bond distance (2.662 Å). This is because the 2π orbital of $A\ell_2$ is used only to form a single $A\ell$-$A\ell$ bond for the diatomic, whereas for planar $A\ell_2CH_2$ these orbitals are also employed in constructing the two $A\ell$-C bonds.

The other noteworthy feature of the planar structure is its small HCH bond angle, only 97.0° at the DZ SCF level of theory. Again resorting to a Walsh like analysis, one finds the methylene a_1 orbital population to be 5.68 electrons. Subtracting off four electrons for the $1a_1$ and $2a_1$ orbitals, one assigns 1.68 Mulliken electrons to the CH_2 fragment $3a_1$ orbital. Since this is the same $3a_1$ population as found for the tetrahedrally bridged structure, it is clear that the correlation between CH_2 angle and $3a_1$ fragment population is not valid in this case. In this sense, such a correlation appears to be of far more value for the terminal metal carbene systems[22,44] than for bridging methylenes. For those wishing to pursue this matter further, the predicted DZ SCF Mulliken populations for all five $A\ell_2CH_2$ structures are given in Table II.

Relative Energies

A summary of relative energies of the different $A\ell_2CH_2$ species is given in Table III. At the DZ SCF equilibrium geometry, the absolute energies (in hartrees) of the tetrahedrally bridged structure are -522.78123 (DZ SCF), -522.94351 (DZ CI), -522.96171 (Davidson corrected DZ CI), -522.80629 (DZ+P SCF), -523.03495 (DZ+P CI), and -523.06145 (Davidson corrected DZ+P CI). Note of course that the Davidson correction[39] for higher excitations (unlinked clusters) gives a nonvariational result, so the absolute energy in such cases is not an upper bound to the exact energy.

Perhaps the most interesting result seen in Table III is the relatively small energy difference between the bridging closed-shell singlet structures corresponding to tetrahedral and planar carbon. At the highest level of theory, Davidson corrected DZ+P CI, this energy difference is predicted to be 30.8 kcal. For the prototype hydrocarbon CH_4, of course, this tetrahedral-planar energy difference is much greater, ∿ 150 kcal.[53] However, Pople and Schleyer[54] have shown that a suitable choice of substituents (as in CH_2Li_2) can reduce the tetrahedral carbon-planar carbon energy difference even below the 31 kcal reported here for $A\ell_2CH_2$, and in a few cases reverse the ordering completely. For the $A\ell_2CH_2$ molecule itself, it is important to state that explorations about the planar bridged stationary point geometry showed this structure not to be an equilibrium geometry, but presumably a transition state for rotation of the methylene group about the C_2 axis.

The only striking qualitative change in the relative energies of Table III due to electron correlation is the reversal of the ordering of the terminally bound electronic states. At both the DZ SCF and DZ+P SCF levels of theory, the two triplet states are predicted to lie below the closed-shell singlet state. However, in every case the introduction of correlation effects causes the singlet to become the ground electronic state of the terminal isomer. At the highest level of theory, the $^3A_2$ (first excited) state is predicted to lie 11.8 kcal above the closed-shell singlet.

The most important single prediction of this paper is that the bridging isomer of $A\ell_2CH_2$ lies significantly below the terminal isomer. At the highest level of theory employed here, this energy difference is 45.8 kcal. Thus it is seen that for $A\ell_2CH_2$ two $A\ell$-C single bonds (bridging structure) provide significantly more binding than does a single Aℓ=C double bond (terminal structure). This observation begs the question, "Just how strong is the π bond in $A\ell{-}A\ell{=}CH_2$?"

