capsule's internal space of 420 Å^3. The proper filling of space is an essential determinant of reversible encapsulation: guests that fill slightly more than half of the available space lead to the most stable complexes.[5] Either guest can interact favorably with the polar seam of hydrogen bonds that hold the capsule together through their modest dipole moments (1.15 **D** for $CHCl_3$ and 2.1 **D** for $ClCH(CH_3)_2$).

The different combinations and isomeric constellations introduced here represent information, temporarily stored in the form of a binary code. The symmetry of the capsule reduces the capacity to six bits from the eight expected. Long-term storage of data on the nanometric scale may follow when their arrangements can be precisely controlled, maintained, and retrieved. In the meantime, reversible assembly provides access to capsules with volumes capable of surrounding numerous guests.[6,7] The well-defined sizes and shapes of the cavities impose limitations on the motions of the guests, both internal, such as ring inversion[8,9] or external, such as molecular translation and tumbling.[10–12] Guest–guest interactions[13] offer even more possibilities for information storage and we explore them in the sequel.

Received: August 5, 2002
Revised: October 29, 2002 [Z19884]

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Modular-Assembled Bowls and Crowns

Modular Cavity-Tunable Self-Assembly of Molecular Bowls and Crowns as Structural Analogues of Calix[3]arenes**

Shu-Yan Yu, Hui Huang, Hong-Bo Liu, Zhong-Ning Chen, Rongben Zhang, and Makoto Fujita*

The construction of container molecules is still an interesting topic in organic synthesis, particularly bowl-shaped molecules, such as calixarenes, because of their potential applications in a variety of areas of supramolecular chemistry.[1] In contrast to the inorganic approach, metal-directed self-assembly has been widely employed to construct well-defined metal–organic container molecules.[2] Metal-assembled bowl-shaped molecules that are structural analogues of calixarenes, such as metallacalix[3]arenes,[3] metallacalix[4]arenes,[4] and others[5,6] have attracted considerable attention. We obtained a metal–organic nanobowl by self-assembly,[7] which was found to assemble in aqueous media to form a dimeric capsule that contains a large hydrophobic pocket inside the framework.[8] This pocket served as a reaction container for a highly stereoselective [2+2] photodimerization of olefins.[9] These findings inspired us to develop structurally and functionally new container molecules with calixarene features to conform with certain molecular architectures, and various reactions. In addition, we noted that among the few inorganic analogues of calixarenes, conformational conversion usually occurred because of the flexibility of the ligand, and because of distortion of the coordination geometry, as found in some metallacalix[3]arenes (with partial cone conformer),[6] and metallacalix[4]arenes (with isomers).[4] Therefore, self-assembled metallacalixarenes with single rigid conformations (i.e., cone conformer, bowl form, and *all-syn* conformation) are

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[*] Prof. Dr. S.-Y. Yu, H. Huang, Dr. H.-B. Liu, Prof. Dr. R. Zhang
State Key Laboratory of Polymer Physics and Chemistry
Center for Molecular Science
Institute of Chemistry
Chinese Academy of Sciences
Beijing 100080 (P.R. China)
Fax: (+86) 10-6255-9373
E-mail: syu@infoc3.icas.ac.cn

Prof. Dr. Z.-N. Chen+
State Key Laboratory of Structural Chemistry
Fujian Institute of Research on the Structure of Matter
Chinese Academy of Sciences
Fuzhou 350002 (P.R. China)

Prof. Dr. M. Fujita
Department of Applied Chemistry
Graduate School of Engineering
The University of Tokyo
bunkyo-ku, Tokyo 113-8656 (Japan)

[+] Crystal structure analysis.

[**] The project supported by National Natural Science Foundation of China No. 90206013.

