[2] a) Y. Inouye, Y. Take, S. Nakamura, *J. Antibiot.* **1987**, *40*, 100; b) Y. Take, Y. Inouye, S. Nakamura, H. S. Allaudeen, A. Kubo, *J. Antibiot.* **1989**, *44*, 107.

[3] R. B. Lingham, A. H. M. Hsu, J. A. O'Brien, J. M. Sigmund, M. Sanchez, M. M. Gagliardi, B. K. Heimbuch, O. Genilloud, I. Martin, M. T. Diez, C. F. Firsch, D. L. Zink, J. M. Liesch, G. E. Koch, S. E. Gartner, G. M. Garrity, N. N. Tsou, G. M. Salituro, *J. Antibiot.* **1996**, *49*, 253.

[4] M. A. Ciufolini, N. Xi, *Chem. Soc. Rev.* **1998**, 437.

[5] D. L. Boger, M. W. Lederboer, M. Kume, *J. Am. Chem. Soc.* **1999**, *121*, 1098.

[6] D. L. Boger, M. W. Lederboer, M. Kume, Q. Jin, *Angew. Chem.* **1999**, *111*, 2533; *Angew. Chem. Int. Ed.* **1999**, *38*, 2424.

[7] D. L. Boger, M. W. Lederboer, M. Kume, M. Searcey, Q. Jin, *J. Am. Chem. Soc.* **1999**, *121*, 11375. Boger's landmark achievement followed an earlier disclosure of the synthesis of sandramycin, a congener of the peptins that contains pipecolinic acid and valine in place of piperazic acid and *N*-methyl-3-hydroxyvaline: D. L. Boger, J. H. Chen, K. W. Saionz, *J. Am. Chem. Soc.* **1996**, *118*, 1629. The Scripps team has also explored in further detail the bioactivity of peptins and related substances: D. L. Boger, J. H. Chen, K. W. Saionz, Q. Jin, *Bioorg. Med. Chem.* **1998**, *6*, 85; D. L. Boger, K. W. Saionz, *Bioorg. Med. Chem.* **1999**, *7*, 315.

[8] See ref. [4] and [12] as well as: a) M. A. Ciufolini, N. Xi, *J. Chem. Soc. Chem. Commun.* **1994**, 1867; b) N. Xi, M. A. Ciufolini, *Tetrahedron Lett.* **1995**, *36*, 6595; c) M. A. Ciufolini, N. Xi, *J. Org. Chem.* **1997**, *62*, 2320; d) M. A. Ciufolini, T. Shimizu, S. Swaminathan, N. Xi, *Tetrahedron Lett.* **1997**, *38*, 4947; e) M. A. Ciufolini, D. Valognes, N. Xi, *Tetrahedron Lett.* **1999**, *40*, 3693.

[9] H. M. Urbanus (Bristol-Myers Co.) NL-T 84 00 237, **1984** [*Chem. Abstr.* **1985**, *102*, 22795q].

[10] Molecular mechanics calculations suggested that the strain energy present in the peptin macrocycle *per monomeric unit* is less than half of the strain energy present in the cyclic form of each monomeric segment. If the transition state for acylative cyclization reactions were sufficiently late along the reaction coordinate, it seemed plausible that the relative energy content of products might influence product distribution. Details will be provided in forthcoming full papers.

[11] T. Ishizuka, T. Kunieda, *Tetrahedron Lett.* **1987**, *28*, 4185.

[12] N. Xi, L. B. Alemany, M. A. Ciufolini, *J. Am. Chem. Soc.* **1998**, *120*, 80.

[13] a) For a valuable review of allyl-type blocking groups see: H. Kunz, *Angew. Chem.* **1987**, *99*, 297; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 294, and references therein; b) a *β,β*-dimethallyl ester was also competent in later steps, but while the crotyl unit was rapidly released with dimedone/[Pd(PPh$_3$)$_4$], the dimethallyl group resisted cleavage.

