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Syntheses of polyaluminium compounds by hydroalumination reactions, chelating Lewis acids possessing two and four coordinatively unsaturated aluminium atoms

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Abstract

Hydroalumination of C≡C triple bonds was achieved by treatment of the tetraalkynylbenzene derivative 1,2,4,5-$(Me_3Si-C\equiv C)_4C_6H_2$ with di(*tert*-butyl)aluminium hydride. Depending on the stoichiometric ratio of the starting compounds multifunctional Lewis acids were obtained with two or four coordinatively unsaturated aluminium atoms. Alkenyl derivatives resulted which have the Al and H atoms in *cis* positions and the di(*tert*-butyl)aluminium and trimethylsilyl groups attached to the terminal carbon atoms of the C=C double bonds.

Keywords: Aluminium; Hydroalumination

1. Introduction

Chelating Lewis acids possessing two or more coordinatively unsaturated atoms of the third main-group elements boron [1], aluminium [2], gallium [3] and indium [4] found considerable interest in current research, because they may find some application in phase transfer processes or in anion recognition, for instance. About 10 years ago we obtained a stable tetraalkyldialuminium derivative which contained a methylene bridge between both its tricoordinate aluminium atoms [$R_2Al-CH_2-AlR_2$, $R = CH(SiMe_3)_2$]. That dialuminium compound was synthesized by the treatment of $Cl_2Al-CH_2-AlCl_2$ with four equivalents of the lithium compound $LiCH(SiMe_3)_2$ [5], and it is a potential acceptor of up to two donor atoms. Indeed, it proved to be a very effective chelating Lewis acid, which gave stable adducts with hydrido (**1**, Scheme 1), nitrato (**2**, Scheme 1), nitrito, diphosphanylmethanido, methylthiolato, acetato and azido ligands [6]. However, those methylene bridged tetraalkyldialanes are stable only when they are effectively shielded by bulky substituents. Insufficient steric shielding by smaller ligands resulted in dismutation reactions [5,7]. One related compound bearing smaller substituents [$Li_2(R_3AlCH_2AlR_3)$; $R = CH_2SiMe_3$] was stabilized by coordinative saturation of its aluminum atoms [8]. In some recent investigations, we found that the hydroalumination [9] of polyalkynes is a facile method for the synthesis of a broad variety of polyaluminium compounds in high yield, and we obtained dialuminium derivatives by the reaction of di(*tert*-butyl)aluminium hydride with 1,4-bis(trimethylsilyl)butadiyne or 1,4-bis(trimethylsilylethynyl)benzene [10]. We hoped to isolate even aluminium richer compounds by the employment of tetraalkynylbenzene derivatives.

2. Results and discussion

Treatment of 1,2,4,5-tetrakis(trimethylsilylethynyl)benzene with two equivalents of di(*tert*-butyl)aluminium hydride in boiling *n*-hexane for 3 days and recrystallization of the rough product of the reaction from the same solvent afforded the colourless product **3**