An attempt was made to answer the above question at all six levels of theory. It should be noted at the outset that all levels of theory used here are expected to underestimate the true dissociation energy, and the most sophisticated (Davidson corrected DZ+P CI) could very well predict an Aℓ=C bond energy that is still 10 kcal less than the exact (unknown) value. The dissociation energy in question here is specifically the energy difference between $^3\Sigma_g^-$ $A\ell_2$ plus $^3B_1$ CH_2 infinitely removed and the $^1A_1$ closed-shell ground state of terminally bound $A\ell{-}A\ell{=}CH_2$. Given this background the predicted dissociation energies are 48.0 kcal (DZ SCF), 68.9 kcal (DZ CI), 71.9 kcal (Davidson corrected DZ CI), 51.6 kcal (DZ+P SCF), 76.8 kcal (DZ+P CI), and 80.5 kcal (Davidson corrected DZ+P CI).

The most completely reliable variational prediction for the Aℓ=C double bond dissociation energy is 76.8 kcal, to be compared with D_e(Aℓ-C) = 77.4 kcal predicted earlier[22] for the single-bonded $A\ell CH_2$ ground state at the DZ+P CI level of theory. However, it should be emphasized that the $A\ell{-}CH_2$ bond cited is somewhat stronger than the typical Aℓ-C single bond, which is more realistically modeled by the $A\ell{-}CH_3$ system, for which the predicted DZ+P CI dissociation energy is 68 kcal. Therefore, it would appear that the π bond in $A\ell{-}A\ell{=}CH_2$ contributes on the order of 10 kcal to the Aℓ-C bond energy. Should this π bond be comparably weak for other

other terminally bound metal-carbene systems, a ready explanation for the preference for bridge bonding is at hand.

Vibrational Frequencies

In principle, theoretical vibrational frequencies can provide a useful fingerprint for the detection of new molecules. In the present case, the $A\ell_2CH_2$ vibrational frequencies may also be quite pertinent to the (eventually) observed vibrational frequencies on metal surfaces.[55] Thus one would expect some of the frequencies of terminal and bridging $A\ell_2CH_2$ to resemble those of methylene chemisorbed in terminal or two-fold bridging sites, respectively, on an aluminum surface (and perhaps on other metal surfaces as well). The harmonic vibrational frequencies of the ground and lowest triplet states of terminal $A\ell_2CH_2$ and of the ground state of bridging $A\ell_2CH_2$ have therefore been predicted at the DZ SCF level, consistent with our earlier study[22] of $A\ell CH$, $A\ell CH_2$, and $A\ell CH_3$. Moreover, since the latter study attracted some interest from surface vibrational spectroscopists,[56] the frequencies of the bridging structure (our lowest energy potential minimum for $A\ell_2CH_2$) were also predicted at the DZ+P SCF level of theory. The theoretical vibrational frequencies are reported in Table IV. The reader should keep in mind the fact that DZ SCF and DZ+P SCF vibrational frequencies are typically $\sim$ 8% higher than the exact harmonic frequencies[57], and that anharmonicity effects will lower the harmonic frequencies several percent further. Thus one may expect the harmonic frequencies predicted here to be perhaps 11% higher than the experimental (as yet unobserved) fundamentals.

It should be noted first that the DZ SCF and DZ+P SCF vibrational frequencies are in reasonable agreement. For example, the energetic ordering by symmetry type is the same. The largest differences between the two sets of predictions are for the CH_2 wag (b_1) and CH_2 twist (a_2) frequencies, both of which are reduced by 100 cm^{-1} by the addition of polarization functions to the basis set. Likewise the CH_2 rocking frequency (b_2) is reduced by 90 cm^{-1} in the larger basis set. Nevertheless, the good qualitative agreement gives us confidence in the earlier reported[22] $A\ell CH_3$, $A\ell CH_2$, and $A\ell CH$ vibrational frequencies, for which only the smaller DZ basis was used.

Before proceeding, it must be noted that the previous reported[22] vibrational frequencies for $A\ell CH_2$ were inadvertantly mislabeled. The proper labels are CH_2 scissor (1070 cm^{-1}), CH_2 wag (660 cm^{-1}), $A\ell$-C stretch (640 cm^{-1}), and CH_2 rock (630 cm^{-1}). This does not affect the discussion in our earlier paper, but does mean that the $A\ell$-C stretching frequencies for the $A\ell CH_3$ (600 cm^{-1}), $A\ell CH_2$ (640 cm^{-1}), and $A\ell CH$ (670 cm^{-1}) ground electronic states now form a monotonic series.

