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Self-Assembly of Trigonal-Prismatic Metallocages Encapsulating $\mathrm{BF_4^-}$ or $\mathrm{CuI_3^{2-}}$ as Anionic Guests: Structures and Mechanism of Formation**

Cheng-Yong Su, Yue-Peng Cai, Chun-Long Chen, Falk Lissner, Bei-Sheng Kang,* and Wolfgang Kaim*

The use of metal ions to promote the self-assembly of discrete, well-defined supramolecular architectures has become an important synthetic strategy during recent years, especially for encapsulating structures which possess an internal cavity capable of accommodating guest molecules.[1] Various large polyhedral structures have been constructed and rationally classified.[2] Among these are the $\mathrm{M_{18}L_6}$ (M = metal, L = ligand) hexahedral cage,[3] $\mathrm{M_{12}L_8}$ and $\mathrm{M_6L_8}$ cube-like cages,[4] and 50-component dodecahedra[5] with high symmetry. However, lower-symmetry hosts can ultimately be expected to show enhanced guest selectivity.[6] Surprisingly, the simplest three-dimensional (3D) canonical cage structure with the fewest number of components ($\mathrm{M_3L_2}$ or $\mathrm{M_2L_3}$), the trigonal prism,[2a] has remained rather uncommon in comparison with the various high-symmetry polyhedra.[7] In contrast to the well studied helical structures,[8] and despite the rapid progress in the construction of various molecular architectures with defined shapes and sizes, the mechanisms of formation for such species are often unknown.[9] To develop synthetically viable pathways for a rational design of discrete molecular architectures, it is important to understand the dynamic behavior of such molecular architectures in solution. In the course of our work on the construction of supramolecular assemblies from tripodal ligands,[10] we now describe the self-assembly of the $\mathrm{M_3L_2}$ trigonal prismatic molecular boxes $[\mathrm{BF_4}{\subset}\{\mathrm{Ag_3(MsTBim)_2}\}](\mathrm{BF_4})_2$ (**1**; MsTBim = 1,3,5-tris(benzimidazol-1-ylmethyl)-2,4,6-trimethylbenzene) and $[\{\mathrm{CuI_3}{\subset}[\mathrm{Cu_3(MsTBim)_2}]\}_2](\mathrm{Cu_2I_4})$ (**2**). The solution ^{1}H NMR spectroscopic study of **1** indicates that the box structure is the thermodynamically stable but kinetically labile product.

The semi-rigid ligand MsTBim,[10e] with an arene core connecting three benzimidazolyl arms is expected to facilitate cage-structure formation instead of encapsulating one or

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[**] This work has been supported by the National Natural Science Foundation of China and the Natural Science Foundation of Guangdong Province. S.C.Y. thanks the Alexander von Humboldt Foundation for a research fellowship.

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

more metal ions as found with other tripodal ligands.[10a–d] Reaction of MsTBim with excess $AgBF_4$ or CuI in MeOH/MeCN (1/1) solution leads to rapid precipitation of solid products, the elemental analyses of which support the formulations $Ag_3(MsTBim)_2(BF_4)_3$ and $(CuI)_{10}(MsTBim)_4$, respectively. While **1** may be readily predicted to contain an M_3L_2 cage structure, the stoichiometry of **2** is less indicative. Even in the case of the 3:2 stoichiometry the topologies may involve an M_6L_4 octahedral cage[11] or square-pyramidal cone,[12] an M_3L_2 trigonal or trigonal-bipyramidal cage[7] as well as unspecified oligomers[10b,c] or well-known (10,3) networks,[13] depending on the size, bond angles, and rigidity of the subunits. The ^1H and ^{13}C NMR spectra of both **1** and **2** show one set of resonance signals comparable with that of the free ligand. The proton signals are shifted downfield, indicative of uniform metal complexation. Furthermore, the simple pattern of the spectrum suggests a single discrete species with a minimum symmetry of C_3. Since larger polyhedral assemblies are disfavored under thermodynamic conditions[9a] and the highly charged polymer structures normally result in broadening of the proton NMR signals,[11c] a trigonal prism of D_{3h} symmetry should be favored. The largest $\Delta\delta$ value of H4 as well as the smallest $\Delta\delta$ value for H2 agrees with the formation of such a metallocage: Although both H4 and H2 hydrogen atoms are expected to lose more electron density upon coordination as a result of being adjacent to a nitrogen donor site, H2 will be shielded through the ring current once a trigonal-prismatic structure is formed.[14]