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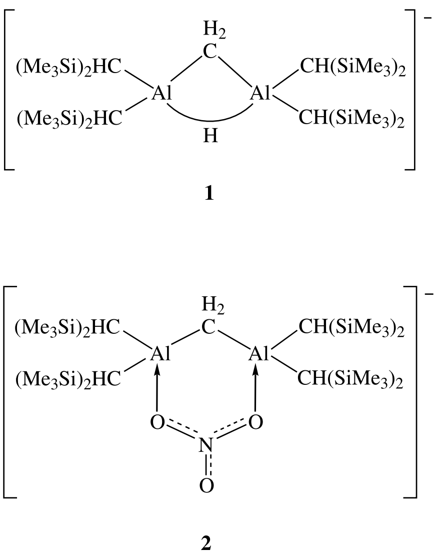
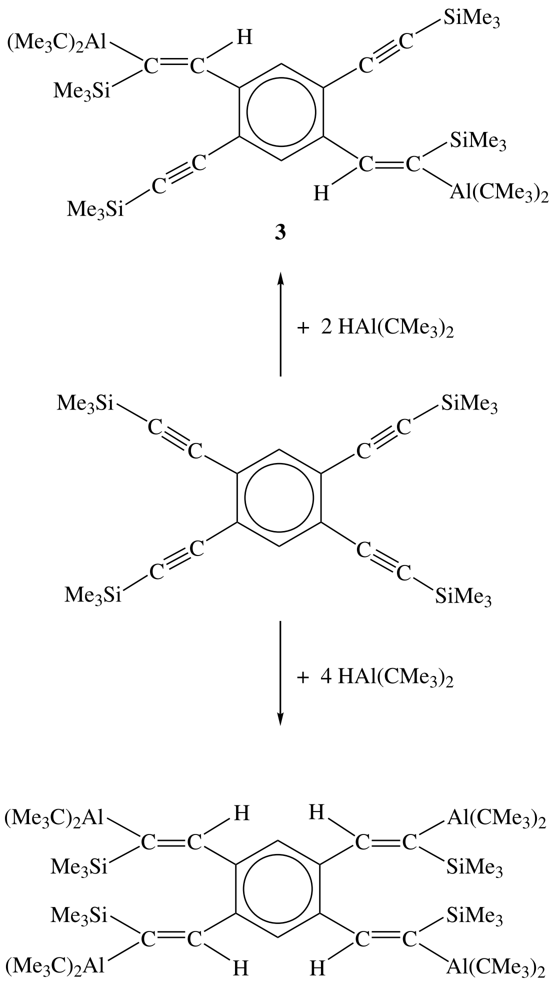


Scheme 1.



(1)

in 37% yield (Eq. (1)). In the ^{1}H-NMR spectrum, compound **3** shows two resonances of trimethylsilyl groups and a singlet for the *tert*-butyl substituents in an intensity ratio of 1:1:2. Two signals of equal intensity were observed at low field ($\delta = 7.88$ and 8.05). They were assigned to both protons attached to the benzene ring and to two alkene protons resulting from the addition of Al–H groups to two alkyne moieties of the tetraalkyne starting compound. In accordance with the result of the crystal structure determination (see below), a centrosymmetric product had formed in which two $C\equiv C$ triple bonds in a *trans* position were hydroaluminated. Two $C\equiv C$ triple bonds remained unchanged. An absorption at 2152 cm^{-1} was observed for these bonds in the IR spectrum, the vibrations of the alkene and benzene groups were detected at 1590 and 1547 cm^{-1}, respectively.

Fig. 1 shows the molecular structure of **3**. The molecules are located on crystallographic inversion centers. Two Al–H groups were added to two alkyne substituents of the tetraalkynyl starting compound in *trans* positions, and we observe the alternating arrangement of hydrogen atoms, alkenyl and alkynyl substituents attached to the central benzene ring. The aluminium and silicon atoms are bonded in geminal positions to the β-carbon atoms of the alkene groups. Negative hyperconjugation [11] with the trimethylsilyl groups may help to stabilize the negative charge of these carbon atoms, which results from the high electronegativity difference between carbon and aluminium, and may thus favour this particular arrangement. The hydroalumination gave a stereoselective *cis* addition, and the hydrogen and aluminium atoms are located on the same sides of the C=C double bonds. As expected, the Al–C distances to the alkenyl carbon atoms are a little shorter (195.5 pm) than those to the inner carbon atoms of the *tert*-butyl groups (198.1 pm). The Si–C distances of the alkynyl SiMe$_3$ groups (C7–Si2 183.7(2) pm; Si2–Me 184.7(3)–185.8(3) pm) are shorter than those of the alkenyl SiMe$_3$ group (C5–Si1 187.2(2) pm; Si1–Me 185.7(3)–188.3(3) pm). The lengths of the C=C double and $C\equiv C$ triple bonds (C4–C5 134.7(3) pm; C6–C7 119.2(3) pm) correspond to standard values [12]. The atoms C6, C7 and Si2 of the linear alkyne groups (angles at C6 and C7 176.6(2) and 177.0(2)°, respectively) are located almost ideally in the plane formed by the benzene carbon atoms (maximum deviation 10 pm of Si2). In contrast, the alkenyl groups are tilted, and the atoms Al and Si1 lie 73 and 171 pm above and below the benzene plane. Torsion angles relevant for the description of that tilting are given in the legend of Fig. 1. The Al atoms have a planar surrounding (sum of the angles 359.5°). The normals of the planes (C5, Al, Ct1, Ct2) and (C1, C2, C3, C1′, C2′, C3′) (benzene) include an