[14] Compounds **11** and **12** obtained in this way were contaminated with Ph$_3$P=O. These substances were extremely polar and difficult to purify; accordingly, they were not fully characterized. By contrast, macrocyclic materials were easily purified by chromatography. It appears that Ph$_3$P=O does not interfere with subsequent coupling operations, and indeed, it might even assist them; cf.: V. A. Efimov, O. G. Chakhmakhcheva, Y. A. Ovchinnikov, *Nucl. Acids Res.* **1985**, *13*, 3651.

[15] D. W. Bayne, A. J. Nicol, G. Tennant, *J. Chem. Soc. Chem. Commun.* **1975**, 782.

[16] L. A. Carpino, *J. Am. Chem. Soc.* **1993**, *115*, 4397.

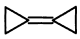
[17] The spectra of **1** are given in ref. [9].

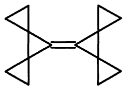
A Third-Generation Bicyclopropylidene: Straightforward Preparation of 15,15′-Bis(hexaspiro[2.0.2.0.0.0.2.0.2.0.1.0]pentadecylidene) and a C_{2v}-Symmetric Branched [15]Triangulane**

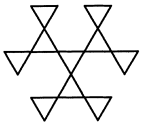
Malte von Seebach, Sergei I. Kozhushkov,
Roland Boese, Jordi Benet-Buchholz, Dmitrii S. Yufit,
Judith A. K. Howard, and Armin de Meijere*

Dedicated to Professor Paul von Ragué Schleyer
on the occasion of his 70th birthday

Bicyclopropylidene (**1**), an interesting laboratory curiosity when first prepared in milligram quantities in 1970,[1] has since become easily available,[2] and due to its unique reactivity, developed into a versatile C_6 building block for organic synthesis.[3] Among other applications, it serves as the best starting material for various branched [*n*]triangulanes—hydrocarbons consisting exclusively of spiroannelated cyclopropane units.[4] The perspirocyclopropanated analogue of **1**, a second-generation bicyclopropylidene **2**, had previously been prepared along a tedious 14-step sequence,[5] and **2** had been further transformed into the perspirocyclopropanated [3]rotane **3** which, with its 10 spiroannelated cyclopropane rings, at that time was the largest achievable [*n*]triangulane.[6]


1


2


3

The classical approach to substituted bicyclopropylidenes by dimerization of 1-halo-1-lithiocyclopropanes generated by treatment of 1,1-dihalocyclopropanes with alkyllithium reagents,[7] has recently been significantly improved by Neu-

---

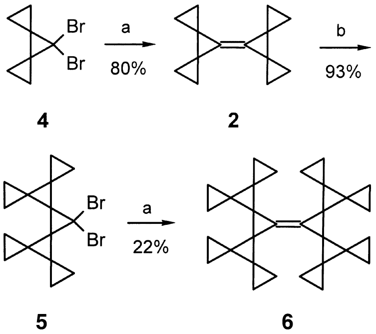
[*] Prof. Dr. A. de Meijere, Dipl.-Chem. M. von Seebach,
Dr. S. I. Kozhushkov
Institut für Organische Chemie der
Georg-August-Universität Göttingen
Tammannstrasse 2, 37077 Göttingen (Germany)
Fax: (+49) 551-399475
E-mail: ameijer1@uni-goettingen.de

Prof. Dr. R. Boese, Dr. J. Benet-Buchholz
Institut für Anorganische Chemie der
Universität-Gesamthochschule Essen
Universitätstrasse 3–5, 45117 Essen (Germany)

Dr. D. S. Yufit, Prof. Dr. J. A. K. Howard
Department of Chemistry, University of Durham
Durham, South Road, DH1 3LE (UK)

[**] This work was supported by the Fonds der Chemischen Industrie and EPSRC (UK). M.v.S. is indebted to the Hermann-Schlosser Foundation for a Graduate Fellowship. The authors are grateful to the companies BASF AG, Bayer AG, Chemetall GmbH, Degussa AG, and Hüls AG for generous gifts of chemicals. We thank Professor H. Butenschön, TU Hannover, for his kind help in providing the DSC measurements, and Professor Burkhard König, Universität Regensburg, for cyclovoltammetric measurements. We are particularly grateful to Dr. B. Knieriem, Universität Göttingen, for his careful reading of the final manuscript.

