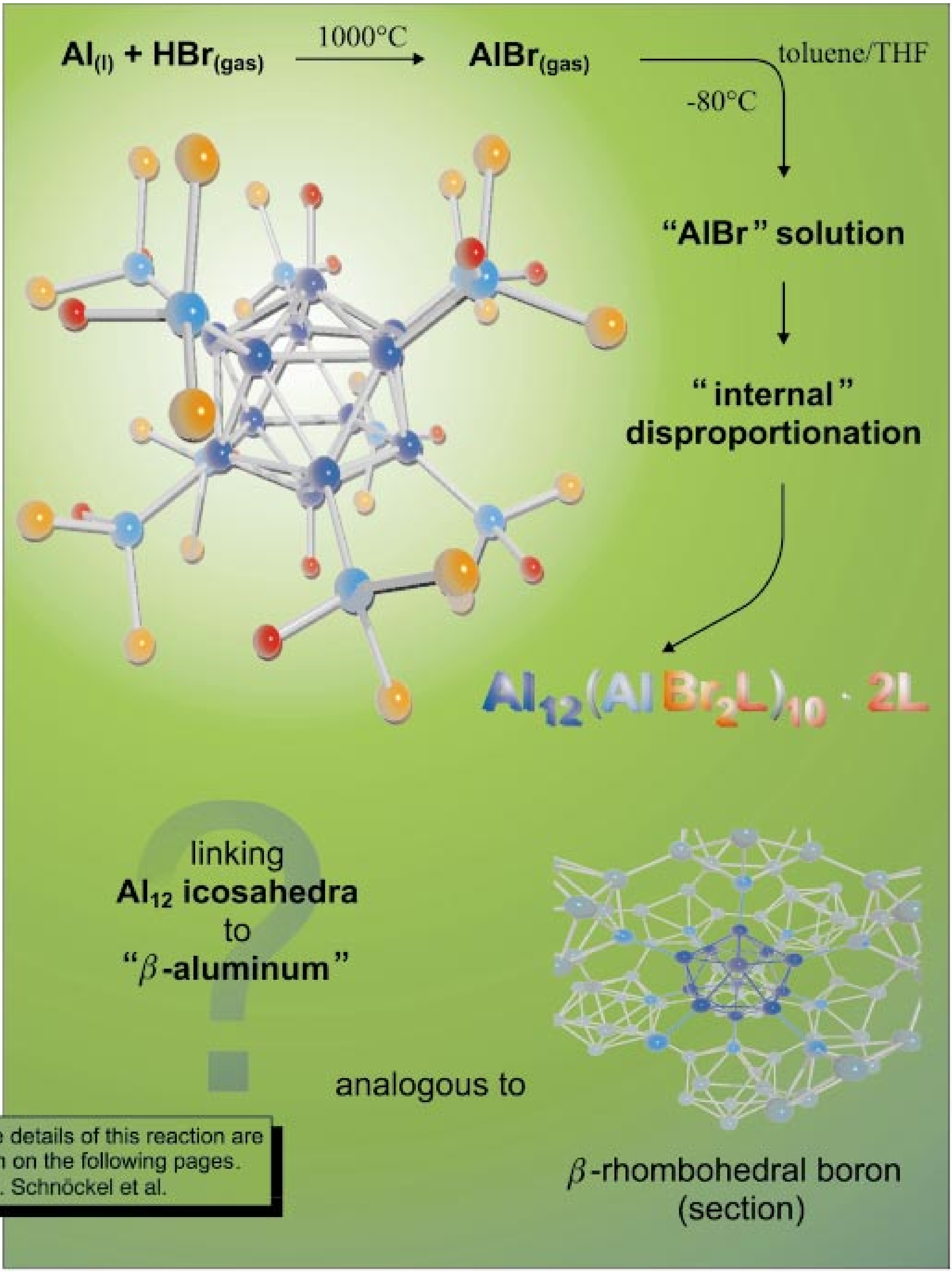


$Al_{(l)} + HBr_{(gas)} \xrightarrow{1000°C} AlBr_{(gas)}$

toluene/THF

-80°C

"AlBr" solution

"internal" disproportionation

$Al_{12}(AlBr_2L)_{10} \cdot 2L$

linking
Al_{12} icosahedra
to
"β-aluminum"

analogous to

β-rhombohedral boron
(section)

More details of this reaction are given on the following pages. by H. Schnöckel et al.