This prediction is confirmed by X-ray crystallographic analyses of the solid-state structures. For compound **1**, three almost linearly coordinated Ag^+ ions (average N-Ag-N angle of 173.3°) join two face-to-face positioned MsTBim ligands (Figure 1) to give a five-component M_3L_2 metallocage. The six benzimidazolyl arms are nearly perpendicular to the central arene bases, thus generating a relatively regular trigonal-prism structure for the $[Ag_3(MsTBim)_2]^{3+}$ ion with a height of approximately 11 Å and distance of about 6 Å between the edges. One BF_4^- ion is a guest inside the cage while two BF_4^- ions stay outside, together with one acetonitrile and one water molecule, leading to a stoichiometry of $\mathbf{1}\cdot MeCN\cdot H_2O$.

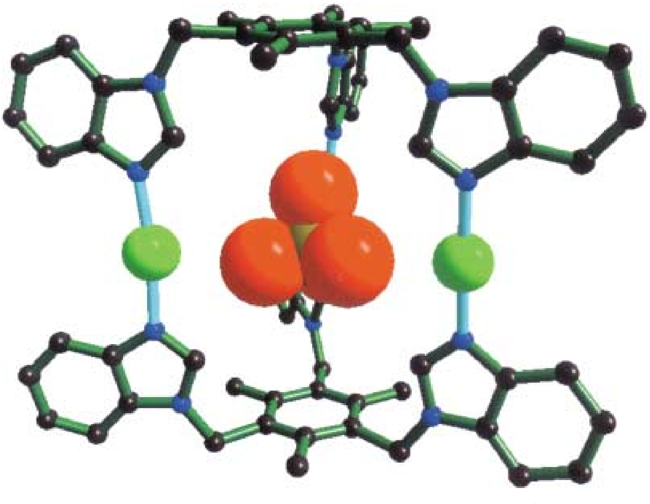

Figure 1. Representation of the $[BF_4\subset\{Ag_3(MsTBim)_2\}]^{2+}$ cage in $\mathbf{1}\cdot MeCN\cdot H_2O$. Key: Ag (green); C (gray); N (blue); F (red), B (gold). The guest is shown in a space-filling mode.

A very similar metallocage is formed in the reaction with CuI. Slow solvent evaporation from the reaction mixture of MsTBim and CuI in MeOH/MeCN/DMF (1/2/2) solution resulted in small crystals the crystallographic analysis of which showed that the structure consists of two independent $[CuI_3\subset\{Cu_3(MsTBim)_2\}]^+$ ions, one $[Cu_2I_4]^{2-}$ ion, and seven water molecules (giving the formulation $\mathbf{2}\cdot 7H_2O$). A essentially identical cage structure, $\mathbf{2}\cdot C_6H_6\cdot 6H_2O$, can be obtained in the presence of benzene. In this latter case, the benzene molecule is located outside the cage as are the six water molecules. In both cases the cations involve the $[Cu_3(MsTBim)_2]^{3+}$ trigonal-prismatic box with slightly bent N-Cu-N (average 158.7°) edges. An additional Cu^+ ion appears to be accommodated in the cage, however, this Cu^+ ion is triangularly surrounded by three iodide anions, therefore, the guest molecule really is the CuI_3^{2-} ion (Figure 2). To the best of our knowledge, such an inclusion of an anionic metal complex into a discrete cationic metallocage has not been reported before; it may be compared with Stang's host–guest molecular squares incorporating coordination of Ag^+ ions by the "π-tweezer effect"[15a–c] or other known ion–cryptate and ion–crown-ether encapsulating systems.[15d–f] Outside the cage there are neutral molecules, and most importantly, an interesting $[Cu_2I_4]^{2-}$ counterion[16] in which two Cu^+ ions are symmetrically bridged by two out of the four I^- ligands leading to the dimer shown in Figure 3.

