Two Isomers with an Al_4C_8 Framework

Christoph Üffing, Achim Ecker, Ralf Köppe, Kurt Merzweiler, and Hansgeorg Schnöckel*

Dedicated to Professor Peter Jutzi on the occasion of his 60th birthday

Abstract: The co-condensation, by annealing from −196 °C to room temperature, of the high-temperature species AlCl and 3-hexyne (EtC≡CEt) with an excess of toluene leads to the formation of the compound $(AlCl \cdot EtC{\equiv}CEt)_4$. Characterisation by X-ray analysis revealed the presence of two isomers in the same crystal: a dimeric 1,4-dialumina-2,5-cyclohexadiene and a 1,4,7,10-tetralumina-2,5,8,11-cyclododecatetraene. Both isomers exhibit aluminium–olefin π-bonding, with the Al_4 entities present in a tetrahedral arrangement. The bonding in both isomers is discussed on the basis of ab initio calculations performed for model compounds.

Keywords: ab initio calculations · alkenes · alkynes · aluminum · pi interactions

Introduction

Some years ago we reported the preparation and structure of the dimeric 1,4-dichloro-2,3,5,6-tetramethyl-1,4-dialumina-2,5-cyclohexadiene $(AlCl \cdot MeC{\equiv}CMe)_4$ (**1**), formed from the high-temperature molecule AlCl and 2-butyne (Figure 1).[1a]

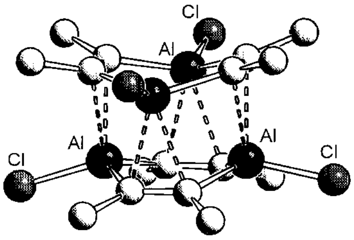

Figure 1. Molecular structure of dimeric 1,4-dichloro-2,3,5,6-tetramethyl-1,4-dialumina-2,5-cyclohexadiene (**1**; H atoms omitted for clarity).

As a unique structural feature, Al–olefin π-bonding was detected for the first time with the aid of X-ray analysis, in contrast to earlier spectroscopic results.[2] These interactions are clearly strong enough to prevent dissociation into monomeric dialuminacyclohexadiene units at about 140 °C under the high-vacuum conditions encountered in the mass spectrometer.[1b]

In order to elucidate this unique π-bonding, ab initio calculations were performed;[1b] they demonstrate that Al–Al interactions also contribute significantly to the stabilisation of these $Al_4Cl_4 \cdot (RC{\equiv}CR)_4$ systems. The bonding description of **1** as a μ_3-alkenyl-bridged Al_4 tetrahedron may therefore be similar to the bonding in some long-known transition metal μ_3-alkyne clusters such as $Ni_4X_4(RC{\equiv}CR)_3$ (X = CO or CN*t*Bu, R = CF_3 or phenyl).[3] In these Ni clusters the alkyne unit with its C≡C axis is oriented orthogonally to one of the edges of the tetrahedron and these interactions must therefore be described as μ_3,η^2-⊥ bonding. NMR spectroscopic investigations show that in contrast to many other transition metal alkyne complexes, there is no detectable rotation of the alkyne units in these Ni compounds.[3] To enable us to study the bonding in **1** by comparison with the Ni clusters and to understand the decomposition of **1** to hexamethylbenzene, we have prepared the analogous ethyl-substituted species $(AlCl \cdot EtC{\equiv}CEt)_4$ (**2**).

Results and Discussion

Preparation and characterisation of 2: The preparation of **2** from 3-hexyne and the high-temperature molecule AlCl proceeds in analogous fashion to the formation of **1**, that is, the co-condensation at −196 °C of gaseous AlCl, 3-hexyne and an excess of toluene. During this annealing process, which is monitored by NMR spectroscopy, many reactions take place.[4] After separating the solid residue, colourless crystals were isolated on cooling to 4 °C. The result of their X-ray analysis (Table 1) was unexpected, revealing the presence of two different isomers in the same crystal: **2b** and either **2a** or **2c** (Figure 2). The space group of **2** is *C*2/*c* with 12 molecules

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Table 1. Crystal structure data of **2**, **4** and **5**.[5]

