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Ab initio molecular orbital study of dialuminum-ethylene complexes

Suk Ping So
Chemistry Department, The Chinese University of Hong Kong, Shatin, N.T. (Hong Kong)

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Abstract

The geometries of the various isomeric dialuminum-ethylene complexes $Al_2C_2H_4$ have been optimized using the STO-3G, 3-21G$^{(*)}$ and 6-31G** basis sets. Vibrational frequency calculations show that only two out of the six structures examined are thermodynamically stable. Unlike the case of $Li_2C_2H_4$, 1,2-dialuminoethane is most stable and more ethane-like than 1,2-dilithioethane perhaps due to the larger covalent character of the C–Al bond. Besides, 1,2-dialuminoethane has been found, in contrast to ethane and 1,2-dilithioethane, to have no stable *gauche* conformer.

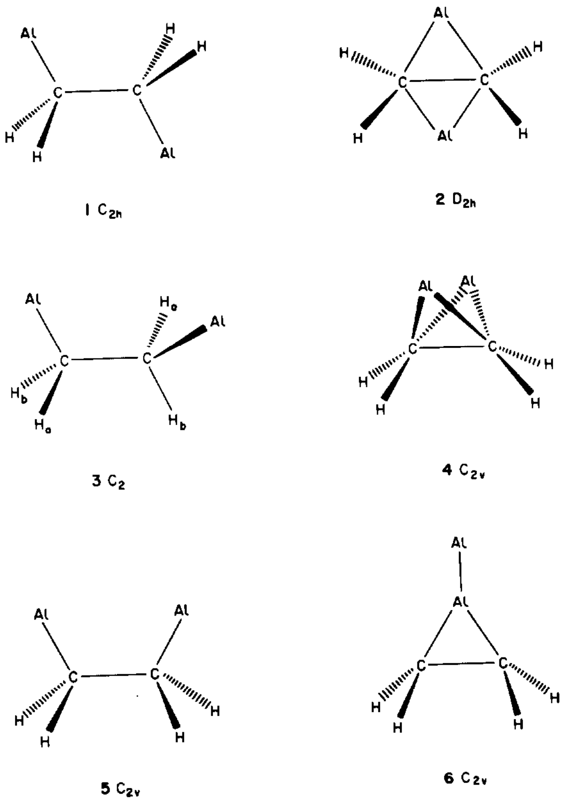
Introduction

The monoaluminum-ethylene complex AlC_2H_4 was first prepared by Kasai et al. [1] in 1975 and trapped in a neon matrix at near liquid helium temperatures. In 1982, Kasai [2] reported the formation of $Al(C_2H_4)_2$ by the photoirradiation of matrices containing AlC_2H_2 complexes. Five years later, Chenier et al. [3] and Howard et al. [4] demonstrated that AlC_2H_4 was stable up to 297 K in an adamantane matrix. From observation of the temperature dependence of the equilibrium constant for the association reaction

$$Al + C_2H_4 \rightleftharpoons AlC_2H_4$$

in the temperature range of 283–333 K, Mitchell et al. [5] have obtained a binding energy greater than 67 kJ mol^{-1} for the association. Recently, Manceron et al. [6] found that condensation of aluminum atoms and ethylene molecules at high dilution in solid argon or solid ethylene produced AlC_2H_4 as the main product, and probably $Al_2C_2H_4$ and $Al_2(C_2H_4)_2$ in small amount. They reported no structural study of the latter two species because of the small number of observed infrared bands attributable to them.

Theoretically, only AlC_2H_4 has been studied by *ab initio* quantum mechanical methods [7,8]. Among the several possible structures of AlC_2H_4, only the π-bonded complex appears to have been observed experimentally to date and has been confirmed theoretically to be strongly bound ($D_0 > 46$ kJ mol^{-1}).



1 C_{2h} 2 D_{2h}

3 C_2 4 C_{2v}

5 C_{2v} 6 C_{2v}

Fig. 1. Structures of dialuminum-ethylene complexes $Al_2C_2H_4$.