$Al_{22}Br_{20} \cdot 12\,THF$: The First Polyhedral Aluminum Subhalide—A Step on the Path to a New Modification of Aluminum?**

Christoph Klemp, Ralf Köppe, Edgar Weckert, and Hansgeorg Schnöckel*

For a long time polyhedral compounds were only known for the element boron in Group 13 (the triels (E)). Large polyhedral clusters such as $B_{20}H_{26}$[1] are accessible by pyrolysis of smaller boron compounds. However, so far no neutral species with a *closo* framework[2] has been found for the binary boranes. In contrast, for the boron halides several examples for this type of framework with its regular deltahedron exist, although according to the Wade's rules[18] one would expect a *precloso* structure. For instance, B_4Cl_4, B_8Cl_8, and recently B_9X_9 (X = Cl, Br, I)[3, 4] have been structurally determined. However, for $B_{12}Cl_{12}$ only the preparation by disproportionation of B_2Cl_4 is known,[5] and the icosahedral $B_{12}F_{12}^{2-}$[6] exists as a dianion. Thus, no neutral icosahedral species has been structurally determined so far. Since B_{12} icosahedra are present in *all* boron modifications as structural elements, the neutral icosahedral boron clusters, in particular, should be important intermediates in the transition from the molecule to the solid state.

For the heavy triels Al, Ga, In, and Tl polyhedral compounds have only been known for a short time. In the last ten years the use of stabilizing ligands has enabled the synthesis of polyhedral E^I compounds, whose first structurally characterized examples were $[AlCp^*]_4$[7] ($Cp^* = C_5Me_5$), $[GaC(SiMe_3)_3]_4$,[8] $[InCp^*]_6$,[9] and $[TlC(SiMe_3)_3]_4$[10]. In the meantime a large number of such polyhedral compounds has been characterized;[11] however, hithero there were no polyhedra with halogen substituents analogous to the boron halides. Although tetrameric halides of monovalent aluminum can be prepared by cocondensation of the high-temperature particle AlX (X = Br, I) with NEt_3 or PEt_3 as the donor and toluene as the solvent (e.g. $[AlBr \cdot NEt_3]_4$[12]), as a result of the high-donor strength of triethylamine and triethylphosphane, respectively, a planar Al four-membered ring with isolated 2e–2c bonds is formed instead of an Al_4 tetrahedron. Consequently, the application of weaker donors for the cocondensation should primarily favor the formation of polyhedral electron-deficient compounds. However, under such conditions the disproportionation of the metastable aluminum monohalide solution to give AlX_3 and elemental aluminum is also favored.

Herein, we report on the cocondensation of AlBr with toluene and THF as donor. This weaker donor with low steric requirements apparently allows the formation of Al multicenter bonds while still preventing the disproportionation to elemental aluminum to a great extent so that isolable intermediates are to be expected. Extremely sensitive pale yellow crystals of the composition $Al_{22}Br_{20} \cdot 12\,THF$ (**1**) were isolated from the solution heated to room temperature. They are mechanically labile and decompose on removal of the solvent or in anhydrous perfluoropolyether (at room temperature within a minute) to give a white amorphous solid. The result of the X-ray structural analysis[13] (Figure 1) shows that this structure is better described by the formula $Al_{12}[AlBr_2 \cdot THF]_{10} \cdot 2\,THF$. The central structural element is a compressed Al_{12} icosahedron. This is the second example of a molecular icosahedral unit for the heavy elements of Group 13; several years ago Uhl et al.[14] prepared an $[Al\textit{i}Bu]_{12}^{2-}$ ion. To our knowledge **1** is the only neutral molecular icosahedral cluster compound outside boron chemistry. The Al–Al distances lie in the expected range for subvalent compounds (see legend for Figure 1).

