DOI: 10.1002/ejic.200700481

Facile Synthesis of Aluminum-Bridged [3,3,3]Cyclophanes by Hydroalumination

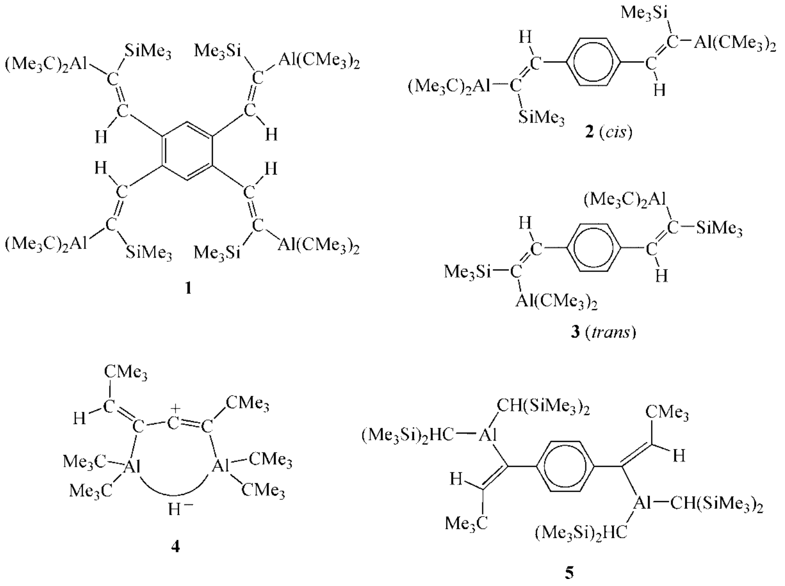
Werner Uhl,*[a] Alexander Hepp,[a] Madhat Matar,[a] and Andrej Vinogradov[a]

Keywords: Aluminum / Hydroalumination / Cage compounds / Cyclophanes

The reaction of 1,3,5-tris(3,3-dimethyl-1-butinyl)benzene $C_6H_3(C{\equiv}C–CMe_3)_3$ with the dialkylaluminum hydrides $HAl(CMe_3)_2$ and $HAl(CH_2CMe_3)_2$ gave the addition of one Al–H bond to each C–C triple bond (hydroalumination). Spontaneous condensation by the release of the corresponding trialkylaluminum derivatives afforded [3,3,3]cyclophane derivatives **6** and **7** in which three tricoordinate Al atoms are in the bridging positions between two functionalized benzene rings. The aluminum atoms behave as Lewis acids, and treatment with thf yielded adduct **6**·3thf.

Introduction

The addition of Al–H bonds to unsaturated compounds containing C=C and C≡C bonds (hydroalumination) is a powerful method for the reduction of organic compounds and the generation of new hydrocarbons.[1,2] In most cases, the organoaluminum intermediates were not isolated, but the organic components were released by hydrolysis. Other derivatives are accessible by particular oxidative workup such as halogenation.[3] Thus, suggestions concerning the structure of the organoaluminum intermediates are rather speculative in most cases. A preferred *cis* addition was postulated owing to the constitutions of the finally isolated hydrocarbons.[1] As was shown by our group only recently,[4,5] silyl-substituted alkynes gave the predicted products of hydroalumination with a dialkylaluminum group attached to that carbon atom that also bears the trimethylsilyl group (**1** and **2** in Scheme 1). This particular constitution may be favored by two reasons. Owing to the electronegativity difference between both elements, the carbon atom attached to silicon bears a negative partial charge and, hence, may be attacked preferentially by the positively charged aluminum ions. Furthermore, the enhanced negative charge at this position in the product, which is introduced by the polarity of the freshly formed Al–C bond, can be stabilized by



Scheme 1.