	2	**4**	**5**
empirical formula	$C_{24}H_{40}Al_4Cl_4$	$C_{16}H_{32}Al_2Cl_2O_2$	$C_{20}H_{40}Al_2Cl_2O_2$
M_r	578.29	381.28	437.38
size [mm]	0.3 × 0.4 × 0.9	0.6 × 0.7 × 0.9	
crystal system	monoclinic	monoclinic	triclinic
space group	$C2/c$ (No. 15)	$P2(1)/c$ (No. 14)	$P\bar{1}$ (No. 2)
a [Å]	19.471(4)	9.751(2)	10.395(9)
b [Å]	29.406(6)	14.616(3)	10.984(11)
c [Å]	18.270(4)	7.5907(15)	12.871(9)
α [°]	90.00	90.00	96.21(7)
β [°]	118.84(3)	91.12(3)	107.04(6)
γ [°]	90.00	90.00	108.02(7)
V [Å^3]	9163.3(33)	1081.6(4)	1303.8(20)
Z	12	2	2
ρ_{calcd} [g cm^{-3}]	1.258	1.171	1.114
μ [mm^{-1}]	0.503	0.385	0.327
$F(000)$	3648	408	472
index ranges	$-17 \leq h \leq 20$; $0 \leq k \leq 30$; $-19 \leq l \leq 0$	$-12 \leq h \leq 12$; $-18 \leq k \leq 18$; $-9 \leq l \leq 9$	$-12 \leq h \leq 12$; $-13 \leq k \leq 13$; $-15 \leq l \leq 15$
2θ range [°]	3.76–44.00°	4.18–54.96°	8.70–50.00°
T [K]	293(2)	200(2)	213
reflns collected	5842	4344	8628
independent reflns	5624 [$R_{int} = 0.0227$]	2474 [$R_{int} = 0.0237$]	4283 [$R_{int} = 0.0622$]
observed reflns	3865 ($F > 4\sigma(F)$)	2016 ($F > 4\sigma(F)$)	3283 ($F > 4\sigma(F)$)
scan range	0.88° (ω)	1.24–1.40° (ω)	
x/y	0.0411/12.5272	0.0582/0.3274	0.0978/1.6641
max/min transm.	0.3478/0.3025	0.8720/0.9984	
data/restraints/param	5624/0/445	2470/0/104	4283/0/235
GOF on F^2	1.023	1.122	1.045
$R1/wR2$	0.0365/0.0885 ($F > 4\sigma(F)$)	0.0391/0.1097 ($F > 4\sigma(F)$)	0.0725/0.1950 ($F > 2\sigma(F)$)
$R1/wR2$ (all data)	0.0772 / 0.1032	0.0529 / 0.1259	0.0915 / 0.2155
largest diff. peak/hole [e Å^{-3}]	0.249/ – 0.193	0.381/ – 0.204	1.065/ – 0.476

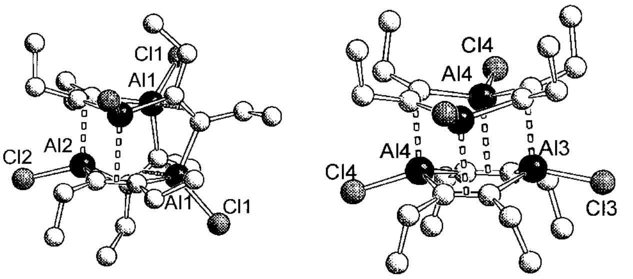


Figure 2. Molecular structures of **2a**, **2c** (left; only one isomer is shown), and **2b** (right) (hydrogen atoms omitted for clarity).

of **2** in the unit cell. The asymmetric unit comprises three half molecules (i.e. dialuminacyclohexadiene rings) of the three isomers (**2a**, **2b**, and **2c**).

