epoxide synthesis. A study of other ligands to expand the scope of the process and enhance asymmetric induction, as well as synthetic applications, is currently underway.

Experimental Section

Typical procedure for lithiation–electrophile trapping of cyclooctene oxide (**1**) in the presence of a diamine:

The diamine (2.6 mmol) was added dropwise to a solution of RLi (1.4 M, 2.5 mmol) in Et_2O (8 mL) at −90 °C. This mixture was stirred for 1 h at −90 °C. A solution of cyclooctene oxide (**1**; 2.0 mmol) in Et_2O (2 mL), precooled to −90 °C, was then added rapidly by cannula to the solution of ligand/RLi and the reaction mixture was then stirred at −90 °C for 3 h. Neat electrophile (3.0 mmol) was added dropwise, and the mixture was then allowed to warm to room temperature over 5 h. After quenching with aqueous H_3PO_4 (0.5 M, 25 mL), the organic phase was washed with saturated aqueous $NaHCO_3$ (25 mL) and brine (25 mL). The aqueous layers were extracted twice with Et_2O (25 mL) and the combined organic phases were dried ($MgSO_4$) and evaporated under reduced pressure. Purification of the residue by column chromatography (SiO_2, Et_2O, petrol) gave the substituted epoxide.

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[1] I. Erden in *Comprehensive Heterocyclic Chemistry II*, *Vol. 1A* (Eds.: A. R. Katritzky, C. W. Rees, E. F. V. Scriven), Pergamon, Oxford, **1996**, pp. 97–171.

[2] a) R. A. Johnson, K. B. Sharpless in *Catalytic Asymmetric Synthesis*, *2nd ed.* (Ed.: I. Ojima), Wiley-VCH, New York, **2000**, pp. 231–285; b) T. Katsuki in *Catalytic Asymmetric Synthesis*, *2nd ed.* (Ed.: I. Ojima), Wiley-VCH, New York, **2000**, pp. 287–325; c) E. N. Jacobsen, M. H. Wu in *Comprehensive Asymmmetric Catalysis* (Eds.: E. N. Jacobsen, A. Pfaltz, H. Yamamoto), Springer, Berlin, **1999**, pp. 649–677.

[3] J. J. Eisch, J. E. Galle, *J. Am. Chem. Soc.* **1976**, *98*, 4646–4648.

[4] a) T. Satoh, *Chem. Rev.* **1996**, *96*, 3303–3325; b) Y. Mori, *Rev. Heteroat. Chem.* **1997**, *17*, 183–210.

[5] a) P. Lohse, H. Loner, P. Acklin, F. Sternfeld, A. Pfaltz, *Tetrahedron Lett.* **1991**, *32*, 615–618; b) T. Satoh, S. Kobayashi, S. Nakanishi, K. Horigushi, S. Irisa, *Tetrahedron* **1999**, *55*, 2515–2528.

[6] D. M. Hodgson, S. L. M. Norsikian, *Org. Lett.* **2001**, *3*, 461–463.

[7] a) D. Hoppe, T. Hense, *Angew. Chem.* **1997**, *109*, 2376–2410; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2282–2316; b) P. Beak, A. Basu, D. J. Gallagher, Y. S. Park, S. Thayumanavan, *Acc. Chem. Res.* **1996**, *29*, 552–560.

[8] a) D. M. Hodgson, G. P. Lee, *Chem. Commun.* **1996**, 1015–1016; b) D. M. Hodgson, G. P. Lee, *Tetrahedron: Asymmetry* **1997**, *8*, 2302–2306; c) D. M. Hodgson, G. P. Lee, R. E. Marriott, A. J. Thompson, R. Wisedale, J. Witherington, *J. Chem. Soc. Perkin Trans. 1* **1998**, 2151–2161; d) D. M. Hodgson, L. A. Robinson, *Chem. Commun.* **1999**, 309–310; e) D. M. Hodgson, C. R. Maxwell, I. R. Matthews, *Tetrahedron: Asymmetry* **1999**, *10*, 1847–1850; f) D. M. Hodgson, L. A. Robinson, M. L. Jones, *Tetrahedron Lett.* **1999**, *40*, 8637–8640.

[9] G. A. Molander, K. Mautner, *J. Org. Chem.* **1989**, *54*, 4042–4050.

[10] K. M. Bertini Gross, Y. M. Jun, P. Beak, *J. Org. Chem.* **1997**, *62*, 7679–7689.

[11] a) D. M. Hodgson, I. D. Cameron, *Org. Lett.* **2001**, *3*, 441–444; b) D. M. Hodgson, I. D. Cameron, M. Christlieb, R. Green, G. P. Lee, L. A. Robinson, *J. Chem. Soc. Perkin Trans. 1* **2001**, 2161–2174.

[12] a) J. K. Crandall, M. Apparu, *Org. React. (N. Y.)* **1983**, *29*, 345–443; b) E. Doris, L. Dechoux, C. Mioskowski, *Synlett* **1998**, 337–343.