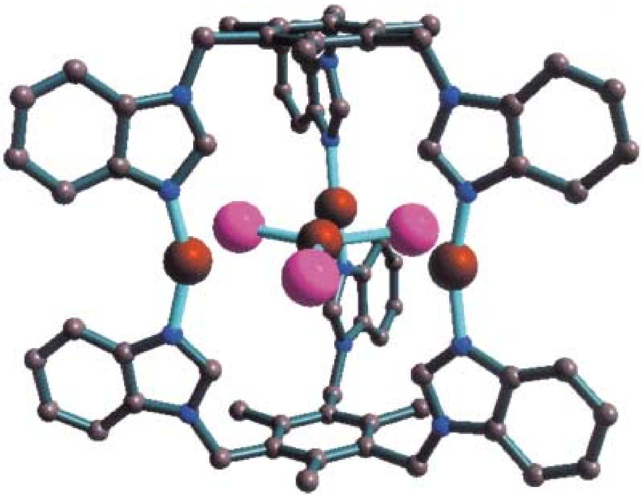

Figure 2. Representation of the $[CuI_3\subset\{Cu_3(MsTBim)_2\}]^+$ cage in $\mathbf{2}\cdot 7H_2O$. Key: Cu (maroon); I (purple); C (gray); N (blue).

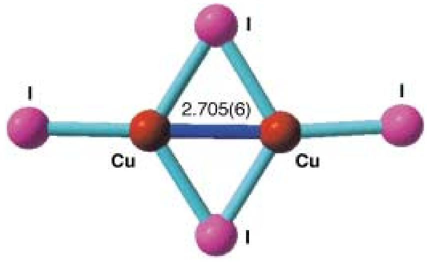

Figure 3. Structure of the counteranion $[Cu_2I_4]^{2-}$ in $\mathbf{2}\cdot C_6H_6\cdot 6H_2O$.

The present metallocages represent the smallest canonical 3D architecture with the shape of a trigonal prism, and are thus counterparts of an M_2L_3 trigonal box, such as $[Ag_2(pbbimb)_3](CF_3SO_3)_2$ (pbbimb = 1,4-bis(benzimidazol-1-ylmethyl)-2,3,5,6-tetramethylbenzene) reported before.[17] Therefore, two complementary strategies to construct compositionally and geometrically different but topologically identical trigonal prismatic boxes can be devised as illustrated in Figure 4. A few other M_3L_2 cages have been designed[7] in which large deviations from the canonical trigonal-prismatic arrangement occur because of the square-planar or tetrahedral coordination of the metal ions used.

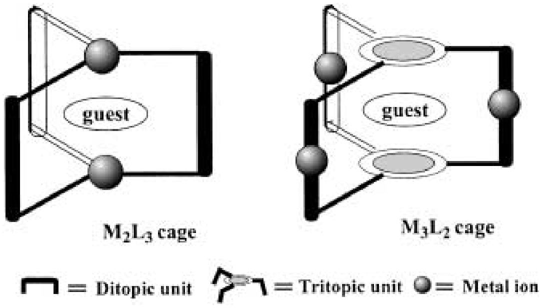

Figure 4. Schematic representation of the complementary trigonal-prismatic metal cages with different compositions but identical topologies.