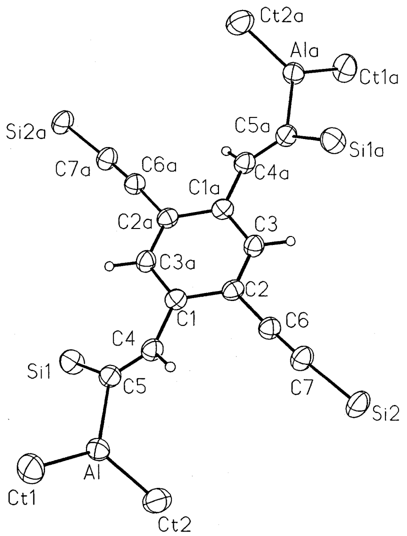


Fig. 1. Molecular structure and numbering scheme of compound **3**; the thermal ellipsoids are drawn at the 40% probability level; methyl groups are omitted for clarity; hydrogen atoms with arbitrary radius. Selected bond lengths (pm) and angles (°): Al–C5 195.5(2), Al–CT1 198.2(3), Al–CT2 198.0(3), Si1–C5 187.2(2), Si2–C7 183.7(2), C1–C4 147.4(3), C4–C5 134.7(3), C2–C6 144.3(3), C6–C7 119.2(3), C1–C4–C5 128.7(2), C4–C5–Al 114.4(2), C4–C5–Si1 130.1(2), C2–C6–C7 176.6(2), C6–C7–Si2 177.0(2). Torsion angles (°): C3′–C1–C4–C5 29.7(3), C1–C4–C5–Si1 6.1(4), C1–C4–C5–Al 171.9(2), C4–C5–Al–CT1 110.7(2), C4–C5–Al–CT2 −61.8(2).

angle of 34.5° so that overall a rather flat molecule results.

A second product was determined by NMR spectroscopy in the rough product of a reaction mixture which was stored at room temperature only. Its concentration was larger than or at least equal to that of **3**. However, it could not be isolated in a pure form or even be enriched by recrystallization of the residue of the mother liquor which remained after isolation of **3**. It showed an ^{1}H-NMR spectrum quite similar to that of **3** with two resonances of trimethylsilyl groups ($\delta = 0.26$ and 0.09) and one signal of *tert*-butyl groups at $\delta = 1.22$ in an intensity ratio of 1:1:2. The alkene and benzene protons resonate at $\delta = 8.06$ and 7.46. We suppose that a compound had formed in which the hydroalumination occurred on neighbouring alkyne groups. Most of the second product rearranged upon heating of a solution of the mixture in hexane to 60 °C to give the sterically less stressed, centrosymmetric compound **3**. This process probably proceeds via elimination of the alane and re-addition of the released Al–H groups to yield the thermodynamically more favored product. The complete consumption of the by-product was not observed even upon elongated heating.

A much more specific reaction was observed when we treated the tetraalkyne with four equivalents of di(*tert*-butyl)aluminium hydride, and the product (**4**) of the fourfold hydroalumination was isolated in 76% yield (1). Its ^{1}H-NMR spectrum showed two singlets of *tert*-butyl and trimethylsilyl groups in an intensity ratio of 2:1, and in the same ratio the resonances of the alkene and benzene protons were observed at low field ($\delta = 8.09$ and 7.39, respectively). Absorptions at 1589 and 1538 cm^{-1} were recorded in the IR spectrum for the C=C double bonds and the benzene ring.

The molecular structure of **4** is depicted in Fig. 2. All alkynyl substituents were transformed to alkenyl groups by the addition of Al–H bonds. Once again a selective *cis* addition was observed. The four coordinatively unsaturated aluminium atoms are attached to the β-carbon atoms of the alkenyl groups, and they are in a geminal position with the trimethylsilyl substituents. Thus, compound **4** has four Lewis acidic centers in one molecule. The alkenyl groups are tilted with respect to the plane of the benzene ring similar as described before for compound **3** and alternately adopt positions above and below the molecular plane. The molecular symmetry approaches D_2. The structural parameters correspond well to those of the alkenyl groups in **3** and do not need a further discussion.