Next we turn to a comparison between the terminally bound $A\ell_2CH_2$ frequencies and those reported earlier[22] for $A\ell CH_2$. For the $A\ell$-C stretching mode the $^1A_1$ ground state $A\ell_2CH_2$ frequency is 890 cm^{-1}, significantly greater than the 640 cm^{-1} predicted for the smaller $A\ell CH_2$ system. This would appear to indicate a somewhat stronger bond between $A\ell_2$ and CH_2 than between $A\ell$ and CH_2, a result consistent with the trend in $A\ell$-C bond distances.

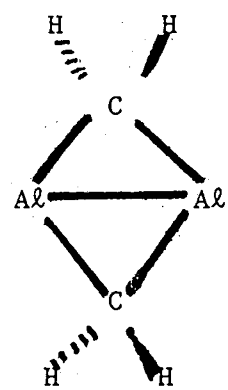
Note that the Aℓ-C bond energies are essentially comparable for $A\ell_2CH_2$ and $A\ell CH_2$. The new modes in $A\ell_2CH_2$ (i.e., those not present in $A\ell CH_2$) are the Aℓ-Aℓ stretch at 220 cm^{-1} and the two Aℓ-Aℓ-C bending modes at 100 and 70 cm^{-1}. For a cluster such as $A\ell_{10}CH_2$ or for aluminum surface–CH_2 systems, there would be additional metal atoms coordinated to each Aℓ atom and this could of course raise these low frequency normal modes, particularly the bending frequencies.

For the tetrahedrally bridged closed shell singlet $A\ell_2CH_2$ the predicted CH stretching frequencies are significantly lower (by 110-260 cm^{-1}) than obtained for either $A\ell CH_2$ or terminal $A\ell_2CH_2$. This suggests reasonably enough that the $A\ell_2$ fragment strongly perturbs the methylene group in the μ-methylene structure. The asymmetric and symmetric carbon-aluminum stretching frequencies are predicted, at 680 and 490 cm^{-1}, to be significantly split. Both lie in the general vicinity of the terminal Aℓ-C stretching frequency predicted for $A\ell CH_2$ (640 cm^{-1}), but significantly below that suggested for $A\ell_2CH_2$ (890 cm^{-1}). Rotation of the methylene bridge is seen to be strongly discouraged by the torsional frequency predicted at 800 cm^{-1} (700 cm^{-1} with the larger DZ+P basis set). The lowest frequency for the tetrahedrally bridging global minimum is 180 cm^{-1} (DZ) or 170 cm^{-1} (DZ+P) and may be described as either the Aℓ-Aℓ stretch or the $CA\ell_2$ scissors motion. Finally, relative to the terminal $A\ell_2CH_2$ structure, the bridging CH_2 frequencies are shifted down (scissors 1510→1470 cm^{-1}), up (wag 800→920 cm^{-1}), and down (rock 610→480 cm^{-1}), respectively.

Concluding Remarks

For the model metal dimer-methylene system studied here the bridging CH_2 structure has been shown to lie ∿ 46 kcal lower in energy than the terminally bound isomer. The reason is very simple, namely that the second M-C σ bond is the bridging structure is significantly stronger than the M-C π bond of the terminal structure. Although this result was obtained specifically for the $A\ell_2CH_2$ system, one expects the same qualitative trend to hold up elsewhere, a view supported by the fact that very few terminal carbene structures have been reported experimentally for binuclear or polynuclear organotransition metal species.[21]

A perhaps unexpected feature found for the bridging $A\ell_2CH_2$ structure (explained in terms of qualitative molecular orbital theory) is its long Aℓ-Aℓ bond. One naturally wonders whether the addition of a second bridging methylene, to form



