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Reaction of AlCl Monomers with Acetylene in a Solid Argon Matrix at 12 K: First Characterization of the Aluminum Acetylide Species Cl(H)AlCCH, Featuring a Short Al−C Bond

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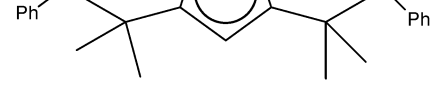
The photoactivated reaction between monomeric AlCl and acetylene in a solid Ar matrix at 12 K is shown to lead to an insertion product, the acetylide species Cl(H)AlCCH. The compound was characterized by its IR spectrum, taking in the effect of isotopic substitution (H/D), and by quantum-chemical calculations. The other possible isomer, the aluminacyclopropene derivative, is not formed. In agreement with the experimental findings, the aluminacyclopropene isomer is calculated to exhibit an energy about 40 kJ mol^{-1} higher than that of Cl(H)AlCCH. The discussion includes also a comparison between possible structures of other homologues of group 13 elements, especially $ClBC_2H_2$ and $ClGaC_2H_2$. While the cyclic structure is stable for XBC_2H_2 (X = H, halogen), the Al and Ga homologues prefer the acetylide isomeric form. Additional experiments were carried out with 2-butyne. The results show that photoactivated AlCl reacts also with 2-butyne upon photoactivation. However, not one but (at least) two products are formed, which are in all probability the insertion product $Cl(H)AlCH_2CCCH_3$ and the corresponding aluminacyclopropene isomer.

Introduction

There are now known numerous stable alkynylaluminum compounds which were synthesized and structurally characterized. The first authenticated compound of this class, reported as early as 1974, was the dimer $[Ph_2AlCCPh]_2$, exhibiting Al−C distances of 199.2 and 218.4 pm.[1] Recently several new molecules were characterized: e.g., compound **1**.[2] An interesting feature of the structure of this and comparable species is the angle Al−C−C, which deviates in several cases from 180°.[3] Thus, in **1** Al−C−C angles of 160.2 and 178.3° are adopted. While small angles are not an exception for alkynyl groups attached to transition-metal centers, compounds composed of main-group elements (E) were believed for a long time to prefer a linear E−C−C arrangement.



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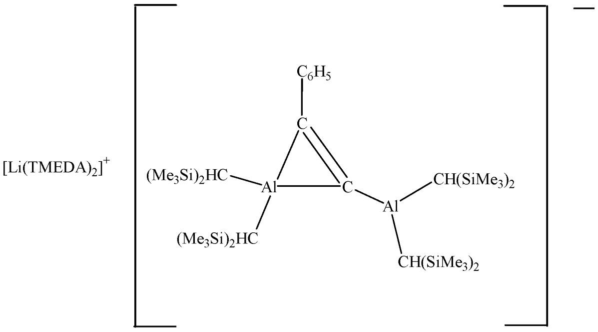
Alkynyl species such as $Me_2AlCCPh$ were used recently to synthesize new exciting carbaalane clusters.[4] Thus, for example, the reaction of dimethylaluminum hydride with an excess of $Me_2AlCCPh$ proceeds to give the carbaalane $(AlMe)_8(CCH_2Ph)_5H$ (and $AlMe_3$)[5] and, if the excess of Me_2AlH is reduced, $(AlMe)_8(CCH_2Ph)_5(CCPh)$.[4] Other examples include $(AlEt)_7(CCHPh)_2(CCH_2Ph)_3H$, prepared from $Et_2AlCCPh$ and an excess of Et_2AlH,[6] and $(AlMe)_8(CCH_2Me)_5H$, made from $Me_2AlCCMe$ and Me_2AlH.[7]

AlC_2 three-membered heterocycles were postulated as reactive intermediates.[8] With compound **2**, the first



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representative of this class was structurally characterized recently.[9] The Al−C distances within the AlC_2 heterocycle were determined to be 195.1(3) and 205.2(3) pm. At 188.6(3) pm, the Al−C distance between the C atom of the ring and the exocyclic Al atom is very short, which argues for the presence of significant π interaction.

The reaction of boron monofluoride, BF, with acetylene was studied already in 1968.[10] In addition to a polymer, some volatile species were obtained as products, one being identified as $(F_2BCHCH)_2BF$. In the vapor phase this species loses BF_3 to form 1,4-difluoro-1,4-diboracyclohexadiene, a species isoelectronic with *p*-benzoquinone. Some stable borirenes were synthesized by reaction of MeB, generated in situ from $MeBBr_2$ and KC_8, with di-*tert*-butylacetylene and other acetylene derivatives in benzene.[11] The aromaticity of these species was assessed in quantum-chemical calculations.[12] According to these calculations, the resonance energy of borirene amounts to about 200 kJ mol^{-1} (ca. 70% of the energy derived for the cyclopropenium cation). Borirene was also characterized in the gas phase[13] and in solid Ar matrixes.[14] Crystals of the dimer of 1,4-dichloro-2,3,5,6-tetramethyl-1,4-dialumina-2,5-cyclohexadiene, $Al_4Cl_4C_{16}H_{24}$, were obtained as products of the reaction between AlCl and 2-butyne.[15] The two units in this dimer are linked via aluminum−olefin π-interactions.

With regard to matrix isolation experiments, the reaction of thermally generated Al atoms with acetylene was studied extensively in the past. Burkholder and Andrews found evidence for the spontaneous formation of a π complex with a $^2B_2$ electronic ground state and a three-membered-ring structure with a $^2A_1$ electronic ground state.[16] Calculations indicate, in agreement with the experimental findings, that the three−membered ring is energetically slightly favored (by 15−30 kJ mol^{-1}) over the π complex.[17] Upon photolysis, two other products, namely the insertion product (the radical species HAlCCH) and AlCCH, were observed. The same products, but with different relative proportions, were observed when the reaction was carried out with laser-ablated Al atoms.[18] This reaction was also studied with EPR spectroscopy.[19]

Herein we report a study of the reactions between AlCl and acetylene, as well as 2-butyne, in a solid Ar matrix at temperatures of 12 K. Matrix-isolated, monomeric AlCl was shown previously to react readily upon photoactivation[20] with a number of small molecules, including HBr,[21] HCl,[22] 1[23] or 2 mol of O_2,[24] and another AlCl molecule (to give the cyclic dimer $[AlCl]_2$).[25]

Experimental Section

C_2H_2 (Messer, purity 2.6) was purified prior to usage by trap-to-trap distillation. C_2D_2 was prepared from CaC_2 (Aldrich) and D_2O. The product was freed from traces of water and other impurities by passage through a cold trap kept at −78 °C.

Details of the matrix isolation methods can be found elsewhere.[26] Very briefly, AlCl was generated by passing HCl over liquid Al in a Knudsen-type evaporation cell heated resistively to 900 °C. The AlCl vapor emitted from the cell was codeposited together with acetylene under an excess of Ar gas onto a Cu block kept at 12 K by means of a closed-cycle refrigerator (Leybold LB510).