To investigate the reactivity of alkali metal atoms with unsaturated hydrocarbon molecules and the structures of the possible products, Manceron and Andrews [9] have carried out a series of infrared work on lithium-ethylene complexes in solid argon. They found that condensation of ethylene molecules and alkali metal atoms at high dilution in argon produced very different results, depending on the nature of the alkali metal. Heavy alkali metal atoms (Na and Cs) yielded only a very weak complex with ethylene virtually unperturbed. Lithium, on the contrary, produced $Li_2C_2H_4$ and $Li(C_2H_4)_n$ ($n = 1$–3) complexes displaying a large degree of perturbation in the ethylene ligand.

The different possible structures of $Li_2C_2H_4$, the lithium analogues of $Al_2C_2H_4$ as shown in Fig. 1, have been studied theoretically [10,11]. Only structures **1**–**5** were considered by Kos et al. [10] and they found **1** to be lowest in energy. However, So [11] recently showed that **6** was the global energy minimum among the six structures at all the levels of theory examined in line with experiment [9].

It was thus thought desirable to perform a theoretical study on the different structures (Fig. 1) of $Al_2C_2H_4$ as a continuation of our work on $Li_2C_2H_4$ [11].

Calculation

The structures **1–6** of singlet $Al_2C_2H_4$ were optimized by the energy gradient method at the SCF level using GAUSSIAN 82 and GAUSSIAN 88 programs [12] implemented on our IBM4381 and Micro VAX2000 computers, respectively. The basis sets employed are the standard STO-3G, 3-21G$^{(*)}$ (3d polarization function on aluminum atoms only) and 6-31G** (2p and 3d polarization functions on hydrogen and non-hydrogen atoms respectively).

The energies of the various structures of $Al_2C_2H_4$ at the optimized 6-31G** geometries were then re-calculated by the third-order perturbation theory with the Møller-Plesset (MP3) partitioning of the Hamiltonian [13] in order to take into account the electron correlation.

Harmonic vibrational frequencies were computed by analytically differentiating the energies twice.

Results and discussion

The structures **1–6** of $Al_2C_2H_4$ have been optimized under the specified symmetries (Fig. 1). The optimization of **3**, however, was somewhat tricky and had to be carried out in two steps. First of all, the Al–C–C–Al dihedral angle was fixed at 60 ° while all other molecular dimensions were being optimized. Then a full optimization was performed using the geometry obtained in the first step as the initial guess. However, when the 3-21G$^{(*)}$ basis was employed, **3** collapsed to **1** in the second optimization when starting geometries obtained with Al–C–C–Al dihedral angles fixed at 60 °, 80 ° and 90 ° were tried. The 3-21G$^{(*)}$ basis has also been found to lead to the collapse of the non-planar structure of trichloromethyl radical to the planar one during geometry optimization [14].

The structural parameters of **1–6** are given in Table 1 in which ethylene is also included for comparison purposes. Results of Table 1 reveal that the 3-21G$^{(*)}$ values of all the bond lengths are generally larger than the corresponding STO-3G values. However, the C–C bonds calculated at the 6-31G** level are shorter than the 3-21G$^{(*)}$ ones, as generally found for these bases [15]. The 6-31G** and the 3-12G$^{(*)}$ C–H and C–Al bond distances, on the other hand, are very similar. As for the bond angles, some are affected by the basis sets to a larger extent than the others. As a whole, 3-21G$^{(*)}$ and 6-31** structures are closer to each other.

In terms of the SCF state energies listed in Table 2, the structures **1–6** of $Al_2C_2H_4$ can be ordered for all levels (STO-3G, 3-21G$^{(*)}$ and 6-31G**) of theory examined in decreasing stability as: **1** > **3** > **5** > **2** > **4** > **6**. However, electron correlation correction at both MP2 and MP3 affects the relative stability of **2** only, placing it energetically below **3** in the above sequence. For the Li analogues, the order of the relative stability (HF/3-21G) is [10,11]: **6** > **1** > **2** > **3** > **4** > **5**.

Vibrational frequency calculations reveal that only **1** and **6** are thermodynamically stable. Structures **2**, **3** and **4** have one imaginary frequency each and hence are transition states. Structure **5** has two imaginary frequencies and represents an energy maximum on the potential surface. For the lithium analogues, no such information has been reported.

