set. For palladium a frozen-core effective-core potential (ECP) was used, i.e., the innermost core orbitals (1s–3p) are parametrized in the potential, and the electrons in the outer-core orbitals (3d–4p) are explicitly treated. Originally[29] these outer-core orbitals were described by a minimal basis set and were frozen in their atomic shapes. In the present calculations we want to incorporate relativistic effects through first-order perturbation theory, and it has been shown[30] that a flexible description of the 4s and 4p orbitals is necessary to obtain a correct atomic splitting for palladium. Therefore only the 3d orbital can be treated as an outer-core orbital, and the 4s and 4p orbitals are described by a double-$\zeta$ basis set, like the valence orbitals (4d, 5s, and 5p). The basis set is further augmented by the usual diffuse d function, yielding a 6s6p4d contracted basis set. The idea to treat the innermost orbitals by a nonrelativistic ECP, where the relativistic effects are expected to be largest, and apply relativistic corrections only on the outermost orbitals may be considered a questionable approach. However, this model has been tested for the palladium atom[30] where the relativistic effects on the excitation energies were very well reproduced, which shows that the important differential relativistic effects show up in the outer orbitals where the orbital characters between the states have their largest difference. A chain effect, where a change in an inner shell caused by relativity will give rise to a change in the outer shells, is anyway not accounted for by first-order perturbation theory. The adequacy of using first-order perturbation theory for problems of the present type has been demonstrated in a large number of previous studies, and we therefore consider our model at this point to be adequate. For the active hydrogens we used the 5s basis set by Huzinaga[31] contracted to three functions and augmented with one p function (0.8). For the hydrogens in the methyl group and on the ligands we used the 4s basis by Huzinaga[31] contracted to double $\zeta$. For carbon, both in the methyl group and in the ligands, like for the ligand oxygens and nitrogens, the MIDI-4 basis set of Tatewaki and Huzinaga[32] was used, which has a minimal basis description of the 1s core and a double-$\zeta$ description of the 2s and 2p valence orbitals. The 1s orbital is for these atoms frozen in the atomic shape. For chlorine and phosphorus the core orbitals (1s–2p) were replaced by ECP:s. For chlorine the 3s and 3p valence orbitals are described by minimal basis contracted basis sets and a diffuse p function is added.[33] For phosporus a 3s,3p valence basis set is used.[34] For flourine the 1s orbital is replaced by an ECP, and a 3s,3p valence basis set is used.[35] It should further be noted that for the nickel–water interaction the presently used basis set has been shown to have rather large superposition errors.[16] We therefore performed test calculations for the water ligand for the $NiH_2$ system using a much larger basis set (basis set F in ref 16), and it was found that the ligand effect on the metal–$R_1R_2$ interaction was practically the same (within 1.5 kcal/mol) for the two basis sets. The Ni–O distance was taken from the optimization using the large basis F in ref 16. We could therefore safely use the smaller water basis set for the other systems.

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# π-Bonded Complex between Aluminum and Ethylene

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**Abstract:** There are several possible isomeric complexes between atomic Al and $C_2H_4$. Only the π-bonded complex appears to have been observed experimentally to date. Ab initio quantum mechanical methods have been applied to this problem and confirm theoretically for the first time that the π-bonded structure is strongly bound ($D_0 > 11$ kcal/mol). The highest level at which a full vibrational analysis has been carried out is configuration interaction including all single and double excitations (CISD) employing a double-$\zeta$ plus polarization (DZ+P) basis set. A second minimum, corresponding to Al–methylcarbene, lies less than 5 kcal/mol above the π-bonded global minimum. The σ-bonded classical ethyl radical structure is predicted to collapse to the π-bonded structure when the effects of electron correlation are considered explicitly.

The aluminum–ethylene complex was first prepared in the laboratory by Kasai and McLeod[1] in 1975. At near liquid helium temperatures Kasai and McLeod trapped the Al–$C_2H_4$ species in a neon matrix. Their analysis of the electron spin resonance (ESR) spectra showed that "the Al atom–ethylene complex is formed through the dative bonds resulting from the interaction of the π orbitals of the olefin and the valence orbitals of the Al atom". This important research by Kasai and McLeod followed the pioneering work of Skell and Wolf[2] on the co-condensation of aluminum atoms with excess propene.

Kasai's 1982 paper[3] on Al–$C_2H_4$ gave a full report of the research communicated earlier[1] and reported new results suggesting the formation of $Al(C_2H_4)_2$ by photoirradiation. Five years later Chenier et al.[4] and Howard et al.[5] reported experiments designed to interrogate the Al–$C_2H_4$ complex under higher temperature conditions in hydrocarbon matrices. They found the aluminum–ethylene complex to be stable up to 297 K in an adamantane matrix. The most recent experimental study of Al–$C_2H_4$ appears to be that of Mitchell, Simard, Rayner, and Hackett (MSRH).[6] From observations of the temperature dependence of the equilibrium constant for

$$Al + C_2H_4 \rightleftharpoons Al\text{–}C_2H_4 \qquad (1)$$

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[†] Contribution CCQC no. 47.