IR spectra were recorded on a Bruker 113v IR spectrometer equipped with two DTGS detectors and one MCT detector to cover the spectral range 200−4000 cm^{-1}. Photolysis was achieved with the aid of a medium-pressure mercury lamp (Philips LP 125) operating at 100 W.

Quantum-chemical calculations relied on the TURBOMOLE program package.[27] The BP method in combination with TZVPP basis sets for Al, B, and Ga and a SVP basis set for all other elements were used.

Results

The IR spectrum taken upon deposition of AlCl together with acetylene under an excess of Ar showed all the absorptions characteristic of acetylene and AlCl.[21] An additional feature appearing at 438.5/433.0 cm^{-1} belongs in all probability to the weak adduct $AlCl{\cdot}C_2H_2$ (see Figure 1). For comparison, in experiments in which AlCl was cocondensed together with HBr, the adduct AlCl·HBr is responsible for a broad absorption at 425 cm^{-1}.[21] However, there was no sign of any additional product from the interaction of AlCl with C_2H_2.

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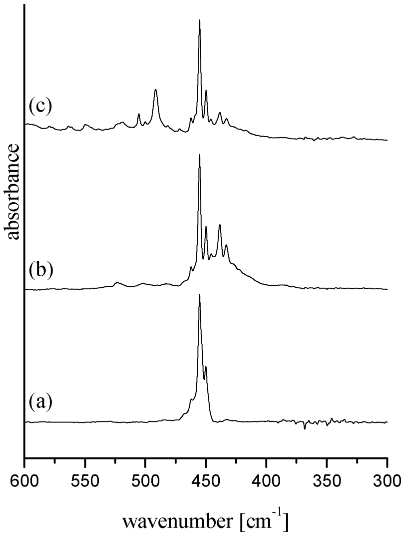

Figure 1. IR spectra in the region 600−300 cm^{-1} taken for AlCl in a solid Ar matrix: (a) upon deposition together with CH_4, providing an example for no detectable interaction;[42] (b) upon deposition together with C_2H_2; (c) following subsequent photolysis of the matrix as in (b).

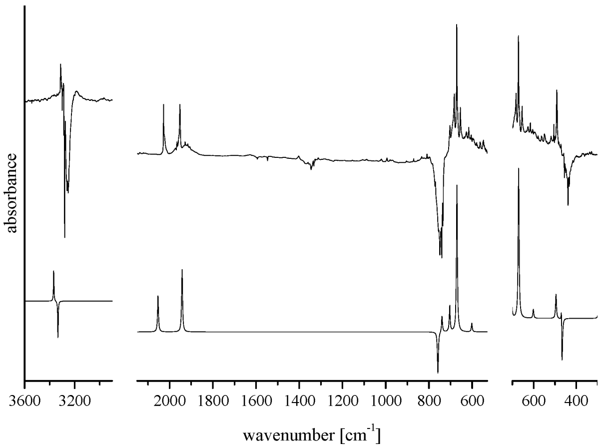

Figure 2. (a, bottom) Difference between the IR spectrum taken following photolysis of an Ar matrix containing AlCl and C_2H_2 and the IR spectrum taken immediately upon deposition. (b, top) Difference between the simulated IR spectrum of Cl(H)AlCCH and those of C_2H_2 and AlCl.

Photolysis is needed to initiate further reaction. Upon 45 min of photolysis of the matrix with broad-band UV−vis radiation (200 < λ_{max} < 800 nm), the signals due to C_2H_2 and perturbed AlCl decreased sharply. At the same time, a group of new absorptions appeared, all belonging to the same absorber (the relative intensities remained unchanged in experiments in which the concentrations of C_2H_2 and/or AlCl were modified). The strongest absorption of this group occurred at 671.4 cm^{-1} (see Figure 2a). Strong absorption maxima were also detected at 2027.9, 1952.2, and 491.4 cm^{-1}. Of these, the feature at 1952.2 cm^{-1} appears in a region in which ν(Al−H) modes of Al(III) species are expected to occur (cf. AlH_3 1882.7 cm^{-1},[28,29] H_2AlNH_2 1899.3/1891.0 cm^{-1},[30] H_2AlPH 1874.1/1866.1 cm^{-1},[31] $HAlCl_2$ 1967.6 cm^{-1},[22] HAl(F)Cl 2005 cm^{-1},[21] HAl(F)Br 1990 cm^{-1},[21] HAlClBr 1959.6 cm^{-1} [21]) The absorption at 2027.9 cm^{-1} has a wavenumber suggesting a ν(C−C) stretching mode of an acetylide group. For BeCCH,[32] MgCCH,[32] AlCCH,[16] and SiCCH,[33] all isolated in solid Ar matrixes, wavenumbers of 2018.9, 1984.2, 1976.4, and 1989.8 cm^{-1}, respectively, were measured for the corresponding ν(C−C) stretching fundamentals. Additional sharp but weaker features were detected at 3312.0, 703.0, 683.0, 615.9, 505.8, and (very weak) 327.3 cm^{-1}. Of these, the band at 505.8 cm^{-1} lies in a region in which ν(Al−Cl) stretching modes of Al(III) species appear, although, of course, mode coupling may be substantial (cf. $HAlCl_2$ 578.9/481.3 cm^{-1},[22] HAlFCl 524.6 cm^{-1},[21] HAlBrCl 552.4 cm^{-1} [21]). The band at 683.0 cm^{-1} lies in a region in which the deformation mode of an acetylide group, δ(HCC), is expected to appear (cf. AlCCH 683.5 cm^{-1},[16] BeCCH 675.7 cm^{-1},[32] MgCCH 660.8 cm^{-1} [32]). The band at 3312.0 cm^{-1} is likely to belong to a mode with a high contribution from the ν(C−H) stretching fundamental, which is shifted slightly to higher wavenumbers compared to acetylene. For comparison, the ν(C−H) mode in the free $[CCH]^-$ anion isolated in an Ar matrix appears at 3318.5 cm^{-1}.[34]

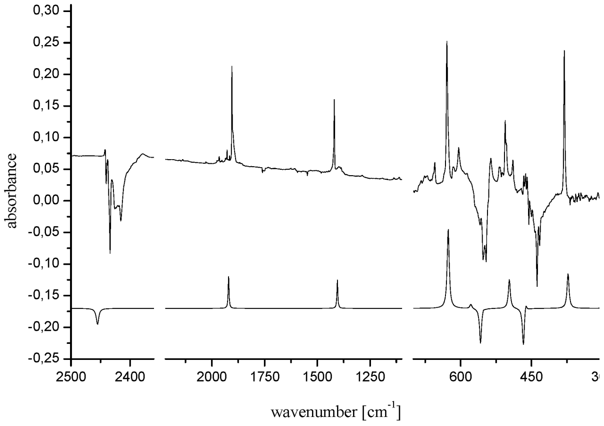

Figure 3. (a, bottom) Difference between the IR spectrum taken following photolysis of an Ar matrix containing AlCl and C_2D_2 and the IR spectrum taken immediately upon deposition. (b, top) Difference between the simulated IR spectrum of Cl(D)AlCCD and those of C_2D_2 and AlCl.