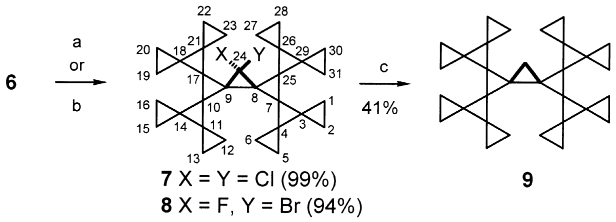
enschwander et al. who observed that copper(II) salts assist the coupling of 1-bromo-1-lithiocyclopropanes generated from 1,1-dibromocyclopropanes to give a variety of substituted bicyclopropylidenes in well reproducible yields.[8] As we now found, this method can also be applied to 7,7-dibromodispiro[2.0.2.1]heptane (**4**),[9] the dibromocarbene adduct of bicyclopropylidene (**1**), to yield the perspirocyclopropanated bicyclopropylidene **2** (80% isolated), making this exotic hydrocarbon easily available in preparatively useful quantities (Scheme 1). It is really spectacular that the dibromide **5**, the dibromocarbene adduct of **2**,[6] can be reductively "dimerized" again to give the third-generation bicyclopropylidene **6** (Scheme 1).[10]



Scheme 1. Synthesis of the third-generation bicyclopropylidene **6**. a) $CuCl_2$, THF, $-95\,^\circ C$, addition of BuLi over 1 h, then $-95\,^\circ C$, 1 h; b) $CHBr_3$, KOH (powder), TEBACl, CH_2Cl_2, $0 \rightarrow 30\,^\circ C$, 5 h. TEBA = benzyltriethylammonium.

Although its total strain energy exceeds 517 kcal mol^{-1},[11] the new cyclopropyl-overcrowded bicyclopropylidene **6** is virtually as stable thermally (up to ca. 230 °C according to differential scanning calorimetry (DSC) measurements) as the perspirocyclopropanated bicyclopropylidene **2**. The oxidation potentials of these alkenes decrease on going from bicyclopropylidene (**1**) (1.58 V) to **2** (1.12 V, $\Delta E = 480$ mV) and further to **6** (0.98 V, $\Delta E = 140$ mV). It is remarkable that the outer sphere cyclopropyl groups in **6** still exert a significant influence, albeit a smaller one than the outer sphere groups in **2**, as indicated by the smaller difference between the values for **6** and **2** compared to that between **2** and **1**.

As expected, the steric congestion arising from the increased number of spiroannelated three-membered rings in **6** prevents certain cycloadditions. Thus, dibromocarbene did not add onto the double bond in **6**,[12] neither under phase-transfer catalysis nor under classical conditions as developed by Doering et al.[13] and Seyferth et al.[14] The addition of bromochlorocarbene also failed under all of these conditions, while 7-bromo-7-chlorodispiro[2.0.2.1]heptane was obtained from **1** in 77% yield using Doering's procedure. Also, **6** did neither react with diazocyclopropane, generated in situ from *N*-nitroso-*N*-cyclopropylurea,[15] nor with diazomethane in the presence of $Pd(OAc)_2$.[16] However, with less sterically demanding carbenes such as dichloro- and bromofluorocarbene the corresponding dihalo[15]triangulanes **7** and **8** were obtained in excellent yields (Scheme 2).[17]



Scheme 2. Preparation of the branched [15]triangulanes **7**–**9**. a) $CHCl_3$, 50% aq. NaOH, TEBACl, room temperature, 3 d; b) $CHBr_2F$, 50% aq. NaOH, TEBACl, CH_2Cl_2, room temperature, 3 d; c) Li, *t*BuOH, THF, 15–20 °C, 3 d.

