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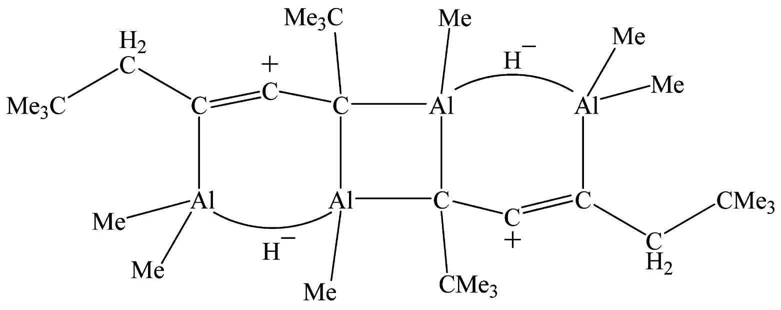

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C−H Bond Activation by Hyperconjugation with Al−C Bonds and by Chelating Coordination of the Hydride Ion

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Abstract: On treating di(*tert*-butyl)butadiyne with dimethylaluminum hydride under different reaction conditions two unprecedented organoelement compounds, containing cationic carbon atoms stable in solution at room temperature, were obtained. A vinyl cation (**2**) in which the cationic carbon atom is part of a C═C double bond was produced from 3 equiv of the hydride, whereas a large excess of the hydride yielded an aliphatic carbocation (**3**) by complete hydroalumination of all C−C multiple bonds. Each compound is zwitterionic with the hydride counterion effectively coordinated in a chelating manner by two strongly Lewis acidic aluminum atoms. In agreement with quantum-chemical calculations the C−H bond activation and the stabilization of the cationic species are further supported by a strong hyperconjugation with Al−C single bonds. This considerably diminishes the effective positive charge at the respective cationic carbon atoms.

Introduction

Hydroalumination is a very powerful method for the reduction of unsaturated organic compounds containing homo- or heteronuclear multiple bonds.[1] In most cases the organoaluminum intermediates of these reactions were not isolated and characterized but immediately destroyed by hydrolysis, and the reduced organic material was finally isolated. The knowledge of the constitution of those intermediates is therefore quite limited, and rather speculative suggestions on the structures and reaction mechanisms can be found in former publications or in text books. In some recent investigations we observed that the course of hydroalumination reactions is much more interesting than may be derived from that general knowledge, and several novel and unexpected products could be isolated. On treating dialkylaluminum alkynides in which the aluminum atoms are attached to carbon atoms of C≡C triple bonds, with the corresponding dialkylaluminum hydrides for example, the new class of carbaalanes were formed by the release of trialkylaluminum. These compounds possess clusters formed by carbon and aluminum atoms, e.g., $(AlMe)_8(CCH_2C_6H_5)_5H$, and have a delocalized bonding situation in their molecular cores.[2] Similar condensation reactions with the formation of cyclophane type molecules were observed on treating benzene centered *tert*-butyl ethynes with aluminum hydrides.[3] Secondary reactions could only be prevented, when a very bulky dialkylaluminum hydride was employed[4] or when trimethylsilylethynes bearing $SiMe_3$ groups attached to their triple bonds were treated with dialkylaluminum hydrides.[5] Similar hydrogallation reactions appear to be more selective than hydroaluminations and were investigated in still greater detail.[6]

In a recent paper we reported on the remarkable reaction of di(*tert*-butyl)butadiyne, $Me_3C{-}C{\equiv}C{-}C{\equiv}C{-}CMe_3$, with di(*tert*-butyl)aluminum hydride.[7] Instead of condensation, a singular persistent butadienyl cation resulted (**1**, Scheme 1). Formally, **1** is produced by hydroalumination of both triple bonds, heterolytic cleavage of one C−H bond, and a very effective chelating coordination of the hydride anion by two unsaturated aluminum atoms. Such butadienyl cations have not been isolated before and were detected in superacidic media only.[8] Comparable silyl-substituted vinyl cations in which the cationic carbon atom is part of a localized C═C double bond were published only recently.[9] Owing to the general importance

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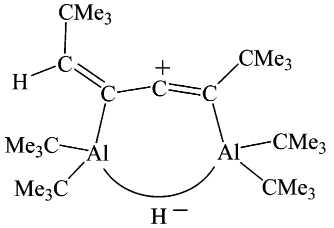
Scheme 1