---

[a] Institut für Anorganische und Analytische Chemie der Universität Münster
Corrensstraße 30, 48149 Münster, Germany
Fax: +49-251-8336660

hyperconjugation with the Si–C bonds. In all cases the *cis* addition products are formed with the hydrogen and aluminum atoms on the same side of the C=C bonds. A *cis*/*trans* rearrangement was observed only for **3** (Scheme 1) upon elongated heating of solutions in benzene.[4] In contrast, spontaneous rearrangement occurred upon the similar addition of Ga–H bonds to silylalkynes (hydrogallation).[6] Exceptions were observed only for the reactions of the sterically shielded di(*tert*-butyl)gallium hydride. The products of these reactions contain up to three coordinatively unsaturated, tricoordinate aluminum or gallium atoms; however, only the *trans* isomers are able to act as powerful chelating Lewis acids. Secondary reactions with the release of trialkylaluminum derivatives occurred upon treatment of dialkylaluminum alkynides with dialkylaluminum hydrides. Clusters similar to carbaboranes were formed that contained aluminum and carbon atoms and had a delocalized bonding situation.[7] Analogous reactions of gallium compounds afforded heteroadamantane-type molecules possessing localized Ga–C bonds.[8] An unexpected and unprecedented product was formed upon treatment of di(*tert*-butyl)butadiyne with di(*tert*-butyl)aluminum hydride. C–H bond activation by hyperconjugation with Al–C bonds and the chelating coordination of the resulting hydride anion by two aluminum atoms afforded **4** as a singular, persistent butadienyl cation (Scheme 1), which was zwitterionic and did not require the application of a strictly noncoordinating counterion for its stabilization.[9] In contrast, benzene centered *tert*-butylethynes showed a more complicated reaction behavior. Secondary reactions occurred that could be clarified completely for the more selective hydrogallation reactions only.[10] Bulky substituents attached to the aluminum atoms as in $R_2Al–H$ [$R = CH(SiMe_3)_2$] prevented these secondary processes.[11] The persistent simple addition products, **5** (Scheme 1), had the aluminum atoms attached to the carbon atoms in the α position to the aromatic ring. This particular constitution may allow optimum mesomeric stabilization of the negative charge, which is localized at these atoms and resulted from the polarity of the Al–C bonds. We report here the first successful reactions of that type conducted with sterically less-shielded dialkylaluminum hydrides.

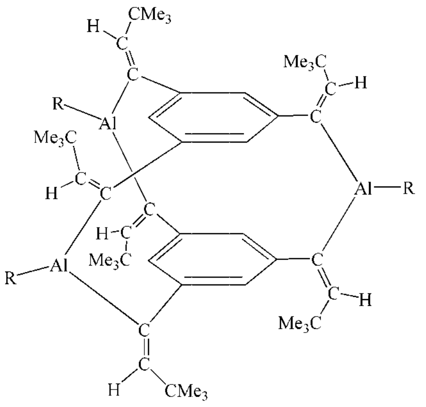
Results and Discussion

Complete consumption of the starting compounds was observed when mixtures of 1,3,5-tris(*tert*-butylethynyl)benzene and the corresponding dialkylaluminum hydrides in *n*-pentane or *n*-hexane were stirred at r.t. for about 20 h [Equation (1)]. Thus, the hydroalumination reactions are much faster than hydrogallation reactions, which do not start at ambient temperature at all and require boiling *n*-hexane over a period of about 16 h for completion.[6,10] The difference in the reaction behaviors of the hydrides may depend on the lower polarity of the Ga–H bond relative to the Al–H bonds. Two aluminum hydrides $R_2Al–H$ ($R = CMe_3$, CH_2CMe_3) were employed. The ^1H NMR spectroscopic analysis of the reaction courses verified the release of the corresponding trialkylaluminum derivatives, tri(*tert*-butyl)- and trineopentylaluminum, respectively, in both cases. The reaction of di(*tert*-butyl)aluminum hydride proved to be complicated. Unknown byproducts were formed, and the yield of compound **6** varied between 10 and 80%. Despite intensive efforts with dozens of experiments, we did not succeed in finding suitable conditions for a more reproducible reaction course. A second problem arose from the poor crystallization behavior, which made the purification by recrystallization from different solvents rather difficult. Sometimes solutions of **6** must be stored at –45 °C for several weeks to isolate colorless crystals of the product. In contrast, the reaction of dineopentylaluminum hydride with the trialkyne was rather unproblematic. Colorless product **7** precipitated directly from the reaction mixture after concentration and cooling to –30 °C. The pure compound was isolated in 63% yield. Smaller substituents attached to aluminum such as methyl or ethyl groups or the application of the dialkyne 1,4-bis(*tert*-butylethynyl)benzene resulted in the formation of insoluble products or complicated reaction mixtures. Thus far, we were not able to isolate any product in a pure form or to unambiguously identify one component of the reaction mixtures.