The experiment was repeated with C_2D_2 in place of C_2H_2. Except for a band at 438.5/433.0 cm^{-1} due to perturbed AlCl, no absorption attributable to a reaction product appeared immediately upon deposition. However, strong bands which can be assigned to a single reaction product were visible in the IR spectrum taken upon UV photolysis of the matrix (see Figure 3a). These bands belong in all probability to the same product as those detected in the experiments using C_2H_2, but this time in its perdeuterated guise. The vibrational modes were all red-shifted with respect to those observed in the experiments with C_2H_2. The strongest absorption in the spectrum shifted from 671.4 cm^{-1} (experiment

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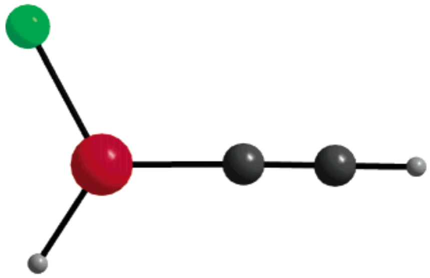
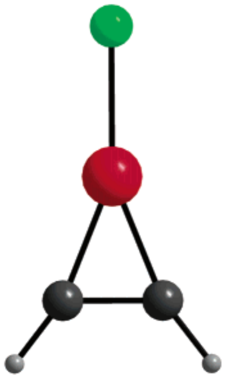
with C_2H_2) to 629.0 cm^{-1} (experiment with C_2D_2), giving a $\nu(H)/\nu(D)$ ratio of 1.0674:1. The strong absorption at 2027.9 cm^{-1} in the experiment with C_2H_2 experienced also only a relatively small shift to 1905.9 cm^{-1} ($\nu(H)/\nu(D)$ = 1.0640:1). In contrast, the band at 1952.2 cm^{-1} suffered a substantial isotopic shift to 1419.3 cm^{-1} ($\nu(H)/\nu(D) = 1.3755:1$), indicating that the corresponding mode involves a large movement of one of the hydrogen atoms. The strong feature at 491.4 cm^{-1} was now detected at 380.5 cm^{-1} ($\nu(H)/\nu(D) = 1.2915:1$). The other bands experienced shifts from 3312.0 to 2584.6 cm^{-1}, from 703.0 to 604.3 cm^{-1}, from 683.0 to 505.6 cm^{-1}, from 615.9 to 541.9 cm^{-1}, from 505.8 to 466.4 cm^{-1}, and from 327.3 to 309.0 cm^{-1}.

Discussion

The experiments give clear evidence that AlCl reacts upon photoactivation with C_2H_2 to give a single new product. The IR absorptions of this product indicate the presence of terminal C−H, Al−H, and Al−Cl bonds. In addition, the product is likely to contain a C−C triple bond. The obvious inference is that the product is the acetylide species H(Cl)AlCCH. Quantum-chemical calculations that were carried out to get more information about this product indicated a C_s symmetric global energy minimum structure of H(Cl)AlCCH:



Cl(H)AlCCH



ClAl(C_2H_2)

At 190.6 pm, the Al−C bond distance is very short (see later discussion). The C−C distance of 123.3 pm indicates the presence of an intact C≡C triple bond. The Al−Cl and the Al−H distances amount to 211.1 and 159.0 pm, respectively. These values are very close to those calculated previously for Al(III) species such as HAlFCl (210.2 and 157.5 pm).[21] The Al−Cl distance is thus significantly reduced compared with that in the AlCl reactant (216.5 pm). The angles Cl−Al−H, H−Al−C, and Cl−Al−C at the Al atom measure 119.1, 123.0, and 117.9°, respectively. In agreement with what is predicted on the basis of the VSEPR model,[35] the angles including the electronegative Cl are smaller than the H−Al−C angle. At 178.9°, the angle Al−C−C deviates only very slightly from 180°.

Table 1. Measured and Calculated IR Properties of Cl(H)AlC$_2$H (in cm^{-1}, with IR Intensities (in km mol^{-1}) in Parentheses)

Cl(H)AlC$_2$H		Cl(D)AlC$_2$D			
obsd	calcd	obsd	calcd	assign	approx descripn
3312.0	3366.9 (29)	2584.6	2614.3 (2)	$\nu_1(a')$	ν(C−H)
2027.9	2054.4 (71)	1905.9	1920.7 (80)	$\nu_2(a')$	ν(C−C)
1952.2	1941.9 (124)	1419.3	1404.8 (71)	$\nu_3(a')$	ν(Al−H)
683.0	693.3 (58)	505.6	497.0 (72)	$\nu_4(a')$	δ(CCH)
671.4	668.1 (288)	629.0	626.4 (201)	$\nu_5(a')$	δ(HAlCl)
615.9	600.6 (13)	541.9	552.1 (7)	$\nu_6(a')$	ν(Al−C)
505.8	494.9 (46)	466.4	462.3 (23)	$\nu_7(a')$	ν(Al−Cl)
327.3	295.6 (22)	309.0	282.4 (23)	$\nu_8(a')$	δ(AlCC)
a	130.3 (1)	*a*	125.0 (1)	$\nu_9(a')$	δ(AlClC)
703.0	722.4 (33)	604.3	578.4 (11)	$\nu_{10}(a'')$	ρ(C−H)
491.4	496.8 (108)	380.5	372.7 (87)	$\nu_{11}(a'')$	ρ(Al−H)
b	218.7 (7)	*a*	191.1 (1)	$\nu_{12}(a'')$	

[a] Out of the range of detection in our experiment. [b] Too weak to be detected.