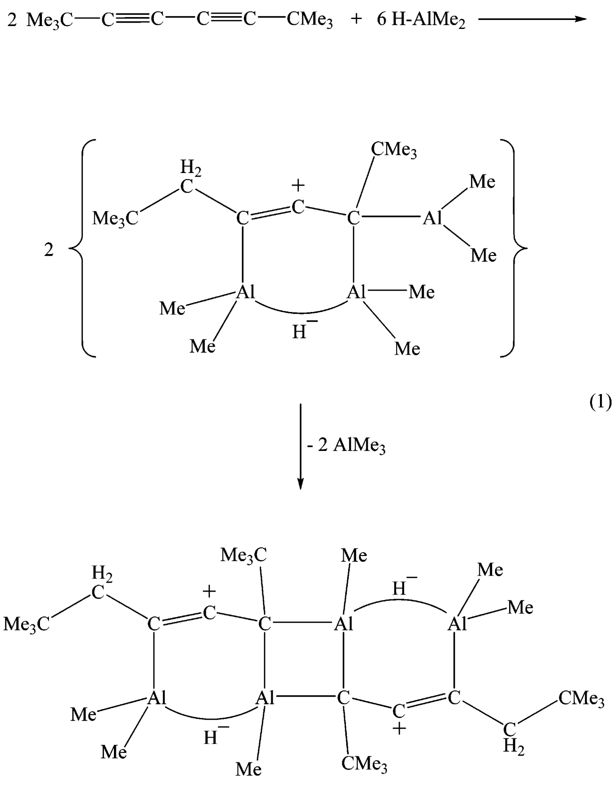


1

of those carbocationic species, more systematic investigations on the applicability of that particular method for generating further derivatives were conducted. The synthesis of two new compounds possessing carbocations but having completely different structures compared to that of **1** is reported here.

Results and Discussion

Synthesis and Molecular Structure of Compound 2. Di-(*tert*-butyl)butadiyne and dimethylaluminum hydride did not react in solution at room temperature. Successful reactions required the treatment of the diyne with an excess of the hydride without any solvent and heating of the mixture to 100 °C until a homogeneous, colorless liquid had formed (eq 1). After cooling to room temperature all volatiles were removed in vacuum, and the residue was recrystallized from *n*-hexane to yield colorless crystals of **2**. Trimethylaluminum was unambiguously identified by NMR spectroscopy as an essential byproduct of the reaction. Compound **2** has a relatively complicated ^{1}H NMR spectrum with three different resonances of equal intensity for the methyl groups attached to aluminum. Two chemically different *tert*-butyl groups could be detected, and two doublets indicated the occurrence of a CH_2 group with diastereotopic protons. The unusual chemical shift of one carbon atom (C3, see below) in the ^{13}C NMR spectrum ($\delta = 196.6$) verified the formation of a carbocation. The remaining carbon atoms of the inner C_4 moiety resonated at $\delta = 42.3$, 70.1, and 86.9. The low-field resonance is in the characteristic range of carbocations stabilized by hyperconjugation; see for instance a vinyl cation stabilized by hyperconjugation with C−Si bonds ($\delta = 202.7$).[9]



(1)

2

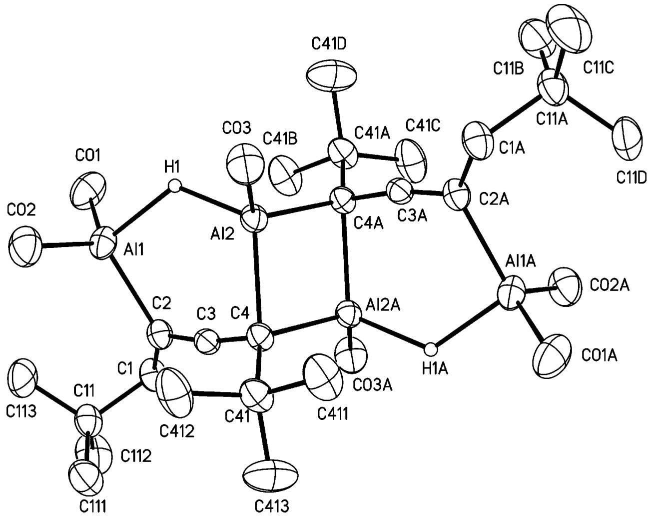
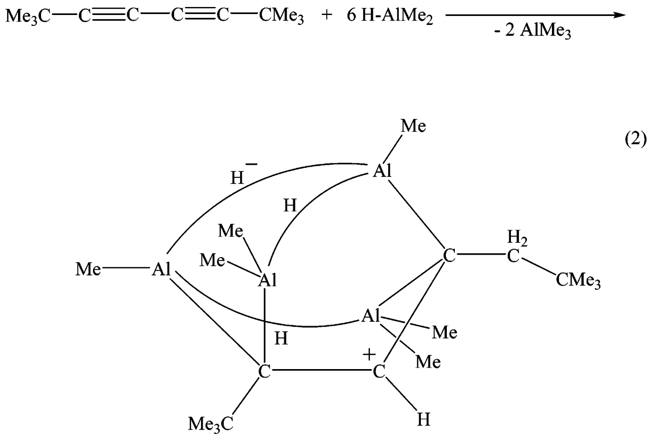