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in the range 283–333 K, MSRH[6] have determined a binding energy greater than 16 kcal/mol for the association (1).

Thus far theory has not been successful in interpreting the experimental observations for Al–$C_2H_4$. This is in contrast to the simpler Al–$C_2H_2$ system, for which theory has guided experiment in a constructive way. For the latter system, the $\pi$-bonded structure is not observed,[3,7] but rather a $\sigma$-bonded vinyl structure AlCH=$\dot{C}$H. While theory[8,9] shows the existence of the observed $\sigma$-bonded vinyl structure, it also demonstrates clearly that the global minimum for Al–$C_2H_2$ is the vinylidene structure, which may be qualitatively understood as something like :Al—$\dot{C}$=$CH_2$. The predicted 39.1 kcal/mol barrier[9] between the initially formed :AlCH=$\dot{C}$H and the lower energy :Al—$\dot{C}$=$CH_2$ prevents the latter from being observed under the low-temperature noble-gas matrix conditions.

In their initial theoretical study of the Al–$C_2H_2$ isomers, Trenary, Casida, Brooks, and one of us (TCBS)[8] included one sentence describing some preliminary studies of $\pi$-bonded Al–$C_2H_4$. With a rigid $C_2H_4$ geometry, the attraction to atomic Al was expected to be $\leq 5$ kcal/mol. A similar result was found quantitatively in the recent theoretical paper by Miralles-Sabater et al.[10] Thus, to date there is no theoretical explanation of the rather strong (>16 kcal/mol) association[6] between Al and $C_2H_4$. Here we show that a satisfactory description of the $\pi$-bonded Al–$C_2H_4$ requires simultaneous geometry optimization and proper treatment of the effects of electron correlation.

## Theoretical Approach

The standard basis set used in this research was of double-$\zeta$ plus polarization (DZ+P) quality. Specifically the atomic contracted Gaussian basis sets may be designated Al(11s7p1d/6s4p1d),[11,12] C(9s5p1d/4s2p1d),[13,14] and H(4s1p/2s1p).[13,14] Chosen polarization function orbital exponents were $\alpha_d(\mathrm{Al}) = 0.4$, $\alpha_d(\mathrm{C}) = 0.75$, and $\alpha_p(\mathrm{H}) = 0.75$. The scale factor for the hydrogen primitive Gaussian s functions was $(1.2)^2 = 1.44$.

Stationary point geometries were fully optimized by using both self-consistent field (SCF) and configuration interaction (CI) analytic gradient methods[15,16] for open-shell systems. The CI wave functions included all Hartree–Fock-interacting[17,18] single and double excitations (CISD) with respect to the single-configuration SCF wave function.

The $^2P_u$ electronic ground state of the aluminum atom is spatially 3-fold degenerate. For perpendicular approaches of Al to $C_2H_4$ the $^2P_u$ atomic state resolves into $C_{2v}$ states of $^2A_1$, $^2B_1$, and $^2B_2$ symmetry. The Hartree–Fock wave functions for these three states have the qualitative form (with core molecular orbitals $1a_1^2\ 2a_1^2\ 1b_2^2\ 3a_1^2\ 2b_2^2\ 1b_1^2\ 4a_1^2$ included implicitly):

$$5a_1^2\ 3b_2^2\ 2b_1^2\ 6a_1^2\ 1a_2^2\ 7a_1^2\ 8a_1^2\ 9a_1 \qquad {}^2A_1 \tag{2}$$

$$5a_1^2\ 3b_2^2\ 2b_1^2\ 6a_1^2\ 1a_2^2\ 7a_1^2\ 8a_1^2\ 3b_1 \qquad {}^2B_1 \tag{3}$$

$$5a_1^2\ 3b_2^2\ 2b_1^2\ 6a_1^2\ 1a_2^2\ 7a_1^2\ 8a_1^2\ 4b_2 \qquad {}^2B_2 \tag{4}$$

In the CISD wave functions, the seven corelike SCF MOs (1s,2s,2p Al and 1s C) are constrained to be doubly occupied in all configurations. Similarly the seven highest virtual orbitals (core counterparts for a DZ quality basis set) are deleted from the CI procedure. In this way, with the DZ+P basis set, there are 24 114 configurations for the $^2B_1$ state and 24 444 configurations for the $^2B_2$ state.