The calculated IR spectrum is depicted together with the experimental one in Figure 2b for Cl(H)AlCCH and in Figure 3b for the perdeuterated version, Cl(D)AlCCD. Table 1 contains a comparison of the wavenumbers calculated and observed for both isotopomers. From the figures and the table it is obvious that the general level of agreement is very good, thus lending strong support to our assignment. For each mode a description of the molecular motion is also given in Table 1. Because of the presence of mode coupling under the relatively low symmetry of the moledule (C_s), some of these descriptions are necessarily somewhat tentative. However, it can be said, for example, that the mode responsible for the absorption observed at 505.8 cm^{-1} in the experiment with C_2H_2 and at 466.4 cm^{-1} in the experiment with C_2D_2 has a high contribution from the ν(Al−Cl) mode, as already mentioned above. This mode has also the smallest $\nu(H):\nu(D)$ ratio of all observed modes (calculated 1.0705:1, observed 1.0845:1). Shoulders at 500.4 cm^{-1} in the experiment with H_2 and at 462.4 cm^{-1} in the experiments relying on D_2 are presumably due to $^{35}Cl/^{37}Cl$ isotopic splitting. The absorption at 2027.9 cm^{-1} in the experiment with C_2H_2 and at 1905.9 cm^{-1} in the experiment with C_2D_2 can be assigned to the ν(C−C) stretching fundamental. This mode is calculated to appear at 2054.4 cm^{-1} for Cl(H)AlCCH and at 1920.6 cm^{-1} for Cl(D)AlCCD ($\nu(H):\nu(D)$ ratio calculated 1.0697:1, observed 1.0640:1). For comparison, our calculations give a value of 2010.0 cm^{-1} for the wavenumber of the ν(C−C) stretching fundmental in C_2H_2. The experiments also succeed in detecting absorptions attributable to the ν(C−H) stretching fundamental. In summary, the combination of experimental results and quantum-chemical calculations leave no doubt that Cl(H)AlCCH is indeed formed as the single product of the photoinduced reaction between monomeric AlCl and acetylene.

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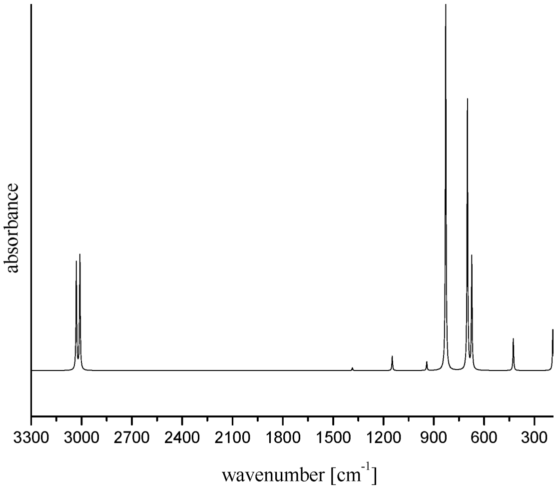

Figure 4. Calculated IR spectrum of the C_{2v}-symmetric cyclic isomer $ClAlC_2H_2$.

Additional calculations were carried out to get information about the second possible isomer bearing the general formula $AlClC_2H_2$, the aluminacyclopropene derivative $ClAl(C_2H_2)$. This species is of interest because of its potential aromatic character. According to the calculations, this species is characterized by a C−C distance of 139.2 pm, showing the double-bond character of the C−C bond. At 186.4 pm, the Al−C bonds are even shorter than in the insertion isomer (190.6 pm). The C−H distance measures 111.0 pm and the Al−Cl distance 209.4 pm. The small H−C−C angle of 127.6° indicates once again that the electronic situation is changed dramatically with respect to that in acetylene. The C−Al−C and Cl−Al−C angles measure 43.9 and 158.1°, respectively. The C_{2v} symmetric molecule exhibits 12 vibrational modes spanning the irreducible representation $5a_1 + a_2 + 4b_1 + 2b_2$. The calculated IR spectrum is visualized in Figure 4. The calculated wavenumbers (in cm^{-1}, with intensities (in km mol^{-1}) and symmetry assignment given in parentheses) are as follows: 3031.0 (37, a_1), 3009.7 (40, b_1), 1385.7 (1, a_1), 1147.8 (5, b_1), 1028.2 (0, a_2), 942.1 (3, a_1), 829.0 (134, a_1), 699.9 (93, b_2), 673.8 (39, b_1), 426.1 (11, a_1), 190.5 (14, b_2), 180.8 (10, b_1). An inspection of the calculated and observed spectra shows that the presence of even traces of this species (up to the limit of detection) can be excluded. The strongest absorption in the calculated spectrum of the C_{2v} symmetric isomer is located at 829.0 cm^{-1}, whereas the experimentally observed spectrum is free of any absorptions in this region. The region 2030−1950 cm^{-1}, which contains the two strong absorptions at 2027.9 and 1952.2 cm^{-1} detected in the experiments, is predicted, on the other hand, to show no absorptions of the C_{2v} symmetric isomer. Thus, a comparison with the observed spectrum makes it clear that the cyclic isomer is not formed in the experiments and that the species detected is indeed the insertion product.

Table 2. Comparison of the Al−C Distances in Organometallic Compounds Featuring Direct Al−C Bonds

compd	d(Al−C) (pm)	ref
$AlCH_3$	200.7	
AlCCH	198.3	
$HAlCH_3$	198.5	
H_2AlCH_3	196.6	
H_2AlCCH	191.7	
Cl(H)AlCCH	190.6	
$[Ph_2AlCCPh]_2$	199.2/218.4	1
$\{[(tBu)_2C_3N_2]Al(CCPh)_2\}_2$	191.3/192.9	2
$Al_4Cl_4C_{16}H_{24}$	199.0	13

Table 3. Energy Difference (in kJ mol^{-1}) between the Acetylide and the Cyclic Isomers for Compounds of the General Formula XMC_2H_2 (X = H, F, Cl, Br and M = B, Al, Ga)

compd	ΔE	compd	ΔE
FBC_2H_2	−21.8	$BrAlC_2H_2$	38.1
$FAlC_2H_2$	48.9	$HAlC_2H_2$	21.1
$ClAlC_2H_2$	40.1	$ClGaC_2H_2$	69.0

The energy difference between the two isomers amounts to 40.1 kJ mol^{-1} (51.1 kJ mol^{-1} with zero point energy corrections) in favor of the insertion product Cl(H)AlCCH.[36] This result is again in good agreement with what is observed in the experiment. To assess the factors that influence the relative stabilities of both isomers, calculations were carried out for different molecules bearing the general formula XEC_2H_2, with X = F, Cl, Br and E = B, Al, Ga. The energy of the acetylide form relative to the cyclic structure with C_{2v} symmetry is given in Table 3 for several representative species of this kind. For E = B, the cyclic structure is favored over the acetylide form. It has been shown previously that these compounds exhibit considerable aromatic character (70% of the resonance energy of the cyclopropenium cation).[12] This aromaticity is certainly one of the most important factors at work here. In the case of the heavier homologues, the acetylide form becomes energetically more favored.[37] The two π electrons in the aluminacyclopropene derivative are certainly less delocalized than those in borirene. The stability of the cyclic form should therefore be reduced. Thus, this class of compounds provides another example of the experimentally verified changes in structure for homologues composed of B on one hand and Al, Ga, or In on the other hand. Other simple examples, studied in matrix experiments in our laboratory and in others, include E_2H_2 (linear for E = B and cyclic for E = Ga, In),[38] $E_2(CO)_2$ (linear for E = B and cyclic for E = Al, Ga),[39] and ENH_2 (linear HBNH, but C_{2v} symmetric amide species ENH_2 for E = Al, Ga, In).[30,40] The energy difference between the cyclic and the acetylide forms for $XAlC_2H_2$ decreases in the sequence X = F > Cl > Br > H. The more electronegative X is, the larger the energy difference, favoring the acetylide form.