Figure 1. Molecular structure and numbering scheme of **2**; hydrogen atoms of methyl groups are omitted for clarity. Important bond lengths [pm] and angles [deg]: Al1−C2 204.2(2), C1−C2 151.8(2), C2−C3 127.3(2), C3−C4 135.5(2), C4−Al2 210.0(2), C4−Al2′ 204.5(2), Al−C(Me) 194.7 (av.), Al1−C2−C3 105.5(1), C1−C2−C3 128.7(2), C2−C3−C4 170.3(2), C3−C4−Al2 95.6(1), C3−C4−Al2′ 100.6(1); Al1′ generated by $-x + 1$, $-y$, $-z + 1$. Structural parameters of the optimized structure of **2** [PBE-D/TZVPP,SV(P)]: Al2−C4 205.7, Al2−C4′ 210.0, Al1−C2 205.5, C1−C2 150.2, C2−C3 128.6, C3−C4 135.6, C2−C3−C4 169.3.

Determination of the crystal structure revealed a centrosymmetric dimeric formula unit (Figure 1, schematic drawing in eq 1). Two tetracarbon skeletons are bridged by two common aluminum atoms. An Al_2C_2 heterocycle having slightly different Al−C bond lengths of 210.0 (Al2−C4) and 204.5 pm (Al2−C4′) is formed. These distances are relatively long compared to standard Al−C bond lengths (e.g., Al−Me 195 pm on average) and may indicate some hyperconjugative stabilization as discussed later on. C3 is the cationic carbon atom. It has only two neighboring atoms (C2 and C4) in an almost ideally linear surrounding (angle C2−C3−C4 170.3°). The C−C distances in the organic backbone vary in accordance with the respective bonding situation. The C1−C2 bond length (151.8 pm) indicates a C−C single bond resulting from the double hydroalumination of one C≡C triple bond. The bonds C2−C3 (127.3 pm) and C3−C4 (135.5 pm) are considerably shorter than the values characteristic of C−C double or single bonds. They indicate some stabilization of the unsaturated cationic carbon atom by hyperconjugation with the Al−C bonds Al2−C4 and Al1−C2 (204.2 pm). The hydrogen atom formally abstracted from C3 is coordinated by both aluminum atoms Al1 and Al2 to form a 3c−2e bond. The result is therefore a ladder type tricyclic molecular structure having two six-membered Al_2C_3H rings connected by a four-membered Al_2C_2 ring. The dimer is formed from a condensation reaction similar to those described in the Introduction. The hypothetic intermediate obtained by triple hydroalumination of the butadiyne with three $AlMe_2$ groups attached to the tetracarbon backbone (schematic drawing in eq 1) eliminates one $AlMe_3$ molecule per formula unit to yield the inner Al_2C_2 ring.

Synthesis and Molecular Structure of Compound 3. Complete hydroalumination of all multiple bonds was observed upon treatment of di(*tert*-butyl)butadiyne with a large excess of dimethylaluminum hydride without a solvent at 100 °C. Compound **3** was isolated in 70% yield, and once again trimethylaluminum was formed as a byproduct (eq 2). NMR spectroscopic characterization verified the formation of another carbocationic species. The ^1H NMR spectrum showed the occurrence of six chemically different methyl groups attached to aluminum. One resonance with an unusual chemical shift of $\delta = 9.28$ was assigned to a hydrogen atom bonded to a positively charged carbon atom, although it is considerably shifted to a higher field compared to, e.g., the isopropyl cation which is only available in superacidic media ($\delta = 13.5$).[10] These differences are probably caused by hyperconjugation and the reduction of the positive charge localized at the cationic carbon atom by transfer of electron density from Al−C bonds. A similar effect may influence the ^{13}C NMR shift of that particular carbon atom ($\delta = 217.5$) to a higher field by about 100 ppm as compared to the resonances of more naked cations in superacidic solvents.[10]



$$Me_3C{-}C{\equiv}C{-}C{\equiv}C{-}CMe_3 + 6\ H\text{-}AlMe_2 \xrightarrow[-\ 2\ AlMe_3]{} \qquad (2)$$