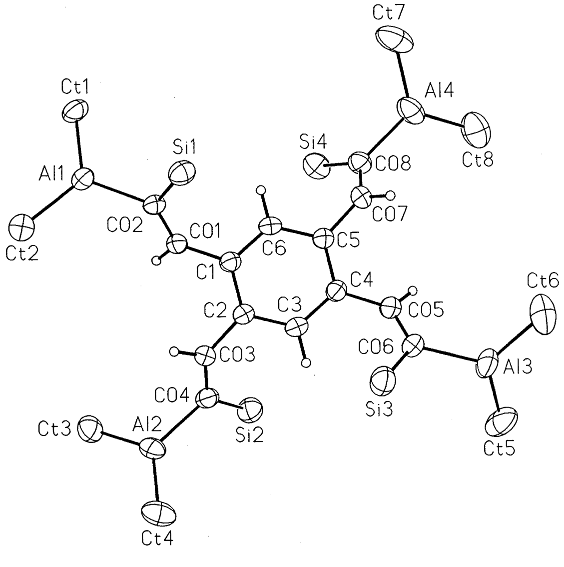


Fig. 2. Molecular structure and numbering scheme of compound **4**; the thermal ellipsoids are drawn at the 40% probability level; methyl groups are omitted for clarity; hydrogen atoms with arbitrary radius. Selected bond lengths (pm) and angles (°): C1–C01 148.0(4), C01–C02 135.5(4), C02–Al1 195.8(3), C02–Si1 187.7(3), C2–C03 147.9(4), C03–C04 135.2(4), C04–Al2 196.0(3), C04–Si2 187.6(3), C4–C05 148.0(4), C05–C06 135.5(4), C06–Al3 194.7(3), C06–Si3 187.5(3), C5–C07 148.3(4), C07–C08 134.9(4), C08–Al4 195.7(3), C08–Si4 187.9(3), C1–C01–C02 126.4(3), C01–C02–Al1 124.9(2), C01–C02–Si1 124.7(2), C2–C03–C04 128.0(3), C03–C04–Al2 120.4(2), C03–C04–Si2 128.0(3), C4–C05–C06 126.9(3), C05–C06–Al3 121.7(2), C05–C06–Si3 126.9(2), C5–C07–C08 125.7(3), C07–C08–Al4 122.7(2), C07–C08–Si4 124.0(2). Torsion angles (°, average values): (H)C–C–C=C −46.8, C–C=C–Si −12.7, C–C=C–Al 178.4, C=C–Al–CT 70.1 and −101.9.

3. Experimental

All procedures were carried out under purified Ar in dried solvents ($C_6H_5CH_3$ over Na–benzophenone; *n*-C_6H_{14} over $LiAlH_4$). The starting compounds di(*tert*-butyl)aluminium hydride [13] and 1,2,4,5-tetrakis(trimethylsilylethynyl)benzene [14] were synthesized according to literature procedures.

