

The hydroalumination of diethynes with di(*tert*-butyl)aluminium hydride: a facile method for the synthesis of organometallic dialuminium compounds

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Abstract

Di(*tert*-butyl)aluminium hydride reacted with the diynes 1,4-bis(trimethylsilyl)-1,3-butadiyne and 1,4-bis(trimethylsilyl)ethynylbenzene by hydroalumination and addition of one Al–H bond to each C≡C triple bond. A selective *cis* addition was observed in both cases to yield alkenes with *Z* configuration exclusively. The aluminium atoms were attached to those carbon atoms which bear the trimethylsilyl groups. While the butadiyne product (**1**) decomposed upon heating in benzene solution, the diene (**2**), obtained by the twofold hydroalumination of 1,4-bis(trimethylsilyl)ethynylbenzene, showed a remarkable rearrangement and gave the thermodynamically favoured product (**4**) almost quantitatively, which has two alkenes in *E* configuration. All products were characterized by crystal structure determinations. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Aluminium; Hydroalumination; Rearrangement

1. Introduction

The addition of Al–H bonds to alkenes or alkynes is an important method for the syntheses of alkylaluminium derivatives and found technical application in the ‘Ziegler–Direktverfahren’ [1]. Preparative organic chemistry employed hydroalumination in several reactions in order to synthesize alkenes or to form cyclic compounds from unsaturated chain molecules [2], for instance. In most of these cases the organoaluminium compounds were not isolated and characterized but were hydrolyzed *in situ* to release the organic component. Thus, only poor information is available from the literature about the constitution of the organoaluminium intermediates. The groups of Eisch and Wilke investigated the selectivity of hydroalumination reactions and found that under kinetic control the *cis* addition is preferred [3–5]. Upon heating or addition of catalysts these products isomerize to the thermodynamically more favoured products, which formally may be

described by the *trans* addition of the Al–H bonds to the C≡C triple bonds. The further substituents attached to the C=C double bonds of the products have a strong influence on the rate of the rearrangements, and the trimethylsilyl substituted compound $\text{H}_5\text{C}_6\text{-(H)C=C(SiMe}_3\text{)(Al-}i\text{-Bu}_2\text{)}$ gave the completely rearranged *trans* product already at a low temperature (–10°C) [4]. The position of the alkylaluminium group in the product was determined by the kind of the further substituents of the starting alkyne $\text{R-C}\equiv\text{C-E}$ ($\text{R} = \text{C}_6\text{H}_5$). If E was a *tert*-butyl group, the dialkylaluminium substituent was attached to that carbon atom which was further bonded to the phenyl group. In the cases of E = trimethylsilyl or trimethylgermyl, a product was formed almost quantitatively in which aluminium and silicon or germanium were bonded to the same carbon atom of the C=C double bond [4]. The preferred formation of geminal silyl or germlyl aluminium compounds may be caused by the better stabilization of the negative charge at this position owing to a hyperconjugative interaction with the silyl groups, while alkyl groups may influence the course of the reaction and the structure of the products mainly by steric reasons.