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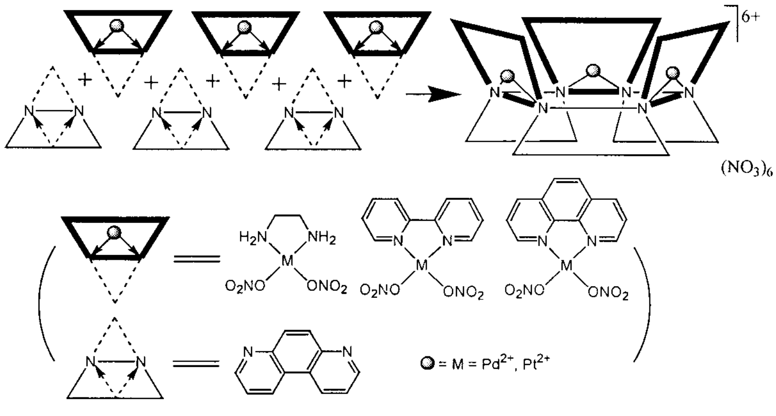

Scheme 1. Modular self-assembly of the crowns. See text for details.

rare.[3] To obtain the cone conformer, which is a structural analogue of calix[3]arenes, we prepared modular, cavity-tunable self-assembly molecular bowls and crowns with unique (*syn, syn, syn*) conformations, the basic principle of which is shown in Scheme 1.

These metallacalix[3]arenes are self-assembled from six planar modules, three metal-coordination-complex ions, and three rigid aromatic ligands (4,7-phenanthroline; L). The metal-coordination complexes are *cis*-protected metal centers that direct the coordination angle to 90°, such as $[Pd(NO_3)_2(en)]$, $[Pt(NO_3)_2(en)]$ (en = ethylenediamine), $[Pd(NO_3)_2(bpy)]$, $[Pt(NO_3)_2(bpy)]$ (bpy = 2,2′-bipyridine), $[Pd(NO_3)_2(phen)]$, and $[Pt(NO_3)_2(phen)]$ (phen = 1,10-phenanthroline). In the ideal case, the three L modules form rigid 60° corners, which favor coordination to three linear metal complexes to self-assemble into an equilateral triangle;[10] but in the examples reported herein, the three ligand modules form a cone to link the three metal-complex units, which results in the formation of a trimetal bowl or crown with a charge of 6+. The lower cavity (below the trimetal triangular plane) consists of the three modules of L; while the upper cavity (above the trimetal triangular plane) consists of the three modules of the square-planar-coordinated metal Pd or Pt. Both cavities exhibit *syn, syn, syn* orientation and cone conformation, confirmed by solution NMR spectroscopy and X-ray crystallographic studies.

The treatment of $[Pd(NO_3)_2(en)]$ with a solution containing one equivalent of L in D_2O at room temperature over several minutes leads to formation of $[\{Pd(en)\}_3L_3](NO_3)_6$ (**1**) in quantitative yield. The ^1H NMR spectra shown in Figure 1a are consistent with a highly symmetrical structure and are indicative of a single product in solution. The resonance signals labeled □ correspond to the ligand 4,7-phenanthroline. Surprisingly, the resonance signals at approximately $\delta = 3.0$ ppm assigned to the CH_2 group of ethylenediamine are a pair of doublets, indicative of two different environments that cannot be averaged. This is characteristic of a cone conformer, as exemplified by *p-tert*-butylcalix[4]arene,[11] rather than metallacalix[4]arenes, where other isomers exist (1,3-alternate conformer, cone),[4] or metallacalix[3]arene (partial cone).[6] The Pt analogue, $[\{Pt(en)\}_3L_3](NO_3)_6$ (**1′**) was obtained at elevated temperature (100 °C, 24 h) by a similar route to that of **1**, and the resonance signals assigned to CH_2 of the ethylenediamine are similar to those of **1** (compare Figure 1a and Figure 1b). Therefore, **1′** has the same structure as **1**, that is, a trimetal-center molecular bowl with a charge of 6+. The self-assembly of **1′** is thermodynamically favored, since the slow transformation from the kinetic products into **1′** was observed at room temperature over 24 h (Figure 1c). NMR monitoring experiments showed that the addition of an excess quantity of a solution containing the nitrate anion to a solution of **1** or **1′** does not lead to any significant chemical shift, which indicates that the binding of the nitrate anion to the bowl reached saturation during the formation of the bowl. Furthermore, when the nitrate anion was replaced with the acetate anion as the leaving group in the starting material, again the bowl formed, which was confirmed by NMR spectroscopy. Three acetate anions were found to be encapsulated within the bowls resulting in a downfield shift of 1.0 ppm of the resonance signals associated with the acetate anion relative to those of the free acetate anion. It seems that the formation of the bowl is not affected by varying the counter anion.