3.1. Treatment of $C_6H_2(C\equiv C{-}SiMe_3)_4$ with two equivalents of $HAl(CMe_3)_2$

3.1.1. Compound **3**

A solution of $HAl(CMe_3)_2$ (0.80 g, 5.63 mmol) in 20 ml of *n*-C_6H_{14} was slowly added to a solution of $C_6H_2(C\equiv C{-}SiMe_3)_4$ (1.30 g, 2.82 mmol) in 50 ml of *n*-C_6H_{14} at room temperature (r.t.). The colour of the mixture changed to yellow. The solution was heated under reflux for 3 days. The solvent was removed in vacuo, and the residue was recrystallized twice from *n*-C_6H_{14} (20/−15 °C). Yield: 0.78 g (37%), colourless solid. M.p. (sealed capillary, Ar): 57 °C. Molar mass (in C_6H_6 by cryoscopy): Found: 700. Calc. 747.4 g mol^{-1}. ^1H-NMR (C_6D_6, 400 MHz, 298 K): $\delta = 8.05$ (2H, s, C=CH), 7.88 (2H, s, C_6H_2), 1.20 (36H, s, CMe_3), 0.27 (18H, s, $SiMe_3$ of alkynyl), 0.21 (18H, s, $SiMe_3$ attached to C=C double bond). ^{13}C-NMR (C_6D_6, 100.6 MHz, 298 K): $\delta = 161.9$ (C=C, carbon atoms attached to Al and Si), 151.8 (C=C, carbon atoms attached to phenyl), 143.5 (phenyl, carbon atoms attached to alkenyl), 133.0 (phenyl, carbon atoms attached to hydrogen), 122.1 (phenyl, carbon atoms attached to alkynyl), 104.0 (C≡C, carbon atoms attached to phenyl), 101.0 (C≡C, carbon atoms attached to $SiMe_3$), 29.9 (C*Me*$_3$), 19.3 (Al*C*Me$_3$), 1.7 ($SiMe_3$ attached to C=C), 0.1 ($SiMe_3$ attached to C≡C). IR (CsBr, paraffin, cm^{-1}): 2153 m νC≡C; 1590 w, 1547 w νC=C, aryl; 1464 vs, 1377 vs paraffin; 1249 vs δCH_3; 1176 w, 1048 m νCC; 843 vs, 760 s νCC, $\delta,\rho CH_3$(Si); 698 w ν_sSiC; 638 m ν_{as}SiC; 596 w, 468 vw, 451 w, 414 w νAlC.

3.2. NMR data of the by-product of the synthesis of **3**

The NMR spectra were recorded in a mixture with **3**. ^1H-NMR (C_6D_6, 300 MHz, 298 K): $\delta = 8.06$ (2H, s, C=CH), 7.46 (2H, s, C_6H_2), 1.22 (36H, s, CMe_3), 0.26 and 0.09 (each 18H, s, $SiMe_3$). ^{13}C-NMR (C_6D_6, 75 MHz, 298 K): $\delta = 162.2$, 153.0, 145.1, 137.9, 128.7, 121.3, 103.4 and 99.9 (phenyl, C=C, C≡C), 29.9 (C*Me*$_3$), 19.3 (Al*C*Me$_3$), 1.7 and 0.2 ($SiMe_3$).

3.3. Treatment of $C_6H_2(C\equiv C{-}SiMe_3)_4$ with four equivalents of $HAl(CMe_3)_2$

3.3.1. Compound **4**

A solution of 0.71 g (1.54 mmol) of $C_6H_2(C\equiv C{-}SiMe_3)_4$ in 50 ml of *n*-C_6H_{14} was slowly added to a solution of 0.88 g (6.18 mmol) of di(*tert*-butyl)aluminium hydride in 20 ml of *n*-C_6H_{14} at r.t. The colour changed to yellow. The mixture was stirred for 2 h at r.t. All volatile components were removed in vacuo. The residue was dissolved in 2–3 ml of *n*-C_6H_{14}. Colourless crystals of **4** precipitated from that solution upon cooling to −15 °C. Yield: 1.20 g (76%). M.p. (Ar, sealed capillary): 135 °C (dec.). Molar mass (in C_6H_6 by cryoscopy): Found 1075. Calc. 1031.8 g mol^{-1}. ^1H-NMR (C_6D_6, 400 MHz, 298 K): $\delta = 8.07$ (4H, s, C=CH), 7.36 (2H, s, C_6H_2), 1.23 (72H, s, CMe_3), 0.19 (36H, s, $SiMe_3$). ^{13}C-NMR (C_6D_6, 100.6 MHz, 298 K): $\delta = 160.9$ (C=C, carbon atoms attached to Al and Si), 154.0 (C=C, carbon atoms attached to phenyl), 140.8 (phenyl, carbon atoms attached to alkenyl), 129.8 (phenyl, carbon atoms attached to hydrogen), 29.9 (C*Me*$_3$), 19.1 (Al*C*Me$_3$), 2.0 ($SiMe_3$). IR (CsBr, paraffin, cm^{-1}): 1589 w, 1538 s phenyl, νC=C; 1463 vs, 1377 vs paraffin; 1307 w, 1246 vs δCH_3; 1176 m, 1153 w, 1072 m, 1035 m, 1006 m νCC; 940 s, 916 m, 837 vs, 807 s, 784 m, 753 m νCC, δCH_3; 651 m νSiC; 595 m, 552 w, 530 w, 457 m, 427 m, 417 m, 399 w νAlC, δCC.