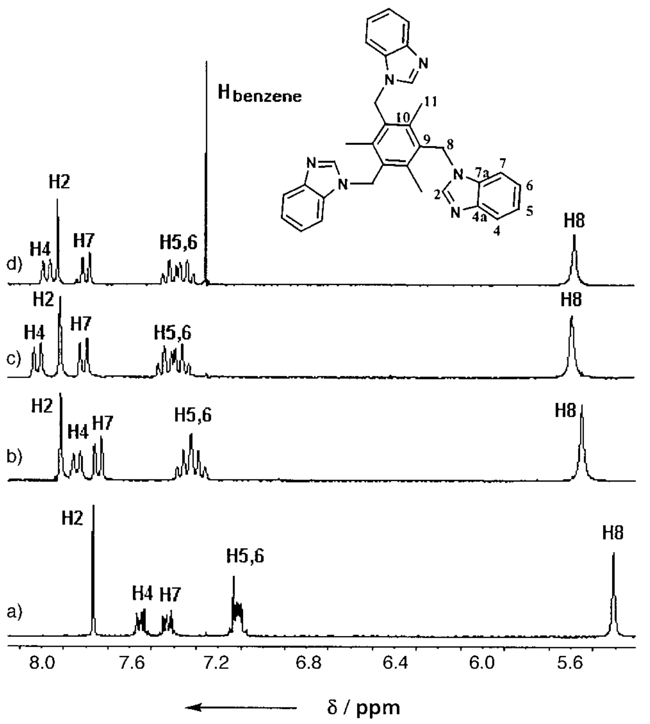

Figure 5. ^1H NMR spectra of a) the ligand MsTBim, b) the reaction mixture from an M:L = 1:1 ratio, c) the reaction mixture from an M:L = 2:1 ratio, d) **1**·C_6H_6.

Considering the varied structural topologies possible even for the same metal-to-ligand ratio, the study of solution dynamics adds information beyond what may be just serendipitous solid-structure analysis. Therefore, the reaction between MsTBim and $AgBF_4$ was carried out in $[D_6]$DMSO solution and monitored by proton NMR spectroscopy (Figure 5). When the metal salt was slowly added to the solution of the ligand (excess of MsTBim), the ^1H NMR spectrum shows one set of ligand signals shifted downfield. This is indicative of complexation, and since no signals of the "free" ligand appear, it also suggests rapid chemical exchange. Continued addition of metal salt leads to further downfield shifts until the metal-to-ligand molar ratio reaches a value of 3:2. The maximum shift is found at this stoichiometry when a spectrum identical with that of the isolated complex is obtained. Excess addition of metal salt has little influence on the proton NMR spectra which establishes quantitative self-assembly of the trigonal prismatic cage **1**. In contrast, on *reverse* order of addition (ligand added to metal salt), only the *reverse* shift of the signals (upfield) was observed without indication of any new resonance. These experiments suggest that the reaction is thermodynamically controlled and that the equilibria are rapidly achieved on the NMR time scale. Such solution dynamics is quite different from that of other known discrete molecular architectures[3,7a,11c,18] in which the formation of oligomeric species or interconversion between several different assemblies can be detected. Although the intermediate is not clear, the rapid exchange between the labile components is prominent even after lowering the temperature to −20 °C. This behavior is a great synthetic advantage in converting all the intermediates into a single product by a "self-correction" mechanism, which leads in this particular case to a trigonal-prismatic box as the smallest possible discrete 3D species.[13] In contrast, the assembly of larger polyhedra is believed to be kinetically controlled[9a] while guest-induced[7a,9b,18a,18c] assembly processes are found for other small metallosupramolecules.

The template effect of the guests in our case seems not specific because they can vary from the spherical BF_4^- ion to the planar CuI_3^{2-} motif. In an effort to increase the anion size while maintaining the same cage structure $AgCF_3SO_3$ was used as starting material; the $CF_3SO_3^-$ ion may not fit inside the final cage. An ^1H NMR spectrum of the complex $[Ag_3(MsTBim)_2](CF_3SO_3)_3 \cdot C_6H_6 \cdot C_6H_5CH_3$[19] formed from the reaction of MsTBim with $AgCF_3SO_3$ in MeOH/MeCN/C_6H_6/$C_6H_5CH_3$ (3/2/1/1) showed almost the same signal pattern as that of **1**, indicative of formation of the same metallocage. X-ray diffraction analyses of crystals grown from this reaction mixture failed to clearly reveal the location of the anions because of the poor data quality. However, reliable structural results are available for $[Ag_3(MsTBim)_2](CF_3SO_3)(BPh_4)_2$[20] which was prepared by carefully adding two molar equivalents of $NaBPh_4$ to the above reaction mixture. Since the BPh_4^- ion is too large to be accommodated inside the cage, the $CF_3SO_3^-$ ion would remain the only anionic template to induce the formation of the cage structure (if necessary). Structural analysis shows that the $CF_3SO_3^-$ ion is located *beside* the cage with the SO_3^- group facing one of the three "windows" of the cage (see Figure S1, Supporting Information). The two BPh_4^- ions occupy the other two windows with one phenyl ring each pointing inward. Therefore, the center of the cage is undoubtedly empty (Figure S2). This finding suggests that formation of such thermodynamically stable cages may not necessarily involve an anionic template effect. Further confirmation of this suggestion by preparation of the same cage with exclusively BPh_4^- ions was prevented by the low solubility of $AgBPh_4$. Recrystallization of **1** in the presence of benzene, toluene, 1,3,5-triethylbenzene, or triphenylamine, only resulted in formation of **1**·C_6H_6. ^1H NMR spectroscopic investigations showed no noticeable shift of the resonance signals of both **1** and benzene (Figure 5 d), which suggests that benzene does not enter the cage, in agreement with the solid-structure analysis result of **2**·C_6H_6·6 H_2O.

