[2] a) R. Sessoli, D. Gatteschi, A. Caneschi, M. A. Novak, *Nature* **1993**, *365*, 141; b) A. Caneschi, D. Gatteschi, N. Lalioti, C. Sangregorio, R. Sessoli, G. Venturi, A. Vingigni, A. Rettori, M. G. Pini, M. A. Novak, *Angew. Chem.* **2001**, *113*, 1810; *Angew. Chem. Int. Ed.* **2001**, *40*, 1760; c) A. L. Barra, A. Caneschi, D. Gatteschi, D. P. Goldberg, R. Sessoli, *Solid State Chem.* **1999**, *451*, 484.

[3] a) A. L. Barra, D. Gatteschi, R. Sessoli, *Chem. Eur. J.* **2000**, *6*, 1608; b) L. Thomas, F. Lionti, R. Ballou, D. Gatteschi, R. Sessoli, A. L. Barra, *Nature* **1996**, *383*, 145; c) J. R. Friedman, M. Sarachik, J. Tejada, R. Ziolo, *Phys. Rev. Lett.* **1996**, *76*, 3830.

[4] a) A. Yamaguchi, H. Ishimoto, K. Awaga, J. S. Yoo, M. Nakano, D. N. Hendrickson, E. K. Brechin, G. Christou, *Phys. B* **2000**, *284*–288, 1225; b) D. Gatteschi, A. Caneschi, L. Pardi, R. Sessoli, *Science* **1994**, *265*, 1054; c) A. Müller, F. Peters, M. T. Pope, D. Gatteschi, *Chem. Rev.* **1998**, *98*, 239.

[5] a) K. L. Taft, C. D. Delfs, G. C. Papaefthymiou, S. Foner, D. Gatteschi, S. J. Lippard, *J. Am. Chem. Soc.* **1994**, *116*, 823; b) R. R. Crichton, *Angew. Chem.* **1973**, *85*, 53; *Angew. Chem. Int. Ed. Engl.* **1973**, *12*, 57; c) K. L. Taft, G. C. Papaefthymiou, S. J. Lippard, *Science* **1993**, *259*, 1302.

[6] a) K. Wieghardt, *Angew. Chem.* **1994**, *106*, 765; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 725; b) R. J. Debus, *Biochim. Biophys. Acta* **1992**, *1102*, 269; c) G. W. Bruvig, H. H. Thorp, R. H. Crabtree, *Acc. Chem. Res.* **1991**, *24*, 311; d) G. Christou, *Acc. Chem. Res.* **1989**, *22*, 328.

[7] a) A. Caneschi, A. Cornia, S. J. Lippard, *Angew. Chem.* **1995**, *107*, 511; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 467; b) S. P. Watton, P. Fuhrmann, L. E. Pence, A. Caneschi, A. Cornia, G. L. Abbati, S. J. Lippard, *Angew. Chem.* **1997**, *109*, 2917; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2774; c) R. W. Saalfrank, I. Bernt, E. Uller, F. Hampel, *Angew. Chem.* **1997**, *109*, 2596; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2482; d) G. L. Abbati, A. Cornia, A. C. Fabretti, A. Caneschi, D. Gatteschi, *Inorg. Chem.* **1998**, *37*, 3759; e) O. Waldmann, R. Koch, S. Schromm, J. Schülein, P. Müller, I. Bernt, R. W. Saalfrank, F. Hampel, E. Balthes, *Inorg. Chem.* **2001**, *40*, 2986; f) A. L. Dearden, S. Parsons, R. E. P. Winpenny, *Angew. Chem.* **2001**, *113*, 155; *Angew. Chem. Int. Ed.* **2001**, *40*, 151; g) H. Oshio, N. Hoshino, T. Ito, *J. Am. Chem. Soc.* **2000**, *122*, 12602.

[8] Crystal data for **1**-Cl$_3$ ($C_{66}H_{90}Cl_3Fe_7N_6O_{24}$): dark-red block (0.2x0.2x0.3 mm^3), $M = 1848.75$, trigonal, space group $P\bar{3}c1$ (No. 165), $a = 14.5632(15)$, $c = 22.374(3)$ Å, $V = 4109.4(9)$ Å^3, $Z = 2$, $T = -70$°C; A total of 22130 (R(int) = 0.0807) unique reflections ($3° < 2\theta < 50°$) were measured. Nonhydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in calculated positions and refined with isotropic thermal parameters riding on those of the parent atoms. Full-matrix least-squares refinement on F^2 (194 variables) converged to $R1 = 0.0650$, $wR2 = 0.1785$ ($I > 2\sigma(I)$). CCDC-192326 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit @ccdc.cam.ac.uk).