Schematic drawings of the molecular structures are given in Equation (1). The integration ratio of the ^1H NMR spectra clearly confirms the condensation reaction and the formation of cyclophane-type molecules. The resonances of the vinylic hydrogen atoms and the protons attached to the aromatic ring are close together and resonate at $\delta = 6.00$ and 6.32 ppm for **6** and at $\delta = 6.24$ and 6.22 ppm for **7**. The

$$2\ \ 1,3,5\text{-}(Me_3C\text{-}C{\equiv}C\text{-})_3C_6H_3\ +\ 6\ H\text{-}AlR_2\ \xrightarrow[-\ 3\ AlR_3]{}$$

$(R = CMe_3,\ CH_2CMe_3)$



6: $R = CMe_3$
7: $R = CH_2CMe_3$

$$\xrightarrow[(R\ =\ CMe_3)]{+\ 3\ thf}\ [Al(thf)(CMe_3)]_3[C_6H_3(C{=}CH\text{-}CMe_3)_3]_2$$

6(thf)$_3$

(1)

carbon atoms of the C=C bonds show chemical shifts of δ = 152 and 156 ppm on average; the resonances at higher field belong to the carbon atoms attached to the phenyl rings and to the aluminum atoms. This situation is in complete accordance with data obtained for the corresponding gallium compounds.[10]

Crystal-structure determinations verified the condensation reactions by the release of the corresponding trialkylaluminum derivatives and the formation of cyclophane-type molecules. All C≡C bonds of the starting trialkyne were reduced by the addition of Al–H bonds to yield alkenyl groups containing C=C bonds. The aluminum atoms attacked exclusively those carbon atoms of the triple bonds that are in the α position to the aromatic ring. Aluminum and hydrogen adopt a *cis* configuration across the double bonds, which is the expected arrangement under kinetically controlled conditions. Spontaneous *cis*/*trans* rearrangement with the formation of the *trans* products occurred only with the addition of Ga–H bonds to trimethylsilyl-substituted alkynes.[6] Condensation and release of trialkylaluminum species from the hypothetical intermediates containing dialkylaluminum groups attached to the C=C bonds gave three C–Al–C bridges between two aromatic rings with coordinatively unsaturated three-coordinate aluminum atoms. Thus, these compounds may be described as [3,3,3]cyclophanes. The molecular structures are depicted in Figures 1, 2, and 3. Considerable problems occurred with respect to the generation of single crystals and the determination of the molecular structure of compound **6** (see Experimental Section). Severe disorder was observed for two of the three independent molecules, which prevents a concise discussion of all the structural parameters. However, the result can be taken as clear structural evidence for the suggested constitution. Further evidence was achieved by the generation and structural characterization of the thf adduct, **6**·3thf, in which the cyclophane-type structure is retained and one thf molecule is bonded to each of its aluminum atoms. This compound is not only valuable for the structural characterization of **6**. It impressively shows that this particular type of compound is suitable to act as multipodal Lewis acids. Relevant bond lengths and angles of the adduct are quite similar to those of the ether-free products. The phenyl rings are almost ideally coplanar with angles between the normals of both rings smaller than 1°. They are not in an ideal

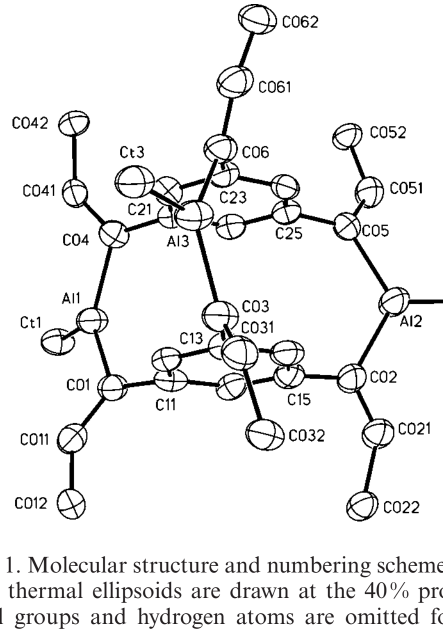


Figure 1. Molecular structure and numbering scheme of compound **6**. The thermal ellipsoids are drawn at the 40% probability level. Methyl groups and hydrogen atoms are omitted for clarity. The molecule located on a general position (see Experimental Section) is considered only. Selected bond lengths [pm] and angles [°]: Al*x*–C0*y* (*x* = 1 to 3; *y* = 1 to 6) 195.7 (av.), Al*x*–Ct*x* 198.4 (av.), C0*y*=C0*y*1 134.6 (av.), C0*y*–Al*x*–C0*y* 120.6 (av.), Al*x*–C0*y*–C0*y*1 115.9 (av.), C0*y*–C0*y*1–C0*y*2 133.0 (av.).

