

A Calix[4]arene Carceplex with Four Rh₂⁴⁺ FastenersF. Albert Cotton,^{*,†} Peng Lei,[†] Chun Lin,[†] Carlos A. Murillo,^{*,†} Xiaoping Wang,[†] Shu-Yan Yu,^{†,‡} and Zhong-Xing Zhang[‡]

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Abstract: It is shown that a spheroidal carceplex can be assembled by linking two bowl-shaped calix[4]-arenes via four dimetal units, (DAniF)₂Rh₂ (DAniF = *N,N*-di-*p*-anisylformamidinate), with a molecule (diethyl ether) or a cation (tetraethylammonium ion) trapped inside. The tetraethylammonium carceplex, **1b**, has been characterized by X-ray crystallography, ¹H NMR, IR, and mass spectrometry. The tetraethylammonium ion fits snugly in the interior of the spheroidal carceplex. A two-fold axis of the tetrahedral cation coincides with the idealized four-fold axis of the cage, and the cation is disordered over two rotational orientations. Only one axial position on each dirhodium unit is occupied by a ligand, CH₃CN or H₂O. The carceplex is very stable, and the axial ligands can be exchanged in single crystals without disrupting the crystallinity of the samples. In this way, a red crystal of the complex with all axial positions occupied by acetonitrile can be transformed to a green crystal of the complex with two axial positions having acetonitrile and the other two having water by simply putting the crystal in contact with distilled water. The calix[4]arene used to make the carceplex structure is 25,26,27,28-tetra-*n*-propoxycalix[4]arene-5,11,17,23-tetracarboxylic acid. By employing 25,26,27,28-tetrapropoxy-5,17-dibromo-calix[4]arene-11,23-dicarboxylic acid, two 1:1 dimetal: calixarene compounds have also been made and characterized: **2**, *cis*-Rh₂(DAniF)₂(calix)(CH₃OH), and **3**, *cis*-Mo₂(DAniF)₂(calix). The Rh–Rh distances in **1b** are in the range of 2.410(2)–2.428(2) Å, that in **2** is 2.4383(4) Å, and the Mo–Mo distance in **3** is 2.0931(4) Å.

Introduction

There is currently great interest in the design and preparation of supramolecular materials. Many may be constructed with single metal atom vertices (e.g., square planar Pd^{II} and Pt^{II} or tetrahedral Zn^{II}),¹ or as in our laboratory by using metal–metal bonded (M₂) dimetal atom vertices (especially those with M₂ = Mo₂⁴⁺,² Rh₂⁴⁺,² and Ru₂⁵⁺³). Useful precursors for preparing the latter have *cis*-M₂(formamidinate)₂ⁿ⁺ moieties with two cisoid formamidinate anions which remain fixed along with some labile ligands such as acetonitrile molecules or acetate. These react with appropriate polyfunctional linkers (e.g., di-

carboxylates) to give various kinds of supramolecular assemblies such as loops, squares, triangles, and more complex polyhedra.⁴ The use of Rh₂⁴⁺ units is especially appealing because many dirhodium compounds have important and varied catalytic activity.⁵

Another possible application that we have envisioned for our polygonal assemblies is their use as hosts for guest molecules of appropriate size. Arrangements capable of encapsulating molecules have been the target of many studies.⁶ Of special interest are the so-called carceplexes, that is, complexes with permanently imprisoned guests.⁷ In this context, an attractive

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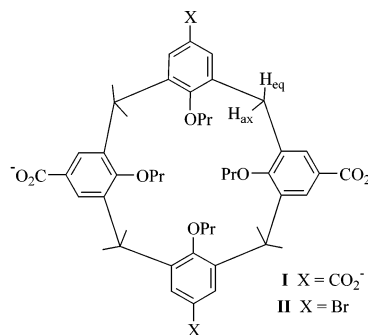
[‡] Chinese Academy of Sciences.

- (1) (a) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853 and references therein. (b) Swiegers, G. F.; Malefetse, T. J. *Chem. Rev.* **2000**, *100*, 3483. (c) Espinet, P.; Soulantica, K.; Charmant, J. P. H.; Orpen, A. G. *Chem. Commun.* **2000**, 915. (d) Navarro, J. A. R.; Lippert, B. *Coord. Chem. Rev.* **1999**, *185/186*, 653. (e) Whang, D.; Kim, K. J. *Am. Chem. Soc.* **1997**, *119*, 451. (f) Mann, S.; Huttner, G.; Zsolnai, L.; Heinze, K. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2808. (g) Scherer, M.; Caulder, D. L.; Johnson, D. W.; Raymond, K. N. *Angew. Chem., Int. Ed.* **1999**, *38*, 1588. (h) Lai, S.-W.; Chan, M. C.-W.; Peng, S.-M.; Che, C.-M. *Angew. Chem., Int. Ed.* **1999**, *38*, 669. (i) Jones, C. J. *Chem. Soc. Rev.* **1998**, *27*, 289. (j) Klausmeyer, K. K.; Wilson, S. R.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **1999**, *121*, 2705. (k) Li, H.; Eddaoudi, M.; O'Keeffe, M.; Yaghi, O.-M. *Nature* **1999**, *402*, 276.
- (2) Cotton, F. A.; Lin, C.; Murillo, C. A. *Proc. Nat. Acad. Sci. U.S.A.* **2002**, *99*, 4810.
- (3) Angaridis, P.; Berry, J. F.; Cotton, F. A.; Murillo, C. A.; Wang, X. *J. Am. Chem. Soc.* **2003**, *125*, 10327.