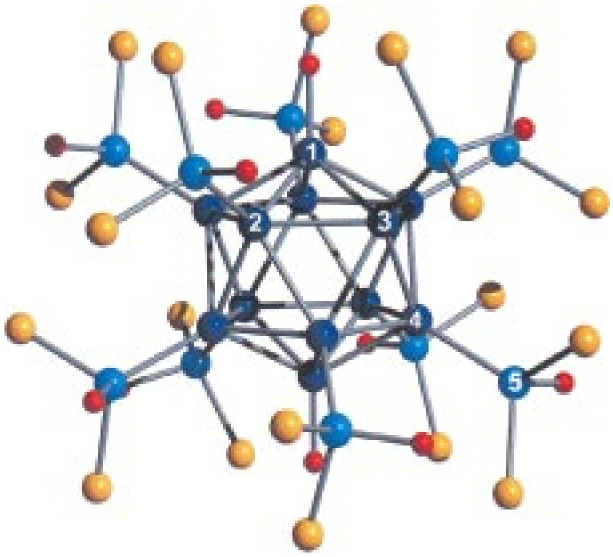


Figure 1. Molecular structure of **1** (C and H atoms are omitted for clarity). Dark blue: Al atoms of icosahedral core; light blue: Al atoms of $AlBr_2$ ligands; orange: Br atoms; red: O atoms of THF molecules. Selected distances [Å] (average ± maximal deviation determined from analogous bonds; results of the DFT calculations in parentheses): Al1–Al2 2.650 ± 0.023 (2.615), Al2–Al3 2.762 ± 0.005 (282.4), Al3–Al4 2.692 ± 0.016 (2.684), Al4–Al5 2.526 ± 0.019 (2.541), Al5–O1 1.892 ± 0.038 (1.937), Al5–Br1 2.299 ± 0.039; for comparison: selected Al–Al distances in other Al compounds (see text): $[Al\textit{i}Bu]_{12}^{2-}$: 2.670–2.696, $[AlCp^*]_4$: 2.769, $[AlBr_2 \cdot OMePh]_2$: 2.530, metal: 2.860.

$AlBr_2$ units are bonded to ten of the twelve Al atoms of the icosahedron. As shown in Figure 2 the 20 bromine atoms are arranged above the triangular faces of the icosahedron in such a way that they adopt the geometry of a distorted pentagonal dodecahedron;[15] a THF molecule (omitted for clarity in Figure 2) protrudes from the center of each of these faces. Therefore, two *para*-positioned Al atoms of the icosahedron

---

[*] Prof. Dr. H. Schnöckel, C. Klemp, Dr. R. Köppe
Institut für Anorganische Chemie der Universität Karlsruhe (TH)
Engesserstrasse, Geb. 30.45, D-76128 Karlsruhe (Germany)
Fax: (+49) 721-608-4854
E-mail: hg@achpc9.chemie.uni-karlsruhe.de.

Priv.-Doz. E. Weckert
Institut für Kristallographie der Universität Karlsruhe (TH)
(Germany)

[**] This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. We are grateful to Alusuisse for their contribution towards financing the frontispiece picture. We thank E. Baum, E. Möllhausen, A. Schnepf, H. Piotrowski, and Priv.-Doz. G. Linti for their support with regard to problems with the crystallography.

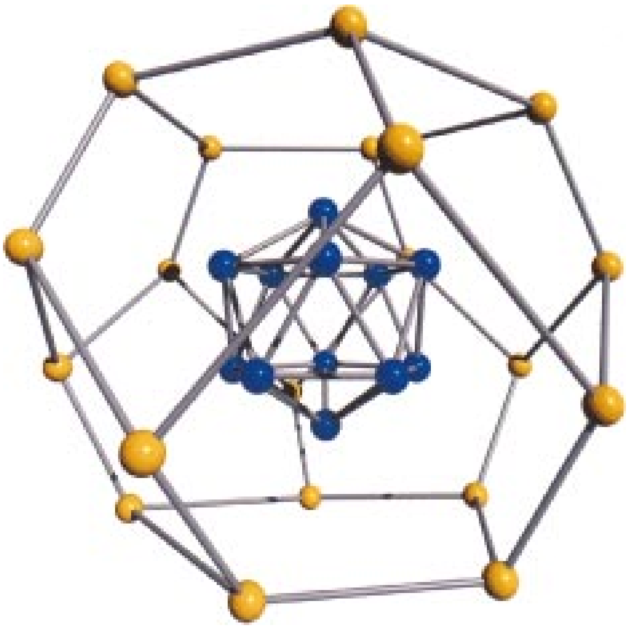


Figure 2. Pentagonal dodecahedron of the Br atoms around the Al icosahedron. The Br–Br distances lie in the range of the sum of the van der Waals radii of 3.80 Å. Color code see Figure 1.

are not bound to $AlBr_2$ units but are each only coordinated by a THF molecule. Thus, in analogy to the 1,12-carboranes an icosahedral framework is formed which is compressed in 1-12 direction. A compound topologically comparable with **1** was reported by Hawthorne:[16] deca(dichloromethyl)-*para*-carborane,[17] which, owing to the good steric shielding of the icosahedral framework by its substituents, was described as a „camouflaged carborane“. As shown in the space-filling model in Figure 3 the subvalent Al atoms in **1** are also completely surrounded by a closed shell of Br atoms and the methylene groups of the THF molecules.