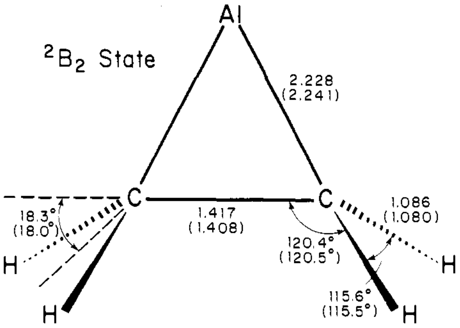

**Figure 1.** Ab initio equilibrium geometries for the $^2B_2$ electronic ground state of $\pi$-bonded Al-$C_2H_4$ (structure **1**). The DZ+P CISD geometrical parameters are given first, followed by the analogous DZ+P SCF results in parentheses. All bond distances are in angstroms.

## Conventional Perpendicular Approach of $^2P_u$ Al to Ethylene

The qualitative considerations discussed in Swope's 1976 paper[19] suggest (see Swope's Figure 3) that the $^2B_2$ potential energy curve should be most attractive as Al approaches $C_2H_4$ in a perpendicular manner. The $^2B_1$ curve should be less attractive and the $^2A_1$ curve repulsive.

The above qualitative predictions were borne out by our ab initio results for Al–$C_2H_4$. The DZ+P SCF and CISD equilibrium geometries for the $^2B_2$ state (structure **1**) are displayed in Figure 1. As expected, the $^2B_2$ electronic state is tightly bound compared to the $^2B_1$ state, with predicted Al–C distance 2.228 Å (DZ+P CISD). This distance represents a bond somewhat weaker than a conventional aluminum–carbon single bond. For example, the Al–C distance (2.228 Å) in the present $\pi$-bonded complex is 0.271 Å longer than that determined experimentally[20] (1.957 Å) for monomeric trimethylaluminum in the gas phase.

Also of interest is the distortion of the ethylene molecule within the Al–$C_2H_4$ complex. For comparison, we have carried out a CISD geometry optimization for the supermolecule in which ethylene is separated by 100 bohrs from the aluminum atom. The $C_2H_4$ structure thus obtained (DZ+P CISD) is

$$r_e(\mathrm{C{=}C}) = 1.338\ \text{Å}$$

$$r_e(\mathrm{C{-}H}) = 1.085\ \text{Å}$$

$$\theta_e(\mathrm{CCH}) = 121.5°$$

$$\theta_e(\mathrm{HCH}) = 117.0°$$

Parenthetically, we note that the above theoretical structure agrees well with the experimental[21] vibrationally averaged structure of ethylene $r_0(\mathrm{C{=}C}) = 1.339$ Å, $r_0(\mathrm{C{-}H}) = 1.085$ Å, $\theta_0(\mathrm{HCH}) = 117.8°$.

In light of the above, there is significant lengthening of the C=C double bond in ethylene upon complexation with the Al atom. Specifically the C=C distance increases by 0.079 Å from free ethylene (1.338 Å) to Al–$C_2H_4$ (1.417 Å). The best qualitative description of the carbon–carbon bond in the $^2B_2$ ground state of $\pi$-bonded Al–$C_2H_4$ is as a weak (or long) C=C double bond.

Another geometrical parameter of interest is the bending-back angle of the $CH_2$ groups with respect to the plane of the free ethylene molecule. For the $^2B_2$ ground state of $\pi$-bonded Al–$C_2H_4$ this bending back angle is 18.0° at the DZ+P SCF and 18.3° at the DZ+P CISD level of theory. It is seen that the attachment

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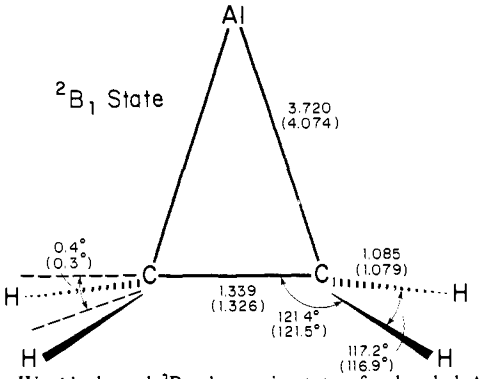


**Figure 2.** Weakly bound $^2B_1$ electronic state of π-bonded Al–$C_2H_4$ (structure **2**). DZ+P CISD structural parameters are given first, followed by the analogous DZ+P SCF results in parentheses. All bond distances are in angstroms.

of the Al atom causes a significant nonplanarity in the ethylene molecule.

Since the recent experiments of MSRH[6] suggest a dissociation energy $D_0(\mathrm{Al{-}C_2H_4}) \geq 16$ kcal/mol, this quantity is of special interest. DZ+P SCF theory predicts a tiny dissociation energy, namely, 1.1 kcal/mol. However, DZ+P CISD does much better, yielding a dissociation energy of 10.1 kcal/mol. When the Davidson correction[22] for the effects of certain (i.e., unlinked clusters) quadruple excitations is appended, the predicted dissociation energy is 11.6 kcal/mol. Although this is still short of the experimental 16 kcal/mol, it does appear to provide a qualitatively correct description of the bonding. Given the fact that the $^2B_2$ state is so weakly bound at the DZ+P SCF level of theory, it is perhaps surprising that DZ+P SCF does such a good job in predicting the equilibrium geometry.