It has been found that once an assembled structure is "locked" into a kinetically stable form, a lot of important properties may be available as manifested by the report of a thermally switchable molecular lock,[18c] resolution of a chiral supramolecular assembly made from labile components,[18b] and, more recently, postmodification of molecular rectangles resulting in enhanced structural stability.[6] Therefore, the present thermodynamically stable but kinetically labile metallocages may provide good models for similar studies which are currently under way.

Experimental Section

General procedure for preparation of **1** and **2**: A MeOH solution of MsTBim was added to a solution of MeCN containing excess $AgBF_4$ or CuI and the resulting mixture was stirred for 10 min. The solid products were collected by filtration and dried. **1**: Yield 90 %. Elemental analysis calcd (%) for $C_{66}H_{60}N_{12}Ag_3B_3F_{12}$: C 49.38, H 3.77, N 10.47; found: C 49.46, H 3.79, N 10.40; ^1H NMR (250 mHz, $[D_6]$DMSO): $\delta = 8.12$ (d, 6 H, H_4), 8.02 (s, 6 H, H2), 7.91 (d, 6 H, H7), 7.54 (m, 6 H, H6), 7.46 (m, 6 H, H5), 5.69 (s, 12 H, H8), 2.36 ppm (s, 18 H; Me); ^{13}C NMR (250 mHz, $[D_6]$DMSO): $\delta =$ 143.70 (C2), 141.14 (C4a), 140.72 (C7a), 133.43 (C9), 130.82 (C10), 124.80 (C4), 124.26 (C7), 119.71, (C5), 112.06 (C6), 44.32 (C8), 16.73 ppm (C11). **2**: Yield 83 %. Elemental analysis calcd (%) for $C_{132}H_{120}N_{24}Cu_{10}I_{10}$: C 40.17, H 3.06, N 8.52; found: C 40.47, H 3.08, N 8.99; ^1H NMR ($[D_6]$DMSO): $\delta =$ 8.10 (s, 6 H, H2), 8.08 (d, 6 H, H4), 7.79 (d, 6 H, H7), 7.53 (m, 6 H, H6), 7.48 (m, 6 H, H5), 5.71 (s, 12 H, H8), 2.31 ppm (s, 18 H; Me); ^{13}C NMR ($[D_6]$DMSO): $\delta = 145.88$ (C2), 140.49 (C4a), 140.19 (C7a), 135.73 (C9), 130.20 (C10), 124.14 (C4), 124.01 (C7), 119.43, (C5), 112.04 (C6), 45.61 (C8), 15.82 ppm (C11).

Crystal data for **1**·MeCN·H_2O: $M_r = 1664.4$, tetragonal, space group $P4(2)/n$, $a = 27.824(4)$, $c = 18.108(4)$ Å, $V = 14020(4)$ Å^3, $T = 173$ K, $Z = 8$, 10367 unique reflections measured, final $R1 = 0.0801$ and $wR2 = 0.1859$ for 6184 observed $[I > 2\sigma(I)]$ reflections. **2**·7 H_2O: $M_r = 4083.11$, triclinic, space group $P\bar{1}$, $a = 16.935(3)$, $b = 17.165$ (3), $c = 30.625(6)$ Å, $\alpha = 101.72(3)$, $\beta = 102.94(3)$, $\gamma = 91.36(3)°$, $V = 8473(3)$ Å^3, $T = 293$ K, $Z = 2$, 10822 unique reflections measured, final $R1 = 0.0847$ and $wR2 = 0.2301$ for 8007 observed reflections. **2**·C_6H_6·6 H_2O: $M_r = 4133.12$, monoclinic, space group $P2(1)/n$, $a = 19.893(6)$, $b = 40.398$ (13), $c = 23.814(9)$ Å, $\beta = 108.19(2)°$, $V = 18182(11)$ Å^3, $T = 173$ K, $Z = 4$, 16630 unique reflections measured, final $R1 = 0.0817$ and $wR2 = 0.1726$ for 5856 observed reflections. CCDC-177761 (**1**·MeCN·H_2O), CCDC-177762 (**2**·7 H_2O), CCDC-177763 (**2**·C_6H_6·6 H_2O) 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).