- (4) Cotton, F. A.; Lin, C.; Murillo, C. A. *Acc. Chem. Res.* **2001**, *34*, 759.
- (5) See, for example: (a) Doyle, M. P.; Ren, T. *Prog. Inorg. Chem.* **2001**, *49*, 113. (b) Estevan, F.; Herbst, K.; Lahuerta, P.; Barberis, M.; Pérez-Prieto, J. *Organometallics* **2001**, *20*, 950. (c) Doyle, M. P.; Phillips, I. M.; Hu, W. *J. Am. Chem. Soc.* **2001**, *123*, 5366. (d) Doyle, M. P.; McKervey, M. A.; Ye, T. *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds – From Cyclopropanes to Ylides*; John Wiley & Sons: New York, 1998.
- (6) (a) Seidel, S. R.; Stang, P. J. *Acc. Chem. Res.* **2002**, *35*, 972. (b) Fujita, M. *Chem. Soc. Rev.* **1998**, *27*, 417. (c) Yu, S.-Y.; Kusakawa, T.; Biradha, K.; Fujita, M. *J. Am. Chem. Soc.* **2000**, *122*, 2665. (d) Kusakawa, T.; Fujita, M. *J. Am. Chem. Soc.* **1999**, *121*, 1397. (e) Terpin, A. J.; Ziekler, M.; Johnson, D. W.; Raymond, K. N. *Angew. Chem., Int. Ed.* **2001**, *40*, 157. (f) Fujita, M.; Nagao, S.; Ogura, K. *J. Am. Chem. Soc.* **1995**, *117*, 1649. (g) O'Leary, B. M.; Szabo, T.; Svenstrup, N.; Schalley, C. A.; Lützen, A.; Schäfer, M.; Rebek, J., Jr. *J. Am. Chem. Soc.* **2001**, *123*, 11519. (h) Shivanyuk, A.; Rebek, J., Jr. *J. Am. Chem. Soc.* **2002**, *124*, 12074. (i) Reek, J. N. H.; Schenning, A. P. H. J.; Bosman, A. W.; Meijer, E. W.; Crossley, M. J. *Chem. Commun.* **1998**, 11.

family of compounds are the calix[*n*]arenes because these well-known toroidal or chalice-like molecules are capable of accommodating various organic molecules within the bowl.⁸ The thrust of the work we report here is to design systems in which two such bowls are united to form spheroidal cages. A few such molecules have already been made with the aid of hydrogen bonding interactions,⁹ or with organic covalent linkers,¹⁰ but we report here for the first time the use of dimetal moieties to link two calixarene bowls to form a spheroidal carceplex.¹¹

Several years ago, a study of the reaction of a corner piece precursor [*cis*-Rh₂(DAniF)₂(CH₃CN_{eq})₄(CH₃CN_{ax})₂]²⁺, DAniF = *N,N'*-di-*p*-anisylformamidinate, and the anions of a calix[4]arenetetracarboxylic acid, **I**, produced a cage compound with two calix[4]arene ligands united by covalent bonds to four [Rh₂] units (where [Rh₂] represents the *cis*-Rh₂(DAniF)₂²⁺ unit) through the eight carboxylate groups of the ligands. This compound was characterized by ¹H NMR spectroscopy and a crystal structure, and it was found that an ether molecule was inside a cage, **1a**. Further work showed that this synthesis was difficult to reproduce, but a highly reproducible preparation of a more stable product has now been found. This compound encapsulates a NEt₄⁺ cation and has a BF₄⁻ counteranion external to the cage, so that the formula can be compactly represented as {NEt₄C[*cis*-Rh₂(DAniF)₂L]₄[calix[4]arene-(CO₂)₄]₂}BF₄, **1b**, where L = acetonitrile or H₂O. The core is very stable and remains intact even under the conditions necessary for mass spectrometric measurements. This compound has been characterized structurally and in other ways including ¹H NMR and mass spectrometry. For comparison, simple dinuclear compounds with one *cis*-M₂(DAniF)₂ unit, M = Rh and Mo, and a calix[4]arene dicarboxylate ligand, **II**, have also been made. These are *cis*-Rh₂(DAniF)₂(Br₂calix[4]arene-(CO₂)₂)(CH₃OH_{ax}), **2**, and *cis*-Mo₂(DAniF)₂(Br₂calix[4]arene-(CO₂)₂), **3**.



Experimental Section

Materials, Methods, and General Procedures. Unless otherwise stated, all manipulations were carried out under nitrogen using standard Schlenk techniques. Solvents were dried by conventional methods and were freshly distilled under nitrogen before use. The starting materials, *cis*-[Rh₂(DAniF)₂(CH₃CN_{eq})₄(CH₃CN_{ax})₂](BF₄)₂,¹² *cis*-[Mo₂(DAniF)₂(CH₃CN_{eq})₄(BF₄)₂],¹³ calix[4]arene(CO₂H)₄ = 25,26,27,28-tetra-*n*-propoxycalix[4]arene-5,11,17,23-tetracarboxylic acid¹⁴ and 25,26,27,28-tetrapropoxy-5,17-dibromo-calix[4]arene-11,23-dicarboxylic acid^{14a} were prepared following published methods. Et₄NOH (35% aqueous solution) and Buⁿ₄NOH (1 M methanol solution) were purchased from Aldrich. All other commercially available chemicals were used as received.