One referee has suggested that the predicted dissociation energies might be corrected for basis set superposition effects. Our position is that the only truly reliable way to make such a correction is to increase the basis set size and carry out an entirely new set of theoretical studies. In fact, it is well-known from experience that the DZ+P CISD method yields dissociation energies less than experiment. Therefore a counterpoise correction would be counterproductive for the present work.

The DZ+P SCF and CISD equilibrium geometries for the $^2B_1$ (structure **2**) electronic state are displayed in Figure 2. As expected from the qualitative ideas of Swope,[19] the $^2B_1$ Al–$C_2H_4$ complex is very weakly bound. The SCF, CISD, and Davidson-corrected CISD dissociation energies $D_e$ are 0.6, 1.3, and 1.4 kcal/mol, respectively. This very weak binding is reflected in Figure 2 in an ethylene geometry that is very little changed from $C_2H_4$ in vacuo. Specifically, the C═C distance is 1.339 Å (only 0.001 Å longer than for free $C_2H_4$) and the methylene bending back angle is only 0.4°. Accordingly the Al–C distance is very long, 3.720 Å with DZ+P CISD.

As expected,[19] the $^2A_1$ potential energy surface is initially repulsive as $^2P_u$ Al approaches ethylene. Nevertheless, after pushing over a barrier one finds a minimum (structure **3**) in this potential curve corresponding to an electron configuration different from (2). This new $^2A_1$ electron configuration is

$$5a_1^2\ 3b_2^2\ 2b_1^2\ 6a_1^2\ 1a_2^2\ 7a_1^2\ 4b_2^2\ 8a_1 \tag{5}$$

However, it must be emphasized that **3** is not low-lying energetically. With the DZ+P basis set this structure lies 11.9 (SCF), 2.3 (CISD), and 1.7 kcal/mol (Davidson-corrected CISD) above separated Al + $C_2H_4$. Thus it is difficult to imagine an experiment that would detect this $^2A_1$ electronic state, even though higher levels of theory will likely make this $^2A_1$ state lower in energy than separated Al + $C_2H_4$.

Despite its energetic unfavorableness, the $^2A_1$ structure (**3**) is of interest because it incorporates two conventional aluminum–carbon single bonds, as demonstrated by the equilibrium geometry. In Figure 3, the DZ+P CISD Al–C bond distances are 1.925 Å, actually a bit shorter than for the experimentally characterized[20] trimethylaluminum, for which $r(\mathrm{Al{-}C}) = 1.957$ Å. Furthermore the predicted C–C distance (1.600 Å) is significantly longer than the standard C–C value of 1.54 Å. Although this $^2A_1$ structure is not low lying energetically, it is probably most representative of the saturated closed-shell

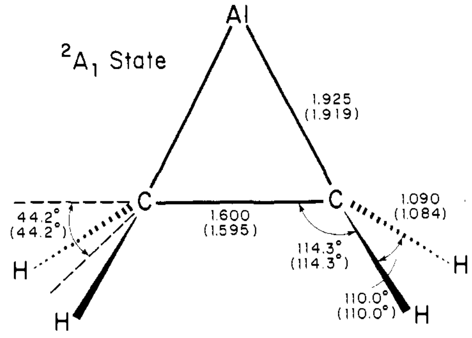
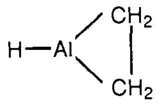


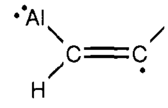
**Figure 3.** Relatively energetically high-lying $^2A_1$ electronic state of (three-membered ring) Al–$C_2H_4$ (structure **3**). DZ+P CISD geometrical parameters are displayed first, followed by the analogous DZ+P SCF results in parentheses. All bond distances are in angstroms.



three-membered ring system. The latter system, for which no experimental data yet exist, should have two fairly normal Al–C single bonds. Presumably, the ground-state electron configuration for closed-shell $HAlC_2H_4$ will simply add one electron to the $8a_1$ orbital of (5).

### σ-Bonded Ethyl-Radical-Like Structures

For the aluminum-acetylene system[8,9] the structure



(6)

which is related to the vinyl radical, is bound by about 17 kcal/mol relative to infinitely separated $^2P_u$ Al + $C_2H_2$. For aluminum–ethylene the analogous structure (structure **4**, Table II) is related to the classical form of the ethyl radical. Therefore, any complete study of the Al–$C_2H_4$ system should include structures of the type **4**.

The σ-bonded structure **4** incorporates at most a single plane of symmetry, i.e., point group $C_s$. The lowest energy electronic state places the unpaired electron as in **4**, corresponding to electron configuration

$$7a'^2\ 8a'^2\ 2a''^2\ 9a'^2\ 3a''^2\ 10a'^2\ 11a'^2\ 12a' \tag{7}$$

in which the core electrons ($1a'^2\ 2a'^2\ 3a'^2\ 4a'^2\ 5a'^2\ 1a''^2\ 6a'^2$) are included implicitly. The CISD wave functions for this $^2A'$ electronic state include a total of 48 697 configurations.