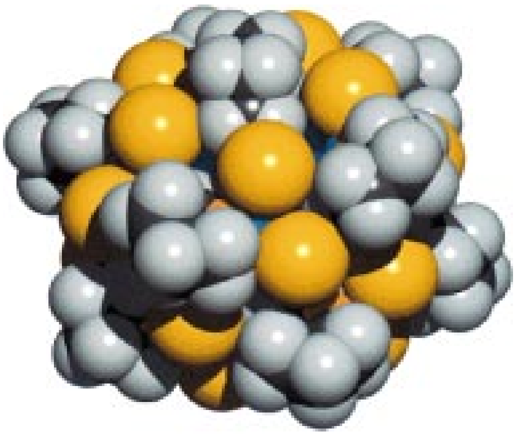


Figure 3. Space-filling model of **1** based on the den van der Waals radii. The Al_{22} cluster is completely surrounded by dodecahedrally arranged Br atoms and icosahedrally arranged THF molecules. In the crystal the molecules adopt an almost hexagonal primitive arrangement. Disordered solvent (toluene) is found in the spaces. Color code see Figure 1.

The bonding in **1** can be interpreted according to Wade's rules.[18] Owing to the coordinated THF molecules the two *para*-positioned Al atoms of the icosahedron can each provide the polyhedral framework with three electrons, whereas the remaining ten icosahedron Al atoms can only each provide two electrons because of their bond to the $AlBr_2$ groups. This results in 26 framework electrons ($=2n+2$ with $n=12$) for the bonding in the Al_{12} polyhedron; that is in accordance with the experiment the electron balance indicates the formation of a molecule of the *closo*-type (icosahedron). Thus, the discussion on three-dimensional aromaticity, for example, for *closo*-polyhedra of boron, should probably be extended to aluminum.[19, 20]

Under formal considerations on the oxidation states in the Al_{22} group the atoms of the icosahedral unit have the oxidation state 0, whereas the remaining ten atoms have the oxidation state +2, that is in total this results in the mean oxidation state of 0.91. Thus, this aluminum subhalide can be considered as the product of an *internal* disproportionation of 24 AlBr units with formal elimination of $[AlBr_2]_2$.[21]

For a better understanding of **1** density functional theory (DFT) calculations were carried out on the analogous but simpler model system $Al_{22}Cl_{20}\cdot 12\,H_2O$ (**1a**).[22] The calculated Al–Al distances are shown in parentheses in the caption of Figure 1 and are in good agreement with the measured values. Furthermore, Figure 4 shows a comparison of the calculated energetic position of this model system (**1a** + Al_2Cl_4) with the energetic positions of the corresponding starting materials ($24\,AlCl+12\,H_2O$) as well as with the thermodynamically most stable final products ($16\,Al_{(f)}+8\,AlCl_3\cdot H_2O+4\,H_2O$): During the formation of **1a** almost the complete disproportionation energy is liberated.[23] However, in the light of the polyhedral structure of **1**, it is questionable whether **1a** and **1** can be interpreted as intermediates of the disproportionation to AlX_3 and a*luminum metal*.

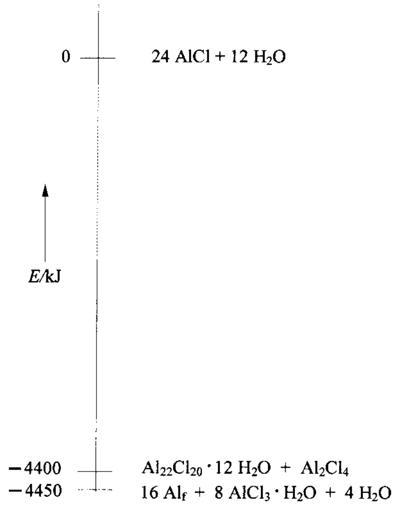


Figure 4. Energy diagram for the position of $Al_{22}Cl_{20}\cdot 12\,H_2O$ (**1a**) relative to the starting material AlCl and the thermodynamic end products Al and $AlCl_3$.