Abbreviations Used. DAniF = *N,N'*-di-*p*-anisylformamidinate; [Rh₂] = *cis*-(DAniF)₂Rh₂²⁺; calix[4]arene(CO₂H)₄ = 25,26,27,28-tetra-*n*-propoxycalix[4]arene-5,11,17,23-tetracarboxylic acid; Br₂calix[4]arene-(CO₂H)₂ = 25,26,27,28-tetrapropoxy-5,17-dibromocalix[4]arene-11,23-dicarboxylic acid; [Rh₂⁴⁺] = the unit [*cis*-Rh₂(DAniF)₂L]²⁺, where L is a neutral axial ligand such as water or acetonitrile; {NEt₄Ccage}-BF₄ = [*cis*-Rh₂(DAniF)₂L]₄[calix[4]arene(CO₂)₄]₂·NEt₄BF₄ (also referred to as **1b** or **1c**); TBAH = Buⁿ₄NPF₆.

Physical Measurements. The ¹H NMR spectra were recorded on either a Varian Inova-500 or a Bruker Avance DMX500 spectrometer for **1b** or a Varian XL-300 instrument for **1a**, **2**, and **3**. The infrared spectrum was collected on KBr pellets on a Bruker Tensor 27 spectrophotometer. The MALDI-TOF mass spectrum of **1b** was collected on a Bruker Biflex instrument. Mass spectral simulation was carried out using the software provided free of cost by the University of Sheffield (<http://www.shef.ac.uk/chemistry/chemputer/isotopes.html>). Cyclic voltammetry was performed in dichloromethane using a CH Instruments model CH1620A electrochemical analyzer equipped with Pt working and auxiliary electrodes and 0.1 M TBAH as the supporting electrolyte. Potentials were referenced to an Ag/AgCl electrode. The values of *E*_{1/2} were taken as (*E*_{pa} + *E*_{pc})/2, where *E*_{pa} and *E*_{pc} are the anodic and cathodic peak potentials. Elemental analyses were performed by the Microanalytical Laboratory at the Institute of Chemistry, Chinese Academy of Sciences for **1b**, or Canadian Microanalytical Service, Delta, British Columbia, Canada for **2** and **3**.

Preparation of (NEt₄)₄(calix[4]arene(CO₂)₄). To a solution of calix[4]arene(CO₂H)₄ (77 mg, 0.10 mmol) in methanol (5 mL) was carefully added a solution of NEt₄OH (20% aqueous solution:methanol, 1:5) until a pH of 6.5 to 7.0 was attained and some solid had formed. After filtration, the solid was washed with methanol which dissolved most of it. The colorless filtrate and the methanol washing were combined, and the solvent was removed at room temperature under vacuum. The solid was then heated under vacuum at 35 °C for 72 h. A white powder (128 mg) was obtained in essentially quantitative yield.

- (7) (a) Cram, D. J.; Cram, J. M. *Container Molecules and Their Guests*; Royal Society of Chemistry: Cambridge, 1994. (b) Jasat, A.; Sherman, J. C. *Chem. Rev.* **1999**, *99*, 931. (c) Chapman, R. G.; Sherman, J. C. *Tetrahedron* **1997**, *53*, 15911. (d) Naumann, C.; Sherman, J. C. In *Calixarenes 2001*; Asfari, Z.; Böhmer, V.; Harrowfield, J.; Vicens, J., Eds.; Kluwer Academic Publishers: Dordrecht, 2001. (e) Hardie, M. J.; Raston, C. L. *J. Chem. Soc., Dalton Trans.* **2000**, 2483. (f) Rebek, J., Jr. *Chem. Commun.* **2000**, 637. (g) Warmuth, R.; Yoon, J. *Acc. Chem. Res.* **2001**, *34*, 95. (h) Mungaroo, R.; Sherman, J. C. *Chem. Commun.* **2002**, 1672.
- (8) (a) Gutsche, C. D. *Calixarenes Revisited*; Royal Society of Chemistry: London, 2000. (b) *Calixarenes in Action*; Mandolini, L., Ungaro, R., Eds.; Imperial College Press: London, 2000. (c) *Calixarenes 2001*; Asfari, Z.; Böhmer, V.; Harrowfield, J.; Vicens, J., Eds.; Kluwer Academic Publishers: Dordrecht, 2001. (d) *Calixarenes: A Versatile Class of Macrocyclic Compounds*; Vicens, J.; Böhmer, V., Eds.; Kluwer Academic Publishers: Dordrecht, 1991. (e) Fan, M.; Zhang, H.; Lattman, M. *Chem. Commun.* **1998**, 99. (f) Yu, S.-Y.; Huang, H.; Liu, H.-B.; Chen, Z.-N.; Zhang, R.; Fujita, M. *Angew. Chem., Int. Ed.* **2003**, *42*, 686. (g) *Macrocyclic Synthesis: A Practical Approach*; Parker, D., Ed.; Oxford University Press: Oxford, 1996.
- (9) (a) Kobayashi, K.; Shirasaka, T.; Yamaguchi, K.; Sakamoto, S.; Horn, E.; Furukawa, N. *Chem. Commun.* **2000**, 41. (b) Shimizu, K. D.; Rebek, J., Jr. *Proc. Natl. Acad. Sci. U.S.A.* **1995**, *92*, 12403. (c) Scheerder, J.; van Duynhoven, J. P. M.; Engbersen, J. F. J.; Reinhoudt, D. N. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1090. (d) Mogck, O.; Bohmer, V.; Vogt, W. *Tetrahedron* **1996**, *52*, 8489. (e) Gibb, C. L. D.; Stevens, E. D.; Gibb, B. C. *J. Am. Chem. Soc.* **2001**, *123*, 5849.
- (10) (a) MacGillivray, L. R.; Atwood, J. L. *Angew. Chem., Int. Ed.* **1999**, *38*, 1018. (b) Gibb, C. L. D.; Stevens, E. D.; Gibb, B. C. *Chem. Commun.* **2000**, 363.
- (11) The use of single-metal atom units to create calix[*n*]arene or resorcin[*n*]arene cages has been reported, but the number of structurally characterized molecules is very limited. See, for example: (a) Fox, O. D.; Dalley, N. K.; Harrison, R. G. *J. Am. Chem. Soc.* **1998**, *120*, 7111. (b) Fox, O. D.; Dalley, N. K.; Harrison, R. G. *Inorg. Chem.* **1999**, *38*, 5860. (c) Fochi, F.; Jacopozzi, P.; Wegelius, E.; Rissanen, K.; Cozzini, P.; Marastoni, E.; Fiscaro, E.; Manini, P.; Fokkens, R.; Dalcanale, E. *J. Am. Chem. Soc.* **2001**, *123*, 7539. (d) Fox, O. D.; Drew, M. G. B.; Beer, P. D. *Angew. Chem., Int. Ed.* **2000**, *39*, 136.