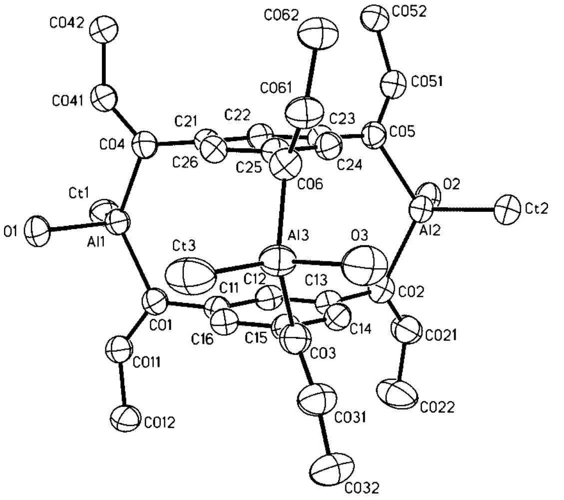


Figure 2. Molecular structure and numbering scheme of compound **6**·3thf. The thermal ellipsoids are drawn at the 40% probability level. Methyl groups and hydrogen atoms are omitted for clarity. Only the oxygen atoms of the thf molecules are considered. Selected bond lengths [pm] and angles [°]: Al*x*–C0*y* (*x* = 1 to 3, *y* = 1 to 6) 198.8 (av.), Al*x*–Ct*x* 201.2(av.), Al*x*–O*x* 193.0 (av.), C0*y*=C0*y*1 134.6 (av.), C0*y*–Al*x*–C0*y* 119.8 (av.), Al*x*–C0*y*–C0*y*1 115.3 (av.), C0*y*–C0*y*1–C0*y*2 133.9 (av.).

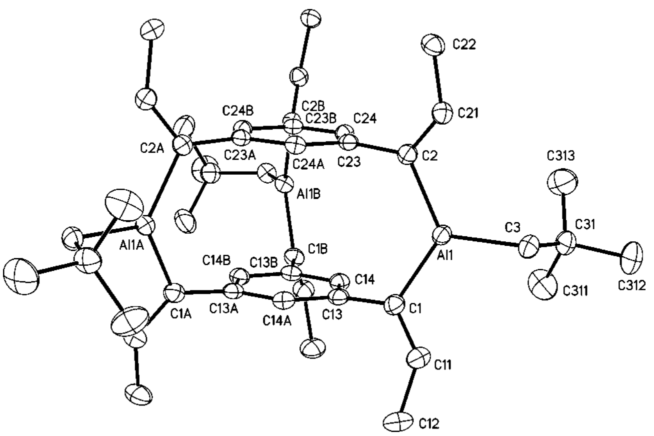


Figure 3. Molecular structure and numbering scheme of compound **7**. The thermal ellipsoids are drawn at the 40% probability level. Methyl groups and hydrogen atoms are omitted for clarity. Selected bond lengths [pm] and angles [°]: Al1–C1 195.6(2), Al1–C2 196.2(1), Al1–C3 196.9(2), C1–C11 134.6(2), C2–C21 134.6(2), C1–Al1–C2 122.40(6), Al1–C1–C11 114.7(1), Al1–C2–C21 112.9(1), C1–C11–C12 132.6(2), C2–C21–C22 132.6(1).

eclipsed arrangement. This may also be deduced from the fact that the normals of the planes of the benzene rings and the C–Al–C groups deviate considerably from the ideal value of 90° (75 to 87°). The distance between the benzene rings of one molecule is close to 360 pm on average, which is in the characteristic range of van der Waals interactions.[12] Thus, the cavity seems to be suitable for the coordination of transition-metal atoms, and it may be an interesting task for future work to generate those products containing an encapsulated metal atom. The C=C bond lengths (135 pm on average) correspond to standard values.[13] The inner cage Al–C distances are quite similar to those including the terminal alkyl groups. Thus, there is no hint of steric stress in the cages. The angles at the aluminum atoms are close to 120°. Expectedly, only in the thf adduct did we observe an approach of the angles to the ideal tetrahedral angle with the exception of the inner cage angle, which remained unchanged relative to the ether-free compounds (about 120° on average).