Abstract in German: *Wird die Hochtemperaturspezies AlCl mit 3-Hexin (EtC≡CEt) und Toluol im Überschuß unter Hochvakuumbedingungen bei −196°C ausgefroren und das Cokondensat langsam auf Raumtemperatur erwärmt, so bildet sich die Verbindung (AlCl·EtC≡CEt)$_4$. Der Röntgenstrukturanalyse zufolge liegen in den Kristallen dieser Verbindung zwei Isomere vor, die als 1,4-Dialumina-2,5-cyclohexadien bzw. als 1,4,7,10-Tetraalumina-2,5,8,11-cyclododecatetraen formuliert werden können. Beiden Isomeren gemeinsam ist das Vorliegen von Aluminium–Olefin-π-Bindungen und die tetraedrische Anordnung der Al$_4$-Einheiten. Die Bindungssituation in beiden Isomeren wird auf der Basis von Ab-initio-Rechnungen diskutiert.*

Of the three independent molecules, one (**2b**) exhibits the expected structure observed for **1**, that is, two six-membered Al_2C_4 rings connected by four Al–olefin π bonds. In contrast, the remaining molecules (**2a**/**2c**) are not dimeric 1,4-dialumina-2,5-cyclohexadienes, but may be described instead as 1,4,7,10-tetralumina-2,5,8,11-cyclododecatetraenes, in which a twelve-membered Al_4C_8 ring system is formed, with the 12 atoms following the seam of a tennis ball (Figure 3). Similarly to **2b**, the Al_4Cl_4 units may be described as distorted tetrahedra. Furthermore, in all three isomers (**2b** and **2a**/**2c**, Figure 2), there are four 3c2e-Al–olefin π bonds and eight Al–C σ bonds present, each Al atom therefore forming one Al–Cl σ bond, two Al–C σ bonds, and one Al–olefin π bond.

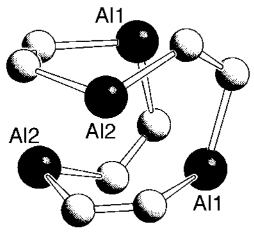


Figure 3. Al_4C_8 framework in **2a** and **2c**.

The bond lengths of **2a**, **2b**, **2c**, and **1** are summarised in Table 2. The similarity of the structural data of **1** and **2b** is obvious; thus, the Al–Al distances within the same six-membered rings measure 338.0 (**2b**) and 337.0 pm (**1**), with distances of 294.2–308.3 pm (**2b**) and 300.5 pm (**1**) between the Al atoms of different six-membered rings. On the other hand, the Al–Al distances in the isomers **2a**/**2c** are on average shorter, since the geometric constraints that arose from the dialuminacyclohexadiene units are no longer present. The remaining interatomic distances (Al–Cl, C=C, Al–C σ) in **2b** and **2a**/**2c** and the Al–C π

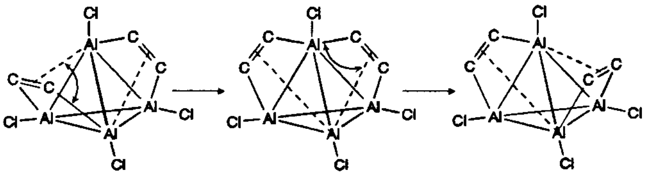
Table 2. Intramolecular distances [pm] (esd) in **1**, **2a**, **2b** and **2c**.

	2a	**2b**	**2c**	**1**[1a]
Al–Cl	211.57(14) / 211.2(2)	211.4(2) / 212.3(2)	212.1(2) / 212.1(2)	210.9
Al–Al	293.5(2) / 316.9(2) / 321.1(2) / 296.5(3)	294.3(2) / 302.5(2) / 338.0(2) / 308.3(2)	299.2(2) / 318.5(2) / 319.1(2) / 297.5(2)	300.5 / 337.0
Al–C(σ)	198.5(4) / 200.0(4) / 200.7(4) / 198.6(4)	201.0(4) / 200.7(4) / 199.7(4) / 200.3(4)	198.4(4) / 201.7(4) / 201.8(4) / 198.6(4)	199.0
Al–C(π)	236.1(4) / 236.0(4) / 240.9(4) / 237.2(4)	232.6(4) / 241.8(4) / 233.7(4) / 242.0(4)	237.3(4) / 239.1(4) / 237.8(4) / 236.9(4)	235.5
C=C	138.2(5) / 136.1(5)	136.4(5) / 137.1(5)	136.6(5) / 136.8(5)	136.7

bonds (232.6–242.0 pm in **2b** and 236.0–240.9 pm in **2a**/**2c**) do not differ very much.