- (12) Catalan, K. V.; Mindiola, D. J.; Ward, D. L.; Dunbar, K. R. *Inorg. Chem.* **1997**, *36*, 2458.
- (13) Chisholm, M. H.; Cotton, F. A.; Daniels, L. M.; Folting, K.; Huffman, J.; Iyer, S.; Lin, C.; MacIntosh, A. M.; Murillo, C. A. *J. Chem. Soc., Dalton Trans.* **1999**, 1387.
- (14) (a) Larsen, M.; Jrgensen, M. *J. Org. Chem.* **1996**, *61*, 6661. (b) Sansone, F.; Barbosa, S.; Casnati, A.; Fabbri, M.; Pochini, A.; Ugozzoli, F.; Ungaro, R. *Eur. J. Org. Chem.* **1998**, 897. (c) Gutsche, C. D.; Pagoria, P. F. *J. Org. Chem.* **1985**, *50*, 5795.

Synthesis of $\{\text{NEt}_4\text{C}[\text{cis-Rh}_2(\text{DAniF})_2\text{L}]_4[\text{calix}[4]\text{arene}(\text{CO}_2)_4]_2\}$ -BF₄**, **1b**.** To $[\text{cis-Rh}_2(\text{DAniF})_2(\text{CH}_3\text{CN}_{\text{eq}})_4(\text{CH}_3\text{CN}_{\text{ax}})_2](\text{BF}_4)_2$ (114 mg, 0.100 mmol) in 2:1 $\text{CH}_3\text{CN}-\text{CH}_2\text{Cl}_2$ (3 mL) was added dropwise 5 mL of an acetonitrile solution of $(\text{NEt}_4)_4(\text{calix}[4]\text{arene}(\text{CO}_2)_4)$ (64 mg, 0.050 mmol), which had been heated to aid the dissolution of the calixarene salt. The reaction mixture was stirred at ca. 37–40 °C for 7 days. After filtration, a dark red solution was collected and layered with diethyl ether. After 2 days, a small amount of unreacted $[\text{cis-Rh}_2(\text{DAniF})_2(\text{CH}_3\text{CN}_{\text{eq}})_4(\text{CH}_3\text{CN}_{\text{ax}})_2](\text{BF}_4)_2$ precipitated as red crystals. After filtration in air, the volume of the filtrate was reduced to 3 mL under vacuum and the resulting solution was chromatographed using a silica gel column and $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ (2:1 v/v) as eluent. Three bands were observed: a major green band, and then a tan band, that was followed by a broad, very slow moving, blue band. As observed by mass spectrometry, the tan band contained a very small amount of $[\text{cis-Rh}_2(\text{DAniF})_2(\text{CH}_3\text{CN}_{\text{eq}})_4(\text{CH}_3\text{CN}_{\text{ax}})_2](\text{BF}_4)_2$. The green band was collected, and the solvent was evaporated under reduced pressure. The product was dried under vacuum. Yield: 16.5 mg (15%). Dark-red, single crystals suitable for X-ray crystallographic analysis were obtained after 2 weeks from a solution of the product in $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ (5:1 v/v), which had been layered with hexane at room temperature. This gave the product with $\text{L} = \text{CH}_3\text{CN}$. Green crystals used for the structural determination were obtained by rinsing single crystals of the acetonitrile analogue with distilled water ($\text{L} =$ a 50% mixture of H_2O and acetonitrile). MALDI-TOF for $([\text{NEt}_4\text{C}\text{cage without axial solvents}]^+)$: 4523.7. Anal. Calcd for $\text{C}_{220}\text{H}_{238}\text{N}_{19}\text{O}_4\text{Rh}_8\text{BF}_4 \cdot \{\text{NEt}_4\text{C}\text{cage}\}\text{BF}_4$ with 2 acetonitrile and 2 water molecules in axial positions): C, 55.86; H, 5.07; N, 5.63. Found: C, 55.46; H, 5.08; N, 5.70. IR (KBr, cm^{-1}): 3442 (br, s), 2960 (br, m), 1614 (s), 1503 (s), 1464 (w), 1400 (s), 1334 (w), 1292 (w), 1244 (s), 1220 (s), 1176 (m), 1122 (m), 1083 (m), 1035 (m), 958 (w), 901 (vw), 831 (w), 807 (w), 776 (w), 725 (vw), 598 (vw), 531 (w). ^1H NMR δ (ppm, in CD_2Cl_2): 7.766 (s, 16H, aromatic/calixarene), 7.255 (s, 8H, NCHN), 6.961 (d, 32H, aromatic/anisyl), 6.707 (d, 32H, aromatic/anisyl), 4.508 (d, 8H, H_{ax} of ArCH_2Ar /calixarene), 3.832 (t, 16H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 3.751 (s, 48H, OCH_3 /anisyl), 3.353 (d, 8H, H_{eq} of ArCH_2Ar /calixarene), 1.941 (s, 12H, CH_3CN), 1.919 (m, 16H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 0.925 (t, 24H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 0.791 (broad, 8H, CH_2CH_3), -1.560 (broad, 12H, CH_2CH_3).