(17)

might reduce the Aℓ-Aℓ distance to that of a more normal single bond. The di-μ-carbene complex (17) is also of interest in that it is a saturated molecule, with each aluminum atom being trivalent. More over, such di-μ-carbene complexes are now being prepared in the laboratory, as evidenced by the recently obtained crystal structure[58] of the ruthenium dimer $Ru_2(CO)_2(\mu\text{-CHMe})(\mu\text{-CMe}_2)Cp_2$, for which the dicarbene metal framework Ru_2C_2 is very nearly planar. As a model for such systems, the $A\ell_2(CH_2)_2$ molecule would appear an attractive target for future theoretical studies.

Acknowledgments

This research was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract Number DE-AC03-76SF00098.

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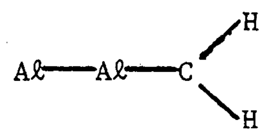
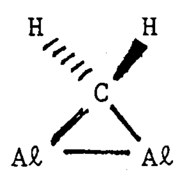
Table I. Valence electron orbital energies (in hartrees) and qualitative descriptions of the occupied molecular orbitals of the ground states of two $A\ell_2CH_2$ isomers.



Designation	Orbital Energy	Description
$8a_1$	-0.8351	methylene $2a_1$ orbital
$3b_2$	-0.5120	methylene $1b_2$ orbital
$9a_1$	-0.4977	$A\ell$ dimer $3s\sigma_g$ + CH_2 $3a_1$
$10a_1$	-0.4417	$A\ell$ dimer $3s\sigma_u$ + CH_2 $3a_1$
$11a_1$	-0.2822	$A\ell$ dimer $3s\sigma_u$
$3b_1$	-0.2337	$A\ell$ $3p\pi$ + CH_2 $1b_1$



Designation	Orbital Energy	Description
$6a_1$	-0.8929	methylene $2a_1$ orbital
$2b_2$	-0.5323	methylene $1b_2$ orbital
$5b_1$	-0.4677	$A\ell$ dimer $3s\sigma_u$ + CH_2 $1b_1$
$7a_1$	-0.4665	$A\ell$ dimer $3s\sigma_g$ + CH_2 $3a_1$
$8a_1$	-0.2942	$A\ell$ dimer $3s\sigma_g$ + CH_2 $3a_1$
$6b_1$	-0.2575	$A\ell$ dimer $3s\sigma_u$ + CH_2 $1b_1$

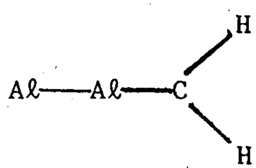
Table II. Summary of Mulliken population analyses for five $A\ell_2CH_2$ geometrical structures.

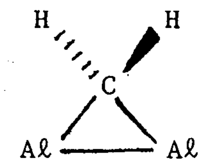
Terminal Structures	CH_2 a_1	CH_2 b_2	CH_2 b_1	$A\ell_1$ 3s	$A\ell_1$ 3p	$A\ell_1$ total	$A\ell_2$ 3s	$A\ell_2$ 3p	$A\ell_2$ total
$^1A_1$	5.50	1.98	1.27	1.89	0.69	12.59	1.20	1.47	12.67
$^3A_2$	5.63	1.97	0.94	1.91	0.92	11.82	1.48	1.15	12.63
$^3A_1$	5.65	1.99	0.95	1.97	1.05	13.02	1.69	0.69	12.39
Bridging Structures									
Planar	5.68	1.91	1.59	1.89	0.52	12.41	1.89	0.52	12.41
Perpendicular	5.68	1.98	1.63	1.84	0.52	12.36	1.84	0.52	12.36

Table III. Relative energies of different isomers and electronic states of $A\ell_2CH_2$. The geometry in each case is the DZ SCF stationary point structure appropriate to the individual species. All energies are in kcal/mole relative to the tetrahedral bridge closed-shell ground state.