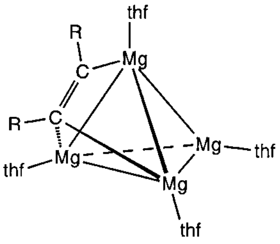
This observation seems plausible, since in the crystallisation of **2** the two isomers are formed in a ratio of 2:1 (**2a**/**2c**:**2b**), and their energy should therefore be very similar. Preliminary quantum chemical calculations for the hydrogen-substituted model compounds confirmed this assumption of nearly equal energy: the compound with the Al–C framework analogous to **2b** is only 12.5 kJ mol^{-1} more stable than the H-substituted isomer with the **2a**/**2c** structure.[6]

In addition to the energetic situation of these isomers, the mechanism for their isomerisation (**2b**$\rightleftharpoons$**2a**/**c**) is also of interest. A rotation of the alkenyl entity across the faces of the Al_4 tetrahedron seems plausible, since a similar mechanism has been discussed for some transition metal clusters (see above). This rotation mechanism, in which the Al–C σ and π bonds are broken and re-form, is presented schematically for two of the four alkenyl units (Scheme 1). However, no significant splitting or broadening of the CH_3 proton signals was detected in their variable-temperature 250 MHz NMR spectra (–80–80 °C); thus, on this basis there is no evidence of any rotation of the alkenyl unit across the Al_3 faces.



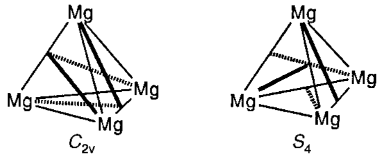
Scheme 1. Schematic representation of the rotation of two alkenyl units across two of the faces of the Al_4 tetrahedron. This is consistent with the interconversion of isomer **2b** to isomer **2a** or **2c**.

A literature search for main-group compounds containing bonding similar to that in **2a**/**2b** revealed the tetrameric magnesium species 1,8-naphthalenediyl-, *o*-phenylene- and diphenylvinylenemagnesium, in which bifunctional organic ligands are situated on the faces of a magnesium tetrahedron.[9, 10] In contrast to the π-like bonding in **1** and **2**, one of the C atoms forms a Mg–C single bond, with the second C atom involved in a μ_2-3c2e bond to the magnesium centres. This bonding situation is illustrated in Scheme 2.



Scheme 2. Schematic representation of the η^2-(σ,μ^2)-bonding of one of the four organic substituents situated on the faces of the Mg_4 tetrahedron.

In the three Mg_4 compounds so far investigated each Mg atom is tetrahedrally coordinated to one σ-bonded C atom, two μ_2-bonded C atoms, and one O atom of a THF molecule. Like the bonding situation in **2b** and **2a**/**2c** and the proposed isomerisation mechanism described above, the divalent organic ligands can be oriented on the faces of the Mg_4 tetrahedra in different ways, resulting in molecules with either C_{2v} or S_4 symmetry, as shown in Scheme 3.



Scheme 3. Two different arrangements for the four divalent organic groups bridging the Mg_4 tetrahedron, with correspondingly different symmetries.[10]

In contrast to **2**, only one of these potential structures is adopted in the solid state for each of the three Mg_4 examples. Their different geometric situations may be one reason for the differences in their behaviour. However, there are also some parallels in the bonding in the Mg_4 and Al_4 compounds, for example by analogy with the observation of a single NMR signal for **2a**/**2c** and **2b**, the two metal-bonded carbon atoms of the Mg_4 compounds could not be distinguished in solution. Such similarities between Al_4 and Mg_4 species are not unexpected, since $[Mg–thf]^{2+}$ and $[Al–Cl]^{2+}$ ions are isolobal. To summarise, the data presented here may give a first insight into the diverse isomerisation processes that may also be possible within the coordination sphere of main group metals.