An important motivational factor for the research on clusters are findings about the change in material properties during the transition from the molecule to the solid state. The $Al_{77}R_{20}{}^{2-}$ cluster ($R=N(SiMe_3)_2$)[24] is the largest metal cluster so far, whose structure has been determined by X-ray diffraction. It consists of a central Al atom, which is surrounded by a series of shells, first by 12 Al atoms, arranged in the form of a distorted icosahedron, then by 44 Al atoms, and finally by a further 20 Al^{I}R units. Since the icosahedral Al$_{12}$ shell is distorted almost to the extent that it is a cuboctahedron, the twelve-coordinate central atom is already situated in an environment that is very remisicent to that in cubic closest packed α-aluminum.

In contrast, compound **1** as the second largest aluminum cluster and as the largest neutral aluminum cluster shows a fundamental structural difference in the Al framework, because in this case the central Al atom is missing. Owing to the reactive Br substituents in the cluster shell further reactions resulting in the growth of the aluminum framework should be possible under comparably mild conditions. Finally, a further disproportionation and/or dehalogenation could lead to the formation of a solid-state structure. As long as no Al atom is present in the center of these icosahedral frameworks the linkage of the icosahedra would be more likely to result in a solid which is structurally more similar to boron and probably nonmetallic. Thus, the Al$_{22}$ unit already is a structurally analogous section from the structure of the β-rhombohedral modification of boron and is unique with regard to the ten M^{0}–M^{II} bonds. Even in boron chemistry so far there has not been an intermediate such as a hypothetical B$_{12}$B$_{10}$R$_{20}$ molecule as the link between molecular B$_{12}$ icosahedra and the linked icosahedra in solid boron. It therefore appears plausible to interpret the formation of **1** as a first step in the direction of a new modification of aluminum.

Experimental Section

AlBr (40 mmol) was cocondensed with toluene (100 mL) and THF (15 mL) according to the method desribed in reference [11a]. A portion (20 mL) of the dark red solution (ca. 0.37 M) was concentrated to about half the volume in the cold and thus freed to a large extent from the donor THF. After several days at room temperature a slightly amorphous precipitate of aluminum occurred. From the further concentrated filtrate, **1** began to crystallize after several days in the form of pale yellow, hexagonal plates, which were mechanically and chemically highly labile. In contrast, in solution **1** is stable to above 110°C. The total yield after several re-precipitations was about 10%.

Received: December 28, 1998 [Z12827IE]
German version: *Angew. Chem.* **1999**, *111*, 1851–1855

Keywords: aluminum · cluster compounds

---

[1] The *conjucto*-borane B$_{20}$H$_{26}$ forms in the pyrolysis of B$_{10}$H$_{14}$, which can be prepared from B$_2$H$_6$.

[2] Binary *closo*-boranes only exist as dianionic species such as B$_{12}$H$_{12}^{2-}$. The neutral 1,12-(SMe$_2$)$_2$B$_{12}$H$_{10}$ recently discovered by Hamilton et al.,[25] however, could be interpreted as a binary borane donor-stabilized by thioether.

[3] In this context also the first neutral *closo*-borane H$_2$B$_9$X$_9$ (X = Cl, Br, I) is presented.

[4] a) W. Hönle, Y. Grin, A. Burkhardt, U. Wedig, M. Schultheiss, H. G. von Schnering, R. Keller, H. Binder, *J. Solid State Chem.* **1997**, *133*, 59–67; b) R. Keller, N. Berger, R. Stöckle, K. Vaas, S. Söylemez, A. Pfitzner, H. Binder, W. Hönle, Y. Grin, A. Burkhardt, M. Schultheiss, U. Wedig, H. G. von Schnering, H. Borrmann, A. Simon, *Advances in Boron Chemistry, IX. International Metting on Boron Chemistry*, **1996**, Session Lecture SA-6, p. 38.

[5] J. A. Morrison, *Chem. Rev.* **1991**, *91,* 35–48.

[6] K. A. Solutsev, A. M. Mebel, N. A. Votinova, N. T. Kuznetsov, O. P. Charkin, *Sov. J. Coord. Chem. (Engl. Transl.)* **1992**, *18*, 296; *Koord. Khim.* **1992**, *18*, 340.