Experimental Section

General: All procedures were carried out under an atmosphere of purified argon. Cyclopentane, *n*-pentane, and *n*-hexane were dried with $LiAlH_4$; thf with Na/benzophenone. Di(*tert*-butyl)aluminum hydride,[14] dineopentylaluminum hydride[15] and 1,3,5-tris(*tert*-butylethynyl)benzene[10] were obtained according to literature procedures. The assignments of the signals in the NMR spectra were made on the basis of HMBC, HSQC, ROESY, and DEPT135 data.

6: A solution of 1,3,5-tris(*tert*-butylethynyl)benzene (0.227 g, 0.714 mmol) in *n*-hexane (20 mL) was added dropwise to a cooled (–10 °C) solution of di(*tert*-butyl)aluminum hydride (0.304 g, 2.14 mmol) in *n*-hexane (20 mL). The mixture was stirred at r.t. for 24 h. The solvent was distilled off in vacuo, and the residue was thoroughly evacuated (10^{-3} Torr) to partially remove the tri(*tert*-butyl)aluminum byproduct. The oily product was dissolved in cyclopentane and stored at –45 °C for several weeks to afford **6** as a colorless solid. Yield: 0.080 g (25%). M.p. (argon, sealed capillary): 185 °C. ^{1}H NMR (400 MHz, C_6D_6): δ = 1.11 (s, 54 H, CMe_3 of alkenyl group), 1.37 (s, 27 H, Al-CMe_3), 6.00 (s, 6 H, vinylic H), 6.32 (s, 6 H, benzene H) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 19.6 (Al-*C*Me_3), 30.9 (Al-C*Me*$_3$), 32.0 (*C*Me_3 of the alkenyl group), 37.4 (C*Me*$_3$ of the alkenyl group), 122.0 (CH of the aromatic rings), 145.9 (*ipso*-C), 150.1 (Al-*C*=C), 154.8 (Al-C=*C*) ppm. IR (CsBr plates, paraffin): $\tilde{\nu}$ = 1580 (vs, *ν*C=C), phenyl, 1460 (vs, paraffin), 1404 (m, *δ*CH_3), 1381 (s, paraffin), 1359 (vs, *δ*CH_3), 1223 (s), 1200 (vs), 1135 (w), 1034 (m), 991 (s), 934 (m), 912 (s), 882 (s), 808 (s), 734 (s), 710 (s, *ν*CC, *δ*CH), 624 (vs), 573 (m), 538 (vw), 487 (s), 439 (w), 386 (m), 361 (s, *ν*AlC, phenyl, *δ*CC) cm^{-1}. $C_{60}H_{93}Al_3$ (895.3): C 80.5, H 10.5; found C 79.8, H 10.3.

6·3thf: An oily residue out of the synthesis of compound **6** was dissolved in thf. Slow concentration of the solution at r.t. over several days afforded crystals of the thf adduct of compound **6**. M.p. (argon, sealed capillary): **6**·3thf did not melt below 230 °C. ^{1}H NMR (400 MHz, [D$_8$]thf): δ = 0.89 (s, 54 H, CMe_3 of alkenyl group), 1.08 (s, 27 H, Al-CMe_3), 1.77 (m, 12 H, thf), 3.62 (m, 12 H, thf), 5.54 (s, 6 H, vinylic H), 5.92 (s, 6 H, benzene H) ppm. ^{13}C NMR (100 MHz, [D$_8$]thf): δ = 15.5 (Al-*C*Me_3), 26.3 (thf), 31.8 (Al-C*Me*$_3$), 32.7 (*C*Me_3 of the alkenyl group), 37.0 (C*Me*$_3$ of the alkenyl group), 68.2 (thf), 119.9 (CH of the aromatic rings), 147.1 (*ipso*-C), 147.8 (Al-*C*=C), 155.9 (Al-C=*C*) ppm. IR (CsBr plates, paraffin): $\tilde{\nu}$ = 1578 (vs), 1556 (vs, *ν*C=C), phenyl, 1465 (vs, paraffin), 1403 (m, *δ*CH_3), 1380 (vs, paraffin), 1355 (vs), 1318 (w), 1299 (w), 1281 (w), 1248 (m, *δ*CH_3), 1224 (vs), 1200 (vs), 1181 (s), 1133 (m), 1071 (m), 1037 (vs), 1003 (vs), 970 (vs), 959 (m), 934 (s), 911 (vs), 893 (vs), 854 (vs), 795 (s), 733 (s), 707 (s, *ν*CC, *ν*CO, δCH), 688 (m), 651 (m), 616 (vs), 571 (s), 549 (s), 484 (vs), 442 (s), 394 (vs), 359 (vs), 336 (s, *ν*AlC, *ν*AlO, phenyl, *δ*CC) cm^{-1}.