3

The molecular structure of **3** (Figure 2) comprises a relatively complicated cage with four heterocycles at its surface, four chemically different aluminum atoms, and owing to the molecular symmetry six different methyl groups bonded to the metal atoms. Three Al−H−Al three-center bonds occur, two of which bridge an Al−Me group with an $AlMe_2$ residue (Al1−H2−Al4 and Al3−H3−Al2), while the remaining one is between two Al−Me groups (Al1−H1−Al3). These particular aluminum atoms (Al1 and Al3) are coordinated by two hydrogen atoms and are therefore involved in two 3c−2e bonds while the others have contact to only one bridging hydrogen atom. Two carbon atoms of the former butadiyne moiety bond each to two aluminum atoms (C1 and C3). C4 represents a methylene group bearing two hydrogen atoms. The cationic carbon atom C2 has one terminal hydrogen atom and an ideal trigonal planar surrounding (sum of the angles 360°). The C−C bond lengths correspond to a normal single bond for the couple C3−C4 (154.2 pm), while shorter ones are observed for the remaining bonds C1−C2 (142.6 pm) and C2−C3 (141.3 pm). They are close to the average values between single and double bonds but significantly longer than those detected for compounds **1** and **2** in which the cationic carbon atoms are part of a π-system. The shortening in **3** compared to C−C single bonds may be caused by a hyperconjugative stabilization of the cation and an electron transfer from Al−C σ-bonds into the empty p-orbital of that carbon atom. There is strong evidence for such an interaction in the structural data. The carbon atoms neighboring the cation are coordinated by two aluminum atoms each with two strongly differing Al−C bond lengths (198.6 and 208.5 pm on average). While the shorter bonds are in the normal range of Al−C distances and are close to the average plane of the atoms C1, C2, H2, and C3, the longer bonds are perpendicular to that plane and are in an ideal position to interact with the empty p-orbital at the cationic carbon atom. The bonds become longer and weaker on electron donation, whereas the corresponding C−C bonds become stronger and shorter. A similar hyperconjugative stabilization with comparable C−C distances in the molecular core was observed for the *tert*-butyl cation which was isolated in the presence of a noncoordinating counterion ($Sb_2F_{11}^-$).[11]

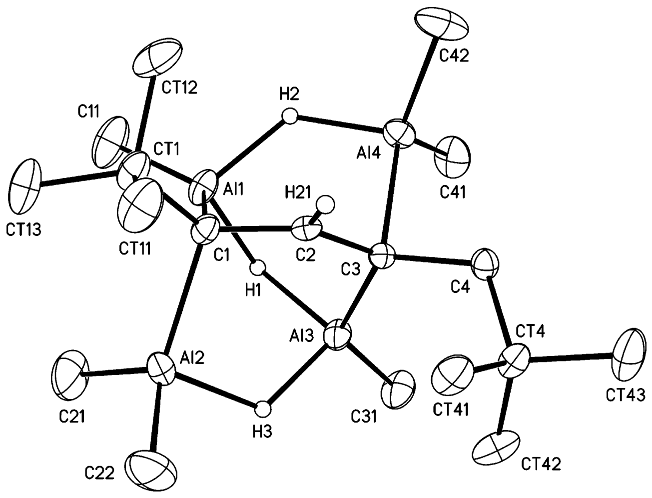


Figure 2. Molecular structure and numbering scheme of **3**; hydrogen atoms of methyl groups are omitted for clarity. Important bond lengths [pm] and angles [deg]: C1−Al1 200.0(2), C1−Al2 207.3(2), C1−C2 142.6(2), C2−C3 141.3(2), C3−C4 154.2(2), C3−Al3 197.2(2), C3−Al4 209.7(2), Al1−C1−Al2 97.62(8), C2−C1−Al1 104.8(1), C2−C1−Al2 109.9(1), C1−C2−C3 128.1(2), C2−C3−C4 116.2(1), C2−C3−Al3 111.8(1), C2−C3−Al4 100.1(1). Structural parameters of the optimized structure of **2** [PBE-D/TZVPP,SV(P)]: C1−C2 142.2, C2−C3 141.6, C3−C4 153.3, C1−Al1 202.5, C1−Al2 210.0, C3−Al4 211.0, C3−Al3 199.2, C1−C2−C3 128.0.