Reactivity of 1 and 2

a) Reactions with diethyl ether: The reaction of **1** with diethyl ether afforded the bisdiethyl etherate **4**, which was characterised by NMR spectroscopy.[1b] Since compound **1**, obtained from the reaction of AlCl with 2-butyne under donor-free conditions, reacts with ethers to form the corresponding etherates—as expected, the formation of an Al–O bond is energetically favoured over that of an Al–olefin bond—it seemed realistic to synthesise **4** by reaction of 2-butyne with a metastable solution of AlCl in toluene/diethyl ether.[11] This reaction yielded colourless crystals with both 2-butyne (**4**) and 3-hexyne (**5**). The crystal structure analyses (Table 1) of the two compounds (Figure 4), at 200 K or 213 K respectively, revealed the space groups $P2_1/c$ for **4** and $P\bar{1}$ for **5**. Bond lengths for the two compounds are summarised in Table 3. As expected, all the structural data presented here for **4** and **5** show similarities to those for a dialuminacyclohexadiene etherate **3** prepared by Hoberg some years ago.[12]

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Table 3. Average intramolecular distances [pm] (esd) in **4** and **5**.

	Al–Al	Al–Cl	Al–O	Al–C	C=C	C_R[a] – C_{Me} / C_R – C_{CH_2}
4	333.5(1)	217.77(9)	191.3(2)	195.9(2)	135.1(3)	152.7(3)
5	332.4(3)	217.7(3) / 217.8(3)	191.8(4) / 191.7(3)	196.2(4) / 196.3(4) / 196.1(4) / 196.4(5)	135.8(6) / 135.2(6)	153.9(6) / 153.6(6) / 153.3(5) / 153.5(5)

[a] C_R: carbon atom of the metallacycle.

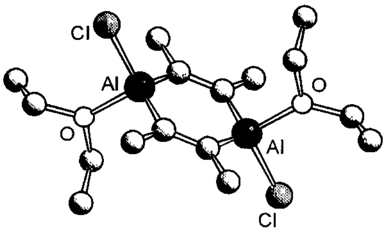
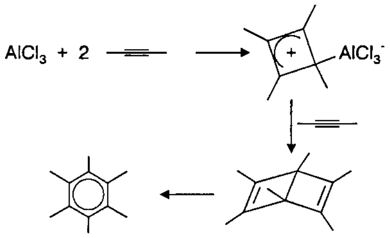


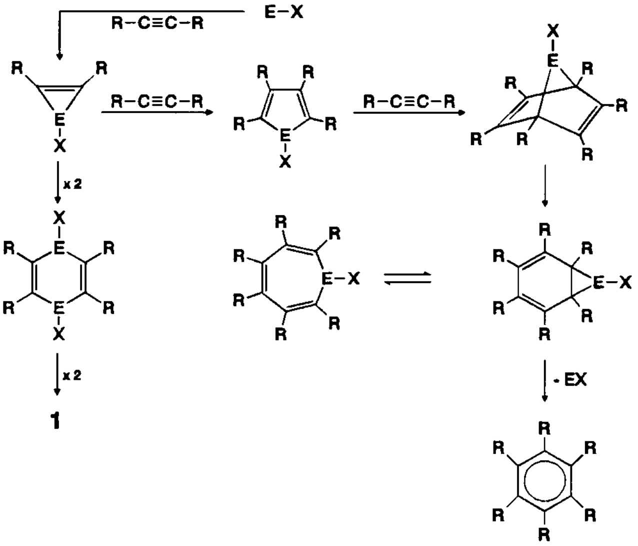
Figure 4. Molecular structure of 1,4-dichloro-2,3,5,6-tetramethyl-1,4-dialumina-2,5-cyclohexadiene-1,4-bis(diethyl etherate) (**4**; the molecular structures of the etherates **4** and **5** are nearly identical; hydrogen atoms are omitted for clarity).

The distances between the Al atoms in **4** and **5** are similar to those in the cyclohexadiene units of **1** and **2b**. Furthermore, the Al–C, Al–O and C–C distances in the two etherates **4** and **5** show no significant differences. Although most of the similarities between **4** and **5** and the donor-free compounds **1** and **2b** are quite plausible, the small difference between the C=C distances of the ether-stabilised and the donor-free species is surprising (136.8 and 135.4 pm, respectively), especially since the Al–Cl bonds in the two donor-stabilised species are about 6 pm longer than in the dimeric molecules **1** and **2**. On the other hand, the Al–C σ bonds in the monomeric etherates are shorter than in the dimers. The decrease in the formal coordination number of the Al atoms from 5 to 4 (dimer to monomer) may be the reason for the strengthening of the Al–C bonds. Moreover, it is interesting to note that the planarity of the Al_2C_4 ring systems in **4** and **5** changes to a boatlike structure in the dimeric species on account of Al–olefin π-bonding. To sum up, nearly all the differences in structural data between the monomeric (donor-stabilised) and dimeric species may be attributed to differences in the coordination sphere of the Al atoms.