Synthesis of $\text{cis-Rh}_2(\text{DAniF})_2(\text{Br}_2\text{calix}[4]\text{arene}(\text{CO}_2)_2)(\text{CH}_3\text{OH}_{\text{ax}})$, **2.** To a stirred solution of red $[\text{cis-Rh}_2(\text{DAniF})_2(\text{CH}_3\text{CN}_{\text{eq}})_4(\text{CH}_3\text{CN}_{\text{ax}})_2](\text{BF}_4)_2$ (57 mg, 0.050 mmol) in 10 mL of CH_3CN was added $(\text{Bu}^n\text{N})_2(\text{Br}_2\text{calix}[4]\text{arene}(\text{CO}_2)_2)$ (50.0 mg, 0.050 mmol) in 15 mL of CH_3CN . The reaction mixture was stirred at ambient temperature (22–25 °C) for ca. 24 h. A reddish precipitate gradually formed. This was collected by filtration and then washed several times with CH_3CN . The crude product was extracted with CH_2Cl_2 (2 \times 5 mL). Methanol was carefully layered on the top of the solution to afford a dark crystalline material after several days. Yield: 69 mg, 86%. ^1H NMR δ (ppm, in CD_2Cl_2): 7.42 (s, 4H), 7.36 (br, 2H), 7.02 (d, 8H), 6.81 (s, 4H), 6.77 (d, 8H), 4.43 (d, 4H), 4.01 (t, 4H), 3.81 (s, 12H), 3.71 (t, 4H), 3.20 (d, 4H), 2.02–1.80 (m, 8H), 1.13 (t, 6H), 0.86 (t, 6H). CV: two reversible waves at 0.21 and 1.07 V in the scan range from -0.10 to +1.30 V. Anal. Calcd for $\text{C}_{73}\text{H}_{78}\text{Br}_2\text{N}_4\text{O}_{13}\text{Rh}_2$: C, 55.32; H, 4.96; N, 3.53. Found: C, 55.01; H, 5.15; N, 3.38.

Synthesis of $\text{cis-Mo}_2(\text{DAniF})_2(\text{Br}_2\text{calix}[4]\text{arene}(\text{CO}_2)_2)$, **3.** To a stirred orange solution of $[\text{cis-Mo}_2(\text{DAniF})_2(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$ (104 mg, 0.100 mmol) in 15 mL of CH_3CN was added $(\text{Bu}^n\text{N})_2(\text{Br}_2\text{calix}[4]\text{arene}(\text{CO}_2)_2)$ (97.8 mg, 0.100 mmol) in 15 mL of CH_3CN . An immediate reaction took place with formation of a bright yellow precipitate, which was collected by filtration, washed several times with CH_3CN , and dried under vacuum. The crude product was extracted with CH_2Cl_2 (3 \times 5 mL). A mixture of isomeric hexane was then carefully layered on top of the solution to afford a yellow crystalline material after several days. The yield was essentially quantitative. ^1H NMR δ (ppm, in CD_2Cl_2): 8.46 (s, 2H), 7.34 (s, 4H), 7.03 (s, 4H), 6.68 (dd, 16H), 4.47 (d, 4H), 4.04 (t, 4H), 3.77 (t, 4H), 3.72 (s, 12H), 3.22 (d, 4H), 1.99–1.82 (m,

8H), 1.14 (t, 6H), 0.86 (t, 6H). CV: one reversible wave at 0.15 V in the scan range from -0.20 to +0.60 V. Anal. Calcd for $\text{C}_{72}\text{H}_{74}\text{Br}_2\text{N}_4\text{O}_{12}\text{Mo}_2$: C, 56.19; H, 4.85; N, 3.64. Found: C, 55.97; H, 5.12; N, 3.44.

X-ray Structure Determinations. For the Rh_8 -cage compounds, three crystal structures were determined, **1a**, **1b**, and **1c**.¹⁵ For each, a single crystal suitable for X-ray diffraction analysis was mounted on the tip of a quartz fiber with a small amount of silicone grease and attached to a goniometer head. Data were collected on a Bruker SMART 1000 CCD system equipped with a low-temperature controller cooled by liquid nitrogen. In each case, 60 frames were collected first to determine the orientation matrix. The cell parameters were calculated using an autoindexing routine, and a hemisphere of data was collected. Data reduction and integration were performed with the software package SAINT,¹⁶ while absorption corrections were applied by using the program SADABS.¹⁷ Positions of the Rh atoms and most of the non-hydrogen atoms were found by using the direct methods program in the Bruker SHELXTL software package.¹⁸ Subsequent cycles of least-squares refinement followed by difference Fourier syntheses revealed the positions of the remaining non-hydrogen atoms. Some of the anisyl groups in the DAniF ligands in **1a**¹⁹ and **1b** were found disordered, and they were refined isotropically. The crystal of **1b** contains two independent cage molecules with an encapsulated Et_4N^+ ion, designated **1b'**, **1b''**. Each resides on a crystallographic inversion center, and the internal volume is occupied by a disordered NEt_4^+ cation. Although **1b'**, **1b''** are not crystallographically equivalent as the result of disorder in the crystal structure, they are chemically equivalent, having one axial ligand in each of the dirhodium units. These are acetonitrile molecules in two of the Rh_2^{4+} units and water in the other two.²⁰ The BF_4^- anions are disordered in two positions in the unit cell, and they were refined with some constraints in bond distances. Hydrogen atoms were placed in calculated positions in the final structure refinement. Data collection for **2** and **3** was similar to that for **1b**; refinement proceeded straightforwardly. Crystal data and structural refinement information are given in Table 1. Selected bond distances and angles are listed in Tables 2–5.