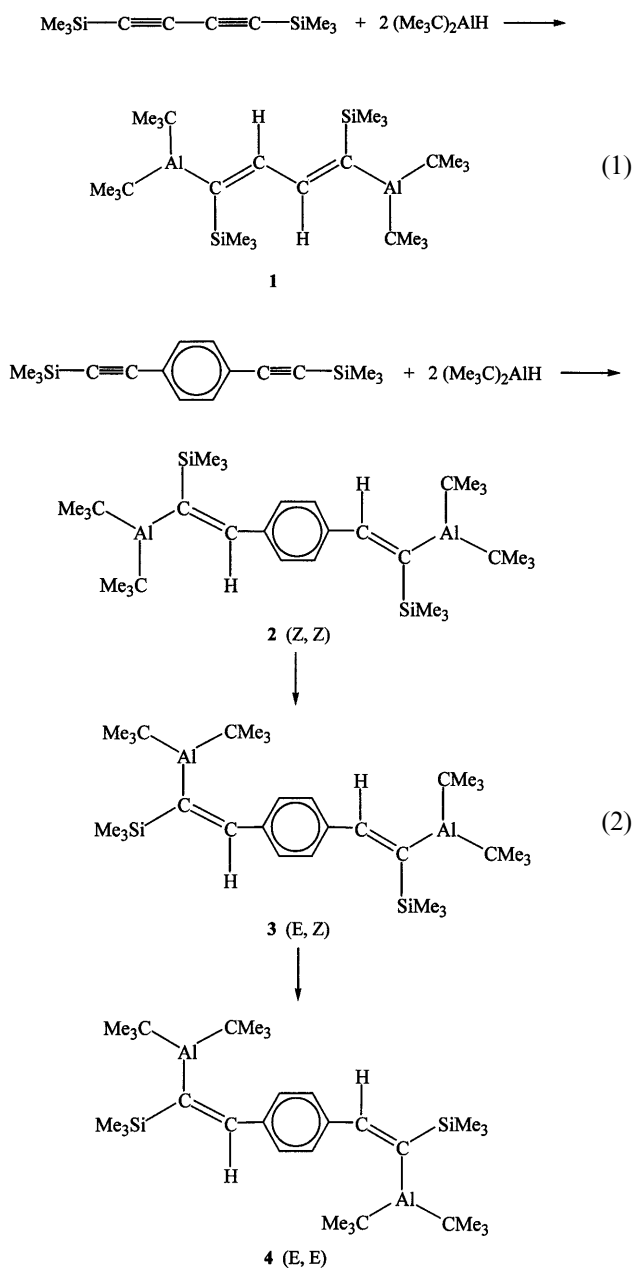
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In a few cases only, hydroalumination was employed for the synthesis of dialuminium compounds, and once again the organoaluminium intermediates were not isolated and characterized [2,3,5,6]. Only recently, we employed the reaction of dialkylaluminium hydrides with dialkylaluminium ethynides for the preparation of carbaalanes such as *arachno*-(AlMe)₈(CCH₂C₆H₅)₅H or *closo*-(AlMe)₇(CCH₂CH₃)₄H₂ [7]. These compounds contain polyhedral clusters of aluminium and carbon atoms and may be described as analogues of carbaboranes [8]. By the hydroalumination of polyalkynes we hope to synthesize polyaluminium compounds containing coordinatively unsaturated aluminium atoms, which may be useful as chelating Lewis acids in phase transfer processes or in anion recognition. The suitability of the dialuminium compound R₂Al–CH₂–AlR₂ [R = CH(SiMe₃)₂] [9] to act as a chelating Lewis acid for the coordination of anions such as nitrite or nitrate was verified by our group in some recently published investigations [10,11]. Much more compounds are required, however, for a systematic approach to this type of chemistry, and the hydroalumination of alkynes seems to be a facile method for the synthesis of a broad variety of polyaluminium compounds containing two, three or even more aluminium atoms. We started our investigations with the hydroalumination of diynes, in order to get a better insight into the rate and the course of these reactions and to obtain detailed information about the structure and stability of those products.

2. Reactions of di(*tert*-butyl)aluminium hydride with diynes

The starting diynes 1,4-bis(trimethylsilyl)-1,3-butadiene and 1,4-bis(trimethylsilylethynyl)benzene were dissolved in *n*-pentane and treated with two equivalents of di(*tert*-butyl)aluminium hydride at room temperature. The components were consumed completely after a reaction time of 15 and 3 h, respectively. After filtration, the solvent was removed in vacuum, and the residue was recrystallized from *n*-pentane to obtain pale yellow (**1**; Eq. (1)) or colourless crystals (**2**; Eq. (2)) of the products in a yield of 40–63%. Both products were obtained in high purity; they are air sensitive and have low melting points of 92 and 108°C, respectively. Their constitution was solved by crystal structure determinations (see below) and by spectroscopic characterization. Besides singlets of the trimethylsilyl and *tert*-butyl groups in an intensity ratio of 1 to 2, both compounds showed very characteristic resonances in the ¹H-NMR spectra with chemical shifts of $\delta = 7.47$ (**1**) and $\delta = 7.72$ (**2**), which are in the normal range [12] of C=C(H)R groups possessing single hydrogen atoms and verify the successful hydroalumination reactions and the addition of only one Al–H bond per C≡C triple bond.



3. Thermal behaviour of compounds **1** and **2**

As discussed below and schematically shown in Eqs. (1) and (2), both products **1** and **2** have *Z* configurations at all C=C double bonds. The aluminium atoms and the hydrogen atoms are on the same side, in agreement with the *cis* addition of the Al–H bonds. As discussed above, these products are usually formed under kinetically controlled conditions, while the *trans* products are thermodynamically favoured. Therefore, we heated solutions of **1** and **2** in benzene to 60°C. The butadiene product gave only a mixture of several unknown products, of which none could be isolated in a

pure form by recrystallization. In contrast, heating of the benzene derivative **2** gave a clearly resolved secondary reaction, which is summarized in Eq. (2).