7: A solution of 1,3,5-tris(*tert*-butylethynyl)benzene (0.244 g, 0.767 mmol) in *n*-pentane (10 mL) was treated with a solution of dineopentylaluminum hydride (0.392 g, 2.30 mmol) in *n*-pentane (20 mL) at r.t. The mixture was stirred under these conditions for 20 h. After concentration and cooling of the solution to –30 °C, product **7** precipitated as a colorless amorphous powder. Yield: 0.227 g (63%). M.p. (argon, sealed capillary): 140 °C (dec.). ^{1}H NMR (400 MHz, C_6D_6): δ = 0.76 (s, 6 H, Al-CH_2), 1.13 (s, 54 H, CMe_3 of alkenyl group), 1.31 (s, 27 H, CMe_3 of neopentyl), 6.22 (s, 6 H, benzene H), 6.24 (s, 6 H, vinylic H) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 25.2 (Al-CH_2), 31.9 (*C*Me_3 of neopentyl and C*Me*$_3$ of the alkenyl groups), 35.8 (C*Me*$_3$ of neopentyl), 37.4 (*C*Me_3 of the alkenyl group), 121.1 (CH of the aromatic rings), 145.3 (*ipso*-C), 153.3 (Al-*C*=C), 157.7 (Al-C=*C*) ppm. IR (CsBr plates, paraffin): $\tilde{\nu}$ = 1574 (s, br. *ν*C=C, phenyl), 1454 (vs, paraffin), 1410 (w, *δ*CH_3), 1373 (s, paraffin), 1293 (w), 1254 (w, *δ*CH_3), 1225 (s), 1202 (s), 1136 (m), 1115 (s), 1094 (m), 1028 (vs), 910 (s), 895 (s), 880 (s), 824 (m), 802 (m), 739 (s), 710 (s, *ν*CC, *δ*CH), 682 (s), 646 (s), 620 (w), 600 (m), 590 (s), 570 (m), 527 (m), 517 (m), 467 (s), 430 (s, *ν*AlC, phenyl, *δ*CC) cm^{-1}. MS (EI, 20 eV): *m*/*z* = 937 (100), 938 (72) [M + H]$^+$, 866 (28), 867 (17) [M – CH_2CMe_3]$^+$. $C_{63}H_{99}Al_3$ (937.4): calcd. C 80.7, H 10.6, Al 8.6; found C 80.2, H 11.3, Al 8.2.

Crystal Structure Determinations of 6, 6·3thf, and 7: Single crystals of solvent-free **6** could only be obtained with enormous difficulties by recrystallization from *n*-pentane (20/–15 °C). It crystallized in the hexagonal space group $P6_3/m$ with 20 molecules in the unit cell. Twelve symmetry related molecules are in general positions. The molecular structure of that species could be refined to reasonable final structural parameters. Six molecules are localized on crystallographic mirror planes. They are severely disordered in particular with respect to the bridging C–Al–C groups. The refinement was done by severe restrictions and gave an insufficient result only, but verified clearly the occurrence of a structure identical to that of the molecule on a general position. Two further molecules are localized on $\bar{6}$ axes. They show a similar disorder of the C–Al–C bridges, but the refinement gave a more consistent result. Overall, the value of that structure determination should be seen in structural evidence only; it clearly does not meet the standard requirement of a sufficiently high quality. Crystals of **6**·3thf were generated by slow concentration of a thf solution at r.t. over several days. The crystals enclosed a thf molecule per formula unit of the adduct, which was refined with atomic occupation factors of 0.5. Recrystallization of the amorphous solid product from *n*-pentane afforded single crystals of **7**, which enclose strongly disordered solvent molecules. The cyclophane molecules of **7** reside on crystallographic threefold rotation axes. Crystal data, data collection parameters, and structure refinement details are given in Table 1. The crystallographic data of **6** and **6**·3thf were collected with a STOE image plate diffractometer, those of **7** were determined with a BRUKER apex diffractometer. The structures were solved by direct methods and refined with the program SHELXL-97[18] by a full-matrix least-squares method based on F^2.