The release of trimethylaluminum in the course of the synthesis of **3** is required to provide the correct number of bridging hydrogen atoms. Formally **3** is produced by the addition of 2 equiv of dimethylaluminum hydride and 2 equiv of methylaluminum dihydride to the starting dialkyne. Each hydride molecule adds one Al−H bond to the π-bonds to give the aliphatic organic backbone, and two hydride atoms remain for the bridging of the metal atoms. The third bridge results from the formal breaking of a C−H bond and the chelating coordination of the eliminated hydride anion by two unsaturated aluminum atoms. It is however by no means clear whether the hydrogen-methyl exchange occurs before the reaction starts in a kind of a preequilibrium or whether it occurs after addition

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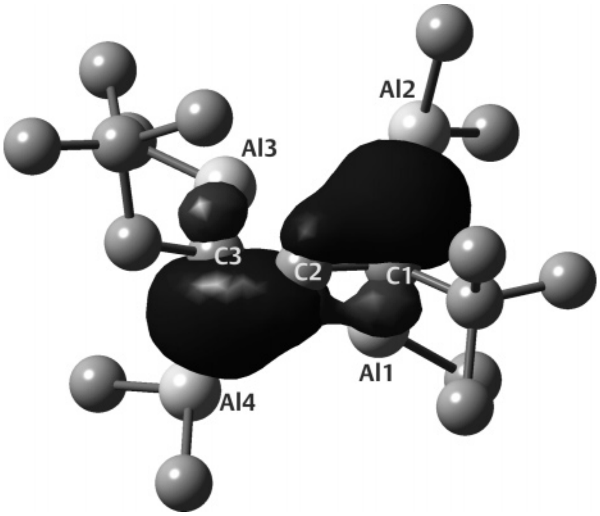

Figure 3. Localized MOs (multicenter-bonds) of **3** (rotated view, only C and Al atoms are shown).

from an intermediate organoaluminum derivative. To the best of our knowledge there is no real evidence for the formation of methylaluminum dihydride in liquid dimethylaluminum hydride at all. Bulky substituents are required to isolate organo aluminum or gallium dihydrides.[12] The maximum hydrogen content with smaller substituents was achieved with the sesquihydrides $[Me_3C\text{-}EH_2]_2[(Me_3C)_2E\text{-}H]_2$ (E = Al, Ga).[13]

Quantum-Chemical Calculations. We first optimized the molecular structure of the vinyl compound **2** in C_i symmetry. The most important bond lengths and angles observed experimentally are reproduced quite accurately (data are included in the legend of Figure 1). The NBO analysis indeed reveals a partial cationic character of C3, bearing a charge of $q = +0.116$. The two directly bonded carbon atoms have a negative charge, the magnitude of which correlates quite well to the number of bonded aluminum atoms [q(C2) = −0.505, q(C4) = −0.920]. A substantial negative charge is further localized at the hydride atom H1 [q(H1) = −0.457]. For comparison we reinvestigated the electronic structure of the butadienyl cation **1** (Scheme 1).[7] The cationic carbon atom has a positive charge similar to that of **2** [q(C2) = +0.130], and those carbon atoms which are attached to AlR_2 groups have around one-half electron charge [q(C3) = −0.516 and q(C5) = −0.440]. A similar value was calculated for the hydrogen atom coordinated in a chelating manner by two aluminum atoms [q(H1) = −0.521].

The optimized structural parameters of compound **3** are added to the legend of Figure 2. NBO analysis attributes almost one electron charge to the carbon atoms that are coordinated by two dialkylaluminum groups [q(C1) = −0.979, q(C3) = −0.959]. In this case, the formal cationic center has a relatively small negative charge (q(C2) = −0.089) which indicates the transfer of electron density from the neighboring atoms. The hyperconjugative interaction is visible in the shape of the corresponding two-electron-multi-center MOs that are found in a Pipek−Mezey orbital localization procedure[14] (Figure 3): The localized MOs definitely verify an interaction of the Al−C bonds with the cationic center at C3. Further evidence results from the calculated Wiberg bond orders[15] between C2 and the metal atoms (C2−Al1 0.147, C2−Al2 0.179, C2−Al3 0.152, C2−Al4 0.214). The numbers indicate a bonding interaction between C2 and all four aluminum centers which supports the description of the bonding situation by multicenter bonds and the hyperconjugative diminution of the electron deficiency at the central carbon atom. Orbital analyses of the butadienyl compound **1** and the vinyl compound **2** reveal very similar interactions. Thus, the stabilization of the formal cationic centers by hyperconjugation with Al−C single bonds seems to be a common property of all three compounds.