The DZ+P SCF equilibrium geometry is shown in Figure 4. Perhaps the most interesting structural feature of this σ-bonded $^2A'$ state (**4**) is the small Al–C–C bond angle, namely, 99.5°. The large deviation (10.0°) from the tetrahedral angle suggests some motion from the expected σ-bonded classical structure toward the π-bonded $^2B_2$ state (**1**) seen in Figure 1. However the Al–C bond distance is reasonable (2.025 Å) for such a σ-complex, being only 0.07 Å longer than that observed experimentally for $\mathrm{Al(CH_3)_3}$. Further, the C–C distance is 1.488 Å, much closer to a standard C–C single-bond distance than a C═C double-bond distance.

When one attempts to optimize the $^2A'$ geometry at the DZ+P CISD level of theory, a striking confirmation of the experimental deductions of Kasai and McLeod[1,3] is found. Namely, there is no DZ+P CISD minimum in the region of the DZ+P SCF

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[22] Davidson, E. R. *The World of Quantum Chemistry*; Daudel, R., Pullman, B., Eds.; D. Reidel: Dordrecht, Holland, 1974; pp 17–30.

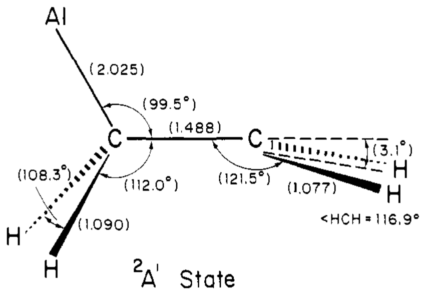

**Figure 4.** Ethyl-radical-like ($\sigma$-bonded) state of Al-$C_2H_4$ (structure **4**). There is no DZ+P CISD equilibrium geometry, as discussed in the text, since this structure collapses to the $\pi$-bonded $^2B_2$ structure depicted in Figure 1. Nevertheless the DZ+P SCF predictions for the equilibrium geometry are given in parentheses. All bond distances are in angstroms.

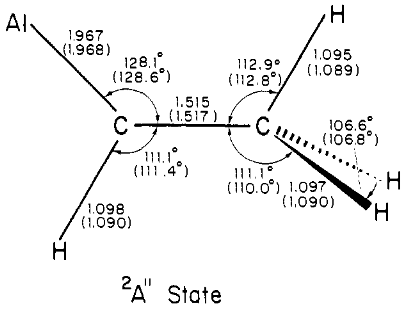

**Figure 5.** Aluminum–methylcarbene isomer of the Al–$C_2H_4$ system (structure **6**). DZ+P CISD geometrical parameters are displayed first, followed by the analogous DZ+P SCF results in parentheses. All bond distances are in angstroms.

equilibrium geometry. An extensive search of structures with larger Al–C–C bond angles still reveals no $^2A'$ minimum. Upon following the DZ+P CISD potential energy surface in the direction of steepest descent, one moves quickly to the $^2B_2$ minimum corresponding to the $\pi$-bonded structure discussed above. This is dramatic evidence in favor of Kasai and McLeod's conclusion from the ESR spectra that Al-$C_2H_4$ has the $\pi$-bonded equilibrium geometry.

An important remaining question concerns the relative energy of the $\sigma$-bonded $^2A'$ state in the region of the SCF minimum. At the DZ+P SCF level of theory the $^2A'$ state is bound by 1.5 kcal/mol relative to infinitely separated Al + $C_2H_4$. At precisely the same geometry, the DZ+P CISD energy is −320.222 17 hartrees, or 6.3 kcal/mol below separated Al + $C_2H_4$ at the same level of theory. The Davidson corrected DZ+P CISD energy for the same structure is −320.259 18 hartrees, or 7.0 kcal/mol below the dissociation limit treated at the same level of theory. Thus the $\sigma$-bonded structure (**4**), which is no longer a minimum at higher levels of theory, is predicted to lie 4.6 kcal/mol above the $^2B_2$ $\pi$-bonded complex (**1**).

One may readily imagine a second low-lying electronic state of the $\pi$-bonded ethyl-radical-like structure of Al-$C_2H_4$. This is the $^2A''$ electronic state (**5**, Table II). In this conformation the Al atom is coplanar with the methylene group, and the unpaired electron occupies an orbital perpendicular to the $CH_2$ plane, with electron configuration

$$7a'^2\ 8a'^2\ 9a'^2\ 2a''^2\ 11a'^2\ 12a'^2\ 3a'' \qquad (8)$$

Conformer **5** is predicted to lie 3.7 kcal/mol above the $^2A'$ state **4** at the DZ+P SCF level. However, a vibrational frequency analysis shows that **5** is a transition state with one imaginary frequency corresponding to internal rotation. The predicted Al–C distance for the higher-energy $^2A''$ state is actually less by 2.006 − 2.025 = 0.019 Å than for the $^2A'$ state. Intuitively, of course, a shorter Al–C distance would be expected to accompany a stronger Al–C bond dissociation energy. One interpretation might be that **4** is partially $\pi$-bonded, while **5** is unable to form a $\pi$-interaction due to spatial orthoganality of the p orbitals. The C–C–Al bond angle in **5** of 115° is much more representative of a $\sigma$-bonded complex than the 99.5° in **4**. Although the relative energy of **4** and **5** is unusual at first sight, it is consistent that both the geometry and energy of **4** is intermediate between **1** and **5**.

