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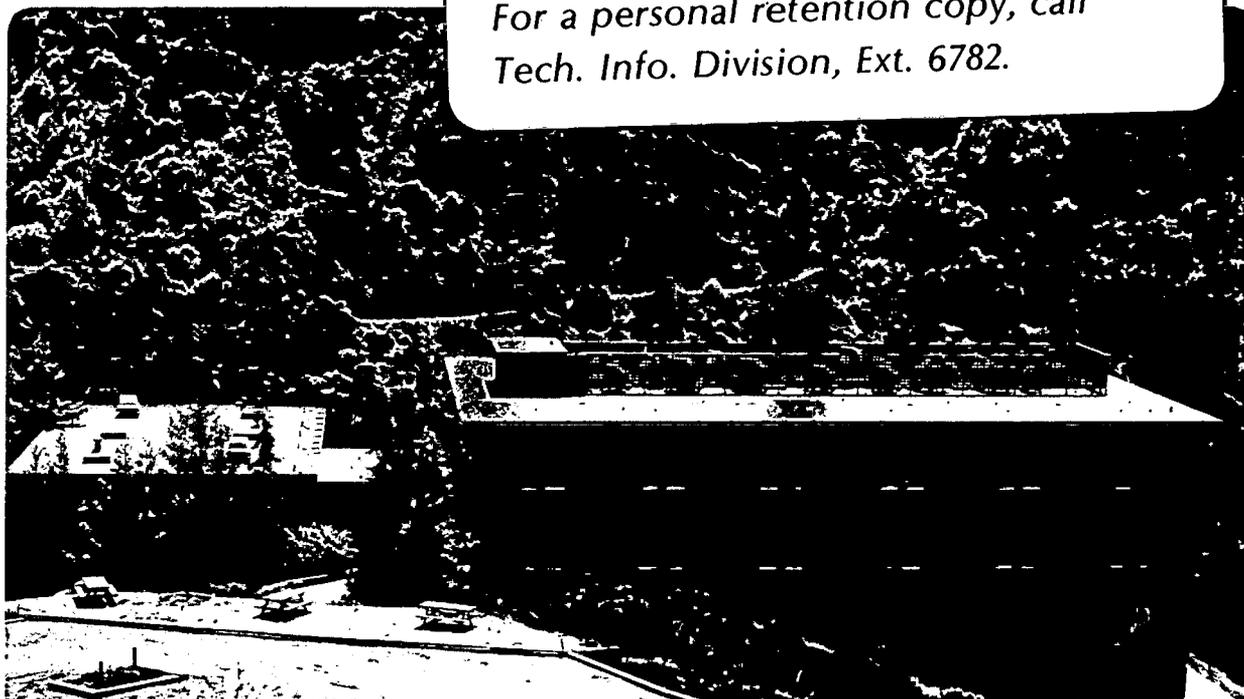
TERMINAL vs. BRIDGE BONDING OF METHYLENE TO METAL  
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## Terminal vs. Bridge Bonding of Methylene to Metal Systems.

 $Al_2CH_2$  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  $M \begin{array}{c} CH_2 \\ \diagup \quad \diagdown \\ \quad \quad \quad \end{array} M$  geometrical structures. Having previously studied the terminal  $Al-CH$ ,  $Al-CH_2$ , and  $Al-CH_3$  metal-organic fragment species, the  $Al_2CH_2$  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  $Al \begin{array}{c} C \\ \diagdown \quad \diagup \\ \quad \quad \quad \end{array} Al$  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

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surface and has  $r_e(\text{Al}-\overset{\circ}{\text{Al}}) = 2.87 \text{ \AA}$ ,  $r_e(\text{Al}-\overset{\circ}{\text{C}}) = 1.81 \text{ \AA}$ , and a methylene bond angle of  $112.2^\circ$ . 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  $\text{AlCH}_2$ . However, for the bridging  $\text{Al}_2\text{CH}_2$ , the  $\text{Al}_2 \cdots \text{CH}_2$  dissociation energy is much larger, 127 kcal. Vibrational frequencies for the bridging and terminal  $\text{Al}_2\text{CH}_2$  species are presented and discussed.

### Introduction

The first mononuclear transition metal methylene complex,  $\text{Cp}_2\text{TaCH}_3\text{CH}_2$ , was synthesized<sup>1</sup> (and its crystal structure  $\underset{\sim}{1}$  simultaneously reported<sup>2</sup>) by Schrock in 1975. However, during the intervening six years, only one other terminally bonded neutral methylene complex, the  $\text{Cp}_2\text{Zr}(\text{PPh}_2\text{Me})\text{CH}_2$  molecule  $\underset{\sim}{2}$  of Schwartz and Gell,<sup>3</sup> has been reported. In addition, a single cationic methylene complex  $\underset{\sim}{3}$ ,  $\text{Cp}[\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2]\text{FeCH}_2^+$ , was characterized in 1980 by Brookhart, Tucker, Flood, and Jensen.<sup>4</sup> A simpler cationic carbene  $\text{CpFe}(\text{CO})_2\text{CH}_2^+$  was quite likely generated as a transient by Jolly and Petit<sup>5</sup> as early as 1966 and reported to react with several olefins to yield cyclopropanes. However, compound  $\underset{\sim}{4}$  has resisted spectroscopic characterization thus far, although the sulfide  $\text{CpFe}(\text{CO})_2\text{CH}_2\text{SCH}_3$  has been developed<sup>6</sup> as a stable precursor to  $\underset{\sim}{4}$ .

The very first transition metal methylene complex reported in the literature was not a terminal structure at all but rather  $\underset{\sim}{5}$ , the bridged molecule  $[\text{CpMn}(\text{CO})_2]_2\text{CH}_2$  of Herrmann, Reiter, and Biersack.<sup>7</sup> 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  $\underset{\sim}{5}$ . Since 1975, quite a number of additional neutral bridging  $\text{CH}_2$  organometallics have been synthesized. Among these, the rhodium complex<sup>8</sup>  $\underset{\sim}{6}$  is analogous to  $\underset{\sim}{5}$ , with the two additional valence electrons of the Rh atoms relative to Mn allowing (in the sense of the 18 electron rule<sup>9</sup>) the displacement of two CO groups.

Moreover, the cobalt complex completely analogous to  $\underset{\sim}{6}$  has very recently been synthesized by Theopold and Bergman,<sup>10</sup> along with the heterobinuclear Co-Rh  $\mu$ -methylene complex.