[13] For selected reviews and recent contributions, see: a) D. M. Hodgson, A. R. Gibbs, G. P. Lee, *Tetrahedron* **1996**, *52*, 14361–14384; b) E. N. Jacobsen, *Acc. Chem. Res.* **2000**, *33*, 421–431; c) S. Matsunaga, J. Das, J. Roels, E. M. Vogl, N. Yamamoto, T. Iida, K. Yamaguchi, M. Shibasaki, *J. Am. Chem. Soc.* **2000**, *122*, 2252–2260; d) M. J. Södergren, S. K. Bertilsson, P. G. Andersson, *J. Am. Chem. Soc.* **2000**, *122*, 6610–6618; e) W. A. Nugent, *J. Am. Chem. Soc.* **1998**, *120*, 7139–7140; f) S. E. Denmark, P. A. Barsanti, K.-T. Wong, R. A. Stavenger, *J. Org. Chem.* **1998**, *63*, 2428–2429.

Synthesis and Structural Characterization of Organometallic Cyclynes: Novel Nanoscale, Carbon-Rich Topologies[**]

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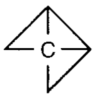
Uwe H. F. Bunz*

Dedicated to Professor Günther E. Szeimies

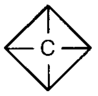
"Carbon-rich" defines an exciting area that spans the world of large arenes to that of highly alkynylated structures including carbon wires, peralkynylated π perimeters, graphdiyne segments, dehydroannulenes, and cyclophane derivatives.[1–9] Carbon-rich organometallic compounds are less explored than their organic counterparts, a tribute to the considerably increased effort in their synthetic access.[10–14] Aesthetic structures, exciting topologies on the nanometer scale, and their modular synthesis, however, make carbon-rich organometallic compounds attractive. Rewards are expected in materials properties that differ from their organic counterparts, such as electroactivity and potential nonlinear optics (NLO) activity. In addition, large carbon-rich organometallic molecules are often surprisingly soluble and form single crystals, which allows their structural characterization in the solid state,[13] a feature that is often elusive for their organic counterparts.

Herein we report the synthesis and structural characterization of three novel organometallic cyclynes[10] with an expanded bicyclo[1.1.0]butane (**A**) and a [2.1.0.0^{1,3}]pentane (**B**) topology. In these structures, the C–C single bonds of the small rings are replaced by alkyne or butadiyne bridges, while the carbon atoms are substituted by benzene rings, cyclobutadiene(cyclopentadienylcobalt) units, or ferrocene centers. Key steps in the synthesis of these targets are the selective *ortho*-metalation of organometallic acetals,[14] and the conversion of aldehydes into alkynes by the Ohira method.[15]

A



B



C

Pd-catalyzed coupling of **1**[14] to the iodide **2a** furnishes **3** in 23% (Scheme 1). The moderate yield of **3** is a result of the two *meta*-positioned alkyne groups in **2a** between which the iodide is sandwiched. Only the active Hartwig catalyst

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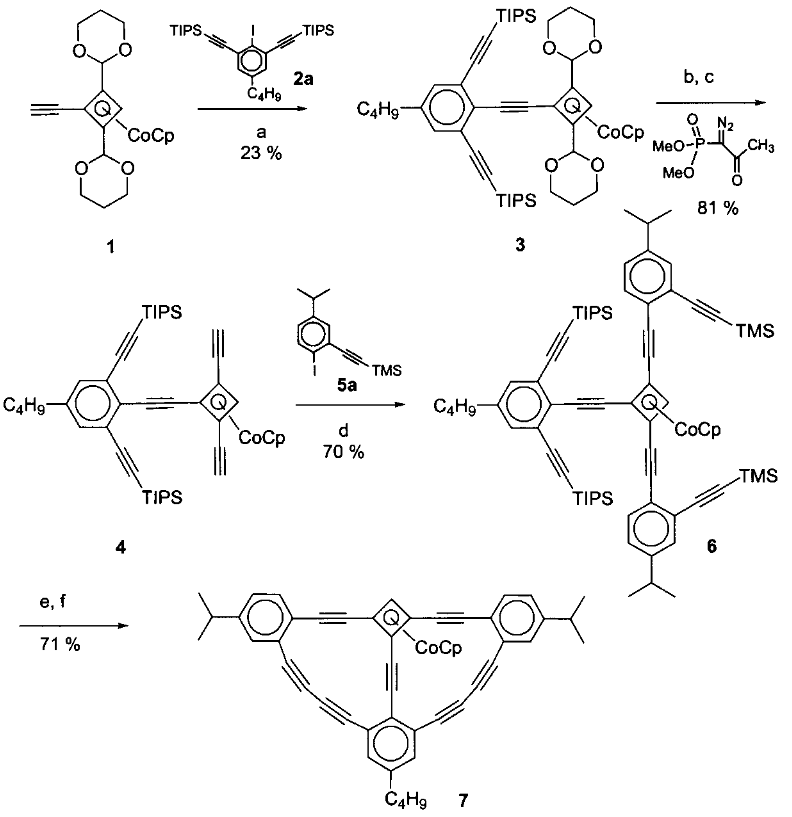
Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

