Keywords: coordination polymers · crystal engineering · nickel · supramolecular chemistry

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[6] Crystals of Ni(tpt)$(NO_3)_2 \cdot$solvate were obtained by layering a solution of $Ni(NO_3)_2 \cdot 6H_2O$ (45 mg) in ethanol (10 mL) on top of a solution of tpt (25 mg) in 1,1,2,2-tetrachloroethane (10 mL); ethanol (5 mL) served as a "buffer layer" between the two solutions. Crystals grew over a period of days as the solutions slowly interdiffused. Crystal stucture data: $0.45 \times 0.25 \times 0.25$ mm^3, trigonal, $P3_121$, $a = 15.216(2)$ $c = 18.650(6)$ Å, $V = 3740(1)$ Å^3, $Z = 3$, $\rho_{calcd} = 1.554$ g cm^{-3}, $2\theta_{max} = 55°$, $\lambda(Mo_{K\alpha}) = 0.71069$ Å, ω:2θ scan mode, $T = 130$ K, 7302 measured reflections, 5719 independent reflections ($R_{int} = 0.0216$). Corrections were applied for Lorentz and polarization effects. Absorption coorrections applied (indexed crystal faces, SHELX-76[9]), $\mu = 1.29$ mm^{-1}, min./max. transmission factors 0.5784, 0.7343. Structure solved by using Patterson methods (SHELXS-86[10]). Full-matrix least squares refinement based on F^2, 321 parameters (SHELXL-97[11]), pyridyl hydrogen atoms placed at geometrically estimated positions, $R1 = 0.0839$, $wR2 = 0.2352$, max. residual electron density 1.049 e Å^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-108609. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Pentacarba-*arachno*-tridecaalane $(AlMe)_8(CCH_2Ph)_5H$ with an Al_8C_5 Skeleton—The First Polyhedral Carbaalane[**]

Werner Uhl[*] and Frank Breher

Carbaboranes contain clusters formed by boron and carbon atoms. Owing to their unique structures and bonding they have been intensively investigated in the last few decades and have been included in inorganic chemistry textbooks for a long time.[1] Up to now the corresponding carbaalanes with a skeleton containing only aluminum and carbon atoms were unknown; however, some compounds in which single aluminum atoms are inserted into borane or carbaborane clusters have been reported.[2] A suitable method for the synthesis of carbaboranes is based on the hydroboration of alkynyldialkylboranes with an excess of dialkylboron hydrides, but often the yields are very low.[3] Recently, our group has begun systematic investigations into the related hydroalumination reaction, in particular with regard to the synthesis of polyaluminum compounds. The latter have been attracting growing interest as chelating Lewis acids in phase-transfer processes or for the recognition of anions.[4] The hydroalumination of aluminum alkynides was described once before, however, the products were never isolated or characterized, and subsequent work up by hydrolysis generally yielded a mixture of hydrocarbons.[5] Similar treatment was reported for the products of the hydroalumination of organic alkynes.[6] The organoaluminum intermediates are, however, of great interest with regard to our investigations, and one of our aims is to isolate them in a pure form for a complete characterization. We report here on the remarkable reaction of dimethylaluminum hydride with dimethylaluminum phenylethynide (**1**).

When **1** was treated with dimethylaluminum hydride in *n*-pentane in a stoichiometric ratio, the color of the reaction mixture changed to red, but the ethynide was recovered in an almost quantitative yield. Compound **1** was only consumed completely when it was dissolved in an excess of the dimethylaluminum hydride and heated without a solvent to 80 °C over a period of two days. Monitoring the reaction by NMR spectroscopy indicated the formation of a large amount of trimethylaluminum, which was distilled off in vacuo at room temperature. Recrystallization of the reddish, solid residue from cyclopentane gave colorless crystals of the product **2** in 60% yield [Eq. (a)].

$$11\ Me_2AlH + 5\ \underset{\mathbf{1}}{Me_2Al{-}C{\equiv}C{-}Ph} \longrightarrow \underset{\mathbf{2}}{(AlMe)_8(CCH_2Ph)_5H} + 8\ AlMe_3 \qquad (a)$$