The simplest (constructed exclusively from Fe, CO, and CH<sub>2</sub> components) and most elegant bridging transition metal methylene complex synthesized to date is  $\underset{\sim}{7}$ , the Fe<sub>2</sub>(CO)<sub>8</sub>CH<sub>2</sub> molecule.<sup>11</sup> In solution, only terminal IR vibrational frequencies are observed, suggesting that the structure therein is  $\underset{\sim}{7b}$ . However, under other circumstances, the structure  $\underset{\sim}{7a}$  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<sub>2</sub> group.

A number of more complicated bridging methylene complexes, involving two<sup>12-17</sup> or three<sup>18-21</sup> metal atoms, have been synthesized. Of the binuclear compounds  $\underset{\sim}{8}$  (R=CH<sub>3</sub>)<sup>12</sup> is of particular relevance to the present study, since one of the two metal atoms which the CH<sub>2</sub> bridges is an aluminum. Among the trinuclear methylene complexes, the Os<sub>3</sub>(CO)<sub>11</sub>CH<sub>2</sub> molecule<sup>20</sup>  $\underset{\sim}{9}$  is impressive in its simplicity in the same sense that Petit's Fe<sub>2</sub>(CO)<sub>8</sub>CH<sub>2</sub> is thus far unique. Shapley and co-workers<sup>20</sup> have found that upon pyrolysis, it is possible to remove from  $\underset{\sim}{9}$  a single CO ligand, yielding the coordinately unsaturated Os<sub>3</sub>(CO)<sub>10</sub>CH<sub>2</sub>. 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.<sup>15</sup>

The weight of the evidence<sup>1-20</sup> 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.<sup>21</sup> 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<sup>22</sup> of  $AlCH$ ,  $AlCH_2$ , and  $AlCH_3$  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  $Al-C$  bond order possible, namely triple ( $Al\equiv CH$ ), double ( $Al\equiv CH_2$ ), and single ( $:Al-CH_3$ ) 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  $AlCH_3$  to  $AlCH$ , namely an increase in the predicted dissociation energy from 68 to 88 kcal and decrease in the  $Al-C$  bond distance by 0.039 Å. But the overall picture for each of the three model species is that of an  $Al-C$  single bond.

Given these theoretical predictions<sup>22</sup> for  $AlCH$ ,  $AlCH_2$ , and  $AlCH_3$ , we have a standard of comparison by which to judge the  $Al_2-CH_2$  system, which is the subject of the present paper.

That is, now that a reasonable understanding of the isolated Al-C terminal bond is at hand, one can compare this both with the terminal M-M-CH<sub>2</sub> results (as noted in the Introduction, very few such molecules have yet been synthesized) and with those for the bridging M'<sup>CH<sub>2</sub></sup>-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  $\delta$ , 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<sup>23</sup> that main group metals (such as aluminum) are not as different from transition metals as is popularly assumed.

#### Theoretical Approach

Although the Al<sub>2</sub>CH<sub>2</sub> 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.<sup>22</sup> 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  $\text{AlCH}_n$  ( $n=1-3$ ), the standard Dunning-Hay<sup>24</sup> DZ basis, designated  $\text{Al}(11s\ 7p/6s\ 4p)$ ,  $\text{C}(9s\ 5p/4s\ 2p)$ ,  $\text{H}(4s/2s)$ . Certain molecular structures were subsequently reoptimized at the double zeta plus polarization (DZ+P) SCF level and the polarization function orbital exponents chosen were  $\alpha_d(\text{C}) = 0.75$ ,  $\alpha_d(\text{A}) = 0.6$ , and  $\alpha_p(\text{H}) = 1.0$ , as in the previous study.<sup>22</sup> All geometrical structures were optimized using closed- and open-shell SCF analytic gradient techniques.<sup>25,26</sup> Subsequently, quadratic force constants in terms of cartesian coordinates were evaluated as central differences of analytic forces and subjected to standard harmonic vibrational analyses.<sup>27</sup>

Given the stationary point geometries determined at the SCF level of theory, relative energies of the various species were examined using correlated wave functions.<sup>28</sup> In the configuration interaction (CI) procedure, the eleven lowest occupied SCF molecular orbitals ( $\text{Al}\ 1s, 2s, 2p; \text{C}\ 1s$ ) 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<sup>29</sup> single and double excitations relative to the appropriate SCF reference configuration. Since all stationary points have  $\text{C}_{2v}$  symmetry, the number of configurations is not excessive, the maximum being 13,955 for the terminal-bonded  $^3\text{A}_2$  state of  $\text{Al}_2\text{CH}_2$ . The correlated wave functions were obtained via

the graphical unitary group approach.<sup>30</sup>

Diatomic Aluminum

Before embarking on our discussion of  $Al_2CH_2$ , it is appropriate to give some attention to the naked aluminum dimer. In addition, since there is some experimental data available for  $Al_2$ , it may be possible to obtain some insight into the reliability of the theoretical methods adopted here.

The definitive work of Dupuis and Liu<sup>32</sup> on the isoelectronic  $B_2$  molecule, together with the experimental background<sup>31</sup> on  $Al_2$ , give us a clear idea of the expected low-lying electronic states of the latter. The observed electronic transition ( $T_e = 17,270 \text{ cm}^{-1}$ ) for  $Al_2$  is  $X \ ^3\Sigma_g^- - A \ ^3\Sigma_u^-$ , and these two states arise from the electron configurations

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

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

The equilibrium bond distances are known to be  $r_e = 2.466 \text{ \AA}$  and  $r_e = 2.560 \text{ \AA}$ , respectively and the ground state dissociation energy is  $\sim 1.6 \text{ eV}$ ,<sup>31</sup> suggesting a single bond between the two aluminum atoms. However, there are other candidates for the  $Al_2$  ground state. Following previous work<sup>32-34</sup> on  $B_2$ , one appreciates (in light of Hund's rules) that the  $^5\Sigma_u^-$  state,



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<sup>35</sup> brought to our attention a low-lying  ${}^3\Pi_u$  state, arising from the electron configuration



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  ${}^3\Pi_u$  ( $r_e = 2.912 \text{ \AA}$ ), followed by  ${}^3\Sigma_g^-$  ( $r_e = 2.661 \text{ \AA}$ ), followed by  ${}^5\Sigma_u^-$  ( $r_e = 2.372 \text{ \AA}$ ). The same ordering of states was found at the DZ+P SCF level of theory, with the predicted bond distances being  $2.815 \text{ \AA}$  ( ${}^3\Pi_u$ ),  $2.592 \text{ \AA}$  ( ${}^3\Sigma_g^-$ ), and  $2.349 \text{ \AA}$  ( ${}^5\Sigma_u^-$ ). The results appear to establish conclusively within that 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<sup>35</sup> (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.<sup>31</sup>

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  $0.195 \text{ \AA}$  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.<sup>36</sup> For example, for thioformaldehyde ( $\text{H}_2\text{C}=\text{S}$ ) the DZ basis set strictly analogous to the present one yields a bond distance<sup>37</sup> of 1.637 Å, in reasonable agreement with experiment,<sup>38</sup> 1.611 Å. Therefore it was decided to further pursue the  $\text{Al}_2$  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<sup>39</sup> for the effect of higher excitations yields  $r_e(\text{Al}-\text{Al}) = 2.496$  Å, a bond distance only 0.030 Å 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  $\text{Al}_2$ . In this regard it may be noted that correlation effects reduce the  $\text{Al}-\text{Al}$  distance by about 0.1 Å, whereas for normal closed-shell molecules the typical result<sup>40</sup> 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<sup>41</sup> 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  $\text{Al}_2$  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  $Al_2CH_2$  might also be somewhat longer than the true (as yet unknown) bond distances.