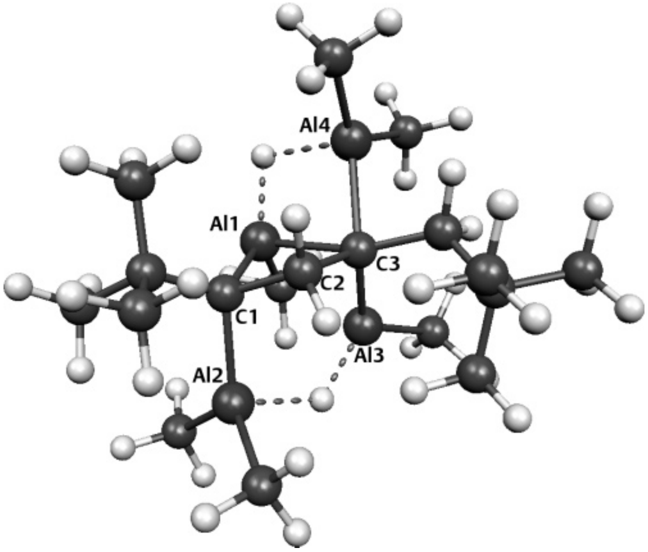

Figure 4. Optimized molecular structure of **4** [PBE-D/TZVPP,SV(P)]. Calculated bond lengths [pm] and angles [deg]: C1−C2 156.9, C2−C3 156.1, C1−Al1 193.9, C1−Al2 204.2, C3−Al3 203.5, C3−Al4 213.3, C1−C2-C3 107.9.

Finally the stability of an alternative isomer (**4**) which has the hydrogen atom H1 shifted to the carbocationic center with an intact C−H bond was investigated in comparison with **3**, in which that particular hydride anion is coordinated in a chelating manner by two aluminum atoms. We obtained a stable structure (Figure 4) of **4** that, however, is significantly higher in energy (+27.9 kcal mol^{-1}) than that of **3**.

Conclusion

Three different types of carbocationic species were realized in the hydroalumination products **1**, **2**, and **3**. Schematic representations are depicted in Scheme 2. They represent a butadienyl cation (**1**), a vinyl cation (**2**), and an aliphatic carbocation (**3**). A steadily increasing number of aluminum atoms attached to the organic backbone from two in **1** to four in **3** is representative for these different structural motifs. All compounds are zwitterionic with an intramolecular compensation of the positive charge. Thus, the problem of applying strictly noncoordinating counterions does not occur in these cases at all. Furthermore, compounds with these particular structures have the considerable advantage of being soluble in nonpolar solvents such as *n*-hexane. Their thermal stability will enable their application in secondary reactions and a thorough inves-

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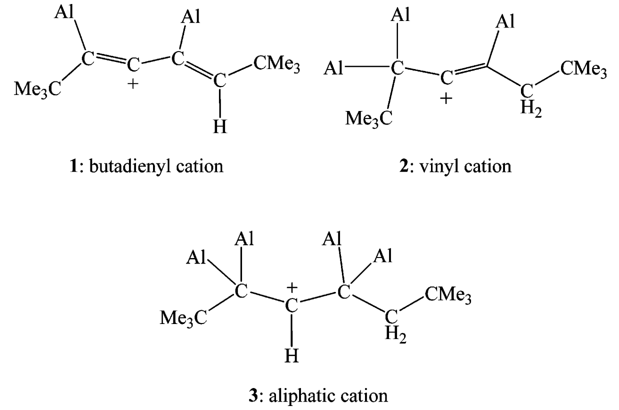
Scheme 2. Schematic Representation of the Different Cationic Systems Obtained by Hydroalumination



1: butadienyl cation **2**: vinyl cation

3: aliphatic cation

tigation of their chemical properties. The successful generation of these cations with the chelating coordination of the hydride ion by two aluminum atoms favored over the formation of a C−H bond depends on two important effects. Hyperconjugation with Al−C bonds at neighboring carbon atoms activates the corresponding C−H bonds and diminishes the positive charge at the inner carbon atoms which remains after the heterolytic C−H bond cleavage. This interpretation is strongly supported by structural data and the results of quantum-chemical calculations. The second point of interest is the effective intramolecular coordination of the hydride ion by two coordinatively unsaturated aluminum atoms which act as a chelating Lewis acid.[16]