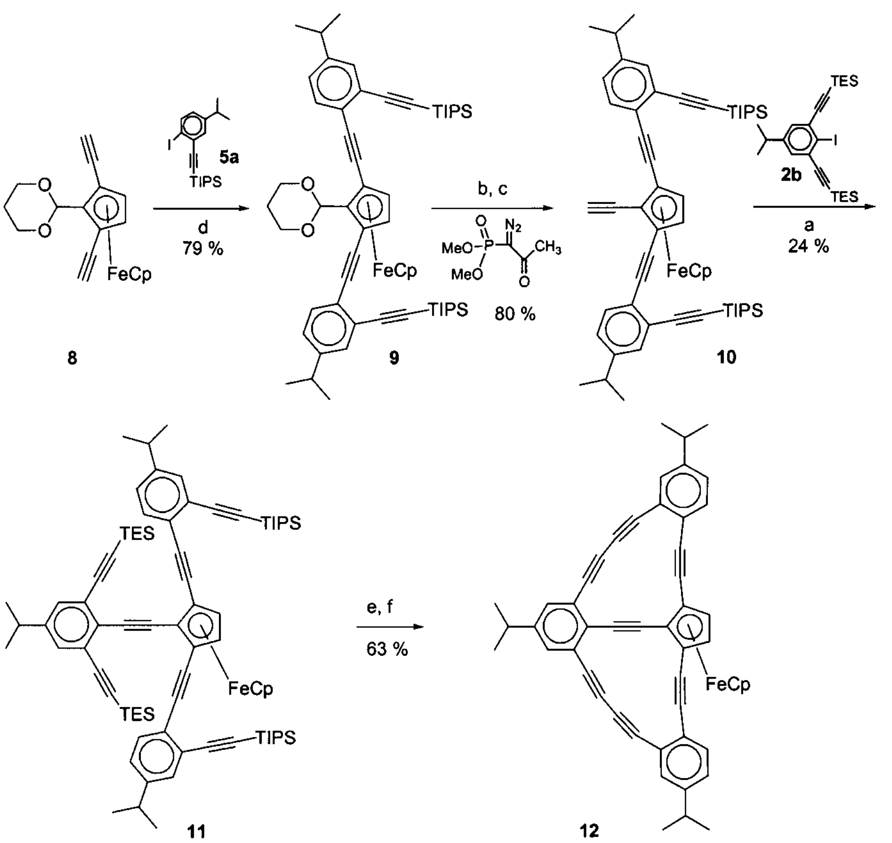


Scheme 1. a) $[\mathrm{Pd}\{\mathrm{P}(o\text{-tolyl}_3)\}_2]$, CuI, NEt_3, THF, 24 °C, 12 h; b) *p*-toluenesulfonic acid, THF, 24 °C, 12 h; c) K_2CO_3, 24 °C, 8 h; d) $[\mathrm{Pd}(\mathrm{PPh}_3)_2\mathrm{Cl}_2]$, CuI, piperidine, THF, 24 °C, 12 h; e) Bu_4NF, THF, 24 °C, 1 h; f) $Cu(OAc)_2$, CH_3CN, 80 °C, 8 h.