For quite a while it appeared, as if the perspirocyclopropanated [3]rotane **3** would be the ultimate size achievable branched triangulane. But the current success in preparing the dihalocarbene adducts **7** and **8** (Scheme 2) from the spirocyclopropyl-overcrowded bicyclopropylidene **6**, fuels new hope that the limits for generating even higher aggregates of spiroannelated cyclopropane rings can be pushed forward still further. Reductive dechlorination of **7** led to the hydrocarbon **9** (Scheme 2) which, with its 15 spirofused cyclopropane rings,[18] already sets a new record.

The structures of compounds **6**–**9** were confirmed by X-ray crystal structure analysis.[19] The lengths of the central double bond turned out to be essentially the same in bicyclopropylidene (**1**) (1.304(2) Å[3b]), perspirocyclopropanated bicyclopropylidene **2** (1.305(4) Å[5a]) as well as the third-generation bicyclopropylidene **6** (1.305(3) Å), and the typical difference between proximal and distal bond lengths observed for the outer spirocyclopropane rings in [3]rotane[20] and perspirocyclopropanated [3]rotane **3**[6] for **6** is observed one sphere further out (Figure 1). The structures of [15]triangulane **9** and its dihalo derivatives **7** and **8** all display a unique feature. The

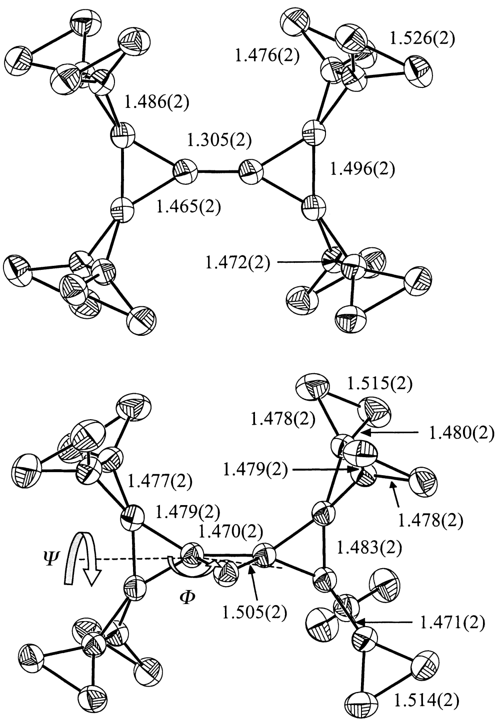


Figure 1. Crystal structures of the third-generation bicyclopropylidene **6** (top) and [15]triangulane **9** (bottom). The bond lengths [Å] are mean values based on assumed D_{2h} symmetry for **6** and C_{2v} symmetry for **9**.[19]

two spiropentane moieties making up the central dispiro[2.0.2.1]heptane units in all of them have lost their usual C_2 symmetry. In **9**, the deformation of these spiropentane units is both by twisting (i. e. rotation of the plane of one cyclopropane ring against that of the other one) by -4.3° and $+5.8^\circ$ ($\Psi = 85.7^\circ$ and 95.8°, respectively, for the left and right spiropentane unit; Figure 1) and bending (i. e. buckling the C_2 axis which usually bisects the two cyclopropane rings; Figure 1) by 11.7° ($\Phi = 168.3^\circ$ for both moieties).[21] This deformation must arise from the mutual repulsion of the two bulky branched [7]triangulane fragments spiroannelated to the central cyclopropane moiety of **9**, and it apparently goes along with a significant change in hybridization of the two central spiro carbon atoms leading to a remarkable shortening of the proximal C–C bond (1.470(2) Å) in the central ring.[22] Such a deformation was also observed in dichloro[15]triangulane **7**, but with slightly less bending ($\Phi = 169.9^\circ$) and significantly less twisting ($\Psi = 89.0^\circ$).