## Aluminum–Methylcarbene Structures

As noted above, for the related Al-$C_2H_2$ system, the global minimum is the vinylidene-like structure $:\mathrm{Al}\text{-}\dot{\mathrm{C}}\text{-}\mathrm{CH}_2$. The analogous structure for Al-$C_2H_4$ would be the $:\mathrm{Al}\text{-}\dot{\mathrm{C}}\mathrm{H}\text{-}\mathrm{CH}_3$ geometry (structure **6**, Table II). However, there are qualitative reasons why such structures should be higher lying energetically than the analogous vinylidene structure for the Al–$C_2H_2$ system. The energy of **6** relative to separated Al + $C_2H_4$ may be visually separated into two energetically distinct parts: (a) the net energy required for the isomerization $C_2H_4 \rightarrow \mathrm{H}\ddot{\mathrm{C}}\text{–}\mathrm{CH}_3$ and (b) the energy regained by bringing Al up to $\mathrm{H}\ddot{\mathrm{C}}\text{–}\mathrm{CH}_3$ to form the $:\mathrm{Al}\text{-}\dot{\mathrm{C}}\mathrm{H}\text{-}\mathrm{CH}_3$ complex. However, part (a) is very expensive energetically, about 75 kcal/mol from the work of Raghavachari et al.[23] By comparison the analogous part (a) for the Al–$C_2H_2$ system requires only about 45 kcal/mol.[24] Therefore the higher energy of $\mathrm{H}\ddot{\mathrm{C}}\text{–}\mathrm{CH}_3$ vs $C_2H_4$ compared to $:\mathrm{CCH}_2$ vs HCCH suggests that the complex $:\mathrm{Al}\text{–}\dot{\mathrm{C}}\mathrm{H}\text{–}\mathrm{CH}_3$ (**6**) should be higher lying energetically compared to Al + $C_2H_4$ than is $:\mathrm{Al}\text{—}\dot{\mathrm{C}}\text{=}\mathrm{CH}_2$ compared to Al + $C_2H_2$.

A trigonal-planar arrangement of AlCH– requires that the unpaired electron in **6** be perpendicular to the plane of the page. This $^2A''$ electronic state for the aluminum–methylcarbene system arises from the electron configuration

$$7a'^2\ 8a'^2\ 9a'^2\ 2a''^2\ 10a'^2\ 11a'^2\ 12a'^2\ 3a'' \qquad (9)$$

This orbital occupancy has one less electron in a″ molecular orbitals than does the $\sigma$-bonded structure (eq 7).

The DZ+P SCF and DZ+P CISD structures for aluminum–methylcarbene are given in Figure 5. The Al–C bond distance (1.967 Å) is now quite normal for an Al–C single bond (only 0.01 Å longer than for $Al(CH_3)_3$ in the gas phase). The C–C bond distance (1.515 Å) now falls within the shorter end of the range of normal C–C single-bond distances. The Al–C–C bond angle (128.1°) is much larger than the H–C(carbene)–C angle (111.1°), but the average of the two angles is close to 120°.

At the DZ+P SCF level of theory $:\mathrm{Al}\text{–}\dot{\mathrm{C}}\mathrm{H}\text{–}\mathrm{CH}_3$ lies 7.7 kcal/mol below infinitely separated Al + $C_2H_4$. At the DZ+P CISD level, this binding energy increases slightly somewhat, to 10.1 kcal/mol. When the Davidson correction is added to the CISD energies, the binding energy remains (to three significant figures) 10.1 kcal/mol. For comparison the $\pi$-bonded structure ($^2B_2$ state **1**) at the same level of theory is bound by 11.6 kcal/mol. Thus the $\pi$-bonded structure lies 1.5 kcal/mol below the Al-methylcarbene equilibrium geometry. For comparison, in the Al–$C_2H_2$ system the $\pi$-bonded structure lies 9.4 kcal/mol *above* the Al–vinylidene equilibrium geometry. Thus our qualitative argument that Al–methylcarbene should be destabilized relative to Al–vinylidene is confirmed.