3.4. Crystal structure determinations

Single crystals of compound **3** were obtained by recrystallization from $C_6H_5CH_3$ (20/−15 °C), single crystals of **4** from *n*-C_6H_{14} (20/−15 °C). Crystal data and structure refinement parameters are given in Table 1. Some *tert*-butyl groups of **4** showed a disorder (CT2, CT4–CT7). Their methyl groups were refined on split positions, with the exception of the group at CT7 (0.63 and 0.37) the occupation factors were near 0.5.

4. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 184180–184181 for compounds **4** and **3**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB1 1EZ, UK (Fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Table 1
Crystal data, data collection parameters and structure refinement for **3** and **4** [a]

	3	**4**
Formula	$C_{42}H_{76}Al_2Si_4$	$C_{58}H_{114}Al_4Si_4$
Temperature (K)	193(2)	193(2)
Crystal system	Triclinic	Monoclinic
Space group [15]	$P\bar{1}$; No. 2	$P2_1/n$; No. 14
a (pm)	680.18(8)	1467.21(9)
b (pm)	1310.1(1)	3353.5(2)
c (pm)	1562.0(2)	1542.3(1)
α (°)	110.789(8)	90
β (°)	95.723(9)	104.094(8)
γ (°)	92.092(9)	90
V (10^{-30} m^3)	1290.9(2)	7360.1(8)
Z	1	4
D_{calc} (g cm^{-3})	0.961	0.931
μ (mm^{-1})	0.173	0.157
Crystal size (mm)	0.5 × 0.2 × 0.1	0.3 × 0.3 × 0.1
Diffractometer	STOE IPDS	STOE IPDS
Radiation	Mo–K$_\alpha$	Mo–K$_\alpha$
Theta range for data collection (°)	1.40–25.97	2.10–25.93
Index ranges	$-8 \le h \le 8$, $-16 \le k \le 16$, $-19 \le l \le 19$	$-18 \le h \le 17$, $-36 \le k \le 41$, $-18 \le l \le 18$
Reflections observed [$I > 2\sigma(I)$]	3622	8508
Independent reflections	5014 [$R_{int} = 0.0894$]	14136 [$R_{int} = 0.0403$]
Parameters	229	680
$R = \Sigma\ \lVert F_o\rvert - \lvert F_c \rVert / \Sigma\ \lvert F_o \rvert [(I > 2\sigma(I)]$	0.0507	0.0647
$wR_2 = \{\Sigma w(\lvert F_o\rvert^2 - \lvert F_c\rvert^2)^2 / \Sigma(F_o^2)^2\}^{1/2}$ (all data)	0.1473	0.1069
Max./min. residual electron density (10^{30} e m^{-3})	0.395/−0.272	0.496/−0.287

[a] Programmes SHELXTL-Plus; SHELXL-93 [16]; solutions by direct methods, full matrix refinement with all independent structure factors.