Upon heating a solution of compound **2** to 60°C for some hours, the signals of two new products (**3** and **4**) were detected by NMR spectroscopy besides the characteristic resonances of the starting compound **2**. One of these products (**3**) disappeared as soon as **2** was completely consumed after about seven days, thus it is only an intermediate in the rearrangement process (Eq. (2)). **3** has two different resonances of *tert*-butyl and trimethylsilyl groups. Furthermore, two resonances were observed for the hydrogen atoms attached to the C=C double bond, and the hydrogen atoms bonded to the aromatic ring gave two doublets in accordance with two chemically different molecular halves. We suppose that **3** is the product of a partial rearrangement of the alkenylaluminium groups. One alkene group has the

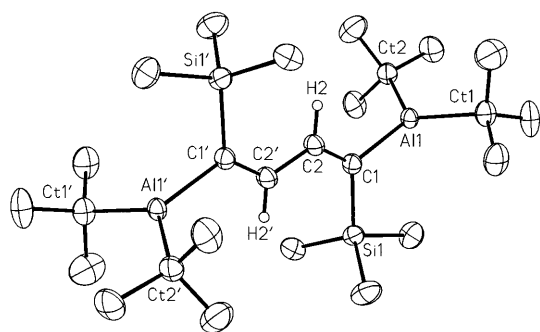


Fig. 1. Molecular structure and numbering scheme of **1**; the thermal ellipsoids are drawn at the 40% probability level. Selected bond lengths (pm) and angles (°): C1–C2 134.1(3), C2–C2' 145.8(4), C1–Si1 187.5(2), C1–Al1 196.5(2), Al1–Ct1 198.6(3), Al1–Ct2 197.6(3), C1–C2–C2' 127.4(3), C1–C2–H2 116.3(1), C2'–C2–H2 116.3(2), C2–C1–Si1 124.2(2), C2–C1–Al1 123.7(2), Si1–C1–Al1 112.1(1), C1–Al1–Ct1 119.2(1), C1–Al1–Ct2 117.3(1), Ct1–Al1–Ct2 122.9(1) (C2' generated by $-x, -y+1, -z+1$).

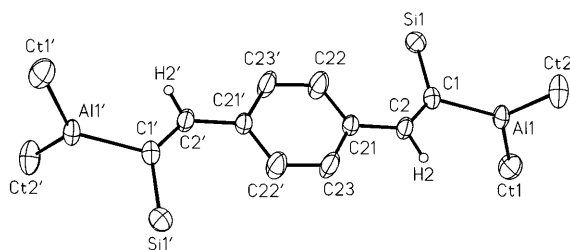


Fig. 2. Molecular structure and numbering scheme of **2**; the thermal ellipsoids are drawn at the 40% probability level; methyl groups are omitted for clarity. Selected bond lengths (pm) and angles (°): C21–C2 148.0(3), C1–C2 133.9(3), C1–Si1 185.9(2), C1–Al1 196.0(2), Al1–Ct1 198.0(3), Al1–Ct2 197.9(3), C21–C2–H2 114.0(1), C21–C2–C1 132.0(2), C1–C2–H2 114.0(1), C2–C1–Si1 132.7(2), C2–C1–Al1 117.6(2), Si1–C1–Al1 109.7(1), C1–Al1–Ct1 117.8(1), C1–Al1–Ct2 117.9(1), Ct1–Al1–Ct2 123.3(1) (equivalent atoms generated by $-x, -y, -z$).

original constitution with the hydrogen and the aluminium atom in a *cis* position, while the second one has the thermodynamically favoured *trans* arrangement of both atoms. Upon longer heating, complete rearrangement occurred with both alkenyl groups in a *trans* configuration and an inversion centre in the middle of the phenyl ring (**4**). The proposed constitution of the final product **4** was verified by a crystal structure determination. The symmetric structure of **4** led to the observation of a quite simple ¹H-NMR spectrum similar to that of compound **2** with singlets for the CMe₃, SiMe₃ and phenyl protons.