### Terminally Bound Methylene Structures

Structures of the general type Al-Al-CH<sub>2</sub> correspond in a qualitative sense to the previously studied Al-CH<sub>2</sub> molecule.<sup>22</sup> Perhaps the simplest intuitive way to think about the electronic structures of Al<sub>2</sub>CH<sub>2</sub> is in terms of the molecular orbitals of the Al<sub>2</sub> and CH<sub>2</sub> fragments. The triplet ground state of methylene arises from the electron configuration



while the first excited state, lying only about 9 kcal higher,<sup>43</sup> emanates from



Since the terminally bonded Al<sub>2</sub>CH<sub>2</sub> structures are expected to have C<sub>2v</sub> symmetry, the next step is to resolve the Al<sub>2</sub> ground state electron configuration (1) into C<sub>2v</sub> symmetry. When this

resolution<sup>42</sup> is carried out in a manner consistent with the  $C_{2v}$  symmetry operations implicit in the nuclear arrangement

$Al-Al-CH_2$ , one obtains

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

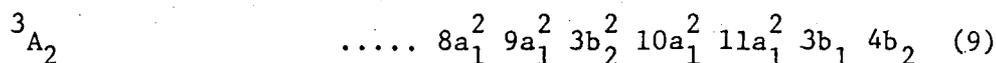
That is, the term symbol  ${}^3\Sigma_g^-$  for the full  $D_{\infty h}$  symmetry becomes  ${}^3A_2$  for the  $C_{2v}$  subgroup specified above.

Perhaps the simplest merger of the ground states (5) and (7) of  $CH_2$  and  $Al_2$  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

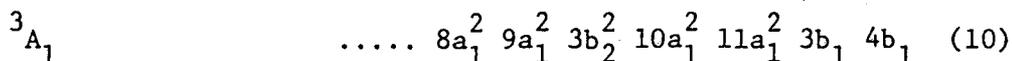
$${}^5B_2 \quad \dots \quad 8a_1^2 \quad 9a_1^2 \quad 3b_2^2 \quad 10a_1^2 \quad 11a_1 \quad 3b_1 \quad 4b_1 \quad 4b_2 \quad (8)$$

However, if one assumes that the  $Al_2$  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  $Al_2CH_2$ . In like manner, as long as the  $11a_1$  orbital of  $Al_2CH_2$  (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  $Al_2$ . 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  $Al_2$ . 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  ${}^3\Sigma_g^-$   $Al_2$ . Alternately, one of the low-lying electronic states of  $Al_2CH_2$  may be envisioned as arising from the merger of ground state  $Al_2$  (7) and singlet methylene (6):

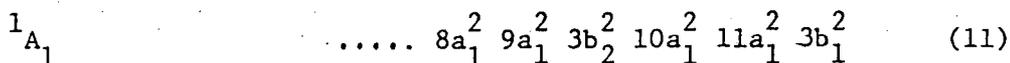


Theoretical exploration of a number of other possible electronic states of  $Al-Al-CH_2$  also showed the  ${}^3A_1$  state



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



which turns out to be the ground electronic state for terminally

bound  $\text{Al}_2\text{CH}_2$ . 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  $\text{Al-Al-CH}_2$  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  $\text{Al}_2\text{-CH}_2$  bonding character. Moreover, the higher lying  $11a_1$  orbital is primarily the  $\text{Al}_2$   $3\sigma_u$  orbital. However, the HOMO, the  $3b_1$  orbital, is a bonding orbital mixing the  $\text{Al}_2$   $\pi$  orbital with the  $\text{CH}_2$  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  $\text{Al}_2$   $3s\sigma_u + \text{CH}_2$   $3a_1$ , in fact the aluminum 3s population on the end Al 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  $\text{Al}_2$  is not strongly populated. More quantitatively, the total Al 3p populations on the end and central Al atoms are 0.69 and 1.20 Mulliken electrons, respectively, and most of this occurs in the above mentioned  $3b_1$   $\pi$ -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  $\text{Al}_2\text{CH}_2$ . This figure shows clearly that the Al-C bond distance for the closed-shell singlet ground state corresponds to that of a true double bond. The predicted  $r_e(\text{Al}=\text{C}) = 1.814 \text{ \AA}$  is much less than the  $2.013 \text{ \AA}$

obtained<sup>22</sup> at the same level of theory for the prototype Al-C single bond in AlCH<sub>3</sub>. Moreover the predicted 1.814 Å agrees well with the 1.802 Å found<sup>22</sup> for the first excited electronic state of AlCH<sub>2</sub>, and the latter state was shown to display a double bond, albeit ~ 21 kcal above the AlCH<sub>2</sub> ground state, which is singly-bonded. Thus a primary difference between Al<sub>2</sub>CH<sub>2</sub> and the previously studied AlCH<sub>2</sub> 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 Al<sub>2</sub>CH<sub>2</sub> do not display Al=C double bonds. Indeed the <sup>3</sup>A<sub>2</sub> and <sup>3</sup>A<sub>1</sub> r<sub>e</sub>(Al-C) distances of 1.960 Å and 1.974 Å fall nicely between the "short single bond" of the AlCH<sub>2</sub> ground state (1.938 Å) and the prototype 2.013 Å predicted for AlCH<sub>3</sub>. This supports the notion that the 3b<sub>1</sub> molecular orbital (doubly-occupied in the closed-shell ground state) is a π-bonding Al-C orbital, while the 4b<sub>1</sub> and 4b<sub>2</sub> 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 Al<sub>2</sub> in its <sup>3</sup>Σ<sub>g</sub><sup>-</sup> ground state, all three Al<sub>2</sub>CH<sub>2</sub> distances are longer. Since the ground state of Al<sub>2</sub> is thought to represent a single bond, logic would suggest that the <sup>1</sup>A<sub>1</sub> ground state (2.868 Å) and <sup>3</sup>A<sub>2</sub> excited

state ( $2.823 \text{ \AA}$ ) represent somewhat weaker Al-Al single bonds. However, the Al-Al distance for the  $^3A_1$  state ( $3.296 \text{ \AA}$ ) 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  $Al_2CH_2$ .