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[**] This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

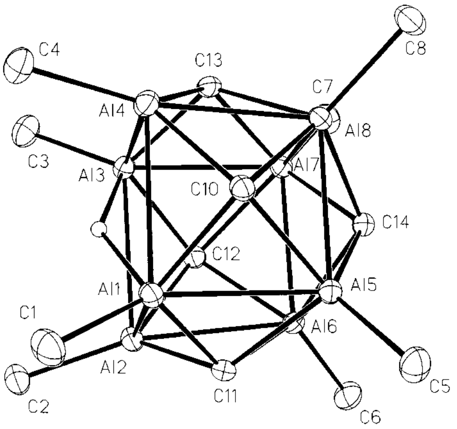

Figure 1. Molecular structure of **2**; the benzyl groups at C10 to C14 were omitted for clarity; bridging hydrogen atom H1 with an arbitrary radius. Selected bond lengths [pm]: Al1–Al2 279.61(9), Al1–Al4 279.19(9), Al1–Al5 259.76(9), Al2–Al3 279.66(9), Al2–Al6 259.95(9), Al3–Al4 280.22(9), Al3–Al7 259.00(9), Al4–Al8 260.98(9), Al5–Al6 262.20(8), Al5–Al8 261.55(8), Al6–Al7 259.96(8), Al7–Al8 260.56(8), Al1–H1 190(3), Al3–H1 191(3), Al1–C10 202.9(2), Al1–C11 202.6(2), Al2–C11 202.2(2), Al2–C12 201.8(2), Al3–C12 203.1(2), Al3–C13 204.0(2), Al4–C10 201.8(2), Al4–C13 202.0(2), Al5–C10 212.5(2), Al5–C11 214.1(2), Al5–C14 203.7(2), Al6–C11 209.3(2), Al6–C12 211.4(2), Al6–C14 208.1(2), Al7–C12 211.5(2), Al7–C13 212.1(2), Al7–C14 205.5(2), Al8–C10 209.4(2), Al8–C13 212.0(2), Al8–C14 208.1(2).

Compound **2** possesses a unique crystal structure (Figure 1)[7] with a skeleton consisting of eight aluminum and five carbon atoms. The eight aluminum atoms form a slightly distorted cube, five faces of which are occupied by the carbon atoms. The remaining face is bridged by the hydrogen atom H1. Every Al atom binds to a terminal methyl group and every carbon atom of the cluster to a benzyl group. While long Al–Al distances (av 279.67 pm) are observed for the hydrogen-bridged face of the Al_8 cube, the remaining eight edges are shortened to 260.50 pm. They are similar to the Al–Al distances in $(AlMe_3)_2$[8] (261 pm) or in organoelement compounds with Al–Al single bonds ($R_2Al–AlR_2$; 265–266 pm).[9] The Al–C bond lengths to the methyl groups are in the expected range (195.0 pm), whereas the strongly differing Al–C distances of the cluster are significantly lengthened. The separations between the atoms C10 to C13 and the aluminum atoms Al1 to Al4 of the hydrogen-bridged face (202.6 pm), which are attached to only three carbon atoms, are shorter than those to the atoms Al5 to Al8 (211.5 pm), which all have four carbon neighbors. In contrast, the distances to C14 are in a narrow range between 204 and 208 pm. That face of the cube, which is bridged by the hydrogen atom H1, is distorted to a rhombus with transannular Al–Al contacts of 363.7 (Al1–Al3) and 424.9 pm (Al2–Al4). This distortion causes different distances of H1 to these aluminum atoms of 191 (Al1, Al3) and 221 pm (Al2, Al4); the Al-H-Al bridge is longer than usually observed in alkylaluminum hydrides.