Structure	DZ SCF	DZ CI	Davidson Corrected DZ CI	DZ+P SCF	DZ+P CI	Davidson Corrected DZ+P CI
$^3A_1$ terminal	43.1	55.3	57.1	44.8	60.9	63.6
$^3A_2$ terminal	41.1	51.2	52.6	41.5	55.6	57.7
$^1A_1$ terminal	47.9	43.0	40.9	47.9	47.3	45.9
planar bridge	33.9	29.3	28.1	32.4	31.1	30.8
tetrahedral bridge	0.0	0.0	0.0	0.0	0.0	0.0

Table IV. Predicted harmonic vibrational frequencies (in cm^{-1}) for $A\ell_2CH_2$.





	$^1A_1$ State	$^3A_2$ State	Normal Mode
b_2	3340	3340	CH asym. stretch
a_1	3250	3240	CH sym. stretch
a_1	1510	1520	CH_2 scissor
a_1	890	700	Aℓ-C stretch
b_1	800	690	CH_2 wag
b_2	610	650	CH_2 rock
a_1	220	180	Aℓ-Aℓ stretch
b_2	100	50	Aℓ-Aℓ-C in-plane bend
b_1	70	90	Aℓ-Aℓ-C out-of-plane bend

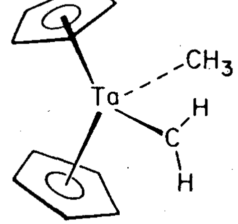
	DZ SCF	DZ+P SCF	Normal Mode
b_2	3080	3080	CH asym. stretch
a_1	3030	3030	CH sym. stretch
a_1	1470	1430	CH_2 scissor
b_1	920	820	CH_2 wag
a_2	800	700	CH_2 twist (torsion)
b_2	680	670	CAℓ asym. stretch
a_1	490	480	CAℓ sym. stretch
b_2	480	390	CH_2 rock
a_1	180	170	Aℓ-Aℓ stretch or $CA\ell_2$ bend (scissor)

Figure Captions

Figure 1. Experimentally known organometallic compounds incorporating the unsubstituted methylene as a ligand.

Figure 2. Theoretical molecular structures for various conformations and electronic states of $A\ell_2CH_2$. All results in this figure were obtained at the double zeta (DZ) basis set, self-consistent-field (SCF) level of theory. Bond distances are in Å.

Figure 3. Ground state geometrical structure of $A\ell_2CH_2$ predicted at two different levels of theory. Bond distances are in Å.



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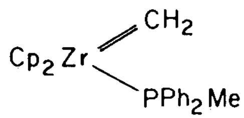

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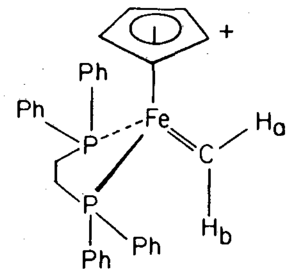

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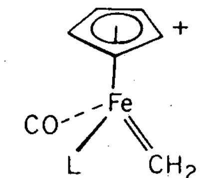

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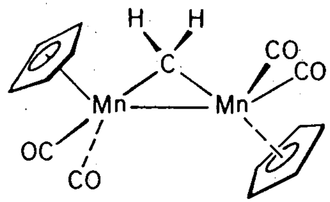

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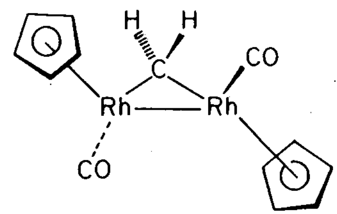

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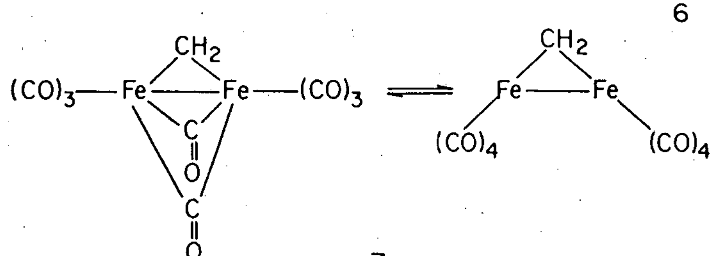