4. Crystal structures of **1**, **2**, and **4**

The molecular structure of compound **1** in the solid state is depicted in Fig. 1. It results from a *cis* addition of Al–H groups to both C≡C triple bonds of the starting diyne and has a *trans* butadiene core in its molecular centre, which is located on a crystallographic centre of symmetry. As expected (see Section 1), the aluminium atoms are bonded to the terminal carbon atoms, which are further attached to trimethylsilyl groups. The bond distances in the electronically delocalized molecular center (C=C 134.1 pm; C–C 145.8 pm) are similar to those of free butadiene C₄H₆ (C=C 134 pm; C–C 148 pm) [13,14] and thus they are only slightly affected by the dialkylaluminium substituents. The Al1–C1 distances (196.5 pm) are as usual, and the Al atoms have an almost ideally planar coordination sphere (sum of the angles 359.4°). The atoms in the molecular centre C1, C2, H2, Al1, Si1 and their equivalents generated by the centre of symmetry form a perfect plane, the maximum derivation of which is observed for the hydrogen atom H2 with only 0.47 pm. That plane is almost perpendicular to the plane around the Al atom, their normals include an angle of 94.7°. Compared to butadiene, some deformations of bond angles in the molecular centre of **1** are observed which may be caused by strong steric interactions. A small angle of 112.1° is found between the dialkylaluminium and trimethylsilyl substituents at the carbon atom C1, while the angles C2–C1–Al1 and C2–C1–Si1 are enlarged to 123.7 and 124.2°, respectively. In butadiene, all angles of the terminal carbon atoms are close to the ideal value of 120° [13]. The angle at the inner carbon atom is enlarged from 122.4° in butadiene to 127.4° in **1**.

Figs. 2 and 3 show the molecular structures of compounds **2** and **4**; both molecules are located on crystallographic centres of symmetry. **2** is the product of a *cis* addition of two Al–H bonds to the ethyne groups of the starting 1,4-bis(trimethylsilylethynyl)benzene, **4** is

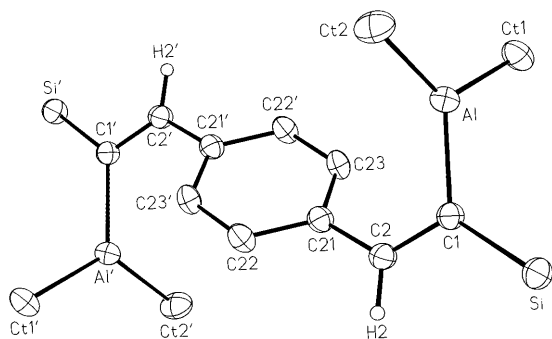


Fig. 3. Molecular structure and numbering scheme of **4**; the thermal ellipsoids are drawn at the 40% probability level; methyl groups are omitted for clarity. Selected bond lengths (pm) and angles ($^{\circ}$): C21–C2 147.7(2), C1–C2 134.7(2), C1–Si 186.3(2), C1–Al 197.1(2), Al–Ct1 199.4(2), Al–Ct2 199.6(2), C21–C2–H2 118.4, C21–C2–C1 123.3(1), C1–C2–H2 118.4, C2–C1–Si 119.1(1), C2–C1–Al 114.1(1), Si–C1–Al 126.10(8), C1–Al–Ct1 120.59(7), C1–Al–Ct2 115.82(8), Ct1–Al–Ct2 122.18(8) (equivalent atoms generated by $-x+1$, $-y+2$, $-z+2$).