One of BF_4^- ion in **1** and the counteranion $[Cu_2I_4]^{2-}$ in **2**·7 H_2O are disordered over two positions. Water molecules in all three compounds are severely disordered. Because of weak diffraction most of C and N atoms in **2**·C_6H_6·6 H_2O were refined isotropically.

Received: February 6, 2002
Revised: April 15, 2002 [Z18663]

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[14] A similar ^1H NMR spectrum of the Cu^+ complex obtained from the reaction of MsTBim with $[Cu(CH_3CN)_4]BF_4$ in MeOH/MeCN/C_6H_6/$C_6H_5CH_3$ (3/2/1/1) solution indicates that the same metallocage is formed. The M_3L_2 metal-to-ligand ratio of 3:2 for $[Cu_3(MsTBim)_2(BF_4)_3]_2$·$C_6H_6$·$C_6H_5CH_3$·$H_2O$ is evident from elemental analysis (%) calcd for $C_{145}H_{136}N_{24}Cu_6B_6F_{24}O$: C 55.59, H 4.38, N 10.73; found: C 55.75, H 4.39, N 10.56; ^1H NMR (CD_3CN): $\delta = 8.01$ (s, 12 H, H2), 7.97 (d, 12 H, H4), 7.89 (d, 12 H, H7), 7.58 (m, 12 H, H6), 7.51 (m, 12 H, H5), 7.37 (s, 6 H, C_6H_6), 7.14–7.28 (m, 5 H, $C_6H_5CH_3$), 5.57 (s, 24 H, H_8), 2.33 (s, 3 H; $C_6H_5CH_3$), 2.27 ppm (s, 36 H; Me).

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[19] Elemental analysis calcd (%) for $C_{82}H_{74}N_{12}Ag_3F_9O_9S_3$: C 50.19, H 3.80, N 8.57; found: C 50.40, H 3.67, N 8.84; ^1H NMR (($[D_6]$DMSO):

$\delta = 8.09$ (d, 6H, H4), 8.02 (s, 6H, H2), 7.91 (d, 6H, H7), 7.54 (m, 6H, H6), 7.46 (m, 6H, H5), 7.36(s, 6H, C_6H_6), 7.13–7.28 (m, 5H, $C_6H_5CH_3$), 5.70 (s, 12H, H8), 2.34(s, 18H; Me), 2.29 ppm (s, 3H; $C_6H_5CH_3$).

[20] Crystal data for $[Ag_3(MsTBim)_2](CF_3SO_3)\cdot(BPh_4)_2$: $M_r = 2132.35$, monoclinic, space group $C2/c$, $a = 25.866(5)$, $b = 18.041(4)$, $c = 22.125(4)$ Å, $\beta = 96.90(3)°$, $V = 10250(4)$ Å^3, $T = 293$ K, $Z = 4$, 8663 unique reflections measured, final $R1 = 0.0744$ and $wR2 = 0.1981$ for 5554 observed $[I > 2\sigma(I)]$ reflections. CCDC-183553 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 CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit @ccdc.cam.ac.uk). The $CF_3SO_3^-$ ion is disordered along the C_2 axis.

Two-Step, Stereoselective Hydrazidoarylation of 1,3-Cyclopentadiene[**]

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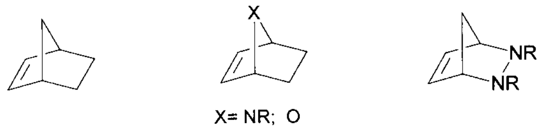
Dieter E. Kaufmann*

The first palladium-catalyzed reductive phenylation of norbornene (**1**) was published by Larock and Johnson[1] in 1989; since then the high synthetic potential of the hydroarylation[2] and especially its asymmetric variant[3] with bicyclic alkenes for the one-step construction of three asymmetric centers has induced a line of follow-up papers. This situation is especially true for the hydroarylation of the 7-aza- and oxabicyclic alkenes **2** (Scheme 1)[2b–d,3c] as this synthetic route even in the case of the asymmetric pathway leads directly to the biologically highly active alkaloid Epibatidine[4] and its analogues.