[7] C. Dohmeier, C. Robl, M. Tacke, H. Schnöckel, *Angew. Chem.* **1991**, *103,* 594; *Angew. Chem. Int. Ed. Engl.* **1991**, *30,* 564.

[8] W. Uhl, W. Hiller, M. Layh, W. Schwarz, *Angew. Chem.* **1992**, *104*, 1378; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1364.

[9] a) O. Beachley, Jr., R. Blom, M. Churchill, K. Feagari, Jr., J. Fettinger, J. Pazik, L. Victoriano, *Organometallics* **1989**, *8,* 346; b) O. Beachley, Jr., M. Churchill, J. Fettinger, J. Pazik, L. Victoriano, *J. Am. Chem. Soc.* **1986**, *108,* 4666.

[10] W. Uhl, S. Keimling, K. Klinkhammer, W. Schwarz, *Angew. Chem.* **1997**, *109*, 64–66; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 64–65.

[11] See for example: a) C. Dohmeier, D. Loos, H. Schnöckel, *Angew. Chem.* **1996**, *108,* 141–161; *Angew. Chem. Int. Ed. Engl.* **1996**, *35,* 129–149; b) W. Köstler, G. Linti, *Angew. Chem.* **1997**, *109,* 2758–2760; *Angew. Chem. Int. Ed. Engl.* **1997**, *36,* 2644–2645; c) N. Wiberg K. Amelunxen, H. Nöth, M. Schidt, H. Schwenk, *Angew. Chem.* **1996**, *108*, 110; *Angew. Chem. Int. Ed. Engl.* **1996**, *35,* 65.

[12] a) M. Mocker, C. Robl, H. Schnöckel, *Angew. Chem.* **1994**, *106,* 1860–1861; *Angew. Chem. Int. Ed. Engl.* **1994**, *33,* 1754; b) A. Ecker, H. Schnöckel, *Z. Anorg. Allg. Chem.* **1998**, *624,* 813–816.

[13] Crystal structure analysis of Al$_{22}$Br$_{20}\cdot$12THF$\cdot x$toluene (**1**): MarResearch image plate diffractometer, Siemens rotating anode 50 kV, 300 mA, Mo$_{K\alpha}$ radiation (λ = 0.71073), measuring temperature 150 K. The crystal was quickly mounted in perfluoropolyether since once in place it decomposes at room temperature in 1–2 min. Crystal dimensions: 0.3 × 0.3 × 0.25 mm, monoclinic, space group $I2/m$, a = 19.848(5), b = 23.018(5), c = 19.153(4) Å, β = 109.56(3)° V = 8245(3) Å^3, Z = 1, ρ_{calcd} = 1.536 Mg m^{-3}, μ_{Mo} = 5.015 mm^{-1}, $\theta_{\min}$ = 3.19°, $\theta_{\max}$ = 25.91°, 29533 measured reflections, of which 7857 were independent, 5127 > 3σ, 500 parameters, absorption correction by local scaling[28] ($T_{\min}$ = 1.3, $T_{\max}$ = 0.65), R_1 = 0.0918, wR_2 = 0.2775, GOF = 1.120, 40 restraints (for THF); max./min. residual electron density 0.814/−0.659 e Å^{-3}. The structure was solved by direct methods and refined against F^2 for all observed reflections. Software packages used: Shelxs, Shelxtl (G. M. Sheldrick, Universität Göttingen), Resviev, Povray. 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-112224. 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). The structure was initially solved as a triclinic system in the space group $P\bar{1}$ with analogous results. This showed an almost equal distribution of two disordered molecules of **1**, which are mirror symmetrical. They can also be interconverted by a C_2 operation (through I and perpendicular to the C_5 axis). Owing to the arrangement in the crystal depending on the Br shell this results in two statistically equally distributed positions for the Al framework in the molecule. The superposition of these two positions leads to the space group $I2/m$. The molecule itself only displays S_{10} symmetry. The highly disordered solvent (toluene) is located between the molecules **1** and could only partly be included in the refinement. The maximum residual electron densities are also located here. The THF groups are also disordered (for their distances restraints were used), which is why the introduction of hydrogen atoms at calculated positions does not seem sensible in this case. All atoms of **1** were refined anisotropically. Since the crystal had decomposed by the end of the measurement an absorption correction was not possible. However, due to the monoclinic crystal symmetry an approximate absorption correction could be achieved by means of local scaling (symmetry-equivalent reflections are averaged).[28]

[14] W. Hiller, K.-W. Klinkhammer, W. Uhl, J. Wagner, *Angew. Chem.* **1991**, *103*, 182–183; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 179.