Results and Discussion

Reaction of the corner piece precursor $[\text{cis-Rh}_2(\text{DAniF})_2(\text{CH}_3\text{CN}_{\text{eq}})_4(\text{CH}_3\text{CN}_{\text{ax}})_2](\text{BF}_4)_2$ in which the cation has a singly bonded Rh_2^{4+} unit, two formamidinate groups in a cisoid conformation, and six labile acetonitrile molecules in equatorial and axial positions with salts of $\text{calix}[4]\text{arene}(\text{CO}_2\text{H})_4$ allows the isolation of a cage complex having four $[\text{Rh}_2^{4+}]$ units capped by two $\text{calix}[4]\text{arene}$ ligands. Depending on the reaction conditions (vide infra), the axial ligand in each of the $[\text{Rh}_2^{4+}]$ units can be water or acetonitrile, and the cage can encapsulate an ether molecule or a NEt_4^+ cation.

Structural Considerations. The cage molecule was characterized in independent crystallographic studies. In **1a** (Figure

- (15) Crystals of **1c** were obtained by allowing the single crystals of the acetonitrile analogue to stand in air over a period of three weeks. These crystals are isomorphous with those of **1b** having two independent cage molecules but differing slightly in composition. In **1c**, a partially occupied CH_3CONH_2 molecule is found on the axial position of a Rh_2 -subunit. The CH_3CONH_2 molecule is formed by reaction of acetonitrile with water, a process that is known to be catalyzed by transition metal species. (See, for example: Eglin, J. E. *Comments Inorg. Chem.* **2002**, 23, 23 and references therein.) Other crystallographic data for **1c** and **1b** are essentially the same, and they are provided in the Supporting Information.
- (16) SAINT. *Data Reduction Software. Version 6.36A*; Bruker Advanced X-ray Solutions, Inc.: Madison, WI, 2001.
- (17) SADABS. *Version 2.05; Area Detector Absorption and Other Corrections*; Bruker Advanced X-ray Solutions, Inc.: Madison, WI, 2001.
- (18) Sheldrick, G. M. *SHELXTL. Version 6.12*; Bruker Advanced X-ray Solutions, Inc.: Madison, WI, 2002.
- (19) Crystals of **1a** were obtained from a reaction similar to that described for the synthesis of **1b**, except that the reaction was done at 22 °C over a period of 2 days, and without chromatographic purification.
- (20) These crystals were prepared, as reported above, by taking single crystals of the acetonitrile analogue and rinsing them with distilled water.

Table 1. Crystal Data and Structure Refinement

	1a·10CH ₃ CN	1b·3.5H ₂ O	2	3
empirical formula	C ₂₄₀ H ₂₆₀ N ₃₀ O ₄₁ Rh ₈	C ₂₂₀ H ₂₄₅ B ₁ F ₄ N ₁₉ O _{45.5} Rh ₈	C ₇₃ H ₇₈ Br ₂ N ₄ O ₁₃ Rh ₂	C ₇₂ H ₇₄ Br ₂ Mo ₂ N ₄ O ₁₂
fw	5044.06	4793.44	1585.03	1539.06
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> , Å	17.577(2)	20.257(9)	12.0208(6)	12.1936(8)
<i>b</i> , Å	19.640(3)	24.161(10)	13.1643(6)	14.496(1)
<i>c</i> , Å	19.871(3)	26.445(11)	23.138(1)	20.993(1)
α , deg	69.092(2)	75.223(7)	77.851(1)	106.990(1)
β , deg	69.336(3)	67.977(7)	77.749(1)	95.559(1)
γ , deg	85.822(3)	66.997(7)	80.174(1)	105.863(1)
<i>V</i> , Å ³	5985(1)	10 955(8)	3467.4(3)	3350.1(4)
<i>d</i> , g/cm ³	1.400	1.453	1.518	1.526
<i>Z</i>	1	2	1	1
<i>T</i> , K	213(2)	173(2)	213(2)	213(2)
R1, ^a wR2 ^b [<i>I</i> > 2σ(<i>I</i>)]	0.0879, 0.2010	0.0824, 0.1834	0.0469, 0.1219	0.0436, 0.1017
R1, ^a wR2 ^b (all data)	0.1683, 0.2363	0.1630, 0.2340	0.0672, 0.1367	0.0728, 0.1178
quality of fit ^c	1.127	1.182	1.028	1.018

^a R1 = $\sum ||F_o| - |F_c|| / \sum |F_o|$, ^b wR2 = $[\sum [w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2]^{1/2}$, $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [\max(0, F_o^2) + 2(F_c^2)] / 3$. ^c Quality of fit = $[\sum [w(F_o^2 - F_c^2)^2] / (N_{\text{obs}} - N_{\text{params}})]$, based on all data.