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(36) A third possible structure, $ClAlCCH_2$ (C_{2v} symmetry), has an energy 164.0 kJ mol^{-1} higher than that of the acetylide form. However, the vibrational analysis yielded one imaginary frequency, showing that this structure is not a minimum on the potential energy hypersurface.

(37) See also: Xie, Y.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1990**, *112*, 5393.

(38) For B_2H_2, see: Tague, T. J., Jr.; Andrews, L. *J. Am. Chem. Soc.* **1994**, *116*, 4970. Knight, L. B., Jr.; Kerr, K.; Miller, P. K.; Arrington, C. A. *J. Phys. Chem.* **1995**, *99*, 4756. For Ga_2H_2 and In_2H_2, see: Himmel, H.-J.; Manceron, L.; Downs, A. J.; Pullumbi, P. *Angew. Chem.* **2002**, *41*, 796; *Angew. Chem., Int. Ed.* **2002**, *114*, 829. Himmel, H.-J.; Manceron, L.; Downs, A. J.; Pullumbi, P. *J. Am. Chem. Soc.* **2002**, *124*, 4448.

(39) For $B_2(CO)_2$, see: Zhou, M.; Tsumori, N.; Li, Z.; Fan, K.; Andrews, L. *J. Am. Chem. Soc.* **2002**, *124*, 12936. For $Al_2(CO)_2$, see: Xu, C.; Manceron, L.; Perchard, J. P. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 1291. For $Ga_2(CO)_2$, see: Himmel, H.-J.; Downs, A. J.; Green, J. C.; Greene, T. M. *J. Phys. Chem. A* **2000**, *104*, 3642.

(40) Thompson, C. A.; Andrews, L. *J. Am. Chem. Soc.* **1995**, *117*, 10125. Thompson, C. A.; Andrews, L.; Martin, J. M. L.; El-Yazel, J. *J. Phys. Chem.* **1995**, *99*, 13839.

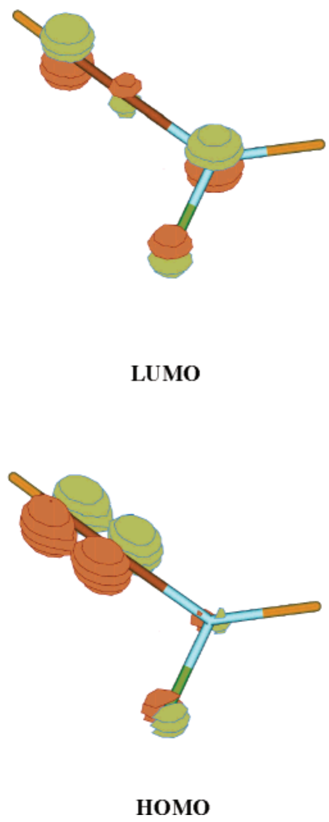
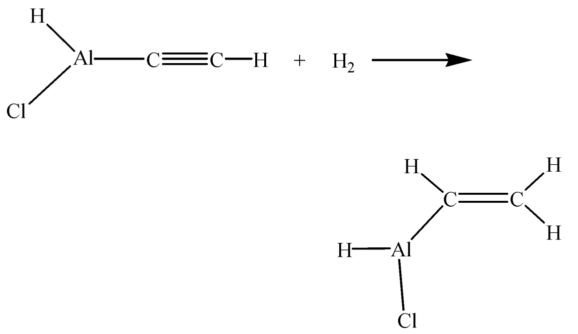


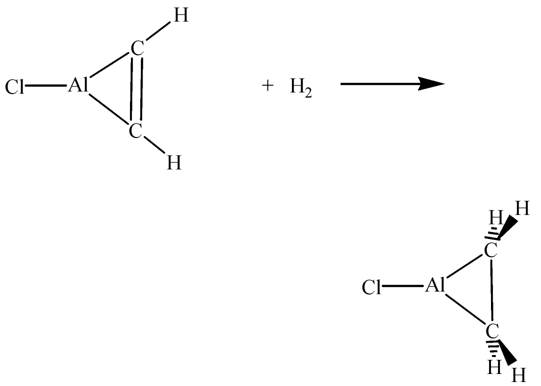
Figure 5. Plot of the HOMO and LUMO of Cl(H)AlCCH.

In Table 2 the Al−C bond distance in $ClAlC_2H_2$ is compared with those found in other related compounds, including some representative alkynyl species which have been characterized by X-ray diffraction. It can be seen that the Al−C distance in Cl(H)AlCCH is relatively short. Thus, in other organometallic compounds such as *t*-$Bu_2AlNMes_2$ and (*i*-$Bu_2AlNMe_2)_2$, Al−C distances of 197.9/199.7[41] and 195.6/198.2 pm[42] are found. For H_2AlCH_3, the calculated Al−C distance is 196.6 pm, and at 198.3 pm, the Al−C distance in AlCCH is calculated to be significantly longer. In $\{[(t\text{-}Bu)_2C_3N_2]Al(CCPh)_2\}_2$, a compound which has been studied using X-ray diffraction, the Al−C distances were determined to be 191.3−192.9 pm.[3] In this compound, therefore, the Al−C distance is close to that calculated for Cl(H)AlCCH. However, as already mentioned, the Al−C−C angle deviates significantly from 180°. As already mentioned, the anion $[(Me_3Si)_2HC]_2AlC(C_6H_5)CAl[CH(SiMe_3)_2]_2^-$ (structure **2**, see Introduction) was structurally characterized recently and shown to exhibit a very short Al−C bond of 188.6(3) pm between the C atom in the AlC_2 heterocycle and the exocyclic Al atom.[9] The short distance is caused by substantial π interaction. In Figure 5, the frontier molecular orbitals of Cl(H)AlCCH are visualized. Most of the electron density in the HOMO is located at the acetylide group (the orbital resembles a bonding π orbital of acetylene). The LUMO has a significant contribution from the empty Al 3p orbital.