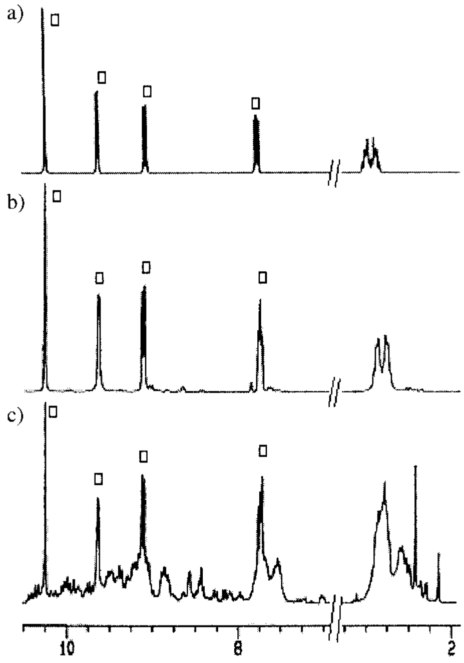

Figure 1. Self-assembly of **1** and **1′**. a) ^1H NMR spectrum of **1**, b) ^1H NMR spectrum of **1′**, c) ^1H NMR spectrum of a sample taken from the reaction of $[Pt(NO_3)_2(en)]$ with L in a 1:1 molar ratio at room temperature after 24 h.

The X-ray crystal structure analysis of **1**[12] shows that the solid-state structure is the same as that in solution. The structure of **1** (Figure 2) comprises a bowl with a binding nitrate anion, together with an empty bowl (omitted for clarity). The three rigid modules of L make up the bowl

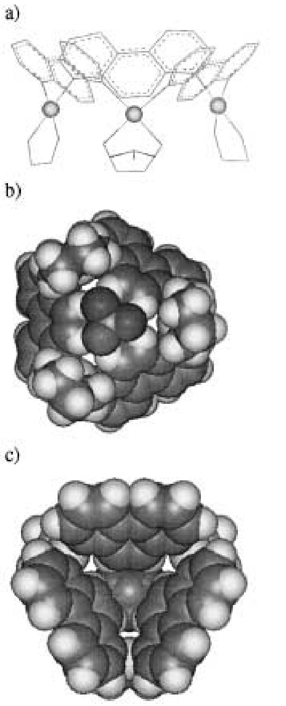

Figure 2. Crystal structure of **1** binding an NO_3^- ion (at the bottom; space-filling CPK presentation): a) side view, b) bottom view along the pseudo-C_3 axis, c) top view along the pseudo-C_3 axis.