As pointed out above, structure **1** of $Al_2C_2H_4$ is more stable than **6** (by 94.9 kcal mol^{-1} at MP3/6-31G**//HF/6-31G**), while the reverse is true for

Table 1
Optimized bond lengths (Å) and bond angles (degrees) of $Al_2C_2H_4$ complexes and ethylene

	STO-3G	3-21G$^{(*)}$	6-31G**		STO-3G	3-21G$^{(*)}$	6-31G**
Structure **1**				*Structure* **4**			
C–C	1.566	1.610	1.575	C–C	1.553	1.550	1.518
C–H	1.091	1.091	1.093	C–H	1.085	1.084	1.083
C–Al	1.969	1.999	2.007	C–Al	2.125	2.228	2.252
C–C–H	108.4	111.3	111.3	C–C–H	113.5	115.8	116.7
C–C–Al	111.6	97.22	101.1	C–C–Al	68.56	69.64	70.31
H–C–H	104.6	108.4	106.7	H–C–H	103.8	105.3	105.7
H–C–Al	111.7	114.2	113.2	Al–X–Al [a]	72.35	74.88	74.15
Structure **2**				*Structure* **5**			
C–C	1.579	1.572	1.541	C–C	1.578	1.605	1.573
C–H	1.069	1.078	1.078	C–H	1.089	1.096	1.096
C–Al	2.066	2.147	2.148	C–Al	1.965	2.002	2.006
C–C–H	120.4	120.5	121.0	C–C–H	108.8	108.3	109.1
C–C–Al	67.54	68.52	68.99	C–C–Al	113.6	121.2	123.6
				H–C–H	104.4	104.5	103.5
				H–C–Al	110.4	106.7	104.9
Structure **3**				*Structure* **6**			
C–C	1.561		1.562	C–C	1.596	1.644	1.603
C–H_a	1.092		1.097	C–H	1.084	1.079	1.080
C–H_b	1.090		1.096	C–Al	1.830	1.919	1.915
C–Al	1.970		2.010	Al–Al	2.021	2.372	2.383
C–C–H_a	109.7		111.6	C–C–H	113.6	113.4	114.2
C–C–H_b	109.6		110.2	C–C–Al	64.15	64.64	65.25
C–C–Al	113.0		114.3	H–C–H	108.8	111.9	111.1
H_a–C–H_b	104.1		104.1				
H_a–C–Al	111.9		110.2	*Ethylene*			
H_b–C–Al	108.1		105.8	C–C	1.306	1.315	1.317
Al–C–C–Al	98.99		96.67	C–H	1.082	1.074	1.076
				C–C–H	122.2	121.9	121.7

[a] X is the midpoint of the C–C bond.

$Li_2C_2H_4$ (by 12.9 kcal mol^{-1} [16]). In the Pauling scale, the electronegativities of Li, Al and C are 0.97, 1.47 and 2.50, respectively. Hence, the C–Li bond is expected to be more ionic and the C–Al bond more covalent. Indeed, according to the formula proposed by Pauling [17], the ionic character can be estimated to be 44% for a C–Li bond and 22% for a C–Al bond. Furthermore, lithium has been shown to utilize its empty 2*p* orbitals to form multicentre bonds in bridging structures [18]. For example, the greater stability of the bridged structures of 1,3-dilithiopropane over the open structure has been attributed to these properties of lithium [19]. Results of Mulliken population analysis are known to be strongly basis set dependent and should not be compared literally for molecules of different compounds. Nevertheless, the Mulliken overlap populations and charge distributions for $M_2C_2H_4$–**1**, $M_2C_2H_4$–**6**, M_2 (M = Li, Al) and C_2H_4 as listed in Table 3 do yield some interesting implications. The covalent overlap population for the C–Li bond of $Li_2C_2H_4$–**6** (0.096) is substantially smaller than those for the carbon–metal bonds of $Li_2C_2H_4$–**1** (0.611), $Al_2C_2H_4$–**1** (0.499) and $Al_2C_2H_4$–**6**

Table 2

Energies (a.u.) of $Al_2C_2H_4$ complexes at optimized geometries

	STO-3G	3-21G$^{(*)}$	6-31G**
1	−555.06360	−558.85370	−561.81162 (−562.19153, MP2) (−562.22899, MP3)
2	−555.00284	−558.83402	−561.78977 (−562.18759, MP2) (−562.22016, MP3)
3	−555.05979	–	−561.80541 (−562.18121, MP2) (−562.22003, MP3)
4	−554.97071	−558.79119	−561.74742 (−562.15145, MP2) (−562.18514, MP3)
5	−555.05195	−558.83890	−561.79800 (−562.17409, MP2) (−562.21314, MP3)
6	−554.78395	−558.69121	−561.64896 (−562.04226, MP2) (−562.07782, MP3)