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References

[1] (a) D.F. Shriver, M.J. Biallas, J. Am. Chem. Soc. 89 (1967) 1078;
(b) D.J. Saturnino, M. Yamauchi, W.R. Clayton, R.W. Nelson, S.G. Shore, J. Am. Chem. Soc. 97 (1975) 6063;
(c) H.E. Katz, J. Org. Chem. 50 (1985) 5027;
(d) H.E. Katz, J. Am. Chem. Soc. 107 (1985) 1420;
(e) H.E. Katz, J. Am. Chem. Soc. 108 (1986) 7640;
(f) H.E. Katz, Organometallics 6 (1987) 1134;
(g) H.E. Katz, J. Org. Chem. 54 (1989) 2179;
(h) L. Jia, X. Yang, C.L. Stern, T.J. Marks, Organometallics 13 (1994) 3755;
(i) M.V. Metz, D.J. Schwartz, C.L. Stern, P.N. Nickias, T.J. Marks, Angew. Chem. 112 (2000) 1368; Angew. Chem. Int. Ed. 39 (2000) 1312;
(j) V.C. Williams, W.E. Piers, W. Clegg, M.R.J. Elsegood, S. Collins, T.B. Marder, J. Am. Chem. Soc. 121 (1999) 3244;
(k) V.C. Williams, C. Dai, Z. Li, S. Collins, W.E. Piers, W. Clegg, M.R.J. Elsegood, T.B. Marder, Angew. Chem. 111 (1999) 3922; Angew. Chem. Int. Ed. 38 (1999) 3695;
(l) V.C. Williams, G.J. Irvine, W.E. Piers, Z. Li, S. Collins, W. Clegg, M.R.J. Elsegood, T.B. Marder, Organometallics 19 (2000) 1619;
(m) W.E. Piers, G.J. Irvine, V.C. Williams, Eur. J. Inorg. Chem. (2000) 2131 (Microreview);
(n) L.D. Henderson, W.E. Piers, G.J. Irvine, R. McDonald, Organometallics 21 (2002) 340;
(o) B. Schilling, V. Kaiser, D.E. Kaufmann, Chem. Ber./Recueil 130 (1997) 923;
(p) M. Reilly, T. Oh, Tetrahedron Lett. 36 (1995) 221;
(q) M. Reilly, T. Oh, Tetrahedron Lett. 36 (1995) 217;
(r) K. Nozaki, M. Yoshida, H. Takaya, Bull. Chem. Soc. Jpn. 69 (1996) 2043;
(s) K. Nozaki, T. Tsutsumi, H. Takaya, J. Org. Chem. 60 (1995) 6668;
(t) J.D. Hoefelmeyer, F.P. Gabbaï, Organometallics 21 (2002) 982.

[2] (a) H. Hoberg, V. Gotor, A. Milchereit, C. Krüger, J.C. Sekutowski, Angew. Chem. 89 (1977) 563; Angew. Chem. Int. Ed. Engl. 16 (1977) 539;
(b) C. Üffing, A. Ecker, R. Köppe, K. Merzweiler, H. Schnöckel, Chem. Eur. J. 4 (1998) 2142;
(c) H. Martin, H. Bretinger, Z. Naturforsch. Teil B: Chem. Sci. 46 (1991) 615;
(d) O. Saied, M. Simard, J.D. Wuest, Inorg. Chem. 37 (1998) 2620;
(e) O. Saied, M. Simard, J.D. Wuest, Organometallics 17 (1998) 1128;
(f) F.A.R. Kaul, M. Tschinkl, F.P. Gabbaï, J. Organomet. Chem. 539 (1997) 187;
(g) M. Tschinkl, R.E. Bachman, F.P. Gabbaï, Chem. Commun. (1999) 1367;
(h) M. Tschinkl, T.M. Cocker, R.E. Bachman, R.E. Taylor, F.P. Gabbaï, J. Organomet. Chem. 604 (2000) 132;
(i) J.J. Eisch, K. Mackenzie, H. Windisch, C. Krüger, Eur. J. Inorg. Chem. (1999) 153;
(j) T. Ooi, M. Takahashi, K. Maruoka, J. Am. Chem. Soc. 118 (1996) 11307;
(k) B. Thiyagarajan, R.F. Jordan, V.G. Young, Jr., Organometallics 17 (1998) 281.

[3] (a) M.A. Dam, T. Nijbacker, F.J.J. de Kanter, O.S. Akkerman, F. Bickelhaupt, A.L. Spek, Organometallics 18 (1999) 1706;
(b) M. Tschinkl, J.D. Hoefelmeyer, T.M. Cocker, R.E. Bachman, F.P. Gabbaï, Organometallics 19 (2000) 1826;
(c) J.D. Hoefelmeyer, D.L. Brode, F.P. Gabbaï, Organometallics 20 (2001) 5653;
(d) P. Jutzi, N. Lenze, B. Neumann, H.-G. Stammler, Angew. Chem. 113 (2001) 1470; Angew. Chem. Int. Ed. 40 (2001) 1424.