framework; these L modules are bridged by three square-planar coordination modules [Pd(en)] in a *syn, syn, syn* orientation, thus the two methylene hydrogen atoms of each en group are in different environments. The bowl can be likened to a calix[3]arene with a cone conformation, in which each [Pd(en)] is related to a methylene group on the backbone of a calix[3]arene. In the metallacalix[3]arene **1**, the three Pd atoms build up an almost equilateral triangle with Pd···Pd distances of 7.64(1), 7.64(1), and 7.69(1) Å. The dimensions of the bowl are as follows: 8.63(1), 8.63(1), and 8.31(1) Å for the upper-rim lengths (i.e. the distances between the midpoints of the 1,10 position of L); 3.62(2) Å in depth; the dihedral angles between L and the tripalladium triangular plane are 52.0(2), 52.0(2), 45.9(1)°. The NO_3^- ion lies below the tripalladium triangular plane (at the bottom of the bowl) with Pd···O distances of 4.01(2), 4.01(2), and 3.78(1) Å, which are significantly longer than those reported by Lippert et al[3] for a complex in which the NO_3^- ion is situated at the center of a triplatinum plane (Pt···O 3.2(1)–3.5(1) Å). The strength of the binding between the NO_3^- ion and the Lewis acidic Pd atoms is limited because of the steric hindrance of the rigid L, since the (L)C···O(NO_3^-) distances of 3.31(2) Å are short (Figure 2b). The N atom of the NO_3^- ion is distorted by 0.337(4) Å out of the plane formed by the three O atoms towards the center of the tripalladium plane, to form a trigonal pyramid. Such a distortion arises from the equilibrium formed between the electrostatic interaction of the metal centers and the anion, and the steric hindrance. To our knowledge, similar examples have not been found in cationic receptors with soft, or symmetrical coordination environments.[13]

The anion binding for the SO_4^{2-} ion was investigated by NMR spectroscopic titration experiments. Increasing concentrations (0.5–2.5 equiv; 0.01–0.05 M) of an aqueous solution of Na_2SO_4, were added to an aqueous solution of the free bowl **1** (0.020 M). The results of NMR spectroscopy support the formation of a 1:1 host–guest complex in aqueous media. Downfield shifts for the signals associated with the 5-H and 6-H of 4,7-phenanthroline (Scheme 1) were observed with the addition of a solution of Na_2SO_4, indicating the substitution of the bound NO_3^- ion. The association constant (K_{ass})[14] for the 1:1 host–guest complex was estimated to be about 250, which is close to that previously reported.[3]

To enlarge the cavity size and to strengthen π-receptor function, aromatic ligands such as bpy and phen were coordinated *cis* to the Pd^{II} or Pt^{II} metal center. Unlike when [Pd(en)] or [Pt(en)] are employed as building blocks, the rigid aromatic-ligand metal complex can construct a second cavity by coupling with L, thus resulting in the formation of a molecular crown such as $[\{Pd(bpy)\}_3L_3(NO_3)_6$ (**2**), $\{[Pt(bpy)]_3L_3\}(NO_3)_6$ (**2′**), $\{[Pd(phen)]_3L_3\}(NO_3)_6$ (**3**), and $\{[Pt(phen)]_3L_3\}(NO_3)_6$ (**3′**).

Compound **2** or **3** readily self-assemble by the combination of $[Pd(NO_3)_2(bpy)]$ or $[Pd(NO_3)_2(phen)]$, respectively with L in a 1:1 molar ratio under mild conditions (40 °C, several minutes). However, the formation of the Pt analogues **2′** or **3′** require harsher conditions (100 °C, 24 h, excess $NaNO_3$). All reactions were monitored by NMR spectroscopy. The spectrum of **2** has highly symmetrical resonance signals, which indicate that the product is a unique tripalladium crown (Scheme 1). The self-assembly product formed under ambient conditions is kinetically favorable because of the labile Pd^{II}–N bonding. The NMR spectra indicate that the predominant species is the triplatinum crown **2′**, which occurs together with some oligomers. According to the concept of a molecular lock,[15] it is necessary to make the inert Pt^{II}–N bond labile if the Pt^{II} ion is to be involved in some self-assembly events. Under the harsher conditions used, the self-assembly gives the thermodynamically most favorable product **2′**, that is, the locked form (cycle closed) as the triplatinum crown. The completion of the self-assembly process is promoted not only by heating, but also by the interaction between NO_3^- ions and the Pt centers.

X-ray crystal structure analysis confirms the crown structure of **2** (Figure 3).[16] The three Pd atoms form an approximately equilateral triangle with Pd···Pd distances of 7.61(2), 7.62(1), and 7.71(3) Å. The lower cavity (below the tripalladium triangle consisting of the three modules of L) presents a bowl structure with a *syn, syn, syn* orientation and cavity size (7.99(1), 8.20(3), and 7.34(2) Å for the rim lengths; 3.6(2) Å in depth; dihedral angles between L and the tripalladium triangular plane are 62.7(2), 58.7(2), 47.4(2)°, slightly smaller than those of **1** because of the decreased flexibility within the metal-complex modules. The lower cavity (consisting of the three L modules) is quite stable, and therefore serves as a scaffold during the assembly process.