The structure of bromofluoro[15]triangulane **8** is one of the very few known structures of compounds containing a geminally bromofluoro-substituted carbon atom. The sterically congested [15]triangulane skeleton apparently accommodates the larger bromine and the smaller fluorine substituents at C24 best with different orientations of the C–F and C–Br bonds. The angle between the C–Br bond axis and the C9-C8-C24 plane is only 49.1°, while that between the C–F axis and the same plane is 58.2°. The crystal packing of the molecules **8** is also noteworthy. The outer-sphere three-membered rings at C4, C11, C18, and C26 form a large enough cavity which accommodates the Br substituent of the adjacent molecule quite nicely: the shortest intermolecular contact Br1···H28B 2.97(1) Å is the same as the shortest intramolecular ones Br1···H312 2.96(1) and Br1···H152 2.98(1) Å, while the sum of van der Waals radii of hydrogen (1.20 Å) and bromine (1.85 Å)[23] atoms is 3.05 Å (Figure 2).

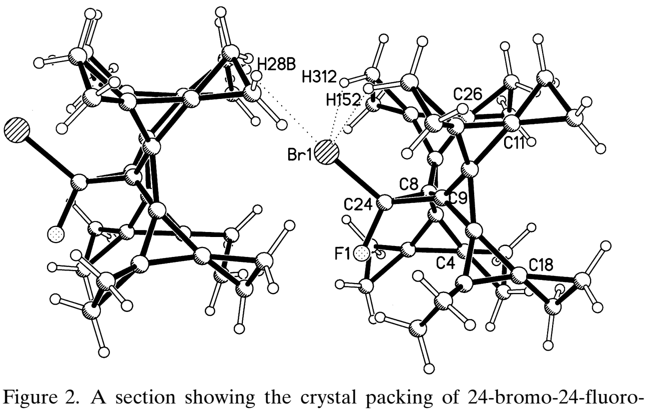


Figure 2. A section showing the crystal packing of 24-bromo-24-fluoro[15]triangulane **8**.[19]

The central dispiro[2.0.2.1]heptane fragment in **8** is also twisted and bent, but the big bromine atom apparently causes the twisting for the two sides to be in the same direction ($\Psi =$ 96.6 and 93.3°) as opposed to compound **9** ($\Psi = 85.7$ and 95.8°), while the degree of bending ($\Phi = 169.9$ and 170.5°) is approximately the same as in **9**.

Thus, the "dimerization" of readily generated bromocuprocyclopropylidenoids has been shown to open a promising route to reasonably large aggregates of spirocyclopropane rings. It remains to be seen, whether the cuprofluorocarbenoids generated from **8** under appropriate conditions can be added to bicyclopropylidene (**1**) or even "dimerized" without rearrangement.

Received: February 16, 2000 [Z14717]

---

[1] P. Le Perchec, J.-M. Conia, *Tetrahedron Lett.* **1970**, 1587 – 1588.

[2] a) A. de Meijere, S. I. Kozhushkov, T. Spaeth, N. S. Zefirov, *J. Org. Chem.* **1993**, *58*, 502 – 505; b) A. de Meijere, S. I. Kozhushkov, T. Späth, *Org. Synth.* **2000**, *79*, in press.

[3] Reviews: a) A. de Meijere, S. I. Kozhushkov, A. F. Khlebnikov, *Zh. Org. Khim.* **1996**, *32*, 1607 – 1626; A. de Meijere, S. I. Kozhushkov, A. F. Khlebnikov, *Russ. J. Org. Chem. (Engl. Transl.)* **1996**, *32*, 1555 – 1575; b) A. de Meijere, S. I. Kozhushkov, A. F. Khlebnikov, *Top. Curr. Chem.* **2000**, *207*, 89 – 147; c) latest application in combinatorial chemistry: A. de Meijere, H. Nüske, M. Es-Sayed, T. Labahn, M. Schroen, S. Bräse, *Angew. Chem.* **1999**, *111*, 3881 – 3884; *Angew. Chem. Int. Ed.* **1999**, *38*, 3669 – 3672.

[4] Reviews: a) A. de Meijere, S. I. Kozhushkov, *Chem. Rev.* **2000**, *100*, 93 – 142; b) A. de Meijere, S. I. Kozhushkov in *Advances in Strain in Organic Chemistry, Vol. 4* (Ed.: B. Halton), JAI Press, London, **1995**, pp. 225 – 282; c) N. S. Zefirov, T. S. Kuznetsova, A. N. Zefirov, *Izv. Akad. Nauk* **1995**, 1613 – 1621; N. S. Zefirov, T. S. Kuznetsova, A. N. Zefirov, *Russ. Chem. Bull. (Engl. Trans.)* **1995**, 1613 – 1621.