[9] An iron ion has unquenched orbital momentum and the spin-Hamiltonian should include the anisotropic term. Analysis of the magnetic data has not been performed.

[10] a) G. Armoi, M. J. Knapp, J.-O. Claude, J. C. Huffman, D. N. Hendrickson, G. Christou, *J. Am. Chem. Soc.* **1999**, *121*, 5489; b) H. J. Eppley, H.-L. Tsai, N. de Vries, K. Folting, G. Christou, D. N. Hendrickson, *J. Am. Chem. Soc.* **1995**, *117*, 301.

[11] V. R. Marath, S. Mitra, *Chem. Phys. Lett.* **1974**, *27*, 103.

[12] The average g value was estimated by the Curie plot of the χ_m values in the temperature range of 200–300 K.

Carborane Cages

Beyond the Icosahedron: The First 13-Vertex Carborane[**]

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The chemistry of carboranes and heterocarboranes is dominated by the 12-vertex icosahedron. The first carborane reported[1] was 1-C(CH$_3$)CH$_2$-1,2-*closo*-$C_2B_{10}H_{11}$ and there are now literally thousands of heterocarboranes known based on the icosahedral geometry. The field of subicosahedral heterocarboranes is also well developed, which reflects the existence of carboranes from $C_2B_3H_5$ to $C_2B_9H_{11}$.

In contrast, the area of supraicosahedral heterocarboranes is relatively unexplored. Although the first 13-vertex metallacarborane was reported over 30 years ago,[2] there are only about a hundred such compounds currently known. The first supraicosahedral p-block metallacarborane was described only last year.[3] We are aware of only a handful of 14-vertex metallacarboranes,[4,5] and no such species of greater cluster size. Crucially, there are no reports of carboranes which extend the homologous family $C_2B_nH_{2+n}$ beyond $n = 10$ nor any reports of the parent borane ions $[B_nH_n]^{2-}$ for $n > 12$. This situation is unfortunate since several of the current applications of boron-cluster compounds, for example, in catalysis as "least-coordinating anions"[6] and in boron–neutron-capture therapy of tumors,[7] would benefit from the existence of carboranes with larger numbers of B atoms.

The most recent computational study of supraicosahedral boranes[8] concluded that a) $[B_{13}H_{13}]^{2-}$, $[B_{14}H_{14}]^{2-}$, and $[B_{15}H_{15}]^{2-}$ ions are thermodynamically unstable with respect to $[B_{12}H_{12}]^{2-}$, and b) the $[B_{12}H_{12}]^{2-} \rightarrow [B_{13}H_{13}]^{2-}$ step is particularly unfavorable and represents a synthetic bottleneck. Tantalizingly, the higher boranes $[B_{16}H_{16}]^{2-}$ and $[B_{17}H_{17}]^{2-}$ are predicted to be progressively more stable than $[B_{15}H_{15}]^{2-}$. In a separate study,[9] other workers have predicted stable, spherical, geometries for $B_{20}H_{20}$, $B_{32}H_{32}$, $B_{42}H_{42}$, and $B_{92}H_{92}$ clusters. Although similar calculations have not been performed on closo carboranes, the results of these computational studies suggest that several stable, large, carboranes could be viable synthetic targets as long as the 12-vertex→13-vertex barrier is overcome. We now report that breakthrough.

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An appealing way to prepare the 13-vertex $C_2B_{11}H_{13}$ or its derivatives from the appropriate $C_2B_{10}H_{12}$ species is by polyhedral expansion, that is, reduction of the closo precursor to the nido dianion[10] $[C_2B_{10}H_{12}]^{2-}$ followed by capitation through treatment with a BRX_2 compound,[11] analogous to the method employed to prepare the first 13-vertex metallacarborane.[2] Starting from 1,2-*closo*-$C_2B_{10}H_{12}$ we tried this many times, under a variety of conditions, and in a variety of solvents, each attempt failing to produce a supraicosahedral species. However, we did note that reduction of 1,2-*closo*-$C_2B_{10}H_{12}$, followed by treatment with BI_3, produced 3-I-1,2-*closo*-$C_2B_{10}H_{11}$, which suggests successful initial production of a 13-vertex carborane that spontaneously degraded by loss of a {BH} unit.