Significantly, the upper cavity (above the tripalladium triangle consisting of the three square-planar $(bpy)Pd^{2+}$ modules)has the following dimensions: 9.38(3), 9.34(2), and 10.16(4) Å for the rim lengths (i.e. the distances between two

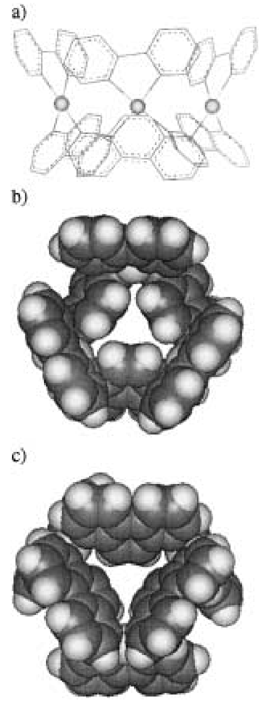

Figure 3. Crystal structure of **2** (space-filling CPK presentation): a) side view, b) bottom view along the pseudo-C_3 axis, c) top view along the pseudo-C_3 axis.

midpoints of the 6,6′ positions of bpy); 5.38(5) Å in depth; dihedral angles between the square planar (bpy)Pd^{2+} modules and the tripalladium triangular plane: 73.2(2), 72.7(2), and 74.7(2)°. The upper cavity, which contains the three Lewis acid centers, is larger than the lower cavity and is expected to exhibit more important receptor chemistry . Noteworthy, no NO_3^- ions are bound to any Pd atoms within the crown. As both the upper and the lower cavity are hydrophobic, the aqueous NO_3^- ions are unable to access the tripalladium Lewis acidic centers. This is in contrast to the situation in **1**, in which the [Pd(en)] modules are unable to form a hydrophobic cavity.

The modular self-assembly was successfully extended to the more rigid, planar, metal-complex modules [Pd(phen)] and [Pt(phen)]. Analysis by NMR spectroscopy confirms the formation of **3** under mild conditions. The resonance signals for **3** and **3′** are similar to those of **2** and **2′**, and again a crown structure is proposed as shown in Figure 4.

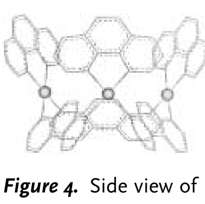

Figure 4. Side view of crown **3** or **3′**.

The dimensions of the upper cavity of the crowns **3** and **3′** are estimated to be about 1.1 nm for the rim lengths (i.e. the distances between the midpoints of the 5,6 positions of phen) and 0.65 nm for the cavity depth. The crowns **3** and **3′** behave as hosts to anions and neutral guests within the upper and lower cavities, which gives rise to strong host–guest interactions and color changes. Moreover, the crowns have strong aromatic receptor properties, and have potential for use as chemosensors for detecting mineral and biological anions. Further investigations will be extended to the self-assembly of calixarene-like metal-organic frameworks with deeper cavities by introducing square-planar coordinated metal complexes with luminescent ligands such as derivatives of 1,10-phenanthroline, as well as to the study of their luminescent responses to host–guest interactions.

Experimental Section

1–**3**: $[Pd(NO_3)_2(en)]$, $[Pd(NO_3)_2(bpy)]$, or $[Pd(NO_3)_2(phen)]$ (0.1 mmol) was added to an aqueous suspension of L (0.1 mmol, 2 mL), and the mixture was stirred for several minutes at room temperature. The resulting solution was allowed to stand at room temperature for several days during which crystals of the product were formed.