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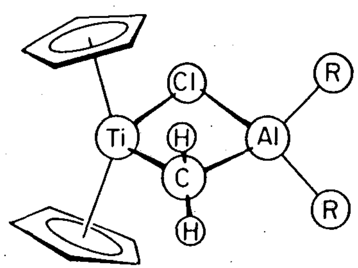

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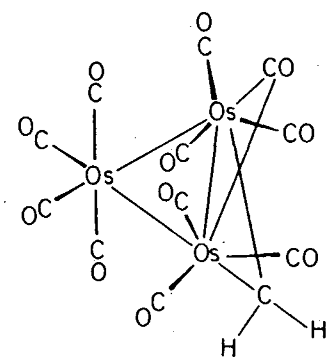

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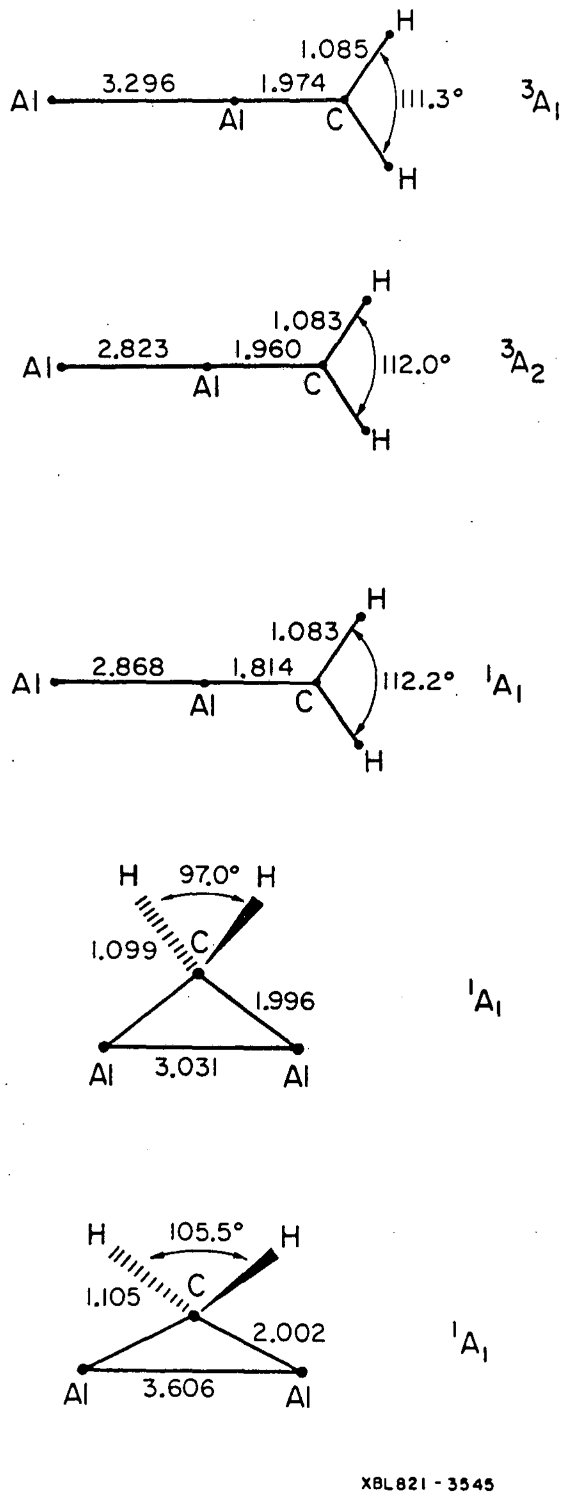
Figure 1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1.085
Al
3.296
1.974
Al
C
111.3°
H
$^3A_1$
H
1.083
Al
2.823
1.960
Al
C
112.0°
H
$^3A_2$
H
1.083
Al
2.868
1.814
Al
C
112.2°
H
$^1A_1$
H
97.0°
H
1.099
C
1.996
Al
3.031
Al
$^1A_1$
H
105.5°
H
1.105
C
2.002
Al
3.606
Al
$^1A_1$
XBL 821 - 3545