b) Formation of hexamethylbenzene and hexaethylbenzene: The preferential formation of hexamethylbenzene was observed in the primary reaction mixture of AlCl, 2-butyne and an aromatic or aliphatic solvent.[4, 18] On the basis of these experiments, we assumed that the formation of hexamethylbenzene as a trimerisation product of the starting compound 2-butyne results from the thermal decomposition of **1**. If this were the case, in the presence of AlCl as a catalytic species, **1** would be formed as an intermediate during the trimerisation process. To test this hypothesis the pure compounds **1** and **2** were heated in different solvents (benzene and cyclohexane). However, neither in these experiments nor after addition of hexamethylbenzene[19] were further hexasubstituted benzene derivatives obtained. This means the above-mentioned formation of hexamethylbenzene and hexaethylbenzene is only possible under the specific conditions of the primary reaction solution. Since small amounts of $AlCl_3$ are present in these solutions as a consequence of the synthetic method, it seemed possible that the well-documented $AlCl_3$ catalysis could be the reason for the observed trimerisation of 2-butyne to hexamethylbenzene (Scheme 4).[23] For this catalytic process a reaction temperature of between 25 and 30 °C has been reported.[23] Since we observed the formation of hexaethylbenzene even at –50 °C, a reaction pathway other than that of $AlCl_3$ catalysis must be responsible in our case. A more plausible reaction mechanism, based on a mechanism proposed for the reaction of methylborylene (BMe) with alkynes, is therefore presented in Scheme 5.[13c]



Scheme 4. Reaction sequence for the $AlCl_3$-catalysed trimerisation of 2-butyne to hexamethybenzene.



Scheme 5. Proposed reaction pathway for the formation of hexamethylbenzene (and **1**) from E–X (E–X = BMe or AlCl) and 2-butyne.

In this scheme an aluminacyclopropene is the reactive intermediate from which either **1**, through a twofold dimerisation, or hexamethylbenzene, through a double addition of an alkyne moiety followed by rearrangement and elimination of AlX, can be formed.

The results presented here demonstrate that AlX species are excellent precursors for unexpected organoaluminium compounds; for example, addition of an alkyne yields

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molecules containing an Al_4C_8 framework. These cagelike compounds, which can be easily broken by donor molecules into two classically bonded dialuminacyclohexadienes, appear to be broadly analogous to the *closo* carboranes (such as $B_{10}C_2$ compounds). However, whereas the stabilisation of carboranes is based on delocalisation through strong multicentre bonding, in the carbalanes discussed here 2e 3c-bonding in the AlC_2 units is of only minor importance because of the higher polarity of Al–C compared with B–C bonds. Consequently, only loose cagelike structures are observed in the Al_4C_8 systems.

Experimental Section

All solvents were dried, distilled (toluene: Na; pentane, heptane, Et_2O: $LiAlH_4$), and degassed before use. All manipulations were carried out under an atmosphere of nitrogen or argon with Schlenk techniques or a glove box (M. Braun). ^1H and ^{13}C NMR spectra were recorded on a Bruker AC 250, ^{27}Al NMR spectra on a Bruker AMX 300 spectrometer, and were referenced to the residual protic impurities of the solvents (^1H NMR: $\delta(C_6D_5H) = 7.16$; $\delta(C_7D_7H) = 2.09$; ^{13}C NMR: $\delta(C_6D_6) = 128.8$; $\delta(C_7D_8) = 137.7$) or to $[Al(H_2O)_6]^{3+}$ ($\delta = 0$; external reference) unless otherwise stated. Mass spectra were recorded on a Finnigan MAT 711 or on a MS 8230 instrument (electron impact, 70 eV). IR spectra were recorded from KBr pellets on a Bruker IFS 113v FT-IR spectrometer and Raman spectra on a DILOR XY 800 instrument (vacuum-sealed glass capillary tubes; λ(excitation) = 514.532 nm). The principles behind the construction of the co-condensation apparatus and the experiments in general are described in ref. [1c].