When 1,2-*closo*-$C_2B_{10}H_{12}$ is reduced the cage carbon atoms separate.[12] Our observation that they become adjacent again when the presumed 13-vertex carborane partially degrades suggested that a system in which such C-atom movement was prevented might represent a way forward. Tethering the cage C atoms with an α,α-*o*-xylylene bridge retains their adjacency on reduction.[13] However, the reduced species has not been structurally characterized in the absence of a coordinated metal ion,[13] so to provide a firm basis for the subsequent capitation step we have determined the structure[14] of the [7,8-μ-{$C_6H_4(CH_2)_2$}-7,8-*nido*-$C_2B_{10}H_{11}]^-$ (**1**) ion as its $[HNEt_3]^+$ salt (Figure 1). This study establishes the presence of a six-atom C_2B_4 open upper face with adjacent C atoms. The structure of the anion is broadly similar to that of the kinetic isomer of the same species coordinated to K^+[13] ions and to that established[12] for the [7,9-Me_2-7,9-*nido*-$C_2B_{10}H_{11}]^-$ ion except that the former is fully triangulated save for a flat six-membered face, and the quadrilateral CB_3 lower face of the latter is replaced by a trapezoidal C_2B_2 face here. The C_6 ring of the phenylene bridge is located over this trapezoidal face.

Removal of the bridging proton from **1** with BuLi or direct two electron (2e) reduction of 1,2-μ-{$C_6H_4(CH_2)_2$}-1,2-*closo*-$C_2B_{10}H_{10}$ with Na yields the [7,8-μ-{$C_6H_4(CH_2)_2$}-7,8-*nido*-$C_2B_{10}H_{10}]^{2-}$ ion which we assume has the same basic structure as the monoanion. Treatment of this compound with $PhBCl_2$ affords the unprecedented 13-vertex carborane 1,2-μ-{$C_6H_4(CH_2)_2$}-3-Ph-1,2-$C_2B_{11}H_{10}$ (**2**) as a moderately stable colorless crystalline solid.

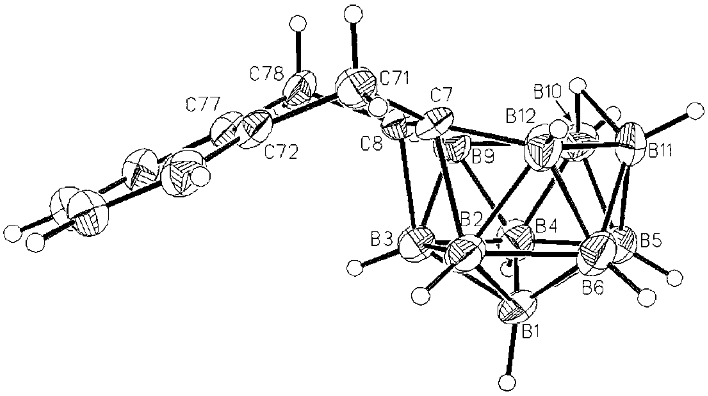

Figure 1. Perspective view of **1** (except for the H atoms, all atoms are drawn as thermal ellipsoids set at 50% probability). The anion has crystallographically imposed C_s symmetry. Selected interatomic distances [Å]: C7-C8 1.444(7), C7-B2 1.833(7), B2-B3 1.949(9), C8-B3 1.816(7), C8-B9 1.546(7), B9-B10 1.851(9), B10-B11 1.836(9), B11-B12 1.842(8), B12-C7 1.551(7).