Hydrogenation energies were also calculated for the two isomers of $ClAlC_2H_2$. These give some additional information about the chemical reactivity and bonding properties.[43] Hence, eq 1, the hydrogenation of the acetylide species, is associated with an energy of −135.5 kJ mol^{-1}, including zero-point energy corrections. Using the same theoretical methods, the energy for the hydrogenation of acetylene to give ethylene was calculated to be −187.2 kJ mol^{-1} (the enthalpy for this reaction was measured to be ca. 170 kJ mol^{-1}). Thus, it appears that the presence of the H(Cl)Al group stabilizes the acetylene, most likely through some degree of extended π interaction. This π interaction should also be present in the product of the hydrogenation reaction. However, the Al−C distance in $Cl(H)AlCHCH_2$ is calculated to be 194.6 pm and, thus, is significantly longer than in the Cl(H)AlCCH reactant (190.6 pm). The larger separation might decrease the possibility for efficient π interaction. Hydrogenation of the hypothetical aluminacyclopropene derivative (see eq 2) is exothermic by −92.3 kJ mol^{-1}. This implies that, as in the case of $ClAlC_2H_4$, the cyclic structure is more energetic than the insertion product (energy difference of 94.4 kJ mol^{-1}). It should be possible to prepare a species with the overall formula $ClAlC_2H_4$ by reaction of AlCl with ethylene.[44]



(1)



(2)

For comparison, the hydrogenation of cyclic $ClBC_2H_2$ was calculated to be exothermic by −80.7 kJ mol^{-1} (including zero-point energy corrections), in good agreement with earlier estimates for the cyclic borirene HBC_2H_2 (ca. −89 kJ mol^{-1}).[12] While this value is close to that derived for the Al homologue, the energy for hydrogenation of the isoelectronic cyclic $[ClC_3H_2]^+$ cation to give the cyclic $[ClC_3H_4]^+$ cation turns out to be

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[41] Petrie, M A.; Power, P. P.; Rasika Dias, H. V.; Ruhlandt-Senge, K.; Waggoner, K. M.; Wehmschulte, R. J. *Organometallics* **1993**, *12*, 1086.

[42] Lagrone, C. B.; Schauer, S. J.; Thomas, C. J.; Gray, G. M.; Watkis, C. L.; Krannich, L. K. *Organometallics* **1996**, *15*, 2458.

[43] Himmel, H.-J.; Schnöckel, H. *Chem. Eur. J.* **2002**, *8*, 2397.

[44] Himmel, H.-J. Unpublished results.

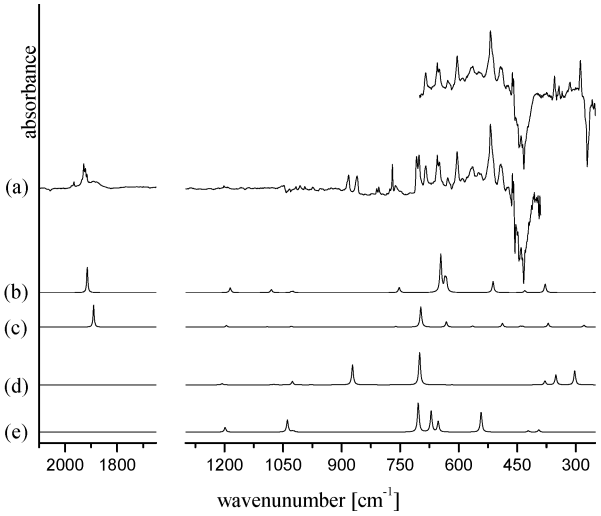


Figure 6. (a) Difference between the IR spectrum taken following photolysis of an Ar matrix containing AlCl and 2-butyne and the IR spectrum taken immediately upon deposition. (b)−(e) Difference between the calculated IR spectra of **I**−**IV** and those of 2-butyne and AlCl.

Table 4. Calculated Energies (in kJ mol^{-1}) for the Hydrogenation of Compounds Having the General Formula $ClEC_2H_2$ (E = C, B, Al, Ga)

reacn	ΔE
$[ClCC_2H_2]^+$ (C_{2v}) + H_2 → $[ClCC_2H_4]^+$ (C_{2v})	−62.5
$ClBC_2H_2$ (C_{2v}) + H_2 → $ClBC_2H_4$ (C_{2v})	−80.7
$ClAlC_2H_2$ (C_{2v}) + H_2 → $ClAlC_2H_4$ (C_{2v})	−92.3
$ClGaC_2H_2$ (C_{2v}) + H_2 → $ClGaC_2H_4$ (C_{2v})	−110.3
HCCH + H_2 → H_2CCH_2	−187.2
Cl(H)AlCCH (C_s) + H_2 → Cl(H)AlCHCH$_2$ (C_s)	−135.5

less exothermic (−62.5 kJ mol^{-1}). All values obtained for the energies of hydrogenation are summarized in Table 4.

Additional experiments were conducted with 2-butyne. These were motivated by the results of further quantum-chemical calculations, suggesting that for a molecule with the general formula $ClAlC_4H_6$ the cyclic structure and the insertion product exhibit almost the same energy. The energy difference amounts to not more than 4.0 kJ mol^{-1} in favor of the cyclic structure, but if zero-point energy corrections are made, the insertion product has an energy which is 9.3 kJ mol^{-1} lower than that of the cyclic form. The cyclic structure was previously suggested to be involved as a nonisolable intermediate during the reaction of “AlCl” (metastable solutions) with 2-butyne, leading finally to $Al_4Cl_4C_{16}H_{24}$ on a preparative scale.[15] Upon deposition of AlCl together with 2-butyne, a band at 437.3/432.8 cm^{-1} can be assigned to a weak adduct of AlCl with 2-butyne. However, no other spontaneously formed products were found, in agreement with what is observed for the analogous experiment with acetylene. Photolysis was again necessary to initiate further reaction. The difference spectrum obtained from the spectra taken immediately upon deposition and following a period of 30 min of UV photolysis is shown in Figure 6a. It contains a band at 1923.8 cm^{-1} in a region in which ν(Al−H) fundamentals are expected to appear. Between 900 and 400 cm^{-1}, several absorptions grow in. The most intense of these are located at 882.9/861.3, 708.3, 702.9, 684.7, 654.5, 650.5, 604.1, 517.4, 354.1, and 287.6 cm^{-1}. The presence of the band assignable to a ν(Al−H) fundamental indicates that one of the possible reaction products is $Cl(H)AlCH_2CCCH_3$.

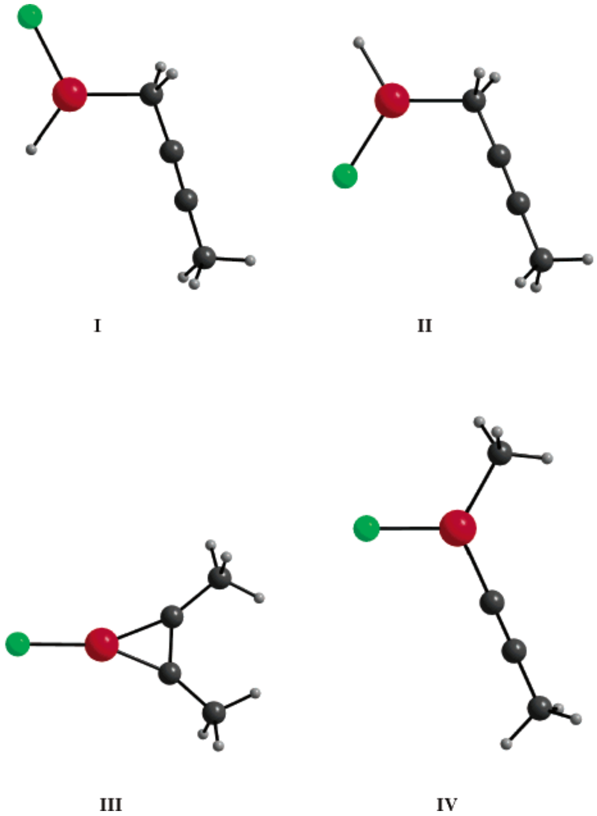


Figure 7. Calculated structures (**I**−**IV**) of possible products of the matrix reaction between monomeric AlCl and 2-butyne.