Table 1. Crystal data and structure refinement for compounds **6**, **6**·3thf, and **7**.[a]

	6	**6**·3thf	**7**
Formula	$C_{60}H_{93}Al_3$	$C_{74}H_{121}Al_3O_{3.5}$	$C_{64.67}H_{99}Al_3$
Crystal system	hexagonal	monoclinic	rhombohedral
Space group[16]	$P6_3/m$ (no. 176)	$P2_1/c$ (no. 14)	$R\bar{3}$ (no. 148)
Z	20	4	6
T [K]	193(2)	193(2)	153(2)
$d_{\text{calcd.}}$ [g cm^{-3}]	0.984	0.980	0.978
a [pm]	2803.53(9)	2327.5(2)	1647.47(6)
b [pm]	2803.53(9)	2320.7(1)	1647.47(6)
c [pm]	4438.7(2)	1444.4(1)	4150.3(2)
α [°]	90	90	90
β [°]	90	94.084(7)	90
γ [°]	120	90	120
V [10^{-30} m^3]	30213(2)	7782.0(9)	9755.4(7)
μ [mm^{-1}]	0.095	0.089	0.092
Crystal size [mm]	$0.24 \times 0.16 \times 0.10$	$0.26 \times 0.14 \times 0.09$	$0.37 \times 0.33 \times 0.26$
Radiation	Mo-K_α; graphite monochromator	Mo-K_α; graphite monochromator	Mo-K_α; graphite monochromator
θ range [°]	$1.24 \le \theta \le 24.01$	$1.24 \le \theta \le 26.31$	$1.73 \le \theta \le 31.26$
Index ranges	$-32 \le h \le 32$	$-28 \le \mathrm{h} \le 28$	$-23 \le \mathrm{h} \le 23$
	$-32 \le k \le 31$	$-28 \le \mathrm{k} \le 28$	$-23 \le \mathrm{k} \le 23$
	$-50 \le l \le 50$	$-18 \le \mathrm{l} \le 17$	$-60 \le \mathrm{l} \le 59$
Independent reflections	16024 [R_{int} = 0.2221]	15640 [R_{int} = 0.1161]	6632 [R_{int} = 0.0418]
Reflections $I > 2\sigma(I)$	5435	6413	4908
Parameters	1107	776	255
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$ [$I > 2\sigma(I)$]	0.1005	0.0608	0.0635
$wR_2 = \{\Sigma w(\|F_o\|^2 - \|F_c\|^2)^2/\Sigma\|F_o\|^2\}^{1/2}$ (all data)	0.2740	0.1735	0.1875
Max./min. residual [10^{30} e m^{-3}]	0.908/–0.373	0.728/–0.273	0.472/–0.260

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

Acknowledgments

We are grateful to the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for generous financial support.

---

[1] a) E. Winterfeldt, *Synthesis* **1975**, *10*, 617–630; b) J. Marek, J.-F. Normant, *Chem. Rev.* **1996**, *96*, 3341–3367; c) J. J. Eisch in *Comprehensive Organic Chemistry* (Eds.: B. Frost, J. Flemming), Pergamon, Oxford **1991**, vol. 8, p. 773.