Compound **2** was characterized by ^1H, ^{13}C, and ^{11}B NMR spectroscopy, mass spectrometry, and single-crystal X-ray diffraction[15] (Figure 2). Ignoring the Ph substituent, the carborane cluster has approximate C_s symmetry about the plane passing through B5, B12, and B13. All the polyhedral faces are triangulated except for C1-C2-B7-B3 which is trapezoidal. With respect to the cluster C1 and C2 are both four-connected, B5 is six-connected, and all other B atoms are five-connected. This polyhedral shape is that of a henicosahedron (**a**, Figure 3) and not the docosahedron previously predicted[8] for the 13-vertex borane $[B_{13}H_{13}]^{2-}$ (**b**, Figure 3) which has C_{2v} symmetry and is fully triangulated, but the two geometries are related by only a single diamond↔square transformation. We have used density functional calculations[16] to study both $[B_{13}H_{13}]^{2-}$ and 1,2-$C_2B_{11}H_{13}$, and find that the structure **b** is preferred over **a** by 3.8 kJ mol^{-1} for the borane dianion, whilst the reverse is the case by 7.4 kJ mol^{-1}

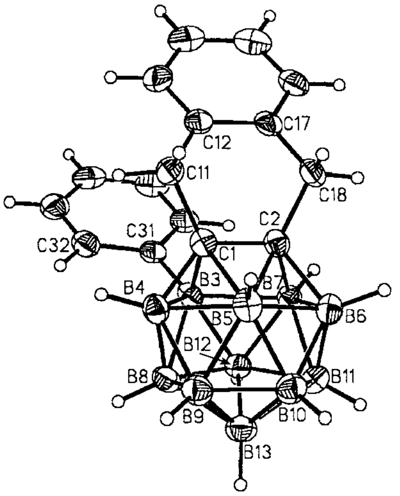

Figure 2. Perspective view of the supraicosahedral carborane **2** (except for the H atoms, all atoms are drawn as thermal ellipsoids set at 50% probability). Selected interatomic distances [Å]: C1-C2 1.427(2), C1-B3 1.898(2), C1-B4 1.569(2), C1-B5 1.841(3), C2-B5 1.917(3), C2-B6 1.632(3), C2-B7 1.766(2), B3-B7 1.987(3).

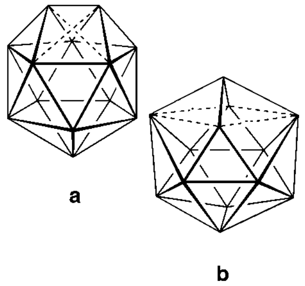

Figure 3. The cluster geometries (**a**, the henicosahedron) found in the supraicosahedral carborane **2** and (**b**, the docosahedron) predicted for the $[B_{13}H_{13}]^{2-}$ ion. Idealized point groups are C_s and C_{2v}, respectively. Theoretically, the henicosahedron is preferred for 1,2-$C_2B_{11}H_{13}$ by 7.4 kJ mol^{-1}, whereas the docosahedron is preferred for $[B_{13}H_{13}]^{2-}$ by 3.8 kJ mol^{-1}. Topologically **a** can be transformed into **b** by making either, and **b** into **a** by breaking any, of the dashed connectivities shown.

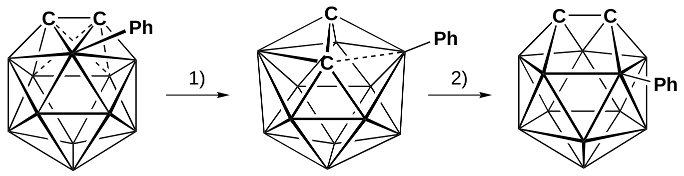

Figure 4. Suggested mechanism for the formation of **2**. The kinetic isomer (left) transforms to the observed thermodynamic isomer (right) by a square→diamond transformation (1, either dashed connectivity made) followed by a diamond→square transformation (2, dashed connectivity broken). The intermediate species has the docosahedral geometry shown as **b** in Figure 3.

for the carborane. We presume the tendency of cluster C atoms to adopt relatively low connected sites is responsible for the latter preference. In **2** the B atom bearing the Ph substituent is not the six-connected boron atom—capitation of deprotonated **1** would be expected to afford **2** in which B3(Ph) and B5(H) were interchanged. We suggest that the kinetic product does indeed have Ph group bonded to a six-connected boron atom, but that it rearranges (Figure 4) into **2** by successive square→diamond then (different) diamond→square transformations via a docosahedral intermediate. Given the marginal differences in calculated energies between the henicosahedron and the docosahedron such a rearrangement is expected to be facile.