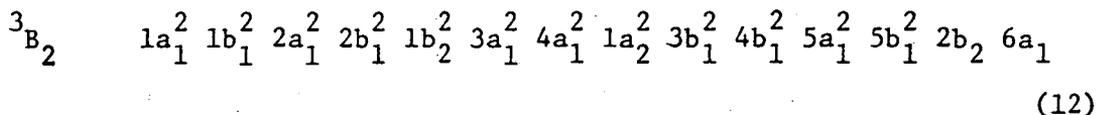
The structure of the methylene fragments in the three  $Al_2CH_2$  are remarkably similar, with CH distances  $1.083 \text{ \AA}$  ( $^1A_1$ ),  $1.083 \text{ \AA}$  ( $^3A_2$ ),  $1.085 \text{ \AA}$  ( $^3A_1$ ) and methylene bond angles of  $112.2^\circ$ ,  $112.0^\circ$ , and  $111.3^\circ$ . Previously we have shown<sup>22,44</sup> that for  $MnCH_2$  and  $AlCH_2$ , the methylene bond angles of the various electronic states may be correlated by a simple Walsh-like argument<sup>45</sup> 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  $\sim 102^\circ$ , while a singly-occupied orbital [as in triplet methylene, electron configuration (5)] yields a  $CH_2$  bond angle of  $\sim 133^\circ$ . In like manner for  $Al_2CH_2$ , 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

$^1A_1$	$3a_1$	$1.50$	$^3A_2$	$3a_1$	$1.63$	$^3A_1$	$3a_1$	$1.65$
		$112.2^\circ$			$112.0^\circ$			$111.3^\circ$

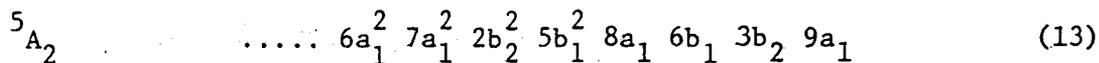
is found. That is, the magnitude of the methylene bond angle is inversely related to the CH<sub>2</sub> fragment 3a<sub>1</sub> orbital population. However, the three bond angles are so nearly the same that this correlation may be fortuitous. Nevertheless, these CH<sub>2</sub> bond angles are intermediate between the known bond angles of isolated singlet and triplet methylene; and in a similar manner the 3a<sub>1</sub> fragment populations lie between the integer values of 2 and 1 inherent in the Hartree-Fock descriptions of <sup>1</sup>A<sub>1</sub> and <sup>3</sup>B<sub>1</sub> 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 Al<sub>2</sub>CH<sub>2</sub> 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<sub>2v</sub> arrangement, the <sup>3</sup>Σ<sub>g</sub><sup>-</sup> ground electron configuration (1) of Al<sub>2</sub> resolves as

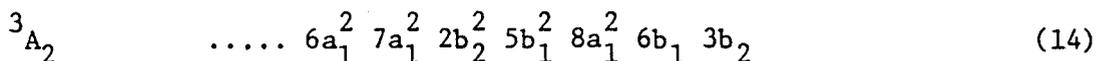


As was illustrated in more detail for the terminally bound isomer, one can merge (12) with the triplet CH<sub>2</sub> configuration (5) to yield a quintet state

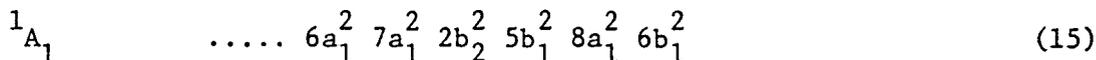


with a formal bond order of zero between the Al<sub>2</sub> and CH<sub>2</sub> fragments.

Starting from the no bond structure (13) a first bond can be constructed by pairing up the  $3a_1$  lone pair orbital of  $\text{CH}_2$  [designated  $8a_1$  in (13)] with the  $a_1$  component of the  $2\pi_u$  bonding orbital of  $\text{Al}_2$  [designated  $9a_1$  in (13)]. The resulting triplet state



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



The valence orbital energies for this  ${}^1A_1$  ground state of bridged-bonded  $\text{Al}_2\text{CH}_2$  are seen in Table I, which also gives a brief description of each molecular orbital. There it is apparent that the two  $\text{Al-C}$  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  $\text{Al-C}$  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  $\text{Al}_2\text{CH}_2$  geometry. Specifically, the  $\text{Al}$  3p populations

(necessarily equal for this  $C_{2v}$  structure) are only 0.52 Mulliken electrons. The bonding is thus primarily between the Al 3s ( $Al_2$   $3\sigma_g$  and  $3\sigma_u$ ) 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.

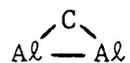
Since the bridge bonded  $^1A_1$  state represents the lowest minimum on the regions of the  $Al_2CH_2$  potential energy hypersurface studied here, this geometrical structure was determined at both the DZ SCF and DZ+P SCF levels of theory. The good agreement between the two structures seen in Figure 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,<sup>46</sup> whereas systems such as  $Mo_2(O_2CH)_4$  seem fairly "normal" with respect to their electronic structure,<sup>47</sup> Also worthy of some mention is the fact that the methylene bond angle

decreases by only  $0.7^\circ$  with the addition of polarization functions to the basis. For the isolated  $\text{CH}_2$  fragment it is well known<sup>48</sup> that the addition of d functions on the carbon atom decreases the HCH bond angle by  $\sim 4^\circ$ . Thus it would appear that the DZ basis set does a better job in predicting the structure of  $\text{Al}_2\text{CH}_2$  than would be anticipated from analogous results for the  $\text{Al}_2$  and  $\text{CH}_2$  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  $2.002 \text{ \AA}$ , quite similar to the  $2.013 \text{ \AA}$  predicted at the same level of theory for the prototype single bond in  $\text{Al-CH}_3$ . The slightly shorter DZ+P SCF distance of  $1.980 \text{ \AA}$  is likewise only a bit longer than the value  $1.957 \text{ \AA}$  determined by electron diffraction experiments<sup>49</sup> for the saturated  $\text{Al}(\text{CH}_3)_3$  molecule. Thus the two Al-C bonds in the ground state bridge-bonded species are conventional single bonds.