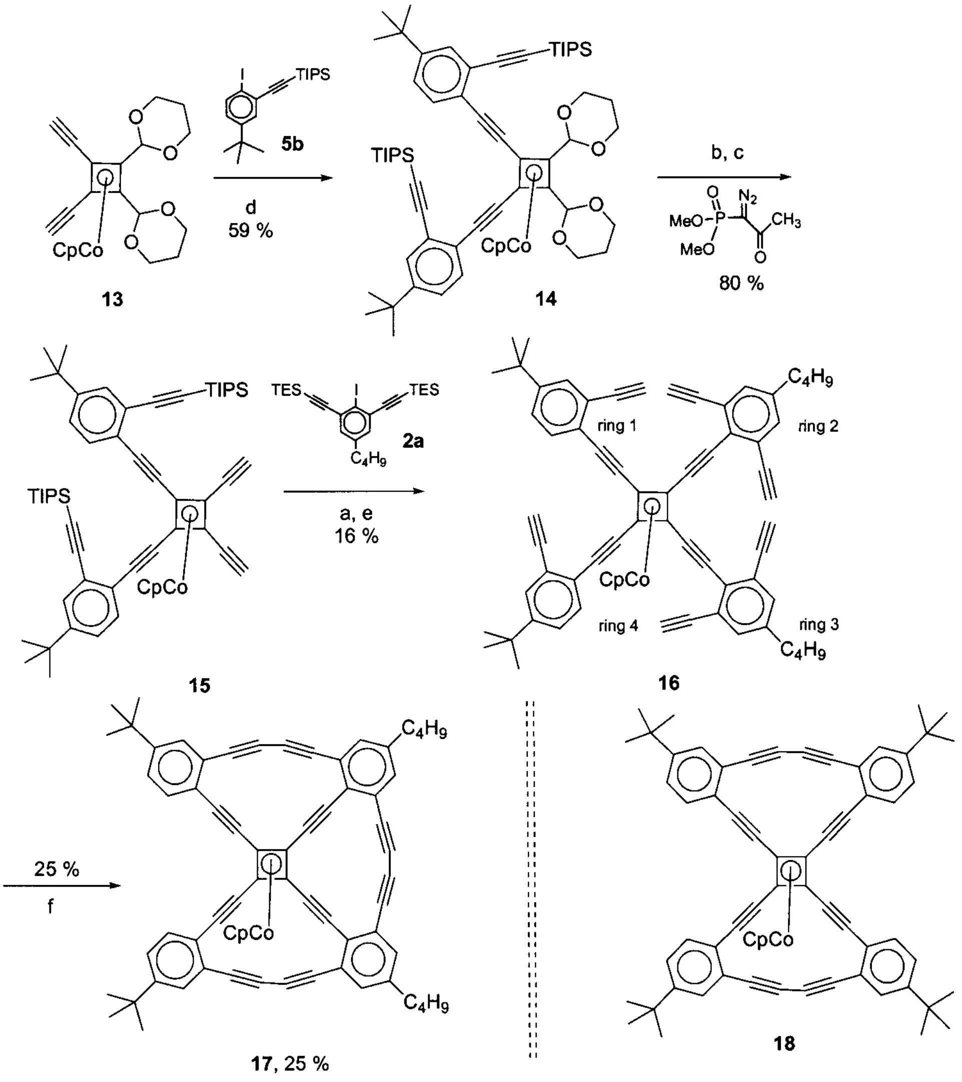
$[\mathrm{Pd}\{\mathrm{P}(o\text{-tolyl})_3\}_2]$[14b] with THF as cosolvent[16] is capable of coupling **1** to **2a**. The coupling product **3** was deketalized and treated with the Ohira–Seyferth reagent $CH_3C{=}OCN_2P{=}O(OMe)_2$[15] to give the pentayne **4** in 81 % yield. Coupling of **4** to **5** furnishes **6** in 70 % yield. Desilylation of **6** proceeds with Bu_4NF in THF; the intermediate heptayne was immediately utilized for the coupling step to close the two cyclyne rings to form **7** in 71 % yield. The six-step synthesis (**1** → **7**) occurs in a respectable overall yield of 9 %.

The ferrocene-containing "super-bicyclo[1.1.0]butane"(**12**) was targeted to show the general applicability of the method. Diyne **8** was treated with **5a** under Pd catalysis (Scheme 2) to furnish **9** in 79 % yield. Deketalization with *para*-toluenesulfonic acid (TsOH) followed by Ohira alkynylation[15] transforms **9** into the pentayne **10** in 80 %. The critical step is the Pd-catalyzed coupling of **10** to **2b** that furnishes **11** in 24 %. The yield of the coupling reaction is only moderate, again as a result of the decreased reactivity the iodide **2b** experiences as a consequence of being positioned between two alkyne substituents. Deprotection of **11** and a double cyclization using $Cu(OAc)_2$ in acetonitrile[15c] gives **12** in 61 % yield as stable, dark-red needles.

It was of interest if a "super-tricyclic" structure analogous to **B** was accessible by this method. A retrosynthetic analysis suggests **13** as the starting point for **17** (Scheme 3). Pd-catalyzed coupling of **13** to **5b** gave **14** in 59 % yield. Deprotection by TsOH and conversion of the two aldehyde groups into alkyne units proceeded under standard conditions[15] to give **15** in 80 %. The critical step is the double Pd-catalyzed coupling of **15** to **2a** that provided **16** in 17 % yield after deprotection with Bu_4NF in THF. The last step in the reaction sequence is the triple ring closure to give **17**, which proceeds in 25 % yield. Significant amounts of insoluble and infusible tan-colored solids are formed as by-products. The relatively low yield of this transformation is a consequence of the underlying statistics of the ring-closing reaction. If the alkynes of benzene rings 1 and 4 in **16** couple, **17** cannot form. Instead cross-linking to form insoluble materials prevails. If the ring-closing reaction proceeds statistically, it is expected that 33 % of **16** will be lost to the unwanted cyclizations, hence, the highest possible reaction yield is 67 %. The actual yield of 25 % suggests that each ring forms



Scheme 2. For reactants and conditions see Scheme 1.



Scheme 3. For reactants and conditions see Scheme 1.

in a satisfactory yield of 72%, if the unproductive coupling pathways are corrected for by a simple statistical analysis.

The novel and intriguing structures of the organometallic super-bicyclo[1.1.0]butanes **7** and **12** as well as the super-tricyclo[2.1.0.0^{1,3}]pentane **17** mandated their single-crystal structure analysis.[17–19] Suitable, coffin-shaped specimens were obtained from mixtures of dichloromethane and hexanes.