the completely rearranged product, in which the hydrogen atoms and the dialkylaluminium substituents are on opposite sides of the C=C double bonds. Once again, aluminium and silicon atoms are attached to the same terminal carbon atoms in both cases. Despite their different configurations, both compounds show almost indistinguishable bond lengths. The C=C double bonds (C1–C2 133.9 and 134.7 pm, respectively), the bonds to the phenyl ring (C2–C21 148.0 and 147.7 pm), the Al–C bonds (C1–Al1 196.0 and 197.1 pm, Al–Ct1/2 198.0 and 199.5 pm) and the Si–C bonds (C1–Si1 185.9 and 186.3 pm) are in an expected range and need no further discussion. In contrast, the bond angles differ significantly between both compounds with a strong deformation of the angles at the C=C double bonds in the *cis* product **2**. While the angles C2–C1–Al and C2–C1–Si are quite normal in the *trans* product **4** (114.1 and 119.1 $^{\circ}$, respectively), the C2–C1–Si1 angle of **2** is enlarged to 132.7 $^{\circ}$ (C2–C1–Al1 117.6 $^{\circ}$) indicating a considerable steric stress in the molecule, which may be caused by a steric repulsion between the phenyl group and the trimethylsilyl substituents. The molecular centre of **2** comprising the benzene ring, the C=C double bonds and the atoms attached to the ethene groups is almost planar. The angle between the normals of benzene (C21 to C23) and the alkenyl group (C21, C2, C1, H2, Si1, Al1) is only 6.4 $^{\circ}$. The coordination sphere of the aluminium atom deviates slightly from planarity, and Al1 is located 11 pm above the plane spanned by the carbon atoms C1, Ct1 and Ct2. This plane is perpendicular to the diethynylbenzene group, and their normals enclose an angle of 87.2 $^{\circ}$. The *trans* product **4** deviates strongly from planarity. The planes

of the aromatic ring and of the ethene groups comprising the atoms C1, C2, H2, Si, Al are tilted by 39.7 $^{\circ}$, and the plane formed by the aluminium atom and its substituents deviates from an ideal perpendicular arrangement (74.2 $^{\circ}$). The aluminium atom is 14 pm above the α carbon atoms of its substituents. Owing to the particular conformation of the molecule, the Al atoms are situated 193 pm above the plane of the benzene ring and in particular above the C–H bond C23–H23. A narrow contact exists between this bond and the coordinatively unsaturated Al atoms (Al $\cdots$ C23 276.6 pm; Al $\cdots$ H23 234.5 pm), which may indicate some weak donor–acceptor interaction.

5. Experimental

All procedures were carried out under purified argon in dried solvents (*n*-pentane and *n*-hexane over LiAlH₄; benzene over Na/benzophenone). Di(*tert*-butyl)aluminium hydride was synthesized as described in Ref. [15], commercially available 1,4-bis(trimethylsilyl)-1,3-butadiyne and 1,4-bis(trimethylsilyl)ethynylbenzene (Lancaster) were thoroughly evacuated at room temperature and used without further purification.

5.1. Synthesis of *s-trans*-[*Z,Z*]-1,4-bis{di(*tert*-butyl)aluminium}-1,4-bis(trimethylsilyl)-1,3-butadiene

1: A solution of 0.951 g (6.70 mmol) of di(*tert*-butyl)alane in 25 ml of *n*-pentane was added dropwise to a solution of 0.641 g (3.30 mmol) of 1,4-bis(trimethylsilyl)-1,3-butadiyne in 25 ml of *n*-pentane at room temperature. The mixture was stirred for 15 h, and the solution adopted a yellow colour. All volatile components were removed in vacuum, and the orange crystalline residue was dissolved in *n*-pentane. Product **1** crystallized in pale yellow, air sensitive crystals upon cooling of the solution to -50°C . Yield: 0.632 g (40%). M.p. (argon, sealed capillary): 92–93 $^{\circ}\text{C}$. ¹H-NMR (C₆D₆, 300 MHz): δ = 0.27 (s, 18 H, SiMe₃), 1.12 (s, 36 H, Al–CMe₃), 7.47 (s, 2 H, Al(Si)C=CH). ¹³C-NMR (C₆D₆, 75.5 MHz): δ = 1.5 (SiMe₃), 19.4 (Al–CMe₃), 29.5 (Al–CMe₃), 154.5 (Al(Si)C=CH–R); the second alkene carbon atom was not detected. IR (CsBr plates, paraffin, cm^{−1}): ν = 1534 w ν C=C; 1462 vs, 1377 s paraffin; 1306 w, 1246 s, 1221 w δ CH₃; 1069 w, 1042 w, 1007 w, 936 w ν CC; 882 sh, 856 vs ρ CH₃; 837 vs, 814 sh ν C₃C; 766 m, 745 m, 723 w ρ CH₃; 689 w, 678 w ν_{as} SiC; 656 vw, 629 m, 596 m, 548 w, 529 w, 478 w ν AlC; 451 m, 424 w δ C₃C, δ SiC₃. Molar mass (cryoscopically in benzene, g mol^{−1}): calc. 478.86; found 514.