The most unexpected feature of the  $\mu$  methylene structures is the relatively long Al-Al bond. Specifically the DZ+P SCF prediction  $r_e = 3.610 \text{ \AA}$  is more than one angstrom longer than for the ground state of  $\text{Al}_2$ . 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  $\text{Al}_2(\text{CH}_3)_6$ , which has the diborane structure,<sup>50</sup> is  $2.60 \text{ \AA}$ , a value not too much longer than that ( $2.47 \text{ \AA}$ ) found experimentally for the  ${}^3\Sigma_g^-$  ground state of  $\text{Al}_2$ . Furthermore, similar Al-Al distances are found for several other carbon-bridged aluminum dimers.<sup>50</sup> Thus one concludes that a typical Al-Al single

bond distance is  $\sim 2.5$  Å, and consequently that the Al-Al bond in bridging Al<sub>2</sub>CH<sub>2</sub> 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<sub>2v</sub> arrangement. Recall that the first Al-C bond was then constructed by pairing up the 8a<sub>1</sub> and 9a<sub>1</sub> orbitals in (13), and the second Al-C bond somehow came into being when the 6b<sub>1</sub> orbital was doubly occupied. Note that the singly-occupied 6b<sub>1</sub> orbital in (13) is the carbon 2p orbital perpendicular to the HCH plane in the isolated triplet methylene fragment. This lb<sub>1</sub> orbital of methylene is called the methylene p orbital in Hoffmann's papers.<sup>51</sup> So, it must be asked "How did the 6b<sub>1</sub> orbital become an Al-C bonding orbital?" This question might in turn be answered by inquiring with which unoccupied orbitals of the Al<sub>2</sub> fragment can the methylene p (or lb<sub>1</sub>) orbital interact. The unequivocal answer to the latter question is the 7b<sub>1</sub> orbital of Al<sub>2</sub>CH<sub>2</sub>, the b<sub>1</sub> component (in C<sub>2v</sub> symmetry) of the 2π<sub>g</sub> antibonding orbital of Al<sub>2</sub>.

The above argument suggests that the second Al-C bond in bridging Al<sub>2</sub>CH<sub>2</sub> might be formed by the interaction between the

methylene p orbital and the antibonding  $2\pi_g$  or  $2\pi^*$  orbital of  $Al_2$ . Thus the total wave function would take on an additional amount of  $Al-Al$  antibonding character with the attachment of the  $CH_2$  bridge to  $Al_2$ . This in turn might explain the unusually long  $Al-Al$  bond distance. If one pursues this oversimplified argument to the extreme and hypothesizes that the  $6b_1$  orbital is 50%  $Al_2 \pi^*$  in character, then the overall complex would have an  $Al-Al$  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  $Al_2$  fragment mitigates against any significant population of its  $\pi^*$  antibonding orbital. The  $Al_2 \pi^*$  character is found to reside rather in the LUMO  $7b_1$  orbital.

Given the electronic population analyses of Tables I and II, the long  $Al-Al$  bond in bridging  $Al_2CH_2$  is seen to be due to the decrease in aluminum 3p character relative to the isolated diatomic  $Al_2$ . Configuration (1) shows that for  $Al_2$  each atom contributes one  $2p\pi$  electron to the single bond. However, in  $Al_2CH_2$ , the  $Al$  3p population is reduced to 0.52 Mulliken electrons. Thus the carbene complex has lost significant bonding character relative to  $Al_2$ , and this results in a longer  $Al-Al$  distance. The terminal  $Al_2CH_2$  structure, in contrast, has about the same total aluminum 3p population. However, the  $Al-Al$  distance in the terminal  $Al_2CH_2$  is also increased (but to a much smaller degree) relative to naked  $Al_2$ . 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  $\text{Al}_2\text{CH}_2$ , a 70% Al-Al bond for terminal  $\text{Al}_2\text{CH}_2$ , and a 100% bond for naked  $\text{Al}_2$ .

The structure of the  $\text{CH}_2$  fragment within the tetrahedrally bridged  $\text{Al}_2\text{CH}_2$  is much closer to that of isolated singlet methylene<sup>52</sup> [DZ SCF  $r_e(\text{CH}) = 1.103 \text{ \AA}$ ,  $\theta_e(\text{HCH}) = 106.6^\circ$ ] than were the previously discussed terminal  $\text{Al}_2\text{CH}_2$  structures. Following our earlier line of reasoning, the  $\text{CH}_2$  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  $\text{CH}_2$   $3a_1$  population within tetrahedrally bridged  $\text{Al}_2\text{CH}_2$  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  $\text{C}_{2v}$  arrangement was also examined in some detail, and the DZ SCF theoretical structure is illustrated in Figure 2. The latter structure is strikingly different from the tetrahedrally bridged  $\text{Al}_2\text{CH}_2$ , which has an Al-Al distance 0.575  $\text{ \AA}$  longer. In fact the Al-Al distance for the planar bridge is 3.031  $\text{ \AA}$ , 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  $\text{Al}_2 \ ^3\Sigma_g^-$  ground state, but this time in a third  $\text{C}_{2v}$  subgroup, which again retains the labeling of the molecular orbitals of the  $\text{CH}_2$  fragment in (5) and (6):

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

Comparison with electron configuration (5) for triplet  $\text{CH}_2$  shows that the two  $\text{Al}-\text{C}$  bonds are trivially constructed by pairing up the  $2b_1$  or  $\text{Al}_2 \ \pi$  orbital with the  $1b_1$  or  $p$  orbital of  $\text{CH}_2$  on the one hand; and the second component of the  $\pi$  orbital ( $6a_1$ ) with the methylene  $3a_1$  or lone pair orbital on the other hand. Since this introduces no  $\text{Al}_2 \ \pi^*$  antibonding character whatever into the wave function, one might not expect the dramatic increase in the  $\text{Al}-\text{Al}$  distance that characterized the tetrahedrally-bridged closed-shell singlet state. However, there is still for the planar structure a significant increase relative to the  $\text{Al}_2 \ ^3\Sigma_g^-$  bond distance (2.662 Å). This is because the  $2\pi$  orbital of  $\text{Al}_2$  is used only to form a single  $\text{Al}-\text{Al}$  bond for the diatomic, whereas for planar  $\text{Al}_2\text{CH}_2$  these orbitals are also employed in constructing the two  $\text{Al}-\text{C}$  bonds.

The other noteworthy feature of the planar structure is its small HCH bond angle, only  $97.0^\circ$  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<sup>22,44</sup> than for bridging methylenes. For those wishing to pursue this matter further, the predicted DZ SCF Mulliken populations for all five  $Al_2CH_2$  structures are given in Table II.