ORTEP representations of **7**, **12**, and **17**, and the packing diagram of **12** are shown in Figures 1–3. The bond lengths and bond angles in **7**, **12**, and **17** are in excellent agreement with the reported values for alkynylated cyclobutadiene and cyclopentadienyl complexes.[13, 20]

The polyyne **7** forms a perfect half-wheel. The three radial alkyne units attached to the cyclobutadiene complex are linear. The butadiyne groupings are moderately bent to accommodate the topological requirements of the structure (Figure 1). The substituents (i.e., spokes and periphery of the large hydrocarbon ligand) on the cyclobutadiene complex are considerably less nonplanar than expected for multiply ethynylated complexes of this type.[13, 20] This effect may be a consequence of the direct interconnection of the three alkyne substituents by a network of cyclyne rings.

The ferrocene-based cyclyne **12** (Figure 2) shows considerable in-plane bending of the outer two of the three radial alkyne units, which leads to a slight ruffling of the large hydrocarbon ligand (Figure 2a), similar to that observed in some porphyrins.[21] This ruffling is caused by the minor mismatch of the circumference of the perimeter compared to the size of the radial spokes, and bears testimony to the way the outer π perimeter adapts to the decreased bond angles (72°) prevalent in the ferrocene module relative to the square cyclobutadiene complexes. The packing of **12** is remarkable and shown in Figure 2b. Six molecules of **12** form a circular arrangement that results in a helical superstructure not observed in the packing of **7**.

The structures of the open congeners of **17** and of the butterfly **18** have been described recently.[13] In these species the alkyne bridges are bent away from the cyclobutadiene nucleus to accommodate for the electronic influence of the {CpCo} fragment. It was of interest whether the same distortion was visible in the polyyne **17**. A suitable specimen was obtained from dichloromethane/hexane mixtures and an ORTEP representation of **17** is shown in Figure 3a. The molecules of **17** are disordered in the crystal, but the large hydrocarbon ligand is visibly flattened out (Figure 3b)

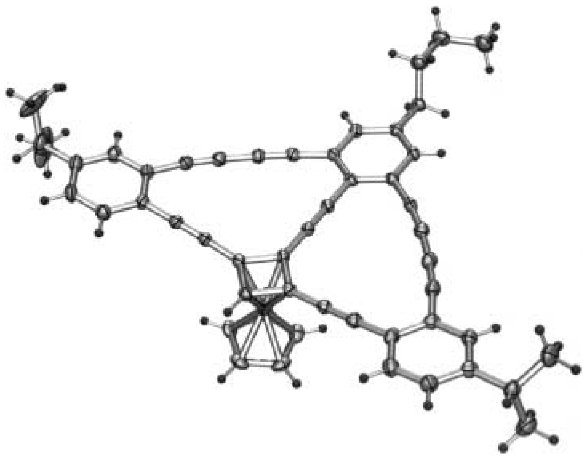


Figure 1. ORTEP representation of the molecular structure of **7**.

compared to the structure of the butterfly-shaped **18**.[13] The flattening is particularly pronounced in the back-side of the large ligand, where the third ring is closed. The full wheel with the topology **C** is expected to be planar, as a result of the geometric relationship of the perimeter to the length of the radial spokes.

In conclusion, a series of novel polycyclic carbon-rich organometallic compounds (**7**, **12**, and **17**) has been prepared by a combination of Ohira alkynylations, Pd/Cu-catalyzed couplings, and $Cu(OAc)_2$-mediated cyclizations. They represent nanoscale versions of **A** and **B**; they have been subjected to single-crystal structure determination and show subtle differences in their structures depending upon the central organometallic core. We will report on the synthesis and characterization of a full wheel with a nanoscale topology of the unknown fenestrane type **C** structure in the future.[22, 23]

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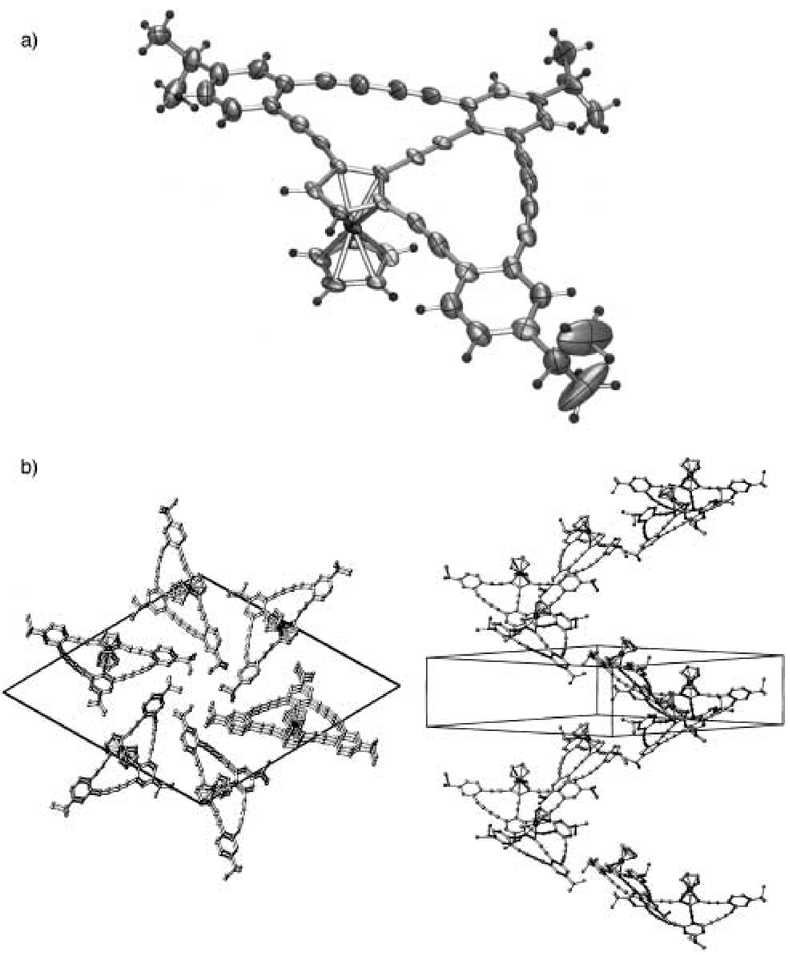