(0.687), while $Li_2C_2H_4$–**6** has practically the same Li–Li and C–H but a smaller C–C overlap population when compared to the free Li_2 and C_2H_4 molecules. It is seen from Table 1 that complexation lengthens the C–C bond of the C_2H_4 subunit (1.317 Å at 6-31G** level) by 0.258 Å, 0.286 Å and 0.250 Å for $Al_2C_2H_4$–**1**, $Al_2C_2H_4$–**6** and $Li_2C_2H_4$–**1**, respectively, but only by 0.007 Å for $Li_2C_2H_4$–**6**. All these indicate that the carbon–metal bonds of the former three species have substantial covalent character and that complexation in the latter involves the overlapping of lithium and carbon orbitals only to a very slight extent. Charge distributions show that lithium in $Li_2C_2H_4$–**6**, accepts into its vacant 2*p* orbitals

Table 3

Mulliken (6-31G**) overlap populations and charge distributions of $M_2C_2H_4$ complexes, M_2 (M = Al, Li) and C_2H_4 molecules.

	M = Al			M = Li			C_2H_4
	1	6	M_2	1	6	M_2	
Overlap populations							
M–M	–	0.626	1.976	–	0.773	0.771	–
C–M	0.499	0.687	–	0.611	0.096	–	–
C–C	0.471	0.296	–	0.308	1.129	–	1.290
C–H	0.786	0.788	–	0.762	0.824	–	0.820
Charge distributions							
M(M)	–	−0.193	0.000	–	−0.002	0.000	–
M(C)	+0.349	+0.513	–	+0.291	−0.124	–	–
C	−0.582	−0.430	–	−0.483	−0.275	–	−0.254
H	+0.116	+0.135	–	+0.096	+0.169	–	+0.127

electronic charge from the C_2H_4 subunit, bridging the two carbon atoms with a three-centre bond. In the other three species, however, metal-to-ligand donations of electrons are, as anticipated, important, giving some ionic character to their carbon–metal bonds. The present predicted (6-31G**) C–Al bonds of 2.007 Å for $Al_2C_2H_4$–**1** and 1.915 Å for $Al_2C_2H_4$–**6** are somewhat longer and shorter, respectively, than a conventional C–Al single bond in view of the experimentally determined [20] C–Al bond of 1.957 Å (the optimized value from this work is 1.979 Å) for gaseous monomeric trimethylaluminum in which aluminum has a planar trigonal local symmetry and hence sp^2 hybridization. Hence, it is not surprising to find that $Li_2C_2H_4$–**6** is more stable than $Li_2C_2H_4$–**1** but the reverse is true for $Al_2C_2H_4$ perhaps, partly at least, due to the three-member ring strain present in $Al_2C_2H_4$–**6** which is, unlike $Li_2C_2H_4$–**6** as discussed above, not a metal-olefin π-bonded complex.

The C–C–Li angle of $Li_2C_2H_4$–**1** is 72.9°, and the corresponding angle for $Al_2C_2H_4$–**1** is 101.1° (6-31G**). Hence, $Li_2C_2H_4$–**1** may be considered as partially bridged while $Al_2C_2H_4$–**1** is more ethane-like.

The vibrational frequencies have been computed using the 3-21G$^{(*)}$ basis for **1**, **2**, **4**, **5** and **6**, but the 6-31G** basis for **3**. This is because, as mentioned earlier, optimization of **3** using the former basis set fails. In addition, the frequencies for the thermodynamically stable $Al_2C_2D_4$ isomers have also been predicted. The agreement between theoretical and experimental vibrational frequencies is generally improved by scaling the theoretical values [21]. The scale factor corrects both for the deficiencies in the theory and for the neglect of anharmonicity. It has been generally found that the HF/6-31G* harmonic frequencies uniformly scaled by a factor of 0.89 lie within 100 cm^{-1} of experiment with a mean absolute error of 49 cm^{-1}. To our belief, such a conclusion would still be valid for the 3-21G$^{(*)}$ and 6-31G** basis sets. The vibrational frequencies calculated in this work after being uniformly scaled by a factor of 0.89 are listed in Table 4. The theoretical C–C stretching vibrational frequency is 765 cm^{-1} for **1** and 804 cm^{-1} for **6**. Comparison of these values with those predicted for ethylene (1639 cm^{-1}; obs. 1623 cm^{-1}) and ethane (894 cm^{-1}; obs. 995 cm^{-1}) suggests, as do the data in Table 1, that the C–C bonds of **1** and **6** are single rather than double in character. Structure **6** when compared to **1** is thus seen to have a longer C–C bond but yet a higher C–C stretching vibrational frequency. This is not too surprising if one realizes that the carbon atoms of **6** are in a three-member ring; hence they are less free to vibrate against each other and also this mode will mix with other vibrations to a larger extent.