#### Relative Energies

A summary of relative energies of the different  $Al_2CH_2$  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<sup>39</sup> 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  $\text{CH}_4$ , of course, this tetrahedral-planar energy difference is much greater,  $\sim 150$  kcal.<sup>53</sup> However, Pople and Schleyer<sup>54</sup> have shown that a suitable choice of substituents (as in  $\text{CH}_2\text{Li}_2$ ) can reduce the tetrahedral carbon-planar carbon energy difference even below the 31 kcal reported here for  $\text{Al}_2\text{CH}_2$ , and in a few cases reverse the ordering completely. For the  $\text{Al}_2\text{CH}_2$  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  $\text{C}_2$  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  $^3\text{A}_2$  (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  $\text{Al}_2\text{CH}_2$  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  $\text{Al}_2\text{CH}_2$  two Al-C single bonds (bridging structure) provide significantly

more binding than does a single  $\text{Al}=\text{C}$  double bond (terminal structure). This observation begs the question, "Just how strong is the  $\pi$  bond in  $\text{Al}-\text{Al}=\text{CH}_2$ ?"

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  $\text{Al}=\text{C}$  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  $^3\Sigma_g^- \text{Al}_2$  plus  $^3B_1 \text{CH}_2$  infinitely removed and the  $^1A_1$  closed-shell ground state of terminally bound  $\text{Al}-\text{Al}=\text{CH}_2$ . 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  $\text{Al}=\text{C}$  double bond dissociation energy is 76.8 kcal, to be compared with  $D_e(\text{Al}-\text{C}) = 77.4$  kcal predicted earlier<sup>22</sup> for the single-bonded  $\text{AlCH}_2$  ground state at the DZ+P CI level of theory. However, it should be emphasized that the  $\text{Al}-\text{CH}_2$  bond cited is somewhat stronger than the typical  $\text{Al}-\text{C}$  single bond, which is more realistically modeled by the  $\text{Al}-\text{CH}_3$  system, for which the predicted DZ+P CI dissociation energy is 68 kcal. Therefore, it would appear that the  $\pi$  bond in  $\text{Al}-\text{Al}=\text{CH}_2$  contributes on the order of 10 kcal to the  $\text{Al}-\text{C}$  bond energy. Should this  $\pi$  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  $\text{Al}_2\text{CH}_2$  vibrational frequencies may also be quite pertinent to the (eventually) observed vibrational frequencies on metal surfaces.<sup>55</sup> Thus one would expect some of the frequencies of terminal and bridging  $\text{Al}_2\text{CH}_2$  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  $\text{Al}_2\text{CH}_2$  and of the ground state of bridging  $\text{Al}_2\text{CH}_2$  have therefore been predicted at the DZ SCF level, consistent with our earlier study<sup>22</sup> of  $\text{AlCH}$ ,  $\text{AlCH}_2$ , and  $\text{AlCH}_3$ . Moreover, since the latter study attracted some interest from surface vibrational spectroscopists,<sup>56</sup> the frequencies of the bridging structure (our lowest energy potential minimum for  $\text{Al}_2\text{CH}_2$ ) 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<sup>57</sup>, 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<sub>2</sub> wag (b<sub>1</sub>) and CH<sub>2</sub> twist (a<sub>2</sub>) frequencies, both of which are reduced by 100 cm<sup>-1</sup> by the addition of polarization functions to the basis set. Likewise the CH<sub>2</sub> rocking frequency (b<sub>2</sub>) is reduced by 90 cm<sup>-1</sup> in the larger basis set. Nevertheless, the good qualitative agreement gives us confidence in the earlier reported<sup>22</sup> AlCH<sub>3</sub>, AlCH<sub>2</sub>, and AlCH vibrational frequencies, for which only the smaller DZ basis was used.

Before proceeding, it must be noted that the previous reported<sup>22</sup> vibrational frequencies for AlCH<sub>2</sub> were inadvertently mislabeled. The proper labels are CH<sub>2</sub> scissor (1070 cm<sup>-1</sup>), CH<sub>2</sub> wag (660 cm<sup>-1</sup>), Al-C stretch (640 cm<sup>-1</sup>), and CH<sub>2</sub> rock (630 cm<sup>-1</sup>). This does not affect the discussion in our earlier paper, but does mean that the Al-C stretching frequencies for the AlCH<sub>3</sub> (600 cm<sup>-1</sup>), AlCH<sub>2</sub> (640 cm<sup>-1</sup>), and AlCH (670 cm<sup>-1</sup>) ground electronic states now form a monotonic series.

Next we turn to a comparison between the terminally bound Al<sub>2</sub>CH<sub>2</sub> frequencies and those reported earlier<sup>22</sup> for AlCH<sub>2</sub>. For the Al-C stretching mode the <sup>1</sup>A<sub>1</sub> ground state Al<sub>2</sub>CH<sub>2</sub> frequency is 890 cm<sup>-1</sup>, significantly greater than the 640 cm<sup>-1</sup> predicted for the smaller AlCH<sub>2</sub> system. This would appear to indicate a somewhat stronger bond between Al<sub>2</sub> and CH<sub>2</sub> than between Al and CH<sub>2</sub>, a result consistent with the trend in Al-C bond distances.

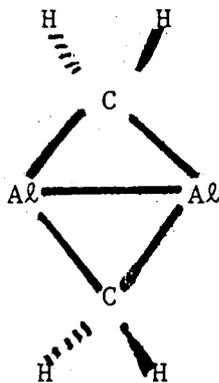
Note that the Al-C bond energies are essentially comparable for  $\text{Al}_2\text{CH}_2$  and  $\text{AlCH}_2$ . The new modes in  $\text{Al}_2\text{CH}_2$  (i.e., those not present in  $\text{AlCH}_2$ ) are the Al-Al stretch at  $220\text{ cm}^{-1}$  and the two Al-Al-C bending modes at  $100$  and  $70\text{ cm}^{-1}$ . For a cluster such as  $\text{Al}_{10}\text{CH}_2$  or for aluminum surface- $\text{CH}_2$  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  $\text{Al}_2\text{CH}_2$  the predicted CH stretching frequencies are significantly lower (by  $110$ - $260\text{ cm}^{-1}$ ) than obtained for either  $\text{AlCH}_2$  or terminal  $\text{Al}_2\text{CH}_2$ . This suggests reasonably enough that the  $\text{Al}_2$  fragment strongly perturbs the methylene group in the  $\mu$ -methylene structure. The asymmetric and symmetric carbon-aluminum stretching frequencies are predicted, at  $680$  and  $490\text{ cm}^{-1}$ , to be significantly split. Both lie in the general vicinity of the terminal Al-C stretching frequency predicted for  $\text{AlCH}_2$  ( $640\text{ cm}^{-1}$ ), but significantly below that suggested for  $\text{Al}_2\text{CH}_2$  ( $890\text{ cm}^{-1}$ ). Rotation of the methylene bridge is seen to be strongly discouraged by the torsional frequency predicted at  $800\text{ cm}^{-1}$  ( $700\text{ cm}^{-1}$  with the larger DZ+P basis set). The lowest frequency for the tetrahedrally bridging global minimum is  $180\text{ cm}^{-1}$  (DZ) or  $170\text{ cm}^{-1}$  (DZ+P) and may be described as either the Al-Al stretch or the  $\text{CAl}_2$  scissors motion. Finally, relative to the terminal  $\text{Al}_2\text{CH}_2$  structure, the bridging  $\text{CH}_2$  frequencies are shifted down (scissors  $1510 \rightarrow 1470\text{ cm}^{-1}$ ), up (wag  $800 \rightarrow 920\text{ cm}^{-1}$ ), and down (rock  $610 \rightarrow 480\text{ cm}^{-1}$ ), respectively.