As already indicated, the calculations suggest that the energy difference between the insertion product and the cyclic form is much smaller in this case. Figure 7 shows the structures for the four possible isomers with the general formula $ClAlC_4H_6$. In the following account, these products will be designated **I**−**IV**. According to our calculations, structure **IV** possesses the lowest energy and thus represents the global energy minimum structure. This product is formed at least formally via insertion of the AlCl molecule into one of the C−CH_3 bonds. **I** and **II** are the two possible conformers of the products arising from insertion into one of the C−H bonds. Structure **I** has a slightly lower energy than does the conformer **II** (by −5.1 kJ mol^{-1}). The energy difference between structures **I** and **IV** amounts to 68.3 kJ mol^{-1} in favor of **IV**. The cyclic aluminacyclopropene derivative **III** has the highest energy of the four isomers. It is 14.7 kJ mol^{-1} higher than that for **I** and 83.0 kJ mol^{-1} higher than that for **IV**.

The calculated IR spectra for **I**−**IV** are shown in Figure 6b−e together with the experimentally obtained spectrum. Table 5 contains all the wavenumbers for the four structures. The presence of an absorption at 1923.8 cm^{-1} in the experimental spectrum clearly argues for the presence of **I** or **II**. It proved difficult to discriminate between **I** and **II**. It might be argued that the strong absorptions at 645.9, 635.4, and 631.4 cm^{-1} in the calculated spectrum of **I** fit well with the observed features at 654.5 and 650.5 cm^{-1} and that **I** is formed. The strong absorption at 517.4 cm^{-1} in the experimen-

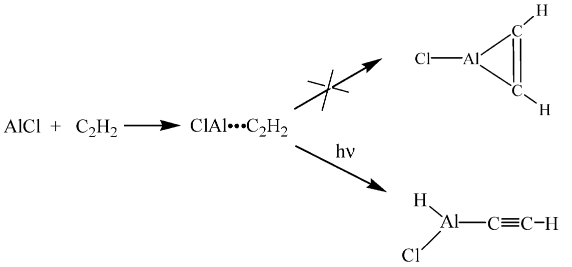
Table 5. IR Properties of the Four Possible Products I−IV (See Figure 6) of the Reaction between Monomeric AlCl and 2-Butene in a Solid Ar Matrix (in cm^{-1}, with IR Intensities (in km mol^{-1}) and Assignments Given in Parentheses)

I	II	III	IV
3008.3 (6, a)	3005.6 (6, a″)	3010.4 (10, b_1)	3047.0 (4, a′)
3002.0 (7, a)	3003.5 (8, a′)	3010.1 (0, a_2)	3029.3 (2, a″)
2967.8 (1, a)	2941.4 (2, a″)	3009.0 (29, a_1)	3019.4 (3, a′)
2926.6 (50, a)	2929.3 (34, a′)	3007.1 (6, b_2)	3016.0 (2, a″)
2924.5 (7, a)	2901.1 (20, a′)	2929.5 (42, a_1)	2943.6 (4, a′)
2278.0 (3, a)	2287.7 (3, a′)	2922.0 (20, b_2)	2936.3 (10, a′)
1914.9 (123, a)	1890.4 (235, a′)	1513.2 (28, a_1)	2189.0 (180, a′)
1415.5 (8, a)	1413.7 (8, a′)	1413.9 (0.1, a_1)	1411.7 (14, a′)
1414.8 (9, a)	1412.5 (9, a″)	1406.2 (19, b_1)	1409.3 (10, a″)
1376.3 (2, a)	1375.5 (3, a′)	1406.2 (0, a_2)	1394.0 (1, a′)
1373.4 (11, a)	1372.5 (9, a′)	1403.0 (17, b_2)	1390.1 (3, a″)
1185.5 (23, a)	1195.0 (17, a′)	1350.0 (0.2, a_1)	1366.4 (1, a′)
1102.8 (1, a)	1106.6 (1, a″)	1341.7 (5, b_2)	1198.6 (20, a′)
1080.1 (15, a)	1090.4 (4, a′)	1206.4 (4, b_2)	1038.9 (51, a′)
1029.5 (4, a)	1029.4 (4, a″)	1073.8 (2, a_1)	1026.6 (4, a′)
1024.6 (6, a)	1028.2 (5, a′)	1026.2 (10, b_2)	1022.0 (4, a″)
752.4 (25, a)	761.4 (7, a′)	1021.3 (0, a_2)	703.6 (123, a′)
645.9 (184, a)	697.1 (211, a′)	977.4 (0.4, b_1)	670.5 (90, a′)
635.4 (56, a)	631.6 (57, a″)	872.1 (56, a_1)	652.5 (45, a″)
631.4 (56, a)	564.3 (12, a′)	700.1 (91, a_1)	542.5 (85, a′)
511.9 (54, a)	487.9 (39, a′)	616.9 (0.1, b_2)	421.7 (6, a′)
430.7 (6, a)	441.3 (10, a′)	451.6 (0, a_2)	409.6 (0.006, a″)
430.2 (4, a)	435.4 (8, a″)	378.8 (11, a_1)	394.7 (10, a′)
378.4 (42, a)	370.7 (41, a″)	351.0 (28, b_2)	230.6 (25, a″)
239.4 (10, a)	278.9 (20, a′)	302.7 (40, b_1)	228.7 (20, a′)
225.1 (11, a)	228.8 (10, a″)	229.4 (0, a_2)	194.7 (0.002, a″)
160.7 (0.3, a)	196.6 (0.3, a″)	228.8 (0.2, a_1)	170.8 (0.002, a″)
156.9 (9, a)	168.8 (5, a′)	218.9 (1, b_1)	157.5 (5, a′)
79.0 (0.2, a)	81.1 (0.1, a″)	121.9 (2, b_2)	114.1 (1, a″)
66.0 (1, a)	64.5 (1, a′)	121.5 (2, b_1)	91.8 (1, a′)

tally observed spectrum is also close to that at 511.9 cm^{-1} in the calculated spectrum of **I**. In contrast, the absorption at 882.9/861.3 cm^{-1} in the experimental spectrum comes in a region which should be free of any absorptions of **I**, **II**, or **IV**. Only **III** has a relatively strong absorption in this region (at 872.1 cm^{-1}). **III** also has strong absorptions at 700.1, 351.0, and 302.7 cm^{-1}, which fit with the experimentally observed bands at 702.9, 354.1, and 287.6 cm^{-1}. Thus, it is likely that **III** is one of the products formed in the experiments, although it exhibits the highest energy of all the isomers. The formation of **IV** can be ruled out, it appears, although it represents the lowest energy structure. This molecule has its strongest absorption at 2189.0 cm^{-1} according to the calculations. However, this region (not shown in Figure 5) is free of any strong absorption which can be associated with a product. In summary, the comparison between the observed and calculated IR spectra suggests that **I** and **III** are formed as the products of the photoactivated reaction between AlCl and 2-butyne. Unfortunately, it was not possible to find photolysis conditions under which the formation of one of the two species is favored.