Table 1

Crystal data, data collection parameters and structure refinement for **1**, **2** and **4**^a

	1	2	4
Formula	C ₂₆ H ₅₆ Al ₂ Si ₂	C ₃₂ H ₆₀ Al ₂ Si ₂	C ₃₂ H ₆₀ Al ₂ Si ₂
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group [16]	<i>P</i> 2 ₁ / <i>n</i> ; no. 14	<i>P</i> 2 ₁ / <i>n</i> ; no. 14	<i>P</i> 2 ₁ / <i>n</i> ; no. 14
<i>Z</i>	2	2	2
Temperature (K)	213(2)	213(2)	213(2)
<i>D</i> _{calc} (g cm ^{−3})	0.956	0.976	0.991
Unit cell parameters			
<i>a</i> (pm)	950.0(1)	1031.1(2)	878.26(6)
<i>b</i> (pm)	1156.03(9)	1231.1(2)	1614.67(8)
<i>c</i> (pm)	1533.9(2)	1546.7(3)	1364.04(9)
β (°)	99.10(1)	105.89(3)	105.917(8)
<i>V</i> (10 ^{−30} m ³)	1663.4(3)	1888.3(6)	1860.2(2)
μ (mm ^{−1})	0.170	0.157	0.159
Crystal size (mm)	0.30 × 0.40 × 0.35	1.00 × 0.47 × 0.46	0.47 × 0.37 × 0.36
Diffractometer	Stoe-IPDS		
Radiation	Mo-K _α ; graphite monochromator		
Exposure; Δφ (°)	207; 1.5	140; 1.5	158; 1.2
2θ range (°)	4.4 ≤ 2θ ≤ 52.1	4.3 ≤ 2θ ≤ 52.1	5.0 ≤ 2θ ≤ 52.0
Index ranges	−11 ≤ <i>h</i> ≤ 11 −13 ≤ <i>k</i> ≤ 13 −18 ≤ <i>l</i> ≤ 18	−11 ≤ <i>h</i> ≤ 11 −15 ≤ <i>k</i> ≤ 15 −19 ≤ <i>l</i> ≤ 18	−10 ≤ <i>h</i> ≤ 10 −19 ≤ <i>k</i> ≤ 19 −16 ≤ <i>l</i> ≤ 16
Independent reflections	3214	3444	3613
Reflections <i>F</i> > 4σ(<i>F</i>)	2492	2712	3005
Parameters	145	172	172
$R = \Sigma F_o - F_c / \Sigma F_o $ (<i>F</i> > 4σ(<i>F</i>))	0.0578	0.0525	0.0421
$wR^2 = \{\Sigma w(F_o ^2 - F_c ^2)^2 / \Sigma w(F_o^2)\}^{1/2}$ (all data)	0.1220	0.1121	0.1323
Maximum/minimum residual electron density (10 ³⁰ e m ^{−3})	0.665/−0.341	0.462/−0.253	0.379/−0.320

^a Programs SHELXL-97, SHELXTL-Plus [17]; solutions by direct methods, full matrix refinement with all independent structure factors.

5.2. Synthesis of *s-trans*-[*Z,Z*]-1,4-bis{2-di(*tert*-butyl)aluminium-2-trimethylsilyl-ethenyl}benzene

2: A solution of 0.274 g (1.93 mmol) of di(*tert*-butyl)alane in 15 ml of *n*-pentane was added dropwise to a solution of 0.262 g (0.97 mmol) of 1,4-bis(trimethylsilylethenyl)benzene in 30 ml of *n*-pentane at room temperature. The mixture was stirred for 3 h. The yellow-brown suspension was filtered, and all volatile components were removed in vacuum. The oily brown residue was dissolved in a small quantity of *n*-pentane and cooled to −50°C to yield compound **2** as colourless, air sensitive crystals. Yield: 0.340 g (63%). M.p. (argon, sealed capillary): 107–109°C. ¹H-NMR (C₆D₆, 300 MHz): δ = 0.19 (s, 18 H, SiMe₃), 1.17 (s, 36 H, Al-CMe₃), 7.30 (s, 4 H, C₆H₄), 7.72 (s, 2 H, Al(Si)C=CH). ¹³C-NMR (C₆D₆, 125.8 MHz): δ = 1.5 (SiMe₃), 19.2 (Al-CMe₃), 29.8 (Al-CMe₃), 141.9 (*ipso*-C of benzene), the other resonance of the benzene ring was covered by the C₆D₆ signal, 153.9 (Al(Si)C=CH-C₆H₄), 158.7 (Al(Si)C=CH-C₆H₄). IR (CsBr plates, paraffin, cm^{−1}): ν = 1593 w, 1551 w, 1501 w aryl, νC=C; 1464 vs, 1377 s paraffin; 1314 vw, 1262 sh, 1246 m δCH₃; 1221 vw, 1175 w, 1107 vw, 1076 vw, 1044 w, 1038 w, 1018 w, 1006 w, 934 w νCC; 854 vs, 841 vs ρCH₃, νC₃C; 812 m, 762 m, 721 w ρCH₃; 691 w ν_{as}SiC;