[4] (a) M. Tschinkl, A. Schier, J. Riede, F.P. Gabbaï, Inorg. Chem. 36 (1997) 5706;
(b) F.P. Gabbaï, A. Schier, J. Riede, M.J. Hynes, Chem. Commun. (1998) 897;
(c) F.P. Gabbaï, A. Schier, J. Riede, Angew. Chem. 110 (1998) 646; Angew. Chem. Int. Ed. 37 (1998) 622;
(d) M. Tschinkl, A. Schier, J. Riede, F.P. Gabbaï, Inorg. Chem. 37 (1998) 5097;
(e) J.D. Hoefelmeyer, M. Schulte, F.P. Gabbaï, Inorg. Chem. 40 (2001) 3833;
(f) M.A. Dam, T. Nijbaker, B.C. de Pater, F.J.J de Kanter, O.S. Akkerman, F. Bickelhaupt, W.J.J. Smeets, A.L. Spek, Organometallics 16 (1997) 511.

[5] M. Layh, W. Uhl, Polyhedron 9 (1990) 277.

[6] (a) W. Uhl, M. Layh, Z. Anorg. Allg. Chem. 620 (1994) 856;
(b) W. Uhl, F. Hannemann, W. Saak, R. Wartchow, Eur. J. Inorg. Chem. (1998) 921;
(c) W. Uhl, M. Koch, M. Heckel, W. Hiller, H.H. Karsch, Z. Anorg. Allg. Chem. 620 (1994) 1427;
(d) W. Uhl, R. Gerding, F. Hannemann, Z. Anorg. Allg. Chem. 624 (1998) 937;
(e) W. Uhl, F. Hannemann, J. Organomet. Chem. 579 (1999) 18;
(f) W. Uhl, M. Koch, A. Vester, Z. Anorg. Allg. Chem. 619 (1993) 359.

[7] (a) W. Uhl, M. Layh, J. Organomet. Chem. 415 (1991) 181;
(b) E.C. Ashby, R.S. Smith, J. Organomet. Chem. 225 (1982) 71.

[8] W. Uhl, M. Layh, W. Massa, Chem. Ber. 124 (1991) 1511.

[9] Recent reports on hydroalumination: (a) U. Dümichen, T. Gelbrich, J. Sieler, Z. Anorg. Allg. Chem. 627 (2001) 1915;
(b) L. Aufauvre, P. Knochel, I. Marek, Chem. Commun. (1999) 2207;
(c) J.A. Francis, S.G. Bott, A.R. Barron, Main Group Chem. 3 (1999) 53;
(d) M.G. Gardiner, S.M. Lawrence, C.L. Raston, Inorg. Chem. 38 (1999) 4467.

[10] W. Uhl, F. Breher, J. Organomet. Chem. 608 (2000) 54.

[11] (a) A.E. Reed, P. von Ragué Schleyer, J. Am. Chem. Soc. 112 (1990) 1434;
(b) C. Jones, C.H.L. Kennard, C.L. Raston, G. Smith, J. Organomet. Chem. 396 (1990) C39;
(c) Y. Mo, Y. Zhang, J. Gao, J. Am. Chem. Soc. 121 (1999) 5737;
(d) W. Scherer, P. Sirsch, D. Shorokhov, G.S. McGrady, S.A. Mason, M.G. Gardiner, Chem. Eur. J. 8 (2002) 2324.

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

[13] (a) W. Uhl, Z. Anorg. Allg. Chem. 570 (1989) 37;
(b) W. Uhl, L. Cuypers, R. Graupner, J. Molter, A. Vester, B. Neumüller, Z. Anorg. Allg. Chem. 627 (2001) 607.

[14] B.C. Berris, G.H. Hovakeemian, Y.-H. Lai, H. Mestdagh, K.P.C. Vollhardt, J. Am. Chem. Soc. 107 (1985) 5670.

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

[16] (a) SHELXTL-Plus, Release 4.2 for Siemens R3 Crystallographic Research Systems, Siemens Analytical X-ray Instruments Inc., Madison, USA, 1990;
(b) G.M. Sheldrick, SHELXL-93, Program for the Refinement of Structures, Universität Göttingen, 1993.