Frequencies of some infrared bands attributed [6] to arise from $Al_2C_2H_4$ or $Al_nC_2H_4$ are reproduced in Table 4 for comparison purposes. It is surprising that, except for two bands, the experimental frequencies of the $Al_2C_2H_4$ complexes containing different isotopic ethylene subunits, namely, C_2H_4 and C_2D_4, have been reported to be practically the same. However, our theoretical results show that, except for the first three lowest frequencies, all other vibrational frequencies are lowered by about 36–767 cm^{-1} on deuteration. Hence comparison of the theoretical and observed frequencies gives no confirmation of the carrier of the observed infrared bands though **1** is more likely. Nevertheless, it is hoped that the present result may serve as a guide and stimulus for future work on these species.

To study the internal rotation of the CH_2Al group about the C–C bond of **1**,

Table 4

Calculated (3-21G$^{(*)}$) vibration frequencies (cm^{-1})[a] of $Al_2C_2H_4$ **1** and **6** and observed infrared bands (cm^{-1})[b]

Sym.[c]	**1**		Sym.[d]	**6**		Observed bands	
	C_2H_4	C_2D_4		C_2H_4	C_2D_4	C_2H_4	C_2D_4
a_u	2837	2100	b_1	2367	2201	~ 1366	
b_g	2826	2097	a_2	2947	2191	1172	1170
a_g	2789	2022	a_1	2895	2102	1160	1160
b_u	2786	2019	b_2	2887	2091	1126	1126
a_g	1417	1036	a_1	1406	1058	742	985
b_u	1402	1038	b_2	1395	1031	~ 600	~ 605
b_g	1234	935	a_2	1134	866	~ 428	~ 498
a_g	1117	902	b_2	992	811		
b_u	994	766	a_1	965	714		
a_u	921	652	b_1	843	609		
a_g	765	723	a_1	804	751		
a_g	568	513	b_1	646	489		
b_u	566	530	b_2	629	571		
b_g	548	418	a_1	535	524		
a_u	464	347	a_2	394	287		
a_g	127	124	a_1	321	314		
b_u	118	113	b_1	133	125		
a_u	70	64	b_2	108	104		

[a] Uniformly scaled by a factor of 0.89. [b] Attributed to $Al_2C_2H_4$ or $Al_nC_2H_4$ in solid argon [6]. [c] The y- and z-axes are along the C–C bond and perpendicular to the skeletal molecular plane, respectively. [d] The x- and the z-axes are perpendicular to the skeletal molecular plane and along the Al–Al bond, respectively.

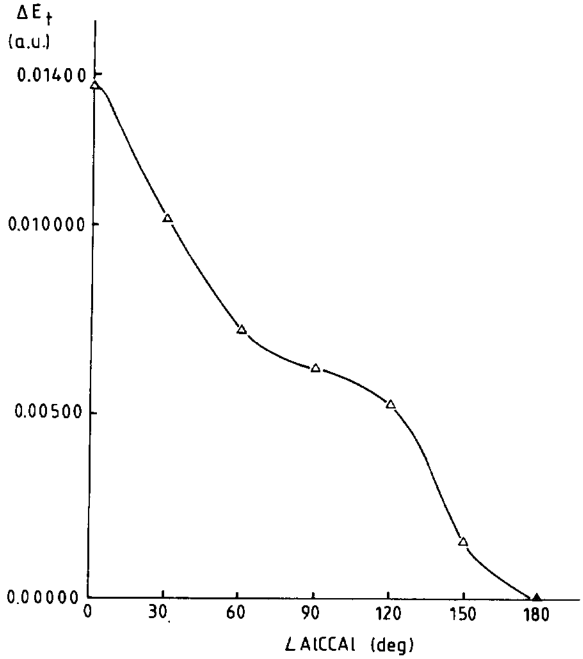


Fig. 2. Relative energy of 1,2-dialuminoethane as a function of the Al–C–C–Al dihedral angle.