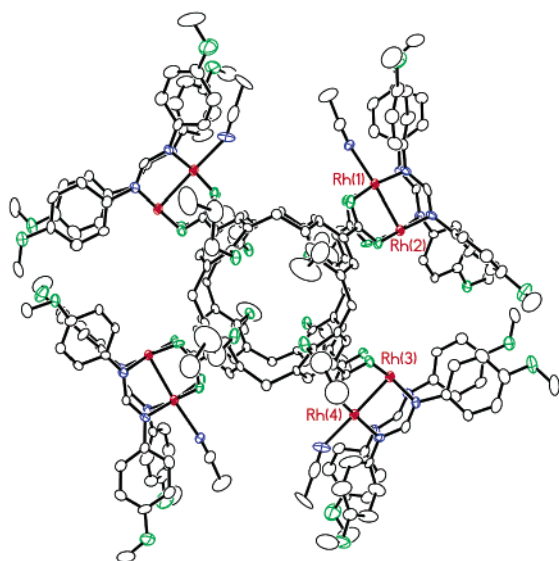


Figure 1. A drawing of the cage **1a** with the encapsulated diethyl ether molecule removed for clarity. Each of the four dirhodium units has one acetonitrile molecule occupying one axial site. An inversion center relates the two halves of the neutral molecule. Displacement ellipsoids are drawn at the 30% probability level.

1), the compound crystallizes in the triclinic space group *P* $\bar{1}$. The center of the cage resides on a crystallographic inversion center, and the inside of the spheroidal cage is occupied by a disordered Et₂O molecule. The cage possesses four dirhodium units but only two independent Rh–Rh distances of 2.429(1) and 2.422(2) Å (Table 2). Each of the Rh₂ moieties is equatorially bound to two formamidinate ligands arranged in a cisoid conformation and two carboxylate groups which are trans to the formamidinate ligands. One of the four carboxylate groups from each calixarene ligand forms bonds to each dirhodium unit. Thus, these dirhodium units serve as fasteners that hold together the two bowls of the calixarenes. Because of this arrangement with two formamidinates and two carboxylates, each dimetal unit has a paddlewheel structure. Additionally, each of the dimetal units has one axial acetonitrile ligand. This is somewhat unusual for dirhodium compounds which typically crystallize with two axial interactions. However, a few examples are known with only one axial interaction.²¹ To understand whether this arrangement is due to the presence of the large molecule or if it is due to the electronic environment created by the ligands, a

Table 2. Selected Bond Lengths [Å] and Angles [deg] for **1a**

Rh(1)–Rh(2)	2.429(1)	Rh(4)–N(8)	2.04(1)
Rh(3)–Rh(4)	2.422(2)	Rh(4)–N(10)	2.16(1)
Rh(1)–N(1)	2.04(1)	Rh(1)–O(9)	2.075(9)
Rh(1)–N(3)	2.04(1)	Rh(1)–O(11)	2.090(9)
Rh(1)–N(9)	2.16(1)	Rh(2)–O(10)	2.043(9)
Rh(2)–N(2)	1.99(1)	Rh(2)–O(12)	2.071(9)
Rh(2)–N(4)	2.03(1)	Rh(3)–O(14)	2.073(8)
Rh(3)–N(6)	2.02(1)	Rh(3)–O(15)	2.048(9)
Rh(3)–N(7)	2.01(1)	Rh(4)–O(13)	2.088(9)
Rh(4)–N(5)	2.05(1)	Rh(4)–O(16)	2.086(8)
N(1)–Rh(1)–N(3)	91.7(4)	O(11)–Rh(1)–N(9)	87.0(4)
N(1)–Rh(1)–O(9)	175.4(4)	N(2)–Rh(2)–N(4)	92.9(4)
N(3)–Rh(1)–O(9)	87.3(4)	N(2)–Rh(2)–O(10)	176.1(4)
N(1)–Rh(1)–O(11)	87.9(4)	N(4)–Rh(2)–O(10)	88.2(4)
N(3)–Rh(1)–O(11)	175.0(4)	N(2)–Rh(2)–O(12)	86.4(4)
O(9)–Rh(1)–O(11)	92.7(3)	N(4)–Rh(2)–O(12)	176.1(4)
N(1)–Rh(1)–N(9)	93.4(5)	O(10)–Rh(2)–O(12)	92.2(3)
N(3)–Rh(1)–N(9)	98.1(4)	N(7)–Rh(3)–N(6)	88.2(4)
O(9)–Rh(1)–N(9)	91.2(4)	N(7)–Rh(3)–O(15)	176.5(5)
N(5)–Rh(4)–O(16)	87.3(4)	N(6)–Rh(3)–O(15)	89.8(4)
N(8)–Rh(4)–O(13)	88.5(4)	N(7)–Rh(3)–O(14)	90.4(4)
N(5)–Rh(4)–O(13)	175.2(4)	N(6)–Rh(3)–O(14)	175.9(5)
O(16)–Rh(4)–O(13)	90.8(3)	O(15)–Rh(3)–O(14)	91.5(3)
N(8)–Rh(4)–N(10)	92.8(5)	N(8)–Rh(4)–N(5)	93.1(4)
N(5)–Rh(4)–N(10)	93.3(5)	N(8)–Rh(4)–O(16)	175.2(4)

simple compound with only one [Rh₂] unit and a calix[4]-arene dicarboxylate derivative was made. It can be seen in Figure 2 that this has essentially the same environment as each of the dirhodium units in the cage with two formamidinate, two carboxylate groups, and only one axial methanol ligand, and has a Rh–Rh distance of 2.4383(4) Å which is comparable to those in the cage. Other Rh–N and Rh–O distances (see Table 3) are also similar. However, in this compound the two carboxylate groups are provided by the same ligand. This arrangement resembles somewhat that found in *cis*-Rh₂(acetate)₂-(*m*-C₆H₄(OCMe₂CO₂)₂)²² and *cis*-Mo₂(DAniF)₂(*m*-C₆H₄(OCMe₂CO₂)₂).²³ The structure of **2** is also very similar to that of the molybdenum analogue **3** (see Supporting Information) except that the latter does not have axial ligands, in accord with the established lesser tendency toward axial ligation of quadruply bonded, dimolybdenum paddlewheel compounds relative to those of the Rh analogues.²⁴