Experimental Section

All procedures were carried out under an atmosphere of purified argon in dried solvents (*n*-hexane and *n*-pentane over $LiAlH_4$). Dimethylaluminum hydride was obtained according to literature procedure.[17] Commercially available di(*tert*-butyl)butadiyne (2,2,7,7-dimethylocta-3,5-diyne, Aldrich) was dried in vacuum prior to use. The assignment of the NMR spectra is based on HMBC, HSQC, ROESY, and DEPT135 data.

Synthesis of 2. Di(*tert*-butyl)butadiyne (0.200 g, 1.23 mmol) was treated with a small excess of dimethylaluminum hydride (0.286 g, 4.93 mmol) without a solvent. The mixture was stirred at 100 °C for 1 h. After cooling to room temperature all volatiles were removed in vacuum. The residue was dissolved in *n*-hexane and cooled to −15 °C to yield colorless crystals of compound **2**. Yield: 0.084 g (26% based on the butadiyne). Mp (argon, closed capillary): 149 °C (dec). MS (EI, 20 eV): *m*/*z* 528 (26%) (M^+); 513 (2%) ($M^+ - CH_3$); 471 (36%) ($M^+ - CMe_3$). ^1H NMR (C_6D_6, 400 MHz): δ 4.03 (2 H, br., AlHAl), 2.45 and 1.96 (each 2 H, d, $^2J_{H-H} = 12.3$ Hz, CH_2), 1.24 (18 H, s, CMe_3 attached to the carbon atoms of the Al_2C_2 ring), 0.92 (18 H, s, CMe_3 of the neopentyl groups), −0.12 (6 H, s, CH_3 attached to the aluminum atoms of the Al_2C_2 ring), −0.14 and −0.23 (each 6 H, s, chemically different methyl groups of the $AlMe_2$ moieties). ^{13}C NMR (C_6D_6, 75.5 MHz): δ 196.6 (cationic carbon atom C3, for numbering see Figure 1), 86.9 (C2), 70.1 (C4), 42.3 (CH_2), 34.2 ($\mathit{C}Me_3$ attached to the Al_2C_2 ring), 32.7 ($C\mathit{Me}_3$ attached to the Al_2C_2 ring), 31.9 ($\mathit{C}Me_3$ of the neopentyl group), 29.6 ($C\mathit{Me}_3$ of the neopentyl group), −3.4 (CH_3 attached to the Al_2C_2 ring), −8.2 and −8.6 (CH_3 of the $AlMe_2$ groups). IR (paraffin, CsBr plates, cm^{-1}): 1856 s,br. νAlH; 1580 m νC=C; 1454 vs, 1386 s (Nujol); 1360 s, 1303 w, 1254 m δCH_3; 1196 s, 1157 m, 1040 s, 1026 s, 995 m, 928 w, 895 m, 872 s, 783 m, br., 695 m, br. νCC, ρCH_3, δAlH; 621 m, 571 m, 538 m, 509 w, 461 m, 451 s νAlC.

Table 1. X-ray Data for **2** and **3**

	2	**3**
formula	$C_{30}H_{60}Al_4$	$C_{18}H_{42}Al_4$
fw	264.35	366.44
crystal system	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a, Å	8.395(1)	9.337(1)
b, Å	9.446(1)	11.450(1)
c, Å	12.695(2)	11.762(1)
α, deg	91.388(3)	78.416(2)
β, deg	102.358(3)	85.403(2)
γ, deg	114.027(2)	89.980(2)
V, Å^3	891.2(2)	1227.7(2)
Z	1	2
D_{calcd}, Mg m^{-3}	0.985	0.991
μ, mm^{-1}	0.146	0.187
θ_{max}, deg	30.08	31.32
temp, K	153(2)	153(2)
no. indep. reflns	5116	7313
no. reflns observed	3935	5387
no. of params	167	223
R1 [$I > 2\sigma(I)$]	0.0612	0.0575
wR2 (all data)	0.1592	0.1514