the Al–C–C–Al dihedral angle (τ) was kept fixed in steps of 30° during the optimization of the other molecular dimensions. As the Al–C–C–Al dihedral angle increases from 0° (**5**) to 180° (**1**), significant changes have been noted in the C–C and C–Al bonds and in the C–C–H_a, H_a–C–Al, H_b–C–Al and C–C–Al bond angles, going rather smoothly through a maximum or a minimum: the C–Al bond and the C–C–Al and C–C–H_a angles are largest (2.010 Å, 122.8° and 122.4°) at $\tau = 90°$, 30° and 120°, while the C–C bond and the H_a–C–Al and H_b–C–Al angles are smallest (1.557 Å, 100.7° and 105.4°) at $\tau = 60°$, 30° and 90°, respectively.

The energies of the various rotomers are plotted against τ in Fig. 2. It is interesting to note that as τ increases from 0° to 180°, an energy minimum occurs only at $\tau = 180°$ (**1**) even though there might be an extremely shallow *gauche* minimum near $\tau = 75$–$80°$ which has not been definitely detected in the present work. This is in contrast to the lithium analogue and the well-known ethane. The former has been reported [10] to have a pronounced *gauche* minimum (**3**) at $\tau = 84.0°$ (3-21G) which however has not been confirmed to be a true minimum by vibrational frequency calculations.

To study the stability of $Al_2C_2H_4$–**1** toward some simple possible dissociations represented by the following equations.

$$Al_2C_2H_4\text{–}\mathbf{1} \rightarrow CH_2{=}CH_2 + 2Al \quad (1)$$

$$Al_2C_2H_4\text{–}\mathbf{1} \rightarrow CH_2{=}CH_2 + Al_2 \quad (2)$$

$$Al_2C_2H_4\text{–}\mathbf{1} \rightarrow CH_2{=}CHAl + HAl \quad (3)$$

$$Al_2C_2H_4\text{–}\mathbf{1} \rightarrow \textit{trans}\text{-}CHAl{=}CHAl + H_2 \quad (4)$$

$$Al_2C_2H_4\text{–}\mathbf{1} \rightarrow AlC_2H_4 + Al \quad (5)$$

the geometries of H_2, Al_2, HAl, C_2H_4, C_2H_3Al, *trans*-$C_2H_2Al_2$ and AlC_2H_4 were also optimized using the 3-21G$^{(*)}$ and the 6-31G** basis functions. Their zero-point vibrational energies (theoretical 3-12G$^{(*)}$ frequencies were uniformly scaled by a factor of 0.89) and MP3 energies (6-31G**) were then computed (0 cm^{-1} and −241.89596 a.u. for Al, 2072 cm^{-1} and −1.16316 a.u. for H_2, 289 cm^{-1} and −483.60380 a.u. for Al_2, 806 cm^{-1} and −242.50019 a.u. for HAl, 10761 cm^{-1} and −78.33997 a.u. for C_2H_4, 8539 cm^{-1} and −319.67492 a.u. for C_2H_3Al, 6265 cm^{-1} and −561.01450 a.u. for *trans*-$C_2H_2Al_2$, and 10496 cm^{-1} [7] and −320.25299 a.u. for AlC_2H_4) at their 3-21G$^{(*)}$ and 6-31G** geometries, respectively. The reaction energies (energy sum of products − energy of reactant) obtained at the highest theoretical level employed (MP3/6-31G**//HF/6-31G**) are found to be 60.9, 179, 33.8, 32.2 and 50.2 kcal mol^{-1} for reactions 1, 2, 3, 4 and 5, respectively. These values become 60.9, 180, 29.7, 25.2 and 49.4 kcal mol^{-1} when the zero-point vibrational energies are taken into consideration. Thus, thermodynamically $Al_2C_2H_4$–**1** is stable toward all the above dissociations. $Li_2C_2H_4$–**1**, on the other hand, has been computed [10] to be unstable toward dissociation into C_2H_4 and Li_2.

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