1′: $[PtCl_2(en)]$ (0.1 mmol) was added to an aqueous solution of $AgNO_3$ (0.1 mmol, 2 mL), and the mixture was stirred for 24 h at 80 °C. An aqueous suspension of L (0.1 mmol, 2 mL) was then added and the mixture was stirred for a further 24 h at 100 °C. The resulting clear solution was allowed to stand at room temperature for several days during which crystals of the product were formed.

2′ and **3′**: $[Pt(NO_3)_2(bpy)]$ or $[Pt(NO_3)_2(phen)]$ (0.1 mmol) was added to a suspended aqueous solution of L (0.1 mmol, 2 mL), and this mixture was stirred for 24 h at 100 °C. Excess $NaNO_3$ was added to the resulting clear solution, which was then stirred for a further 24 h at 100 °C. Excess KPF_6 was then added to the solution and the mixture was refluxed for a further 2 h. The hot solution was filtered and the collected solid was washed with several portions of water then dried in vacuo.

All ^1H NMR experiments were performed under the same conditions (300 MHz, D_2O, 25 °C, TMS).

1: Yield: 90 %. $\delta = 10.26$ (s, 6H), 9.66 (d, 6H, ^3J(H,H) = 5.3 Hz), 9.10 (d, 6H, ^3J(H,H) = 8.5 Hz), 7.83–7.78 (m, 6H), 3.04–2.89 ppm (m, 12H); **2**: Yield: 87 %. $\delta = 10.17$ (s, 6H), 9.92 (d, 6H, ^3J(H,H) = 5.4 Hz), 9.35 (d, 6H, ^3J(H,H) = 8.6 Hz), 8.27 (d, 6H, ^3J(H,H) = 8.1 Hz), 8.13–8.08 (m, 6H), 8.02–7.97 (m, 6H), 7.18–7.14 (m, 6H), 6.90 ppm (d, 6H, ^3J(H,H) = 2.8 Hz); **3**: Yield: 88 %. $\delta = 10.26$ (s, 6H), 10.02 (d, 6H, ^3J(H,H) = 5.4 Hz), 9.43 (d, 6H, ^3J(H,H) = 8.6 Hz), 8.63 (d, 6H, ^3J(H,H) = 8.3 Hz), 8.08–8.03 (m, 6H), 7.97 (s, 6H), 7.49–7.44(m, 6H), 7.28 ppm (d, 6H, ^3J (H,H) = 5.3 Hz). **1′**: Yield: 65 %. $\delta =$ 10.28 (s, 6H), 9.65 (d, 6H, ^3J(H,H) = 4.7 Hz), 9.14 (d, 6H, ^3J (H,H) = 8.6 Hz), 7.80–7.76 (m, 6H), 2.96–2.76 ppm (m, 12H). **2′**: Yield: 64 %. $\delta = 9.98$ (s, 6H), 9.80 (d, 6H, ^3J(H,H) = 5.4 Hz), 9.29 (d, 6H, ^3J(H,H) = 8.6 Hz), 8.16 (d, 6H, ^3J(H,H) = 8.2 Hz), 8.08–8.03 (m, 6H), 7.94–7.89 (m, 6H), 7.19–7.13 ppm (m, 12H); **3′**: Yield: 67 %. $\delta =$ 10.05 (s, 6H), 9.90 (d, 6H, ^3J(H,H) = 5.4 Hz), 9.39 (d, 6H, ^3J(H,H) = 8.4 Hz), 8.50 (d, 6H, ^3J(H,H) = 8.2 Hz), 8.01–7.97 (m, 6H), 7.76 (s, 6H), 7.51–7.42 ppm (m, 12H).