Concluding Remarks

For the model metal dimer-methylene system studied here the bridging  $\text{CH}_2$  structure has been shown to lie  $\sim 46$  kcal lower in energy than the terminally bound isomer. The reason is very simple, namely that the second M-C  $\sigma$  bond in the bridging structure is significantly stronger than the M-C  $\pi$  bond of the terminal structure. Although this result was obtained specifically for the  $\text{Al}_2\text{CH}_2$  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.<sup>21</sup>

A perhaps unexpected feature found for the bridging  $\text{Al}_2\text{CH}_2$  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- $\mu$ -carbene complex (17) is also of interest in that it is a saturated molecule, with each aluminum atom being trivalent. More over, such di- $\mu$ -carbene complexes are now being prepared in

the laboratory, as evidenced by the recently obtained crystal structure<sup>58</sup> of the ruthenium dimer  $\text{Ru}_2(\text{CO})_2(\mu\text{-CHMe})(\mu\text{-CMe}_2)\text{Cp}_2$ , for which the dicarbene metal framework  $\text{Ru}_2\text{C}_2$  is very nearly planar. As a model for such systems, the  $\text{Al}_2(\text{CH}_2)_2$  molecule would appear an attractive target for future theoretical studies.

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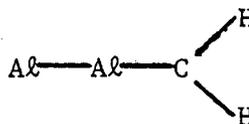
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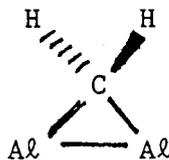
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Table I. Valence electron orbital energies (in hartrees) and qualitative descriptions of the occupied molecular orbitals of the ground states of two  $\text{Al}_2\text{CH}_2$  isomers.



<u>Designation</u>	<u>Orbital Energy</u>	<u>Description</u>
$8a_1$	-0.8351	methylene $2a_1$ orbital
$3b_2$	-0.5120	methylene $1b_2$ orbital
$9a_1$	-0.4977	$\text{Al}$ dimer $3s\sigma_g$ + $\text{CH}_2$ $3a_1$
$10a_1$	-0.4417	$\text{Al}$ dimer $3s\sigma_u$ + $\text{CH}_2$ $3a_1$
$11a_1$	-0.2822	$\text{Al}$ dimer $3s\sigma_u$
$3b_1$	-0.2337	$\text{Al}$ $3p\pi$ + $\text{CH}_2$ $1b_1$



<u>Designation</u>	<u>Orbital Energy</u>	<u>Description</u>
$6a_1$	-0.8929	methylene $2a_1$ orbital
$2b_2$	-0.5323	methylene $1b_2$ orbital
$5b_1$	-0.4677	$\text{Al}$ dimer $3s\sigma_u$ + $\text{CH}_2$ $1b_1$
$7a_1$	-0.4665	$\text{Al}$ dimer $3s\sigma_g$ + $\text{CH}_2$ $3a_1$
$8a_1$	-0.2942	$\text{Al}$ dimer $3s\sigma_g$ + $\text{CH}_2$ $3a_1$
$6b_1$	-0.2575	$\text{Al}$ dimer $3s\sigma_u$ + $\text{CH}_2$ $1b_1$

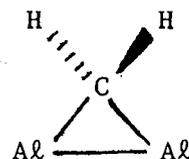
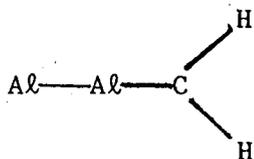
Table II. Summary of Mulliken population analyses for five  $Al_2CH_2$  geometrical structures.

Terminal Structures	$CH_2$ $a_1$	$CH_2$ $b_2$	$CH_2$ $b_1$	$Al_1$			$Al_2$		
				3s	3p	total	3s	3p	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  $\text{Al}_2\text{CH}_2$ . 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		Davidson Corrected	
			DZ CI	DZ+P SCF	DZ+P CI	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  $\text{cm}^{-1}$ ) for  $\text{Al}_2\text{CH}_2$ .



$^1A_1$ State	$^3A_2$ State	Normal Mode	DZ SCF	DZ+P SCF	Normal Mode
$b_2$ 3340	3340	CH asym. stretch	$b_2$ 3080	3080	CH asym. stretch
$a_1$ 3250	3240	CH sym. stretch	$a_1$ 3030	3030	CH sym. stretch
$a_1$ 1510	1520	$\text{CH}_2$ scissor	$a_1$ 1470	1430	$\text{CH}_2$ scissor
$a_1$ 890	700	Al-C stretch	$b_1$ 920	820	$\text{CH}_2$ wag
$b_1$ 800	690	$\text{CH}_2$ wag	$a_2$ 800	700	$\text{CH}_2$ twist (torsion)
$b_2$ 610	650	$\text{CH}_2$ rock	$b_2$ 680	670	CAAl asym. stretch
$a_1$ 220	180	Al-Al stretch	$a_1$ 490	480	CAAl sym. stretch
$b_2$ 100	50	Al-Al-C in-plane bend	$b_2$ 480	390	$\text{CH}_2$ rock
$b_1$ 70	90	Al-Al-C out-of-plane bend	$a_1$ 180	170	Al-Al stretch or $\text{CAAl}_2$ 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  $Al_2CH_2$ . 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  $Al_2CH_2$  predicted at two different levels of theory. Bond distances are in Å.