Figure 2. a) ORTEP representation of **12**. b) Packing diagram of **12**. The sixfold axis in which the single molecules of **12** are packed in the solid state is visible.

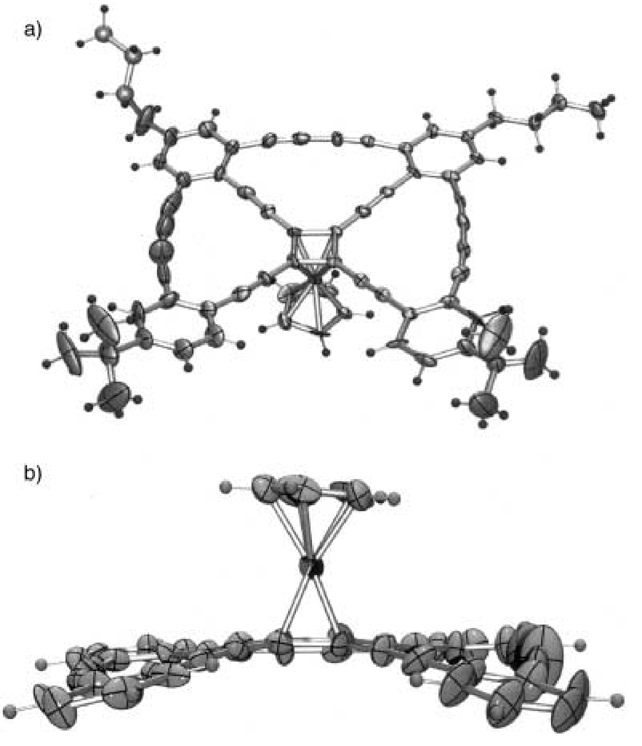

Figure 3. a) ORTEP representation of **17**. b) Side-view ORTEP representation of **17**. Substituents are removed for clarity.

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[1] M. D. Watson, A. Fechtenkötter, K. Müllen, *Chem. Rev.* **2001**, *101*, 1267; A. J. Berresheim, M. Müller, K. Müllen, *Chem. Rev.* **1999**, *99*, 1747; S. Ito, P. T. Herwig, T. Böhme, J. P. Rabe, W. Rettig, K. Müllen, *J. Am. Chem. Soc.* **2000**, *122*, 7698; F. Dötz, J. D. Brand, S. Ito, L. Gherghel, K. Müllen, *J. Am. Chem. Soc.* **2000**, *122*, 7707; T. Weil, U. M. Wiesler, A. Herrmann, R. Bauer, J. Hofkens, F. C. De Schryver, K. Müllen, *J. Am. Chem. Soc.* **2001**, *123*, 8101.

[2] R. Diercks, J. C. Armstrong, R. Boese, K. P. C. Vollhardt, *Angew. Chem.* **1986**, *98*, 270; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 268; P. I. Dosa, C. Erben, V. S. Iyer, K. P. C. Vollhardt, I. M. Wasser, *J. Am. Chem. Soc.* **1999**, *121*, 10430; R. Boese, A. J. Matzger, K. P. C. Vollhardt, *J. Am. Chem. Soc.* **1997**, *119*, 2052.

[3] R. Dembinski, T. Bartik, B. Bartik, M. Jaeger, J. A. Gladysz, *J. Am. Chem. Soc.* **2000**, *122*, 810.

[4] C. Kosinski, A. Hirsch, F. W. Heinemann, F. Hampel, *Eur. J. Org. Chem.* **2001**, 3879; B. Leibrock, O. Vostrowsky, A. Hirsch, *Eur. J. Org. Chem.* **2001**, 4401; G. Schermann, T. Grösser, F. Hampel, A. Hirsch, *Chem. Eur. J.* **1997**, *3*, 1105.