Compound **2** fits well into the electronic concept that was developed originally for the description of borane and carbaborane clusters (Wade rules).[10] Each aluminum atom contributes two electrons and each carbon atom three electrons to the bonding in the cluster. If the bridging hydrogen atom is taken into consideration, 16 electron pairs result, which for the 13-atom cluster in **2** gives an *arachno* configuration. Ab initio calculations[11] on the corresponding *closo* boron cluster ($[B_{15}H_{15}]^{2-}$) revealed an hexagonal antiprismatic structure in which one hexagon was occupied by one boron atom, the second one by two boron atoms. This motif can also be found in **2**, and is best recognized when the cluster is placed on one vertex, for example, Al8. This atom has six nearest neighbors in the cluster and bridges a chairlike six-membered ring (Al4, Al5, Al7, C10, C13, and C14). The next plane comprises only five atoms (Al1, Al3, Al6, C11, and C12), and one vertex of the prism remains unoccupied. This is nearly the position of H1. The atom Al2 is located above this plane. Thus, in comparison to the *closo*-B_{15} cluster, two positions are unoccupied, as expected for an *arachno* structure. However, **2** does not adopt an antiprismatic structure, but owing to the large differences between the Al–Al and Al–C distances the planes are in an almost eclipsed conformation. The polyborane $B_{13}H_{19}$ is isoelectronic to **2**;[12] however, in accordance with the maximum number of twelve boron atoms for each cluster observed so far in boron chemistry not a large cluster, but a *conjuncto*-borane is formed.

In agreement with the crystal structure, two resonances of equal intensity were observed in the ^1H NMR spectrum in the expected range for methyl groups attached to aluminum atoms ($\delta = -0.68$ and -0.30). The two resonances for the CH_2 groups of the benzyl substituents in the intensity ratio of 1:4 at $\delta = 3.52$ and 3.07, respectively, and in particular the resonance of the Al–H proton ($\delta = 5.23$) are shifted to considerably higher field. Apart from some small alterations of the chemical shifts and a small broadening of the resonances, the spectrum did not change up to $-90\,^\circ C$, thus, as expected, the interaction between the four aluminum atoms Al1 to Al4 and the hydrogen atom H1 seems to be highly dynamic. The resonances of the methyl carbon atoms in the ^{13}C NMR spectrum were observed in an expected range at $\delta = -11.7$ and -12.7. However, the carbon atoms of the cluster showed signals with an unusual chemical shift of $\delta = 30.0$ and 24.1. Remarkably, similar ^{13}C NMR shifts were detected experimentally and by quantum chemical calculations for the *arachno*-carbaborane $C_6B_6H_6Et_6$, in which as in **2** the different cluster atoms are arranged in an alternating fashion.[3]

The formation of **2** may be explained by the hydroalumination[13] of dimethylaluminum phenylethynide, in which, as expected, the Al atom of the entering group attacks the negatively charged α-C atom of the alkynide.[5, 6, 13] The twofold addition of R_2AlH results in the formation of a benzyl group. The elimination of trimethylaluminum from the hypothetical intermediate $(R_2Al)_3CCH_2Ph$ may lead to a reactive, unsaturated species as the first building block of the cluster. The hydrogen atom H1 may be introduced by a hydroalumination step with $MeAlH_2$, which is easily formed by the dismutation equilibrium of Me_2AlH. The synthesis of the first known carbaalane **2** by a facile high-yield method has opened the route to a new class of aluminum compounds, which in analogy to carbaboranes may lead to a wide field of activity for preparative and theoretical chemistry.

Experimental Section

All procedures were carried out under argon. *n*-Pentane and cyclopentane were dried over $LiAlH_4$.

1: *n*BuLi (11.4 mL of a 1.6 M solution in *n*-hexane) was added dropwise to a solution of phenylethyne (1.86 g, 2 mL, 18.2 mmol) in *n*-pentane (15 mL) at 0 °C. The suspension was stirred for 2 h at room temperature, cooled to 0 °C, and treated with Me_2AlCl (1.7 mL, 1.68 g, 18.2 mmol) dissolved in *n*-pentane (15 mL). The mixture was stirred for 16 h at room temperature, filtered, and evaporated. The residue was recrystallized from *n*-pentane (20/ – 30 °C). Yield: 1.64 g (57 %); colorless, extremely air-sensitive crystals. M.p. (sealed capillary): 76– 80 °C. ^1H NMR (300 MHz, C_6D_6): $\delta = 7.32$ (2 H, pseudo-d, Ph), 6.89 (1 H, pseudo-t, Ph), 6.78 (2 H, pseudo-t, Ph), 0.03 (6 H, Me); ^{13}C NMR (75 MHz, C_6D_6): $\delta = 135.5$, 133.8, 131.5, and 128.8 (Ph), 119.9 and 96.8 (C≡C), – 6.8 (AlC); IR (Nujol): $\tilde{\nu}$ [cm^{-1}] = 2089 (νC≡C).