[5] a) S. Zöllner, H. Buchholz, R. Boese, R. Gleiter, A. de Meijere, *Angew. Chem.* **1991**, *103*, 1544 – 1546; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1518 – 1520; b) S. Zöllner, Dissertation, Universität Hamburg, **1991**.

[6] S. I. Kozhushkov, T. Haumann, R. Boese, A. de Meijere, *Angew. Chem.* **1993**, *105*, 426 – 429; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 401 – 403.

[7] W. R. Moore, H. R. Ward, *J. Org. Chem.* **1960**, *25*, 2073; W. R. Moore, H. R. Ward, *J. Org. Chem.* **1962**, *27*, 4179 – 4181. For a recent review on the dimerization of halometallocyclopropylidenoids from 1,1-dibromocyclopropanes see ref. [3b].

[8] a) M. Borer, T. Loosli, M. Neuenschwander, *Chimia* **1991**, *45*, 382 – 386; b) T. Loosli, M. Borer, I. Kulakowska, A. Minder, M. Neuenschwander, P. Engel, *Helv. Chim. Acta* **1995**, *78*, 1144 – 1165; c) M. Borer, T. Loosli, A. Minder, M. Neuenschwander, P. Engel, *Helv. Chim. Acta* **1995**, *78*, 1311 – 1324; d) M. Borer, M. Neuenschwander, *Helv. Chim. Acta* **1997**, *80*, 2486 – 2501; e) R. Huwyler, X. Li, P. Bönzli, M. Neuenschwander, *Helv. Chim. Acta* **1999**, *82*, 1242 – 1249.

[9] a) L. Fitjer, J.-M. Conia, *Angew. Chem.* **1973**, *85*, 832 – 833; *Angew. Chem. Int. Ed. Engl.* **1973**, *12*, 761 – 762; b) K. A. Lukin, N. S. Zefirov, D. S. Yufit, Yu. T. Struchkov, *Tetrahedron* **1992**, *48*, 9977 – 9984.

[10] Systematic name: 15,15′-bis(hexaspiro[2.0.2.0.0.0.2.0.2.0.1.0]pentadecylidene).

[11] This estimated total strain energy of **6** is based on a previously published additivity scheme for triangulanes, assuming a strain energy for the central bicyclopropylidene unit of 77.4 kcal mol^{-1}.[3b] See for example H.-D. Beckhaus, C. Rüchardt, S. I. Kozhushkov, V. N. Belov, S. P. Verevkin, A. de Meijere, *J. Am. Chem. Soc.* **1995**, *117*, 11 854 – 11 860.

[12] Several examples of attempted, but unsuccessful dibromocarbene addition to sterically congested bicyclopropylidenes have been reported: a) Y. Fukuda, Y. Yamamoto, K. Kimura, Y. Odaira, *Tetrahedron Lett.* **1979**, 877 – 878; b) A. Tubul, M. Bertrand, *Tetrahedron Lett.* **1984**, *25*, 2219 – 2222. In addition, permethylbicyclopropylidene also did not react with dibromocarbene under different conditions: c) M. von Seebach, Dissertation, Universität Göttingen, **2000**.

[13] a) W. von E. Doering; A. K. Hoffman, *J. Am. Chem. Soc.* **1954**, *76*, 6162 – 6165; b) W. von E. Doering, W. A. Henderson, *J. Am. Chem. Soc.* **1958**, *80*, 5274 – 5277.

[14] D. Seyferth, V. A. Mai, J. Y.-P. Mui, K. V. Darragh, *J. Org. Chem.* **1966**, *31*, 4079 – 4081. For a review on dihalocyclopropanations see: E. V.

Dehmlow, *Methoden Org. Chem. (Houben-Weyl), 4th ed., 1952–, Vol. E 19b*, **1989**, pp. 1461–1627.