[15] Pentagonal dodecahedron, icosahedron, cube, octahedron, and tetrahedron are the five platonic solids. The pentagonal dodecahedron and the icosahedron—like the cube and the octahedron—are duals, since the number of corners of the one body corresonds to the number of the faces of the other body.

[16] M. F. Hawthorne, *Advances in Boron Chemistry, IX. International Meeting on Boron Chemistry*, **1996**, p. 262.

[17] In analogy to **1** the formula here should be B$_{12}$C$_2$[CCl$_2$H]$_{10}\cdot$2H.

[18] K.Wade, *Adv. Inorg. Radiochem.* **1976**, *18*, 1.

[19] a) P. von R. Schleyer, G. Subramanian, H. Jiao, K. Najafian, M. Hofmann, *Advances in Boron Chemistry, IX. International Meeting on*

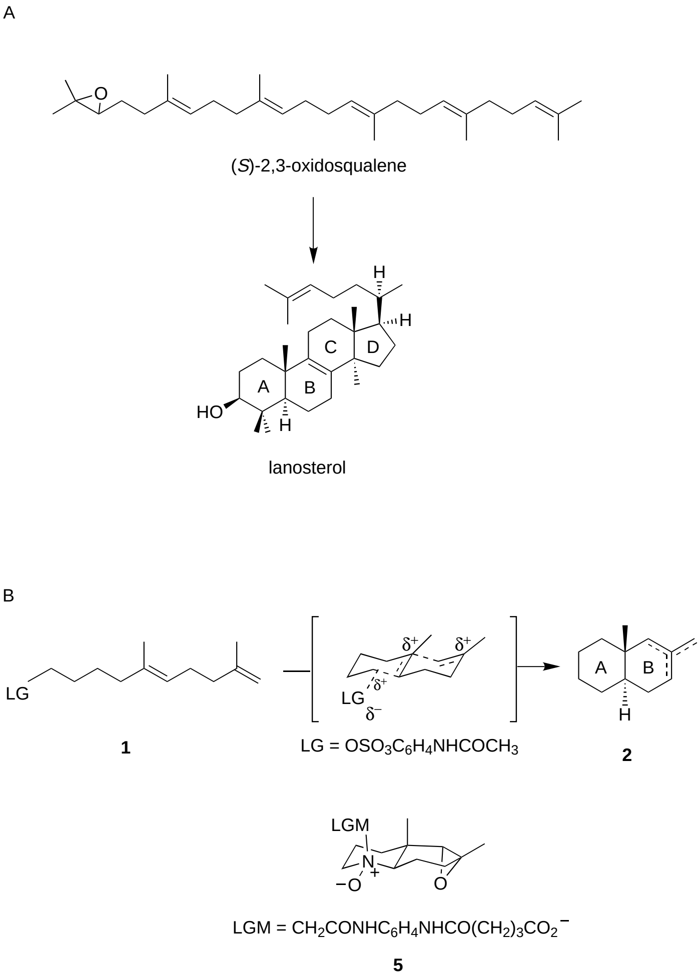
© WILEY-VCH Verlag GmbH, D-69451 Weinheim, 1999
1433-7851/99/3812-1742 $ 17.50+.50/0