We have demonstrated that it is possible to break through the critical 12-vertex→13-vertex bottleneck in polyhedral boron chemistry. For the borane dianions the 12-vertex→13-vertex step has been described as the most difficult to achieve, which suggests that we are now well positioned to synthesize new families of 14-, 15-, 16-, … vertex carborane clusters by successive reduction/capitation steps. Although it has been necessary to tether the cage C atoms to achieve the 12-vertex→13-vertex polyhedral expansion we clearly would not wish to be restricted to tethered supraicosahedral carboranes. We are therefore also investigating the synthesis of supraicosahedral carboranes with removable tethers. Calculations[8] suggest that the stability of 14-vertex and higher polyhedra may make tether removal feasible from this point. Amongst other things tether removal would allow study of the isomerizations of these large carboranes.

Experimental Section

[HNEt$_3$]**1**: Reduction (Na/naphthalene) of 1,2-μ-{$C_6H_4(CH_2)_2$}-1,2-*closo*-$C_2B_{10}H_{10}$ in THF, addition of $BF_3{\cdot}OEt_2$ (1 equiv), hydrolysis (H_2O), and treatment with [HNEt$_3$]Cl, followed by extraction into CH_2Cl_2 and crystallization from CH_2Cl_2/OEt_2 afforded [HNEt$_3$]**1** in 42 % yield. IR (KBr disc): $\tilde{\nu}_{max}$ 2500 (BH) cm^{-1}; ^{1}H NMR (($CD_3)_2CO$, 298 K): $\delta = 7.01$–6.99 (m, 4 H, C_6H_4), 3.96 (br s, 1 H, H_{endo}), 3.86 (d, $J = 15$ Hz, 2 H, $C_{bridge}H_2$), 3.69 (d, $J = 15$ Hz, 2 H, $C_{bridge}H_2$), 3.43 (q, $J = 12$ Hz, 6 H, NCH_2), 1.38 ppm (t, $J = 12$ Hz, CH_3); ^{11}B-{^{1}H} NMR (($CD_3)_2CO$, 298 K): $\delta = 8.2$ (2 B), 2.1 (2 B), −6.5 (2 B), −13.5 (2 B), −16.9 (1 B), −19.0 ppm (1 B); ^{13}C-{^{1}H} NMR (($CD_3)_2CO$, 298 K): $\delta = 138.9$ (2 C, Ar_{quat}), 126.6 (2 C, Ar), 126.4 (2 C, Ar), 49.3 (2 C, C_{bridge}), 48.1 (3 C, NCH_2), 9.6 ppm (3 C, CH_3). Satisfactory microanalytical data were obtained.

2, direct synthesis from closo carborane: Reduction (Na/naphthalene) of 1,2-μ-{$C_6H_4(CH_2)_2$}-1,2-*closo*-$C_2B_{10}H_{10}$ in THF followed by replacement of solvent with 40–60 petroleum ether, cooling to 0 °C and addition of $PhBCl_2$ afforded **2** in 6 % yield (not optimized) following workup involving extraction into CH_2Cl_2, thin layer chromatography on SiO_2 and crystallization from CH_2Cl_2/petroleum ether. IR (CH_2Cl_2): $\tilde{\nu}_{max}$ 2570 (BH) cm^{-1}; ^{1}H NMR ($CDCl_3$, 298 K): $\delta = 7.21$–6.76 (m, 9 H, C_6H_4), 3.91 (s, 4 H, CH_2); ^{11}B-{^{1}H} NMR ($CDCl_3$, 298 K): $\delta = 8.4$ (2 B), 5.3 (3 B, including BPh as a partially obscured signal to higher frequency), 3.7 (2 B), 0.6 (2 B), −1.2 ppm (2 B): ^{13}C-{^{1}H} NMR ($CDCl_3$, 298 K): $\delta = 140.2$ (1 C, Ar_{quat}), 133.2 (2 C, Ar), 129.5 (2 C, Ar_{quat}), 128.4 (1 C, Ar), 127.1 (2 C, Ar), 126.9 (2 C, Ar), 125.2 (2 C, Ar), 48.7 ppm (2 C, C_{bridge}); MS (EI): *m/z* 331 [M^+], 256 [$M^+ - Ph$], 245 [$M^+ - BPh$]. Satisfactory microanalytical data were obtained.

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[1] M. M. Fein, J. Bobinski, N. Mayes, N. Schwartz, M. S. Cohen, *Inorg. Chem.* **1963**, *2*, 1111.