There is at least one additional interesting conformer of the aluminum–methylcarbene system, namely, **7** (Table II) in which the Al atom lies trans to the unique methyl group hydrogen. This structure ($^2A''$ symmetry) has been fully optimized at the DZ+P SCF level of theory and lies 1.3 kcal/mol above **6**. For **7** the Al–C distance is 0.001 Å longer and the C–C distance 0.004 Å longer than for the lower energy conformer **6**. However, structure **7** is not a minimum; it has an imaginary frequency at DZ+P SCF level corresponding to rotation of the methyl group. Note, of course, that for the classical ethyl radical itself, structures **6** and **7** are identical.

## Vibrational Frequencies

After this research was well underway, an unpublished report of the observation of the infrared spectrum of $AlC_2H_4$ by Man-

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[23] Raghavachari, K.; Frisch, M. J.; Pople, J. A.; Schleyer, P. R. *Chem. Phys. Lett.* **1982**, *85*, 145.

[24] Carrington, T.; Hubbard, L. M.; Schaefer, H. F.; Miller, W. H. *J. Chem. Phys.* **1984**, *80*, 4347.

**Table I.** Ab Initio Vibrational Frequencies (in cm$^{-1}$) for the $^2B_2$ Electronic Ground State ($\pi$-Bonded, See Figure 1) of Al–$C_2H_4$ (Infrared Intensities in km/mol Are Given in Parentheses)

| sym | descr | DZ+P SCF | DZ+P CISD |
|---|---|---|---|
| $b_2$ | $CH_2$ asym stretch | 3384 (6.9) | 3329 (5.0) |
| $a_2$ | $CH_2$ asym stretch | 3362 (0) | 3308 (0) |
| $a_1$ | $CH_2$ sym stretch | 3289 (0.7) | 3229 (0.1) |
| $b_1$ | $CH_2$ sym stretch | 3275 (6.2) | 3214 (3.2) |
| $a_1$ | $CH_2$ scissors | 1636 (14.0) | 1575 (9.0) |
| $b_1$ | $CH_2$ scissors | 1549 (10.6) | 1489 (6.6) |
| $a_2$ | $CH_2$ twist | 1313 (0) | 1263 (0) |
| $a_1$ | C–C stretch | 1286 (66.1) | 1260 (44.6) |
| $a_1$ | $CH_2$ wag | 926 (28.9) | 896 (33.2) |
| $b_2$ | $CH_2$ twist | 850 (2.6) | 824 (2.6) |
| $a_2$ | $CH_2$ rock | 793 (0) | 750 (0) |
| $b_1$ | $CH_2$ wag | 836 (13.0) | 745 (10.5) |
| $b_2$ | $CH_2$ rock | 514 (3.9) | 482 (2.7) |
| $a_1$ | Al···$C_2H_4$ stretch | 378 (25.3) | 387 (26.1) |
| $b_1$ | Al···$C_2H_4$ rock | 196 (3.0) | 232 (5.1) |

ceron and Andrews[25] was brought to our attention. Although Manceron and Andrews do not list the values of any of the fundamentals in their conference abstract,[25] they conclude that the $\pi$-bonded structure of Kasai and McLeod[1,3] is the true equilibrium geometry. It seemed important, in light of the forthcoming experiments of Manceron and Andrews,[25] to predict the vibrational frequencies ab initio.

Table I gives the harmonic vibrational frequencies and infrared intensities of $\pi$-bonded Al–$C_2H_4$ ($^2B_2$ electronic ground state) at the DZ+P SCF and DZ+P CISD levels of theory. The latter results were obtained via finite differences of analytic CISD gradients. This requires the evaluation of seven gradients in $C_s$ point group symmetry. In $C_s$ symmetry the largest number of configurations required for the CISD wave functions was 48 967.

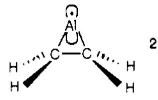
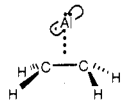
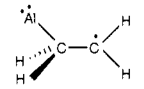
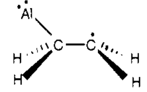
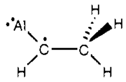
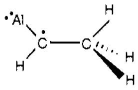
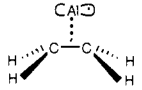
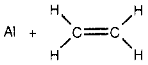
At both the DZ+P SCF and more reliable DZ+P CISD levels of theory, the carbon–carbon vibrational stretching frequency is predicted to have a large IR intensity, specifically 45 km/mol with DZ+P CISD. This high IR intensity is especially interesting since its counterpart for the isolated ethylene molecule is identically zero. The predicted $\omega$(C–C) = 1260 cm$^{-1}$ is probably about 100 cm$^{-1}$ above the true fundamental $\nu$(C–C). At the same level of theory (DZ+P CISD), for isolated ethylene $\omega$(C=C) is predicted[26] to be 1737 cm$^{-1}$, or 477 cm$^{-1}$ higher. Consistent with the structural predictions, the $\pi$-bond to Al significantly weakens the ethylene carbon–carbon bond.