Received: August 16, 2002
Revised: October 15, 2002 [Z19979]

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[12] a) Crystal structure analysis of **1**. A single crystal with dimension of $0.25 \times 0.15 \times 0.05$ mm was coated with a sealing material and mounted on a glass fiber. All measurements were made on a Rigaku RAXIS Rapid IP detector equipped with a graphite monochromated $\mathrm{Mo}_{K\alpha}$ radiation source. The data were collected at 293(2) K. The crystallographic molecule contains half a molecule of **1**. Crystal data: $C_{42}H_{48}N_{18}O_{18}Pd_3 \cdot 2H_2O$, $M_r = 1448.13$; orthorhombic, space group $Pmn21$, $a = 21.8807(4)$, $b = 14.7319(3)$, $c = 23.2315(2)$ Å, $V = 7488.5(2)$ Å^3, $\rho_{\text{calcd}} = 1182$ kg m^{-3}. $Z = 8$, $F(000) = 2696$, $\mu(\mathrm{Mo}_{K\alpha}) = 7.68$ mm^{-1}, $\lambda = 0.71073$ Å. 19837 reflections measured, 7874 observed reflections ($I > 2\sigma(I)$); number of parameters 648; $R_1 = 0.1197$; $wR_2 = 0.3421$. Further refinement was unsuccessful because of the high degree of disorder of the counter anions and the water molecules. b) CCDC-191629 (**1**) and CCDC-191630 (**2**) contain 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).

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[16] Crystal structure analysis of **2**. A single crystal with dimension of $0.25 \times 0.15 \times 0.05$ mm was coated with a sealing material and mounted on a glass fiber. All measurements were made on a Rigaku RAXIS Rapid IP detector equipped with a graphite monochromated $\mathrm{Mo}_{K\alpha}$ radiation source. The data was collected at 293(2) K. The crystallographic molecule contains a molecule of **2**. Crystal data: $C_{66}H_{48}N_{18}O_{18}Pd_3 \cdot 2H_2O$, $M_r = 1736.40$, monoclinic, space group $C2/c$, $a = 39.366(8)$, $b = 24.887(5)$, $c = 18.217(4)$ Å, $\beta = 106.69(3)°$, $V = 17095(6)$ Å^3, $\rho_{\text{calcd}} = 1.544$ kg m^{-3}, $Z = 32$, $F(000) = 8192$, $\mu(\mathrm{Mo}_{K\alpha}) = 0.902$ cm^{-1}, $\lambda = 0.71073$ Å; 19127 reflections measured, 7704 observed reflections ($I > 2\sigma(I)$); number of parameters 891; $R_1 = 0.0931$; $wR_2 = 0.2575$.[12b]

Supported Gold Catalysts

Structure and Reactivity of a Mononuclear Gold-Complex Catalyst Supported on Magnesium Oxide[**]

*Javier Guzman and Bruce C. Gates**

Oxide- and zeolite-supported mononuclear metal complexes are important industrial catalysts, for example, for alkene polymerization,[1] and some have properties not anticipated by known homogeneous catalysis.[2] Some supported transition-metal complexes are close analogues of molecular complexes, with the metal–support-oxygen bonds being as strong as metal–ligand bonds in common transition-metal complexes and strong enough to maintain anchoring during catalysis.[3]

Mononuclear gold complexes are used frequently in organometallic chemistry[4] and have been identified as catalysts for reactions including the addition of alcohols to alkynes,[5] asymmetric aldol reactions,[6] C–C bond formation,[7] oxidative carbonylation of amines,[8] and selective hydrosilylation of aldehydes.[9] Supported gold catalysts have recently been found to be surprisingly active and selective, for example, for CO oxidation and propene epoxidation.[10] Their unique properties have been variously attributed to the smallness of the gold clusters[10b] and to clusters adjacent to cationic gold species at the support surface.[11] Gold supported

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[*] Prof. Dr. B. C. Gates, J. Guzman
University of California Davis
Department of Chemical Engineering and Materials Science
One Shields Ave., Davis, CA95616-5294 (USA)
Fax: (+1) 530-752-1031
E-mail: bcgates@ucdavis.edu

[**] This research was supported by DOE BES (FG02-87ER13790). We thank the Stanford Synchrotron Radiation Laboratory (Beamline 4-1), and the National Synchrotron Light Source (Beamline X-11A), both supported by DOE, for beam time.

0044-8249/03/11506-0714 $ 20.00+.50/0