2: A mixture of **1** (628 mg, 3.97 mmol) and Me_2AlH[14] (1.214 g, 20.9 mmol) was heated for 48 h to 80 °C without a solvent. After about 2 h, a solid started to precipitate from the red solution. All volatile components were distilled off in vacuo after cooling to room temperature. The residue was treated with cyclopentane, filtered, and recrystallized at – 30 °C. The crystals of **2** included up to 0.9 molecules cyclopentane per formula unit after thorough evacuation. Yield: 445 mg (0.486 mmol, 61 %), colorless, slightly air-sensitive crystals. M.p. (sealed capillary): 175 °C (decomp.). ^1H NMR (300 MHz, C_6D_6): $\delta = 7.5 - 7.0$ (m, Ph), 5.23 (1 H, s, AlHAl), 3.52 (2 H, s, CH_2 at C14), 3.07 (8 H, s, CH_2), – 0.30 and – 0.68 (each 12 H, s, AlMe); ^{13}C NMR (75 MHz, C_6D_6): $\delta = 147.9$ (*ipso*-C at C14), 147.5 (*ipso*-C of the other phenyl groups), 129.6, 129.0, 128.7, 126.1 and 125.7 (Ph), 35.5 (CH_2 at C14), 34.2 (CH_2 at C10 to C13), 30.0 (C10 to C13), 24.1 (C14), – 11.7 and – 12.7 (AlMe); assignment on the basis of *j*-modulated and ^1H–^{13}C correlated NMR spectra; IR (Nujol, CsBr plates): $\tilde{\nu}$ [cm^{-1}] = 1599 m (Ph), 1462 vs, 1377 vs (Nujol), 1300 m (ν_{Al-H}), 1186 s, 1154 m, 1072 w, 1030 w (ν_{C-C}), 959 s, 930 m, 907 m, 824 m (Ph), 750 vs, 710 vs, 691 vs, 673 vs, 665 vs (δ_{Ph}, ν_{Al-C}), 581 m, 550 m, 525 m, 505 w, 428 m (ν_{Al-C}); UV/Vis (cyclopentane): λ_{max} [nm] ($\lg \varepsilon$) = 250 (4.1).

Received: January 12, 1999 [Z 12896 IE]
German version: *Angew. Chem.* **1999**, *111*, 1578 – 1580

Keywords: aluminum · cluster compounds · electron deficiency

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Stereospecific Migration of P from N to C_{sp^2}: Ring-Expansion Reaction of Chiral Diazaphospholidine Oxides

Olivier Legrand, Jean Michel Brunel, and Gérard Buono*

Many modern synthetic targets, in particular those of interest for pharmaceutical and agrochemical preparations, are either benzenoid or incorporate key aromatic or heteroatomic components.[1, 2] In this context, *ortho*-lithiation has appeared as one of the most important methods for the regiospecific construction of polysubstituted aromatic compounds.[3] When the *ortho*-lithiation directing group contains an electronegative atom attached to a π-unsaturated or coordinatively unsaturated group, the lithiated species may undergo 1,3-migration to the *ortho* position on the aromatic ring. Such metalation-induced 1,3-migration is very common in benzene systems and has been seen for the rearrangement of 1) arenesulfonamides of N-substituted anilines to N-substituted 2-aminoaryl aryl sulfones,[4] 2) aryl *O*-carbamates to salicylamides,[5] 3) *o*-bromophenyl esters to *o*-hydroxyaryl ketones,[6] 4) arylphosphate esters to 2-hydroxyaryl phosphonates,[7] and 5) (triarylsiloxy)benzenes to *o*-(triarylsilyl)phenols.[8]

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