631 m, 596 w, 523 w, 465 vw νAlC; 446 vw, 419 w δC₃C, δSiC₃. Molar mass (cryoscopically in benzene, g mol^{−1}): calc. 554.96; found 495.

5.3. ¹H-NMR data of the intermediate compound *s-trans*-[*E,Z*]-1,4-bis{2-di(*tert*-butyl)aluminium-2-trimethylsilyl-ethenyl}benzene (**3**)

¹H-NMR (C₆D₆, 300 MHz): δ = 0.20 and 0.28 (each s, 9 H, SiMe₃), 1.05 and 1.15 (each s, 18 H, Al-CMe₃), 7.07 and 7.39 (each d, 2 H, ³*J*_{HH} = 7.9 Hz, C₆H₄), 7.65 and 7.92 (s, 1 H, Al(Si)C=CH).

5.4. Synthesis of *s-trans*-[*E,E*]-1,4-bis{2-di(*tert*-butyl)aluminium-2-trimethylsilyl-ethenyl}benzene

4: A solution of 1.210 g (2.18 mmol) of **2** in 25 ml of benzene was heated to 60°C in a closed glass vessel for 7 days. The colour changed from colourless to yellow. The solvent was removed in vacuum, and the pale yellow residue was dissolved in *n*-pentane. After concentration to about 20 ml and cooling to −30°C the product (**4**) was obtained as yellowish crystals. Yield: 1.150 g (95%). M.p. (argon, sealed capillary): 187°C. ¹H-NMR (C₆D₆, 300 MHz): δ = 0.23 (s, 18 H, SiMe₃), 1.04 (s, 36 H, Al-CMe₃), 7.13 (s, 4 H, C₆H₄), 7.82 (s, 2

H, Al(Si)C=CH). ^{13}C -NMR (C_6D_6 , 125.8 MHz): δ = 0.3 (SiMe₃), 18.8 (Al–CMe₃), 30.0 (Al–CMe₃), 125.8 (*o*-C of C₆H₄), 147.7 (*ipso*-C of C₆H₄), 153.0 (Al(Si)C=CHC₆H₄), 166.9 (Al(Si)C=CHC₆H₄). IR (CsBr plates, paraffin, cm^{−1}): ν = 1532 w, 1487 w aryl, $\nu\text{C}=\text{C}$; 1460 vs, 1377 vs paraffin; 1316 w, 1260 sh, 1244 s δCH_3 ; 1210 vw, 1171 vw, 1158 vw, 1105 w, 1079 vw, 1050 vw, 1007 w, 998 w, 982 vw, 959 w, 934 m, 916 s νCC ; 887 vs $\nu\text{C}_3\text{C}$; 835 vs, 806 s, 743 s, 723 m ρCH_3 ; 687 m $\nu_{\text{as}}\text{SiC}$; 625 w $\nu_{\text{s}}\text{SiC}$; 592 m, 579 m, 542 m, 498 w, 466 vw νAlC ; 434 s, 420 w, 403 w, 388 w, 370 w $\delta\text{C}_3\text{C}$, δSiC_3 .

5.5. Crystal structure determinations

Single crystals of compounds **1**, **2** and **4** were obtained by recrystallization from *n*-pentane. The crystals of compound **1** were grown over a period of 4 weeks from a dilute solution in *n*-pentane at -30°C . All crystals of **1** were twinned, but the reflections of the individuals could be detected separately. The refinement of **1** was carried out with all but 12 reflections, which were probably damaged by an overlap with those of the second individual. Crystal data and structure refinement parameters of all compounds are given in Table 1.

6. Supplementary material

The crystallographic data of compounds **1**, **2** and **4** (excluding structure factors) were deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 142062 (**1**), 142063 (**2**) and 142064 (**4**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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