[5] Y. Rubin, T. C. Parker, S. J. Pastor, S. Jalisatgi, C. Boulle, C. L. Wilkins, *Angew. Chem.* **1998**, *110*, 1353; *Angew. Chem. Int. Ed.* **1998**, *37*, 1226; N. Jux, K. Holczer, Y. Rubin, *Angew. Chem.* **1996**, *108*, 2031; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1986.

[6] For an excellent review, see M. M. Haley, J. J. Pak, S. C. Brand, *Top. Curr. Chem.* **1999**, *201*, 82; W. B. Wan, S. C. Brand, J. J. Pak, M. M. Haley, *Chem. Eur. J.* **2000**, *6*, 2044; M. M. Haley, S. C. Brand, J. J. Pak, *Angew. Chem.* **1997**, *109*, 864; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 836; J. J. Pak, T. J. R. Weakley, M. M. Haley, *Organometallics* **1997**, *16*, 4505.

[7] F. Diederich, *Nature* **1994**, *369*, 199; F. Diederich, Y. Rubin, *Angew. Chem.* **1992**, *104*, 1123; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1101; J. D. Tovar, N. Jux, T. Jarrosson, S. I. Khan, Y. Rubin, *J. Org. Chem.* **1997**, *62*, 3432.

[8] G. J. Palmer, S. R. Parkin, J. E. Anthony, *Angew. Chem.* **2001**, *113*, 2577; *Angew. Chem. Int. Ed.* **2001**, *40*, 2509.

[9] Y. Tobe, K. Kubota, K. Naemura, *J. Org. Chem.* **1997**, *62*, 3430.

[10] For an example of an organometallic cyclyne, see J. D. Bradshaw, L. Guo, C. A. Tessier, W. J. Youngs, *Organometallics* **1996**, *15*, 2582.

[11] G. Scholz, R. Gleiter, F. Rominger, *Angew. Chem.* **2001**, *113*, 2559; *Angew. Chem. Int. Ed.* **2001**, *40*, 2477.

[12] U. H. F. Bunz, *Top. Curr. Chem.* **1999**, *201*, 131; U. H. F. Bunz, Y. Rubin, Y. Tobe, *Chem. Soc. Rev.* **1999**, 107.

[13] M. Laskoski, G. Roidl, M. D. Smith, U. H. F Bunz, *Angew. Chem.* **2001**, *113*, 1508; *Angew. Chem. Int. Ed.* **2001**, *40*, 1460; M. Laskoski, M. D. Smith, J. G. M. Morton, U. H. F. Bunz, *J. Org. Chem.* **2001**, *66*, 5174; U. H. F. Bunz, G. Roidl, M. Altmann, V. Enkelmann, K. D. Shimizu, *J. Am. Chem. Soc.* **1999**, *121*, 10719.

[14] a) M. Laskoski, J. G. M. Morton, M. D. Smith, U. H. F. Bunz, *Chem. Commun.* **2001**, 2590; b) for the active catalyst [Pd{P(o-tolyl)$_3$}$_2$], see F. Paul, J. Patt, J. F. Hartwig, *Organometallics* **1995**, *14*, 3030.

[15] a) S. Ohira, *Synth. Lett.* **1989**, *19*, 561; S. Müller, B. Liepold, G. J. Roth, H. J. Bestmann, *Synlett* **1996**, 521; D. F. Taber, Y. Wang, *J. Am. Chem. Soc.* **1997**, *119*, 22; b) for the diazophosphonate, see D. Seyferth, R. S. Marmor, P. Hilbert, *J. Org. Chem.* **1971**, *36*, 1379; D. G. Brown, E. J. Velthuisen, J. R. Commerford, R. G. Brisbois, T. R. Hoye, *J. Org. Chem.* **1996**, *61*, 2540; c) the most efficient alkyne–alkyne coupling reaction we have utilized so far has been developed by: F. Vögtle, R. Berscheid, *Synthesis* **1992**, 58; P. Siemsen, R. C. Livingston, F. Diederich, *Angew. Chem.* **2000**, *112*, 2740; *Angew. Chem. Int. Ed.* **2000** *39*, 2633.

[16] M. M. Haley, personal communication on related transformations.

[17] For details of X-ray crystallography on **7**, **12**, and **17** see the Supporting Information. Crystal data for **7**: $C_{51}H_{37}Co$, $M_r = 708.74$, triclinic, $P\text{-}1$, $a = 10.9507(8)$, $b = 12.1458(8)$, $c = 15.4401(11)$ Å, $\alpha = 86.981(1)$, $\beta = 79.657(1)$, $\gamma = 65.458(1)°$, $V = 1837.2(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.281$ g cm^{-3}. $2\theta_{max} = 50.2°$; 15359 reflections collected, 6532 independent, 5052 with $I > 2\sigma(I)$. No absorption correction ($\mu = 0.50$ mm^{-1}). $R1$, $wR2$ ($I > 2\sigma(I)$) = 0.0416, 0.814, respectively.