The DFT calculations yielded the following geometrical parameters for the aluminacyclopropene derivative (structure **III**): Al−Cl, 210.4 pm; Al−C, 186.8 pm; C−C, 140.4/149.9 pm; C−Al−C, 44.2°; C−C−C, 130.3°. In the C−H insertion product (structure **I**), the Al−Cl, Al−H, Al−C, and C−C bond distances are 212.5, 159.6, 197.8, and 122.7 pm, while the angles H−Al−C, H−Al−Cl, Cl−Al−C, and C−C−C are 124.9, 117.7, 117.4, and 176.9/178.8°, respectively.

Reaction Pathways. The experiments clearly show that the reaction between AlCl and C_2H_2 proceeds spontaneously only to form the weak adduct ClAl···C_2H_2. Photolysis brings about activation of this adduct, basically through an excitation within the AlCl molecule.[20] The photoinduced reaction between AlCl with C_2H_2 to give Cl(H)AlCCH is calculated to be exothermic by −113.0 kJ mol^{-1} (including zero-point energy corrections). The potential reaction leading to the aluminacyclopropene derivative (see eq 3) is considerably less



(3)

exothermic (−61.9 kJ mol^{-1}). For comparison, the reaction of BCl with C_2H_2 to give the cyclic borirene is associated with an energy change of as much as −354.2 kJ mol^{-1} (also including zero-point energy corrections). As already mentioned, $ClBC_2H_2$ prefers the cyclic structure. In this case the reaction to give the acetylide form is less exothermic (−327.1 kJ mol^{-1}, again taking in zero-point energy corrections). The reaction of GaCl with C_2H_2 to give the acetylide-type product Cl(H)GaCCH is associated with an energy of only −21.4 kJ mol^{-1}, including zero-point energy corrections. The reaction leading to the cyclic isomer is now *endothermic* (+56.4 kJ mol^{-1}, including zero-point energy corrections).

In the case of the reaction of AlCl with 2-butyne, the formation of structure **I** via C−H insertion is exothermic by −57.2 kJ mol^{-1}. This compares with the formation of **III**, which is accompanied by an energy change of −125.5 kJ mol^{-1}. As already mentioned, the aluminacyclopropene derivative **III** was suggested as a possible intermediate on the way to dimeric 1,4-dichloro-2,3,5,6-tetramethyl-1,4-dialumina-2,5-cyclohexadiene from the reaction between "AlCl" in metastable solutions and 2-butyne. These earlier experiments gave no sign of any product resulting from insertion of the AlCl into the C−C or C−H bonds. The barrier to insertion is expected to be higher than that associated with formation of the aluminacyclopropene derivative. For the thermal insertion of AlCl into H_2, a barrier of about 250 kJ mol^{-1} can be assumed.[45] The barrier for C−H insertion might be of comparable magnitude. A photoinduced reaction is anticipated, however, to be associated with little or no barrier.[45] Therefore, the thermal reactions are more likely to yield the aluminacyclopropene derivative. That the mechanisms are complicated is most impressively shown, however, by a comparison of the products obtained from reactions of AlCl with 2-butyne [15] and with 3-hexyne.[46]

Conclusions

AlCl was shown to insert into the C−H bond of acetylene upon photoactivation to give the new alky-

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(45) (a) Himmel, H.-J.; Klaus, C. *Z. Anorg. Allg. Chem.*, in press. (b) Himmel, H.-J. *Eur. J. Inorg. Chem.*, submitted for publication. See also consideration of the cases of the Ga and In analogues in ref 20.

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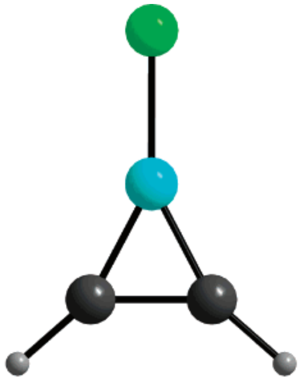
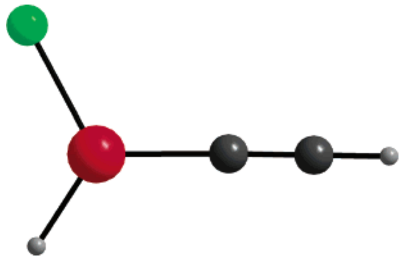
nylaluminum compound Cl(H)AlCCH. This product was characterized by its IR spectrum (taking in the effects of perdeuteration) and by extensive quantum-chemical calculations. The Al−C distance in this species is unusually short (190.6 pm), arguing for a significant degree of π-interaction. An inspection of the valence orbitals shows that the electron density of the HOMO is mainly located in a bonding π-orbital of the acetylide group. The LUMO has a substantial contribution from the Al p orbital and some additional contribution from the p orbitals at the C atoms. The hydrogenation reaction leading to $Cl(H)AlCHCH_2$ is exothermic by -135.5 kJ mol^{-1}. This value is significantly smaller than that derived for hydrogenation of acetylene to give ethylene. The reduced reactivity is caused at least partially by the π interaction present in Cl(H)AlCCH (which is larger than that in $Cl(H)AlCHCH_2$). In agreement with the experimental findings, the calculations predict for the second possible isomer with the general formula $ClAlC_2H_2$, the aluminacyclopropene derivative, an energy which is 51.1 kJ mol^{-1} higher than that of the acetylide form, which represents the global energy minimum isomer.

Calculations carried out for other homologues, especially $ClBC_2H_2$ and $ClGaC_2H_2$, show that the cyclic isomer is favored over the acetylide form for B, whereas the acetylide form offers the global potential energy minimum structure for both Al and Ga. Calculations for $XAlC_2H_2$, where X = F, Cl, Br, H, show that the energy difference between the cyclic and the acetylide-type structures widens with increasing electronegativity of the substituent attached to the Al atom.

Additional experiments were carried out to study the photoinduced reaction of AlCl with 2-butyne. The IR spectra recorded for the products of the reaction suggest that both the C−H insertion product, $Cl(H)AlCH_2CCCH_2$, and the cyclic aluminacyclopropene derivative are formed in this case.



$ClBC_2H_2$



$ClAlC_2H_2$

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