[2] G. B. Dunks, M. M. McKown, M. F. Hawthorne, *J. Am. Chem. Soc.* **1971**, *93*, 2541.

[3] N. M. M. Wilson, D. Ellis, A. S. F. Boyd, B. T. Giles, S. A. Macgregor, G. M. Rosair, A. J. Welch, *Chem. Commun.* **2002**, 464.

[4] W. J. Evans, M. F. Hawthorne, *J. Chem. Soc. Chem. Commun.* **1974**, 38.

[5] W. M. Maxwell, R. F. Bryan, E. Sinn, R. N. Grimes, *J. Am. Chem. Soc.* **1977**, *99*, 4016; J. R. Pipal, R. N. Grimes, *Inorg. Chem.* **1978**, *17*, 6.

[6] K. Shelly, C. A. Reed, Y. L. Lee, W. R. Scheidt, *J. Am. Chem. Soc.* **1986**, *108*, 3117.

[7] for example, L. F. Tietze, U. Griesbach, U. Bothe, H. Nakamura, Y. Yamamoto, *ChemBioChem* **2002**, *3*, 219.

[8] P. von R. Schleyer, K. Najafian, A. M. Mebel, *Inorg. Chem.* **1998**, *37*, 6765.

[9] I. Boustani, A. Rubio, J. A. Alonso in *Contemporary Boron Chemistry* (Eds.: M. G. Davidson, A. K. Hughes, T. B. Marder, K. Wade), Royal Society of Chemistry, Cambridge, **2000**.

[10] D. Grafstein, J. Dvorak, *Inorg. Chem.* **1963**, *2*, 1128.

[11] M. F. Hawthorne, P. A. Wegner, *J. Am. Chem. Soc.* **1968**, *90*, 896.

[12] T. D. Getman, C. B. Knobler, M. F. Hawthorne, *Inorg. Chem.* **1990**, *29*, 158.

[13] G. Zi, H.-W. Li, Z. Xie, *Chem. Commun.* **2001**, 1110.

[14] For both structure determinations: crystals were studied at 160(2) K using a Bruker *P*4 diffractometer with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Intensity data to θ_{max} 25° were collected by ω scans. Data were corrected for absorption by psi scans and the structures solved by direct and difference-Fourier methods. Refinement[20] was by full-matrix least-squares analysis on F^2. All non-hydrogen atoms were refined with anisotropic displacement parameters. Crystal data for [HNEt$_3$]**1**: $C_{16}H_{35}B_{10}N{\cdot}0.5 < CH_2Cl_2 < 1.0$, $M_r^* = 507.50$, monoclinic, $P2_1/c$, $a = 15.658(2)$, $b = 11.543(2)$, $c = 14.580(3)$ Å, $\beta = 110.310(10)°$, $V = 2471.4(7)$ Å^3, $Z = 4$, $\rho = 1.364$ Mg m^{-3}, $\mu^* = 0.286$ mm^{-1}, $F(000)^* = 1064$. 4545 data collected, 4294 independent reflections ($R_{int} = 0.0706$), $R_1 = 0.1168$, $wR_2 = 0.2916$ for data with $I > 2\sigma(I)$, $S = 1.125$, largest peak 0.872 and deepest hole −0.343 e Å^{-3}. (*M_r, ρ, μ, and $F(000)$ values assume 0.5 CH_2Cl_2 of solvation). CCDC-188724 ([HNEt$_3$]**1**) and CCDC-188725 (**2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

[15] Crystal data for **2**: $C_{16}H_{23}B_{11}$, $M_r = 334.25$, monoclinic, $P2_1/n$, $a = 7.345(2)$, $b = 17.393(4)$, $c = 14.786(3)$ Å, $\beta = 99.28(2)°$, $V = 1864.2(8)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.191$ Mg m^{-3}, $\mu = 0.058$ mm^{-1}, $F(000) = 696$. 4355 data collected, 3268 independent reflections ($R_{int} = 0.0336$), $R_1 = 0.0462$, $wR_2 = 0.1081$ for data with $I > 2\sigma(I)$, $S = 1.033$, largest peak 0.140 and deepest hole -0.225 e Å^{-3}.[14]

[16] R. G. Parr, W. Yang, *Density-Functional Theory of Atoms and Molecules*, OUP, New York, **1989**. Calculations used the ADF1999 program[17–19] with the BP86 functional and incorporated a treatment of relativistic effects. A double-ζ plus polarization STO basis set for all atoms and the frozen core approximation was applied (C, B: 1s).