[18] Crystal data for **12**: $C_{51}H_{36}Fe \cdot 0.25\,CH_2Cl_2$, $M_r = 725.88$, hexagonal, $P6_3$, $a = 27.174(2)$, $c = 9.1170(7)$ Å, $V = 5830.4(7)$ Å^3, $Z = 6$, $\rho_{calcd} = 1.240$ g cm^{-3}. $2\theta_{max} = 48.2°$; 22326 reflections collected, 5788 independent, 4316 with $I > 2\sigma(I)$. No absorption correction applied ($\mu = 0.46$ mm^{-1}). $R1$, $wR2$ ($I > 2\sigma(I)$) = 0.0623, 0.1231, respectively; GOF = 1.013. 509 parameters refined, 4 restraints (disordered CH_2Cl_2 solvent).

[19] Crystal data for **17**: $C_{69}H_{59}Co$, $M_r = 939.03$, monoclinic, $P2_1/n$, $a = 10.568(1)$, $b = 35.490(4)$, $c = 15.132(2)$ Å, $\beta = 102.215(3)°$, $V = 5547.0(11)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.124$ g cm^{-3}. $2\theta_{max} = 45.1°$; 21290 reflections collected, 7278 independent, 3104 with $I > 2\sigma(I)$. No absorption correction ($\mu = 0.35$ mm^{-1}). $R1$, $wR2$ ($I > 2\sigma(I)$) = 0.1098, 0.2544, repectively; GOF = 1.008. 605 parameters refined. Molecular disorder corresponding to a 90° rotation around the $Co \cdots Cp_{centroid}$ vector is present, but could not be modeled as a result of the small fraction (< 10 %).

[20] U. H. F. Bunz, V. Enkelmann, *Organometallics* **1994**, *13*, 3823.

[21] W. Jentzen, M. C. Simpson, J. D. Hobbs, X. Song, T. Ema, N. Y. Nelson, C. J. Medforth, K. M. Smith, M. Veyrat, M. Mazzanti, R. Rammaseul, J. C. Marchon, T. Takeuchi, W. A. Goddard, J. A. Shellnutt, *J. Am. Chem. Soc.* **1995**, *117*, 11085.

[22] For an example of a hexagonal fenestrane geometry, see W. B. Wan, M. M. Haley, *J. Org. Chem.* **2001**, *66*, 3893.

[23] For examples of planar carbon and bona fide fenestrane geometries in organic and organometallic chemistry, see D. Röttgers, G. Erker, R. Fröhlich, M. Grehl, S. J. Silvero, I. Hyla-Kryspin, R. Gleiter, *J. Am. Chem. Soc.* **1995**, *117*, 10503; M. Thommen, R. Keese, *Synlett* **1997**, 231; D. Kuck, A. Schuster, R. A. Krause *J. Org. Chem.* **1991**, *56*, 3472; S. Grimme, *J. Am. Chem. Soc.* **1996**, *118*, 1529; D. Kuck, *Chem. Ber.* **1994**, *127*, 409.

Hexameric Mg–O Stacks with Six THF-Solvated Sodium Amide Appendages: "Super" Variants of Inverse Crown Ethers Generated by Cleavage of THF[**]

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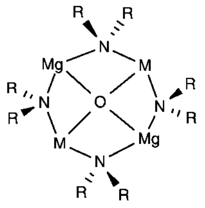
s-Block organometallic compounds are known to be thermodynamically unstable with respect to oxidation or hydrolysis (giving oxides or hydroxides). However, under certain kinetic conditions such reactions may not reach completion but instead stop at intermediate composite structures containing metal cations, oxygen-based anions (usually O^{2-} or OH^-), and organic skeletons. This "oxygen encapsulation" phenomenon[1] has probably existed since these air- and moisture-sensitive compounds first appeared about a century ago, but it is only relatively recently that its detection has become routine (in suitably crystalline samples) through X-ray crystallographic study. Inevitably the proliferation of such studies has meant more structures of this type (mainly formed fortuitously rather than intentionally) coming to light, though the complex factors controlling their formation remain largely in the dark. We are interested in a special class of oxygen-encapsulated compound: inverse crown ethers[2] are mixed alkali-metal magnesium (or zinc) amides, the amido component of which is derived from the exceptionally bulky amines (2,2,6,6-tetramethylpiperidine (tmpH) or 1,1,1,3,3,3-hexamethyldisilazane (hmds(H))). Their common structure is characterized by octagonal $(NM^1NM^2)_2$ rings (e.g. **1**) which act as square-planar tetrametallic hosts for the encapsulation of a *single* anion (either O^{2-} or $(O_2)^{2-}$). Herein we describe a "super" variant to these simple, two-dimensional inverse crown ethers in a new class of heterobimetallic amide, the novel three-dimensional cage construction of which includes *multiple* O^{2-} encapsulation. Moreover we have traced the source of encapsulated O^{2-} ions, often a matter of puzzlement in examples reported previously, to the cleavage of THF solvent molecules used in the reaction.



1

Originally we set out to synthesize hypothetical $[Na_2Mg_2(tmp)_4(O)_x(O_2)_y]$, the missing entry in the series of

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