Compound 1: In a typical 2-h co-condensation experiment, about 40 mmol AlCl was generated and then frozen out with an approximately equimolar quantity of 2-butyne dissolved in *n*-heptane (about 100 mL). The contents of the stainless steel vessel were washed out several times with solvent and the resulting suspension was allowed to warm to room temperature. After being left for some days the solution was filtered and the solvent partially removed in vacuo. On cooling to 4 °C colourless crystals of **1** were formed. Yield: <1% (based on the maximum possible amount of AlCl produced). IR (KBr): $\tilde{\nu}$ [cm^{-1} (rel. int.)] = 2963 (2), 2903 (2), 2839 (1), 1437 (3), 1363 (3), 1137 (1), 996 (1), 913 (2), 677 (8), 535 (6), 516 (10), 470 (4), 427 (9); Raman (solid; λ(excitation) 514 nm): not possible due to fluorescence effects; ^1H NMR (C_6D_6, 25 °C): $\delta = 1.97$ (s, 24H; CH_3); ^1H NMR (C_6D_6, 70 °C): $\delta = 2.00$ (s, 24H; CH_3); ^{13}C NMR (C_6D_6, 25 °C): $\delta = 183.4$ (br), 22.4; ^{27}Al NMR (C_6D_6, 25 °C): $\delta \approx 106$ ($\omega_{1/2} \approx 4000$ Hz); ^{27}Al NMR (C_6D_6, 70 °C): $\delta \approx 106$ ($\omega_{1/2} \approx 1560$ Hz); ^1H NMR (C_6D_{12}, 25 °C, TMS): $\delta = 2.14$ (s; 24H, CH_3); ^{13}C NMR (C_6D_{12}, 25 °C, TMS): $\delta = 183.9$, 21.8; ^{27}Al NMR (C_6D_{12}, 25 °C): $\delta \approx 103$ ($\omega_{1/2} \approx 3500$ Hz).

Compound 2: The co-condensation of AlCl with 3-hexyne dissolved in toluene was carried out as described above. The resulting solution was warmed slowly up to room temperature, the solvent partially removed in vacuo, and the solution held at 4 °C, yielding colourless crystals. ^1H NMR (C_7D_8, 25 °C): $\delta = 2.52$ (q, $^3J(H,H) = 7.6$ Hz, 16H; CH_2), 1.10 (t, $^3J = 7.6$ Hz, 24H; CH_3); ^{13}C NMR (C_7D_8, 25 °C): $\delta = 194.19$, 29.75, 13.68; ^{27}Al NMR (C_7D_8, 25 °C): $\delta \approx 120$ ($\omega_{1/2} \approx 3500$ Hz); ^1H NMR spectra were recorded between −80 °C and +80 °C at intervals of 20°.

Compound 4: AlCl solution (13 mL, about 7 mmol; toluene/Et_2O) was added at −78 °C to a stirred solution of 2-butyne (about 13 mmol) in *n*-pentane (34 mL). A brownish precipitate was formed. The suspension was warmed up slowly to room temperature and filtered, and the red solution was concentrated in vacuo. On cooling of the solution to 4 °C large colourless crystals of **4** were formed; m.p. 120–130 °C (yellow discoloration); Raman (solid): $\tilde{\nu}$ [cm^{-1} (rel. int.)] = 2979.9 (4), 2969.6 (4), 2936.0 (10), 2894.6(5), 2839.3 (3), 1444.6 (3), 1330.2 (2), 1086.5 (1), 991.6 (1), 890.3 (1), 833.6 (1), 767.1 (1), 504.7 (1), 373.8 (4), 322.5 (1), 229.5 (1), 184.2 (1); ^1H NMR (C_6D_6, 25 °C): $\delta = 3.62$ (q, $^3J = 7.0$ Hz, 8H; CH_2), 2.18 (s, 12H; CH_3), 0.80 (t, $^3J = 7.0$ Hz, 12H; CH_3); ^{13}C NMR (C_6D_6, 25 °C): $\delta = 164.6$ (Al–C), 67.9 (OCH_2CH_3), 19.2 (=C–CH_3), 14.1 (OCH_2CH_3); ^{27}Al NMR (C_6D_6, 25 °C): $\delta \approx 117$ ($\omega_{1/2} \approx 3500$ Hz); MS (EI, 70 eV, 35 °C) [*m*/*z* (rel. int.)]:[12e] 463.9 (77; $\mathbf{1}^+$), 448.9 (11; $\mathbf{1}^+$ – Me), 409.9 (6), 402.0 (7), 367.0 (38), 347.9 (35), 293.9 (36), 232.0 (57; $\mathbf{4}^+$ − $2Et_2O$), 197.0 (36), 170 (40), 74 (54; Et_2O^+).