As we are interested in both the hydroarylation of bicyclic alkenes and, herein, in the use of these products in the stereoselective synthesis of substituted cyclopentane derivatives, we have investigated the hydroarylation followed by reductive cleavage of the easily accessible[5] 2,3-diazabicyclo[2.2.1]heptenes **3**,[6] in which the N–N[7] or C–N bond[8] represents an internal point of fracture.



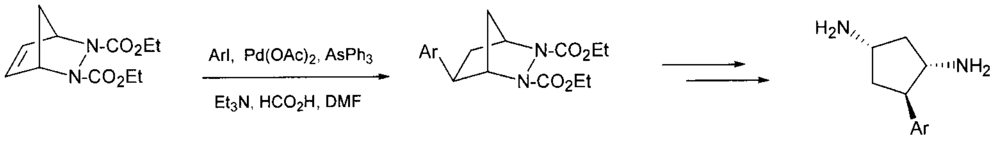
1 **2** **3**

Scheme 1. (Hetero)norbornenes **1**–**3** as starting materials for hydroarylation reactions.

Recently, we have reported the first palladium-catalyzed hydroarylation of the N,N′-diethoxycarbonyl-substituted derivative **4** of **3** with triethylamine as a base.[6] The following selective N–N bond cleavage opens a highly stereoselective way to the *trans*-4-aryl-*cis*-1,3-diaminocyclopentanes **6** (Scheme 2).

Encouraged by this initial result, we turned to the hydroarylation of the sterically more hindered and more rigid, tri- or tetracyclic Diels–Alder adducts of 1,3-cyclopentadiene with the very reactive azodienophiles 4-phenyl-1,2,4-triazoline-3,5-dione (**7a**) and 2,3-phthalazine-1,4-dione (**7b**). The reaction of **7a** with iodobenzene was chosen as a model system with which to optimize the reaction conditions; selected experiments are shown in Table 1.

We started with the reaction conditions (Et_3N, DMF, 65 °C, entry 1) which were optimal in case of the hydroarylation of **4**; besides 21% of the expected hydroarylation product **8a**, compound **9a** was formed in 9% as the product of a C–N cleavage reaction. Formally, the formation of **9a** is the result of a 1,2-hydrazidoarylation on the primarily employed 1,3-cyclopentadiene. From the ^1H and ^{13}C NMR spectroscopic data it appeared that the *trans* isomer **9a** was formed exclusively. The structural assignment is difficult in case of five-membered ring systems; however, the stereochemistry was unambiguously supported by an X-ray analysis (Figure 1).[9,10]



4 **5** **6**

Scheme 2. Stereoselective synthesis of threefold substituted cyclopentane derivatives.

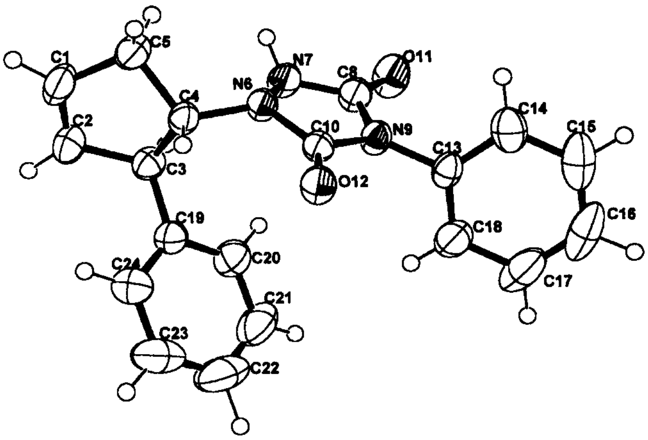


Figure 1. ORTEP plot of **9a**.

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[**] Palladium-catalyzed reactions, part 4; part 3 ref [6]. We thank BAYER AG, Leverkusen and Fond der Chemischen Industrie (Germany) for financial support.