The second strongest IR bond for $\pi$-bonded $^2B_2$ Al–$C_2H_4$ is the $CH_2$ wag predicted at 896 cm$^{-1}$, with intensity 33 km/mol. For isolated $C_2H_4$ this fundamental has an even higher DZ+P CISD IR intensity, namely, 96 km/mol. The Al–$C_2H_4$ harmonic vibrational frequency lies 896 − 983 = 87 cm$^{-1}$ below that predicted at the same level of theory for $C_2H_4$.

The closest one can come for Al–$C_2H_4$ to finding an Al–C stretching vibration is the $a_1$ symmetric Al···$C_2H_4$ stretching. This harmonic vibrational frequency is predicted to be 387 cm$^{-1}$ (DZ+P CI) and to be quite intense in the IR spectrum, namely, 26 km/mol. Counterintuitively, the effect of electron correlation is to increase this Al–C stretching frequency, from 378 cm$^{-1}$ (SCF) to 387 cm$^{-1}$ (CISD), which, however, may be attributed to the shorter Al–C distance in the CISD predicted structure.

Two of the four C–H stretching frequencies (forbidden $a_2$ and the $a_1$ mode predicted at 3229 cm$^{-1}$) of Al–$C_2H_4$ are unlikely to be observable. The other two ($b_2$ 5 km/mol and $b_1$ 3 km/mol) have weak IR intensities by comparison with isolated ethylene (32 and 16 km/mol from DZ+P CISD[26]). The Al–$C_2H_4$ C–H stretch predicted at 3329 is shifted downward by 20 cm$^{-1}$ relative to free $C_2H_4$; the $\pi$-bonded C–H stretch predicted here at 3214 cm$^{-1}$ is shifted downward by 12 cm$^{-1}$ relative to isolated $C_2H_4$.

**Table II.** Summary of Relative Energetic Results (in kcal/mol) for the $AlC_2H_4$ System[a]

| | structure | no. of imaginary freq at SCF level | rel energy SCF | CISD | Davidson corr CSID |
|---|---|---|---|---|---|
| **3** |  $^2A_1$ | 0 | +11.9 | +2.3 | +1.7 |
| **2** |  $^2B_1$ | 0 | −0.6 | −1.3 | −1.4 |
| **5** |  $^2A''$ | 1 | +2.2 | −0.2 | −0.3 |
| **4** |  $^2A'$ | 0 | −1.5 | (−6.3)[b] | (−7.0)[b] |
| **7** |  $^2A''$ | 1 | −6.4 | | |
| **6** |  $^2A''$ | 0 | −7.7 | −10.1 | −10.1 |
| **1** |  $^2B_2$ | 0 | −1.1 | −10.1 | −11.6 |
| |  | | 0.0 | 0.0 | 0.0 |

[a] All theoretical predictions were made with a double-$\zeta$ plus polarization (DZ+P) basis set. [b] This structure collapses to the $\pi$-bonded $^2B_2$ state upon geometry optimization at the DZ+P CISD level of theory.

## Concluding Remarks

The relative energies of the Al–$C_2H_4$ structures are given in Table II. For the separated Al + $C_2H_4$ system the total energies are −319.904 58 (DZ+P SCF), −320.212 15 (DZ+P CISD), and −320.247 99 hartrees (Davidson-corrected DZ+P CISD). For the global minimum $^2B_2$ state ($\pi$-bonded geometry) the total energies are −319.906 29 (DZ+P SCF), −320.228 30 (DZ+P CISD), and −320.266 48 hartrees (DZ+P CISD plus Davidson correction).

The most complete level of theory shows that the $\pi$-bonded $^2B_2$ structure is predicted to lie 1.5 kcal/mol below the aluminum–methylcarbene structure. In fact higher levels of theory are expected to (a) increase the predicted $^2B_2$ dissociation energy and (b) further separate the $\pi$-bonded and methylcarbene structures. Also shown in Table II is the interesting result that the $\sigma$-bonded $^2A'$ structure collapses to the $\pi$-bonded $^2B_2$ state when correlation effects are included in the wave functions.

Our theoretical finding of a $\pi$-bonded global minimum for $AlC_2H_4$ is consistent with the early ESR experiments of Kasai and McLeod[1,3] and also with the (unpublished) infrared experiments of Manceron and Andrews.[25] Not expected from any experimental study is the existence of the aluminum–methylcarbene minimum on the $AlC_2H_4$ potential energy hypersurface. The latter minimum should lie no more than 5 kcal/mol above the $\pi$-bonded structure, and the observation of the Al–methylcarbene structure would be an important experimental discovery.

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[25] Manceron, L.; Andrews, L. *Infrared Spectrum and Structure of the $AlC_2H_4$ Molecule in Solid Argon*; Abstract MH1, Symposium on Molecular Structure and Spectroscopy, Columbus, OH, June, 1988.

[26] Lee, T. J.; Allen, W. D.; Schaefer, H. F. *J. Chem. Phys.* **1987**, *87*, 7062.