Compound 5: The formation of **5** proceeds in the same way as described for **2**. If a nonstoichiometric amount of diethyl ether was present in the tube, compounds **2** and **5** crystallised alongside one another. The NMR data of **5** were taken from spectra of a mixture of the two compounds. ^1H NMR (C_6D_6, 25 °C): $\delta = 3.68$ (q, $^3J = 7.0$ Hz, 8H; CH_2), 2.85 (m, 4H; CH_2), 2.34 (m, 4H; CH_2), 1.37 (t, $^3J = 7.5$ Hz, 12H; CH_3), 0.83 (t, $^3J = 7.0$ Hz, 12H; CH_3); ^{13}C NMR (C_6D_6, 25 °C): $\delta = 67.8$, 26.4, 16.6, 14.1; ^{27}Al NMR (C_6D_6, 25 °C): 119 ($\omega_{1/2} \approx 4000$ Hz). This broad resonance signal is presumably due to the presence of both **2** and **5**.

Crystal structure analyses: A suitable crystal of compound **2** was sealed in a glass capillary tube, and oil-coated crystals of compound **4** and **5** were manipulated onto a glass fibre and transferred under a cold stream of nitrogen to a Stoe Stadi IV (ω scan mode, scan time: variable; 0.5–2.0 s/step; **2**, **4**) or to a STOE IPDS (**5**) diffractometer ($Mo_{K\alpha}$ radiation with graphite monochromator in each case). The structures were solved by direct methods by means of the program package SHELXS-86 (Sheldrick **1990**: H atom treatment: riding model, fixed isotropic *U*; empirical absorption correction; weighting scheme: $w^{-1} = \sigma^2 F_o^2 + (xP)^2 + yP$; $P = (F_o^2 + 2F_c^2)/3$, and refined by full-matrix least-squares techniques using the program package SHELXL-92 (Sheldrick **1993**).

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[5] An X-ray structure analysis performed on a single crystal of **2** at 200 K gave the same result. Further details of the crystal structure investigations can be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany) (Fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-408400 (**2**), CSD-408401 (**4**), and CSD-380163 (**5**).

[6] Distances are in pm and energy values in a.u. (1 a.u ≡ 1 Hartree ≡ 2625.5 kJ mol⁻¹). For the quantum chemical calculations, instead of their alkyl-substituted analogues we used the hydrogen-substituted compounds $[(AlCl \cdot HC{\equiv}CH)_4]$, with D_{2d} (**2b**) or S_4 symmetry (**2a**/**2c**); details of the calculation: HF-SCF, TZP basis, TURBOMOLE;[7] literature values[1b] are given in brackets (HF-SCF, TZDP basis). $\boldsymbol{D_{2d}}$

isomer (2b): energy (total): −3113.739986; (−3113.737347); selected distances: Al–Al: 353.8 (352.3) or 321.7 (321.2); Al–C(σ): 200.3 (199.9); Al–C(π): 246.2 (246.1); Al–Cl: 212.4 (211.7); C=C: 135.5 (135.5). SEN:[8] Al–Al (0.02) or (0.25), Al–Cl (1.24), Al–C(σ) (1.31), Al–C(π) (0.66), C=C (2.22); Al–C=C (0.38), Al–Al–C (0.12). **S_4 isomer (2a, 2c)**: energy (total): −3113.735205; selected distances: Al–Al: 339.5 or 316.6; Al–C(σ): 201.2 or 199.6; Al–C(π): 250.4 or 244.9; Al–Cl: 212.5; C=C: 135.4. SEN: Al–Al (0.09) or (0.27), Al–Cl (1.24), Al–C(σ) (1.32 or 1.30), Al–C(π) (0.65 or 0.64), C=C (2.22); Al–C=C (0.38), Al–Al–C (0.07 or 0.12).

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