Boron Chemistry, **1996**, p. 3; b) K. A. Solutsev, A. M. Mebel, N. A. Votinova, N. T. Kuznetsov, O. P. Charkin, *Sov. J. Coord. Chem. (Engl. Trans.)* **1992**, *18*, 296; *Koord. Khim.* **1992**, *18*, 340.
[20] The recording and calculation (NICS) of the ^{27}Al NMR spectra are subject of ongoing investigations.
[21] The species $Al_2Br_4 \cdot 2D$ has already been structurally characterized with D = OMePh as stabilizing donor.[26]
[22] RIDFT, BP86-functional, SV(P)-basis, Turbomole program package; O. Treutler, R. Ahlrichs, *J. Chem. Phys.* **1995**, *102*, 346; K. Eichkorn, O. Treutler, H. Ohm, M. Häser, R. Ahlrichs, *Chem. Phys. Lett.* **1995**, *242*, 652. Quantum chemical calculations for AlX compounds have shown that the halogen (Cl or Br) and the donor (H_2O or THF) do not have a significant influence on the values considered here of the investigated Al species.[27]
[23] The calculation shows that during the formation of **1** about 99 % of the disproportion energy is liberated. Owing to the mathematical approximation and the connection between the calculated data and the experimentally determined sublimation energy of aluminum (accuracy: $\pm 5\ kJ\,mol^{-1}$), exact quantifications are difficult, that is these results only serve as preliminary information on the energetic situation.
[24] A. Ecker, E. Weckert, H. Schnöckel, *Nature* **1997**, *387*, 379.
[25] E. J. M. Hamilton, G. T. Jordan IV, E. A. Meyers, S. G. Shore, *Inorg. Chem.* **1996**, *35*, 5335.
[26] M. Mocker, C. Robl, H. Schnöckel, *Angew. Chem.* **1994**, *106*, 946–948; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 862.
[27] A. Ecker, E. Baum, M. A. Friesen, M. A. Junker, C. Üffing, R. Köppe, H. Schnöckel, *Z. Anorg. Allg. Chem.* **1998**, *624*, 513–516.
[28] W. Kabsch, *J. Appl. Crystallogr.* **1993**, *26*, 795–800.

Convergence of Catalytic Antibody and Terpene Cyclase Mechanisms: Polyene Cyclization Directed by Carbocation–π Interactions**

Chiana M. Paschall, Jens Hasserodt, Terri Jones, Richard A. Lerner, Kim D. Janda, and David W. Christianson*

Carbocation cyclization cascades catalyzed by terpenoid cyclases rank among the most important and the most complex carbon–carbon bond forming reactions in chemistry and biology.[1, 2] For example, consider the pathway of cholesterol biosynthesis in which the open-chain polyene squalene oxide is cyclized to yield the tetracyclic product lanosterol in a single chemical reaction catalyzed by lanosterol synthase (Scheme 1 A).[2] More than one third of the carbon atoms in the triterpene substrate undergo changes in bonding and/or hybridization during the cyclization cascade to yield a product containing seven precisely formed stereocenters. Remarkably, only 1 out of a possible 128 product stereoisomers is generated, so one key role of the cyclase is to mediate the structural and stereochemical precision of the cyclization reaction. Such precision is the hallmark of most terpenoid cyclases, which are responsible for the biosynthesis of myriad natural products in all forms of life.



Scheme 1. A) Cyclization catalyzed by lanosterol synthase. Lanosterol rings are labeled according to the standard steroid nomenclature. B) Polyene cyclization catalyzed by antibody HA5-19A4 yields a *trans*-decalin skeleton analogous to the lanosterol A and B rings. LGM = leaving group mimic plus carrier protein linker. For further information see the text.

Recent X-ray crystal structure determinations of terpenoid cyclases suggest an independent evolution of two classes of cyclases, yet members of each class exhibit convergent structural features important for catalysis.[3] The active site cavities of each are nested deep within α-helical superstructures, where numerous hydrophobic residues help to sequester the linear polyene substrate from solvent and form

---

[*] Prof. Dr. D. W. Christianson, C. M. Paschall
Roy and Diana Vagelos Laboratories
Department of Chemistry, University of Pennsylvania
Philadelphia, PA 19104-6323 (USA)
Fax: (+1) 215-573-2201
E-mail: chris@xtal.chem.upenn.edu

Prof. Dr. J. Hasserodt, T. Jones, Prof. Dr. R. A. Lerner,
Prof. Dr. K. D. Janda
Department of Chemistry and
The Skaggs Institute for Chemical Biology
The Scripps Research Institute
10550 N. Torrey Pines Road
La Jolla, CA 92037 (USA)

[**] This work was supported by NIH grants GM56838 (D.W.C.) and GM43858 (K.D.J.) and the Skaggs Institute for Chemical Biology. C.M.P is supported by a Fontaine Fellowship from the University of Pennsylvania and an NSF Minority Fellowship Award. We thank Lisa Kerwin for preparation of the Fab. Additionally, we thank J. D. Cox, C. A. Lesburg, T. Stams, and R. Stanfield for helpful discussions during the course of this investigation.