[17] E. J. Baerends, D. E. Ellis, P. Ros, *Chem. Phys.* **1973**, *2*, 41.

[18] G. te Velde, E. J. Baerends, *J. Comput. Phys.* **1992**, *99*, 84.

[19] C. F. Guerra, J. G. Snijders, G. te Velde, E. J. Baerends, *Theor. Chem. Acc.* **1998**, *99*, 391.

[20] G. M. Sheldrick, SHELXTL Version 5.1, Bruker AXS Inc., Madison, Wisconsin, **1999**.

Giant Rings

Macrocycle Synthesis by Olefin Metathesis on a Nanosized, Shape-Persistent Tricationic Platinum Template**

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Macrocyclic compounds are widely used as preorganized host molecules for the selective binding of specific guests.[1] Commonly, these guests are monometallic cations or small polar molecules, such as urea. An alternative possibility is to assemble a given set of molecules around a metal center[2] or molecular pattern[3,4] and then couple the molecules to one host–guest complex. In this reaction sequence the metal center or molecular pattern functions as template.[5] In a number of recent reports the latter strategy has been used for the synthesis of catenanes and knots,[6] and of molecular wires imbedded in an alkane double helix.[7] In these reactions, host and guest often become irreversibly integrated in an assembly with novel molecular properties.

In a recent study, we prepared a series of shape-persistent multimetallic compounds which can be easily converted into the corresponding multicationic species.[8] The cationic sites in the trication of **1** (see Scheme 1) used in the present study are fixed in a two-dimensional space and are at the corners of a triangle with edges of 1.75 nm.[8b] The NCN pincer platinum cations bind new ligands exclusively *trans* to C_{ipso} along the pseudo C_2 axis of the molecule (C_4-C_{ipso}-Pt). Accordingly, binding of pyridine ligands provides a special molecular arrangement having the planes of the tris(phenylene)benzene core and the pyridine ligands coplanar. It turns out that of the combinations ECE pincer ligand/metal/pyridine (E: N, S; metal: palladium, platinum) the NCN pincer platinum pyridine complexes are the kinetically most stable ones.[9] Moreover, the NCN-Pt complexes are the least active catalysts for the isomerization of α-olefins (see below). This makes the trication of **1** an ideal template for interconnecting the pyridine rings at the *ortho* or *meta* positions thereby forming a large tris(pyridyl) macrocyclic compound around the trication.

Here we report the selective linking of 2,6-bis(dec-9-enyloxy)pyridine substituents by alkene metathesis to form a 69-membered tris(pyridyl) macrocycle. Its detachment occurs by addition of nucleophiles, for example, Cl^-. The trisolefinic macrocycle could be hydrogenated and subsequently recoordinated to the tricationic template. This sequence (Scheme 1) provides a new approach to the selective synthesis of large-ring macrocyclic hosts which have as the only preorganization a precise atom connectivity pattern.

2,6-Bisolefin-substituted pyridines **2a**,**b** were prepared from 9-decen-1-ol and 2,6-dibromopyridine or 2,6-bis(chloromethyl)pyridine, respectively. The template precursor **1** (1 mmol) was reacted in CH_2Cl_2 with three equivalents of either **2a** or **2b** in the presence of suspended $AgBF_4$ to give the tricationic compounds **3a** or **3b**, respectively, in quantitative yields. A prolonged reaction time (30 min to 16 h) is necessary because of the poor solubility of $AgBF_4$ in CH_2Cl_2. The compounds **3** undergo alkene metathesis in the presence of the first-generation Grubbs catalyst, $[Cl_2(Cy_3P)_2Ru{=}CHPh]$ (5 mol% per pyridine ligand), leading to the tricationic tris-platinum heteromacrocycle complexes **4**. The alkene metathesis reactions were performed under high dilution (1×10^{-3} M) to prevent intermolecular olefin metathesis polymerization. Easy detachment of the newly formed macroheterocycle from the tricationic template was possible by reacting **4** with an aqueous NaCl solution, affording free macrocycle **5a** or **5b** and the neutral template precursor **1**. In fact, pure **1** was obtained quantitatively and could be reused in subsequent experiments.

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