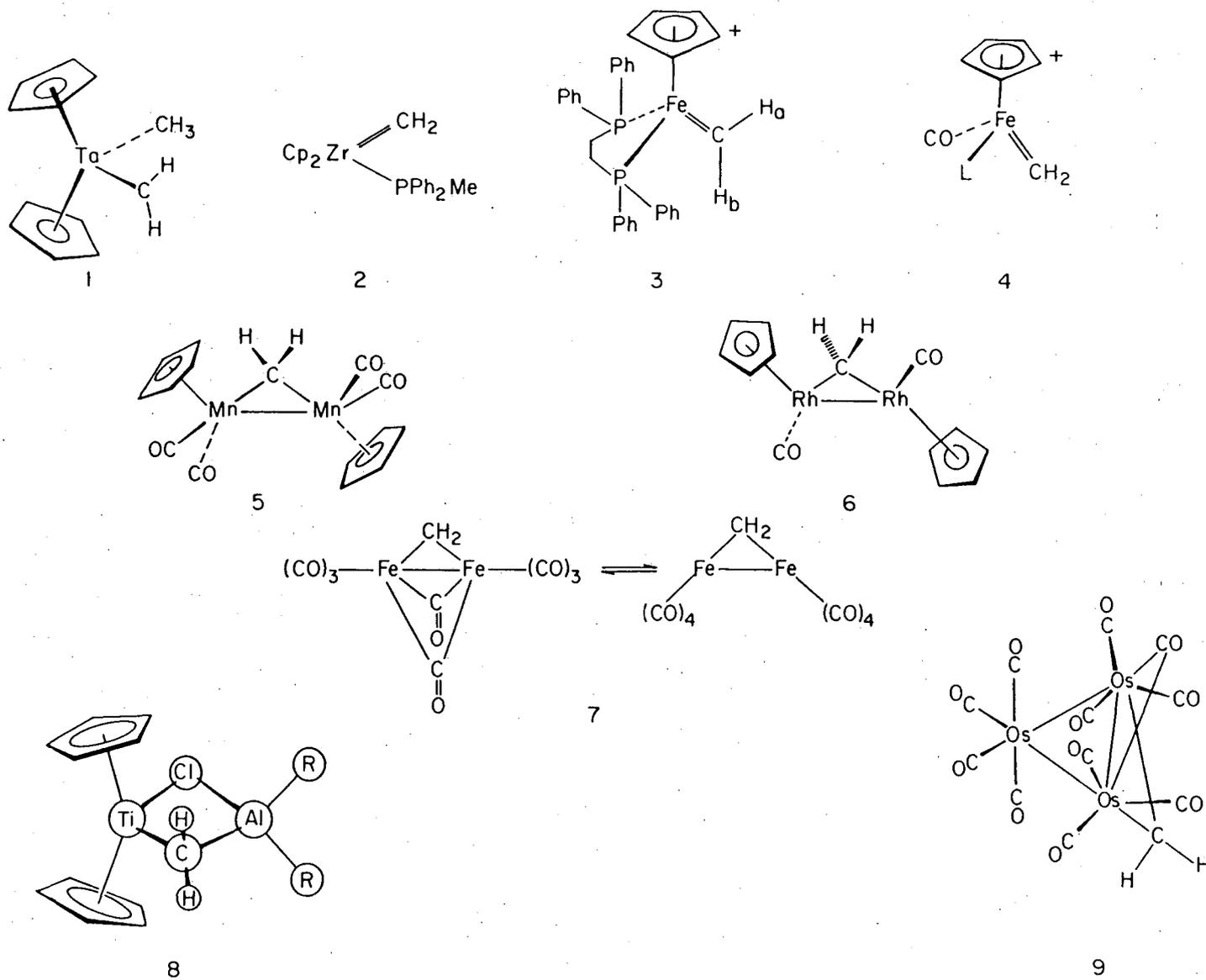


Figure 1

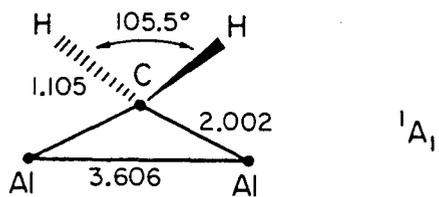
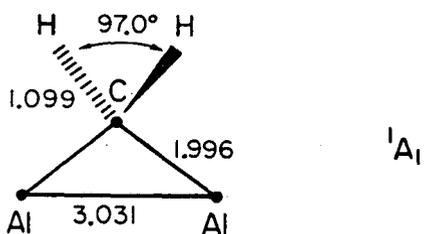
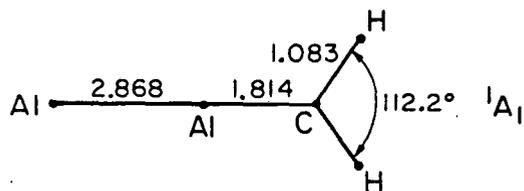
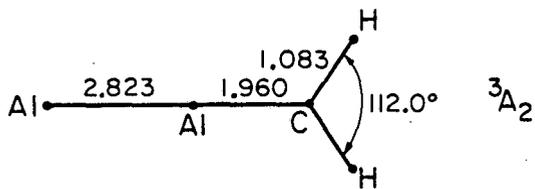
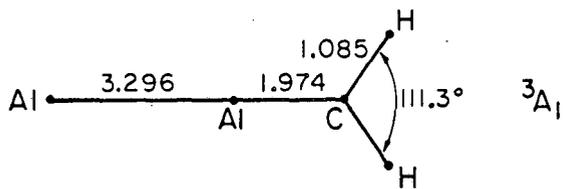
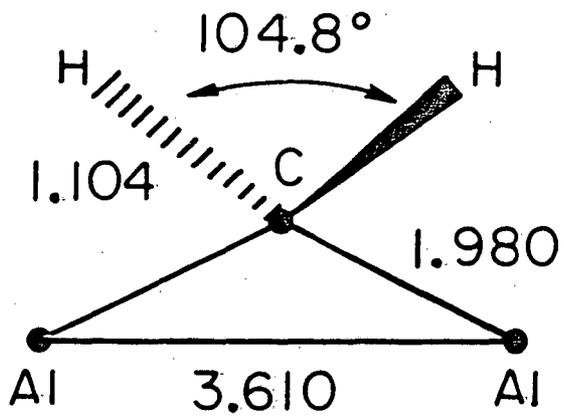
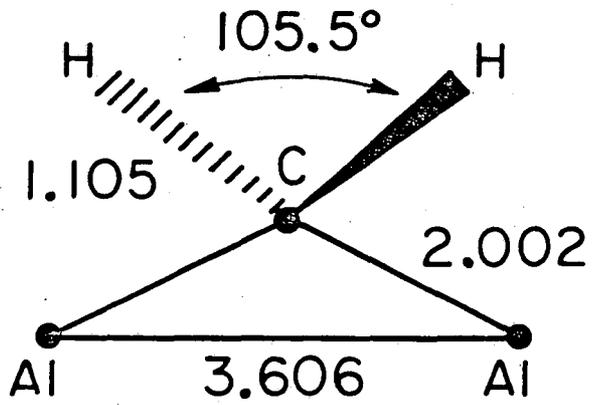


Figure 2

XBL821 - 3545



DZ + P SCF



DZ SCF

Figure 3

XBL 821 - 3541

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