[2] a) G. Wilke, H. Müller, *Chem. Ber.* **1956**, *89*, 444–447; G. Wilke, H. Müller, *Justus Liebigs Ann. Chem.* **1960**, *629*, 222–240; b) J. J. Eisch, M. W. Foxton, *J. Org. Chem.* **1971**, *36*, 3520–3526; c) J. J. Eisch, W. C. Kaska, *J. Am. Chem. Soc.* **1966**, *88*, 2213–2220; d) J. J. Eisch, W. C. Kaska, *J. Am. Chem. Soc.* **1963**, *85*, 2165–2166. Some recent publications on general aspects of hydroalumination: e) U. Dümichen, T. Gelbrich, J. Sieler, *Z. Anorg. Allg. Chem.* **2001**, *627*, 1915–1920; f) J. A. Francis, S. G. Bott, A. R. Barron, *Main Group Chem.* **1999**, *3*, 53–57; g) M. G. Gardiner, S. M. Lawrence, C. L. Raston, *Inorg. Chem.* **1999**, *38*, 4467–4472; h) M. Hoshi, K. Shirakawa, *Chem. Commun.* **2002**, 2146–2147; i) W. Uhl, M. Matar, *Z. Naturforsch.* **2004**, *59b*, 1214–1222; j) W. Uhl, J. Molter, B. Neumüller, *J. Organomet. Chem.* **2001**, *634*, 193–197; k) V. V. Burlakov, P. Arndt, W. Baumann, A. Spannenberg, U. Rosenthal, *Organometallics* **2004**, *23*, 4160–4165.

[3] L. Aufauvre, P. Knochel, J. Marek, *Chem. Commun.* **1999**, 2207–2208.

[4] W. Uhl, F. Breher, *J. Organomet. Chem.* **2000**, *608*, 54–59.

[5] W. Uhl, M. Matar, *J. Organomet. Chem.* **2002**, *664*, 110–115.

[6] W. Uhl, H. R. Bock, F. Breher, M. Claesener, S. Haddadpour, B. Jasper, A. Hepp, *Organometallics* **2007**, *26*, 2363–2369.

[7] a) W. Uhl, F. Breher, *Angew. Chem.* **1999**, *111*, 1578–1580; *Angew. Chem. Int. Ed.* **1999**, *38*, 1477–1479; b) W. Uhl, F. Breher, A. Lützen, W. Saak, *Angew. Chem.* **2000**, *112*, 414–416; *Angew. Chem. Int. Ed.* **2000**, *39*, 406–409; c) W. Uhl, F. Breher, J. Grunenberg, A. Lützen, W. Saak, *Organometallics* **2000**, *19*, 4536–4543; d) W. Uhl, F. Breher, A. Mbonimana, J. Gauss, D. Haase, A. Lützen, W. Saak, *Eur. J. Inorg. Chem.* **2001**, 3059–3066.

[8] W. Uhl, L. Cuypers, B. Neumüller, F. Weller, *Organometallics* **2002**, *21*, 2365–2368.

[9] W. Uhl, J. Grunenberg, A. Hepp, M. Matar, A. Vinogradov, *Angew. Chem.* **2006**, *118*, 4465–4467; *Angew. Chem. Int. Ed.* **2006**, *45*, 4358–4361.

[10] a) W. Uhl, F. Breher, S. Haddadpour, *Organometallics* **2005**, *24*, 2210–2213; b) W. Uhl, S. Haddadpour, M. Matar, *Organometallics* **2006**, *25*, 159–163.

[11] W. Uhl, M. Matar, *Z. Anorg. Allg. Chem.* **2005**, *631*, 1177–1180.

[12] a) G. D. Smith, R. L. Jaffke, *J. Phys. Chem.* **1996**, *100*, 9624–9630; b) W. Uhl, F. Hannemann, R. Wartchow, *Organometallics* **1998**, *17*, 3822–3825.

[13] J. March, *Advanced Organic Chemistry*, 3rd ed., Wiley, New York, **1985**, p. 19.

[14] W. Uhl, L. Cuypers, R. Graupner, J. Molter, A. Vester, B. Neumüller, *Z. Anorg. Allg. Chem.* **2001**, *627*, 607–614.

[15] O. T. Beachley Jr, L. Victoriano, *Organometallics* **1988**, *7*, 63–67.

[16] T. Hahn (Ed.), *International Tables for Crystallography, Space-Group Symmetry*, Kluwer Academic, Dordrecht-Boston-London, **1989**, vol. A.

[17] CCDC-645566 (for **6**), -645565 (for **6**·3thf), and -645564 (for **7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[18] *SHELXTL-Plus*, REL. 4.1, Siemens Analytical X-RAY Instruments Inc., Madison, WI, **1990**; G. M. Sheldrick, *SHELXL-97: Program for the Refinement of Structures*, University of Göttingen, **1997**.

Received: May 3, 2007