Synthesis of 3. Di(*tert*-butyl)butadiyne (0.202 g, 1.25 mmol) was treated with an excess of dimethylaluminum hydride (0.650 g, 11.21 mmol) without a solvent. The mixture was stirred at 100 °C for 1.5 h. After cooling to room temperature all volatiles were removed in vacuum. The residue was dissolved in *n*-pentane and cooled to −15 °C to yield colorless crystals of compound **3**. Yield: 0.320 g (70% based on the butadiyne). Mp (argon, closed capillary): 113 °C (dec). MS (EI, 70 eV): *m*/*z* 366 (6%) (M^+); 351 (4%) ($M^+ - CH_3$); 309 (19%) ($M^+ - CMe_3$). ^1H NMR (C_6D_6, 400 MHz): δ 9.28 (1 H, s, cationic-C−H), 3.58, 3.33 and 3.01 (each 1 H, br., AlHAl), 2.04 and 1.93 (each 1 H, d, $^2J_{H-H} = 13.1$ Hz, CH_2), 1.14 (9 H, s, CMe_3 attached to C1; see Figure 2 for the numbering scheme), 0.80 (9 H, s, CMe_3 of the neopentyl group), −0.12 (3 H, s, CH_3 at Al2), −0.14 and −0.29 (each 3 H, s, CH_3 at Al4), −0.25 (3 H, s, CH_3 at Al3), −0.32 and −0.43 (each 3 H, s, CH_3 at Al1). ^{13}C NMR (C_6D_6, 75.5 MHz): δ 217.5 (cationic carbon atom C2), 84.7 (C1), 79.4 (C3), 50.1 (C4, CH_2), 37.0 ($\mathit{C}Me_3$ at C1), 33.6 ($C\mathit{Me}_3$ at C1), 33.6 ($\mathit{C}Me_3$ at C4), 29.8 ($C\mathit{Me}_3$ at C4), −4.5 and −5.7 (CH_3 at Al4), −7.7 and −10.7 (CH_3 at Al1), −7.8 (CH_3 at Al2), −12.1 (CH_3 at Al3). IR (paraffin, CsBr plates, cm^{-1}): 1652 w, br., 1584 m, br. νAlH, νC=C; 1462 vs, 1377 s (Nujol); 1366 s, 1310 w, 1261 w δCH_3; 1198 m, 1112 s, 1073 m, 1043 vs, br., 940 m, 901 m, 874 m, 845 m, 820 w, 714 m, 685 w νCC, ρCH_3, δAlH; 648 w, 638 w, 618 w, 515 m, 461 s νAlC.

Crystal Structure Determinations. Single crystals of compounds **2** and **3** were obtained by recrystallization from *n*-hexane and *n*-pentane, respectively, at −15 °C. The crystallographic data were collected with a Bruker APEX diffractometer with graphite-monochromated Mo Kα radiation. The crystals were coated with high viscosity mineral oil, picked up with a glass fiber, and immediately mounted in the cooled nitrogen stream of the diffractometer. The crystallographic data and details of the final *R* values are provided in Table 1. All structures were solved by direct methods using the SHELXTL PLUS[18] program and refined with the SHELXL-97[18] via full-matrix least-squares calculations based on F^2. All non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms attached to carbon were calculated at ideal positions and allowed to ride on the bonded

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atom with $U = 1.2U_{eq}(C)$. Hydrogen positions of the Al−H−Al bridges were taken from difference Fourier maps; the atoms were refined isotropically.

Quantum-Chemical Calculations. Density functional theory (DFT) calculations provide a reasonable balance of computational efficiency and chemical accuracy.[19,20] We have used the PBE functional[21] together with an empirical correction term in our calculations to compensate for the insufficient description of dispersion forces in the commonly used functionals.[22] The large number of spatially close-lying bulky alkyl groups make this important for the present study. The AO basis for geometry optimizations consisted of a split valence set with polarization functions [SV(P)][23] on all atoms except Al, the carbon atoms comprising the skeleton, and the hydride atoms for which a triple-ζ basis (TZV)[24] augmented with three sets of polarization functions (2df,2pd) on all elements was employed (TZVPP).[25] The final energies were obtained after replacing the SV(P) basis by TZVP without further optimization (single point energies). Natural population analyses[26] were performed with the NBO program.[27]

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Supporting Information Available: X-ray crystallographic files in CIF format for the compounds **2** and **3**. Further details of the crystal structure determinations are also available from the Cambridge Crystallographic Data Center on quoting the depository numbers CCDC-646838 (**2**) and −646839 (**3**). This material is available free of charge via the Internet at http://pubs.acs.org.

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