[15] W. Kirmse, U. Jansen, *Chem. Ber.* **1985**, *118*, 2607–2625, and references therein.

[16] a) R. Paulissen, A. J. Hubert, P. Teyssie, P. *Tetrahedron Lett.* **1972**, 1465–1466; b) J. Kottwitz, H. Vorbrüggen, *Synthesis* **1975**, 636–637; c) A. J. Anciaux, A. J. Hubert, A. F. Noels, P. Teyssie, *J. Org. Chem.* **1980**, *45*, 695–702. For a review see also: Yu. V. Tomilov, V. A. Dokichev, U. M. Dzhemilev, O. M. Nefedov, *Usp. Khim.* **1993**, *62*, 847–886; Yu. V. Tomilov, V. A. Dokichev, U. M. Dzhemilev, O. M. Nefedov, *Russ. Chem. Rev.* **1993**, *62*, 799–838.

[17] All new compounds were fully characterized by spectroscopic methods (^{1}H NMR, ^{13}C NMR, MS), elemental analyses and crystal structure analyses. **6**: Colorless solid, m.p. 245–246 °C (decomp); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 0.57-0.66$ (m, 8H), 0.73–0.90 (m, 24H); ^{13}C NMR (62.9 MHz, $CDCl_3$, additional DEPT): $\delta = 4.63$ (8 CH_2), 7.25 (8 CH_2), 21.44 (8C), 26.57 (4C), 114.17 (2C); elemental analysis (%) calcd for $C_{30}H_{32}$ (392.6): C 91.78, H 8.22; found: C 91.64, H 8.09. **7**: Colorless solid, m.p. 212 °C (decomp); ^{1}H NMR: $\delta = 0.61-0.94$ (m, 28H), 1.15–1.25 (m, 4H); ^{13}C NMR: $\delta = 4.99$, 6.78, 7.01, 7.67 (4 CH_2), 19.04 (8C), 17.85 (4C), 32.45 (2C), 37.69 (C); elemental analysis (%) calcd for $C_{31}H_{32}Cl_2$ (475.5): C 78.31, H 6.78, Cl 14.91; found: C 78.20, H 6.75, Cl 14.68. **8**: Colorless solid, m.p. 223–225 °C (decomp); ^{1}H NMR: $\delta = 0.61-1.00$ (m, 30H), 1.34–1.42 (m, 2H); ^{13}C NMR: $\delta = 4.87$, 4.98, 6.63, 6.80, 6.86, 6.98, 7.54 (2 CH_2), 6.51 (d, $^5J_{C,F} = 3.8$ Hz, 2 CH_2), 17.55, 18.08, 18.96, 32.46 (2C), 18.63 (d, $^4J_{C,F} = 3.1$ Hz, 2C), 31.88 (d, $^3J_{C,F} = 1.8$ Hz, 2C), 34.08 (d, $^2J_{C,F} = 10.6$ Hz, 2C), 90.60 (d, $^1J_{C,F} = 320.7$ Hz, C); elemental analysis (%) calcd for $C_{31}H_{32}BrF$ (503.5): C 73.95, H 6.41, Br 15.87; found: C 73.84, H 6.38, Br 15.64. **9**: Colorless solid, m.p. 191–193 °C; ^{1}H NMR: $\delta = 0.47-0.60$ (m, 8H), 0.63–0.86 (m, 24H), 0.94 (s, 2H); ^{13}C NMR: $\delta = 3.02$, 4.64, 5.99, 6.49 (4 CH_2), 5.83 (CH_2), 18.00, 18.49, 27.64, 22.55 (2C); elemental analysis (%) calcd for $C_{31}H_{34}$ (406.6): C 91.57, H 8.43; found: C 91.81, H 8.56.

[18] Systematic names: 24-dichloro- (**7**), 24-bromo-24-fluoro- (**8**), tetradecaspiro[2.0.2.0.0.0.0.0.2.0.2.0.0.0.2.0.2.0.0.1.0.0.2.0.2.0.0.0]untriacontane (**9**).

[19] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-142835 (**6**), -142836 (**7**), -142041 (**8**), and -142837 (**9**). 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).