Figure 2

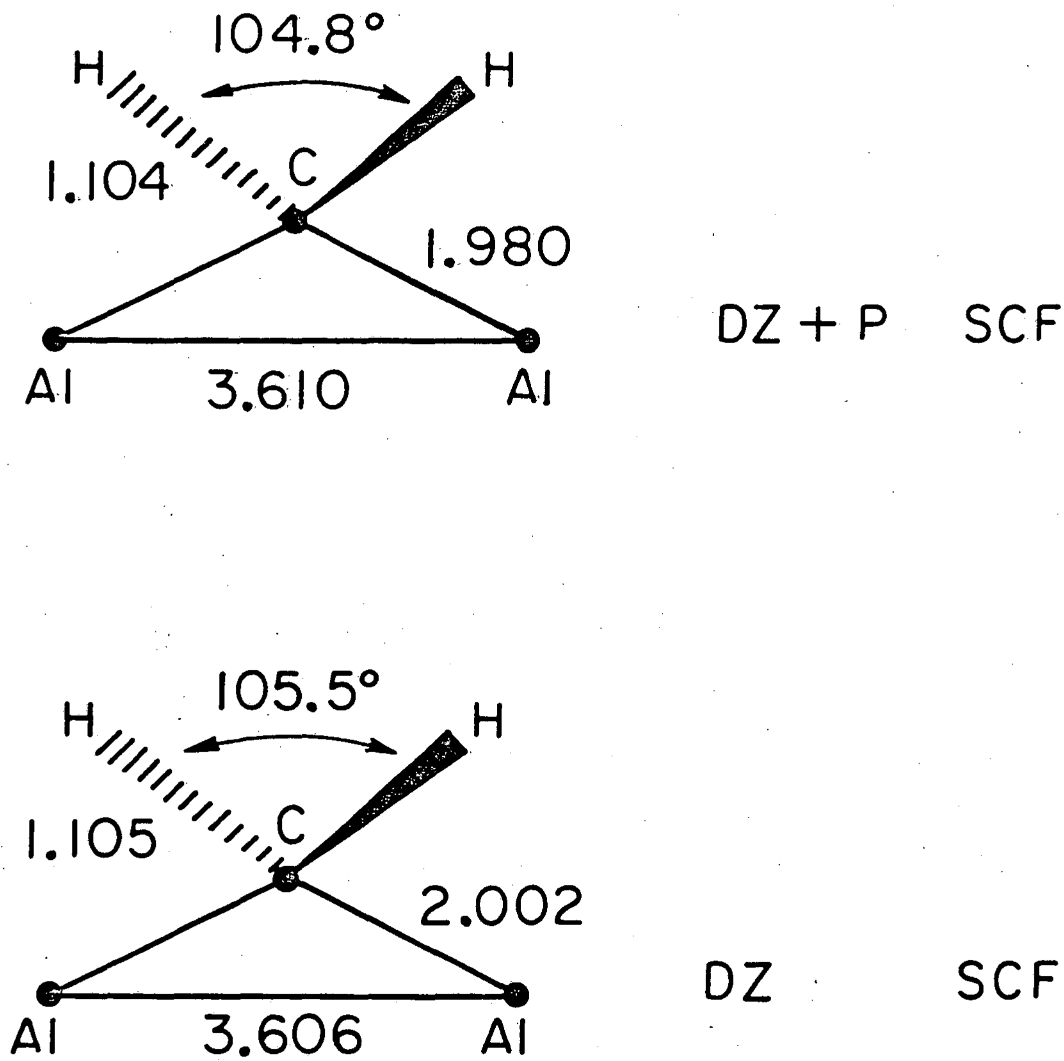

Figure 3

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