[20] R. Boese, T. Miebach, A. de Meijere, *J. Am. Chem. Soc.* **1991**, *113*, 1743–1748.

[21] For comparison, in spiropentane itself the angles Ψ and Φ are 90.2 and 179.6°, respectively, while in ethano-bridged spiropentane Ψ and Φ are 80.0 and 154.0°, respectively. See for example R. Boese, D. Bläser, K. Gomann, U. H. Brinker, *J. Am. Chem. Soc.* **1989**, *111*, 1501–1503.

[22] Thus, the previously published additivity Scheme for bonding parameters in [*n*]triangulanes also hold for [15]triangulane **9**. See for example R. Boese, T. Haumann, E. D. Jemmis, B. Kiran, S. Kozhushkov, A. de Meijere, *Liebigs Ann.* **1996**, 913–919.

[23] A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441–451.

Cross-Linked Scandium-Containing Dendrimers: A New Class of Heterogeneous Catalysts

Manfred T. Reetz* and Dirk Giebel

Dedicated to Professor José Barluenga
on the occasion of his 60th birthday

Interest in metal-containing dendrimers as catalysts[1] is increasing because in principle they combine the advantages of homogeneous and heterogeneous catalysis in one system.[1c] Nevertheless, recyclization and reuse of such catalysts is not always demonstrated, which raises the question of whether in such cases the synthetic effort necessary in their preparation is actually meaningful.[1d] Here we report on scandium-containing dendrimers, which have useful catalytic properties as Lewis acids and which can also be easily recycled and reused without any appreciable loss in activity. In contrast to soluble dendritic catalysts previously described, our materials are heterogeneous catalysts that are insoluble due to a Sc-promoted cross-linking of individual dendrimer units.[2–4] Application in catalysis is based on previous reports by Kobayashi according to which scandium salts having electron-withdrawing ligands as in $Sc(OTf)_3$ (Tf = triflate = F_3CSO_2), $ScCl_3$, $Sc(NTf_2)_3$, $Sc(PF_6)_3$, or polyallyl scandium trifylamido ditriflate (PA-Sc-TAD) are effective catalysts in Mukaiyama aldol additions to aldehydes and aldimines, Diels–Alder and Michael additions as well as Friedel–Crafts acylations.[5]

The commercially available dendrimer DAB-dendr-$(NH_2)_{32}$ **1**[6] with 32 outer primary amino groups was first subjected to sulfonylation using Tf_2O/Et_3N. The reaction afforded a solid compound **2** which turned out to be only slightly soluble in conventional solvents. The IR spectrum does not show any bands near 3359 cm^{-1} typical of primary amino groups; rather, absorption at 3489 cm^{-1} characteristic of $(R)HNSO_2CF_3$ functions is clearly visible. Thus, most of the outer amino groups appear to have been sulfonylated. We then envisioned that these functional groups can bind to scandium with concomitant cross-linking of the dendritic units **2**. For this purpose a suspension **2** in THF was treated with different amounts of the cross-linking agent $Sc(OTf)_3$ in the presence of KH as base. As a typical result the completely insoluble solid material **3** was formed, which according to elemental analysis has a Sc/N ratio of 0.2 corresponding to about 40 % Sc-loading (see Experimental Section). Although a large proportion of the outer amino groups are likely to exist as $N(Tf)[Sc(OTf)_2]$ units, some of them serve as cross-linking points with two (or three) sulfonamido ligands at scandium (symbolized by **3**). The X-ray powder diffractogram points to a completely amorphous solid. Thus, the possible presence of nonreacted $Sc(OTf)_3$ trapped in the solid matrix can be excluded.

In order to obtain some information concerning the surface morphology and the actual cross-linking, a scanning electron

---

[*] Prof. Dr. M. T. Reetz, Dipl.-Chem. D. Giebel
Max-Planck-Institut für Kohlenforschung
Kaiser-Wilhelm-Platz 1, 45470 Mülheim an der Ruhr (Germany)
Fax: (+49)208-306-2985
E-mail: reetz@mpi-muelheim.mpg.de