- (21) Cotton, F. A.; Hillard, E. A.; Liu, C. Y.; Murillo, C. A.; Wang, W.; Wang, X. *Inorg. Chim. Acta* **2002**, 337, 233.
 (22) Bonar-Law, R. P.; McGrath, T. D.; Singh, N.; Bickley, J. F.; Steiner, A. *Chem. Commun.* **1999**, 2457.
 (23) Berry, J. F.; Cotton, F. A.; Ibragimov, S. A.; Murillo, C. A.; Wang, X. *J. Chem. Soc., Dalton Trans.* **2003**, 4297.

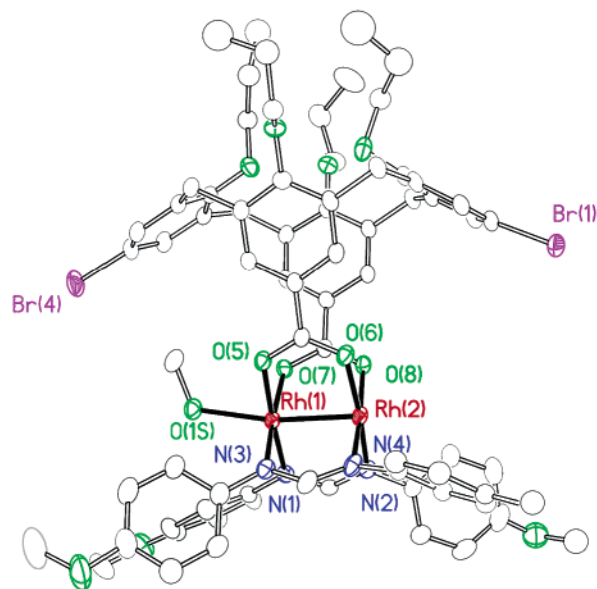


Figure 2. A plot of **2** with displacement ellipsoids drawn at the 40% probability level. The drawing shows the similarity of the dirhodium unit with those of the cages **1a** and **1b**. Note, however, that in the cage compounds each of the carboxylate groups is provided by a different calixarene ligand.

Table 3. Selected Bond Lengths [Å] and Angles [deg] for **2**

Rh(1)–Rh(2)	2.4383(4)	Rh(1)–O(1S)	2.301(2)
Rh(1)–N(1)	2.026(3)	Rh(1)–O(5)	2.048(2)
Rh(1)–N(3)	2.038(3)	Rh(1)–O(7)	2.088(2)
Rh(2)–N(2)	2.026(3)	Rh(2)–O(6)	2.088(2)
Rh(2)–N(4)	2.012(3)	Rh(2)–O(8)	2.063(3)
N(1)–Rh(1)–N(3)	91.4(1)	N(2)–Rh(2)–O(6)	173.6(1)
N(1)–Rh(1)–O(5)	175.9(1)	O(8)–Rh(2)–O(6)	84.0(1)
N(3)–Rh(1)–O(5)	91.2(1)	N(4)–Rh(2)–Rh(1)	89.28(9)
N(1)–Rh(1)–O(7)	92.8(1)	N(2)–Rh(2)–Rh(1)	88.23(8)
N(3)–Rh(1)–O(7)	173.1(1)	O(8)–Rh(2)–Rh(1)	88.46(6)
O(5)–Rh(1)–O(7)	84.3(1)	O(6)–Rh(2)–Rh(1)	86.70(7)
N(1)–Rh(1)–O(1S)	96.3(1)	O(5)–Rh(1)–Rh(2)	88.26(6)
N(3)–Rh(1)–O(1S)	101.7(1)	O(7)–Rh(1)–Rh(2)	86.47(6)
O(5)–Rh(1)–O(1S)	86.24(9)	O(1S)–Rh(1)–Rh(2)	168.81(7)
O(7)–Rh(1)–O(1S)	83.29(9)	N(4)–Rh(2)–N(2)	91.9(1)
N(1)–Rh(1)–Rh(2)	88.70(8)	N(4)–Rh(2)–O(8)	175.5(1)
N(3)–Rh(1)–Rh(2)	88.12(8)	N(2)–Rh(2)–O(8)	91.9(1)

The second cage, **1b**, also forms crystals in the triclinic space group $P\bar{1}$, but there are two independent cage molecules, **1b'** and **1b''**. These are chemically equivalent, and their cores are structurally similar to that of **1a**. Each has an inversion center, but the internal volume is occupied now by a disordered NEt_4^+ cation; a BF_4^- counteranion is located outside the cage. Again, however, only one axial position is occupied on each of the crystallographically independent dirhodium units. Four of the eight axial sites are occupied by two acetonitrile and two water molecules. The Rh–Rh distances are in the narrow range of 2.410(2)–2.428(2) Å (Table 4). The structure of the core of one of the molecules and a schematic representation of the reaction are shown in Figure 3. The molecule has been drawn with all axial ligands and anisyl groups removed, and with a space filling diagram of the encapsulated tetraethylammonium ion. It appears that this is trapped and thus unable to escape from inside the cage (vide infra). Therefore, the species can be represented by the formula $\{\text{NEt}_4\text{Cage}\}\text{BF}_4$.

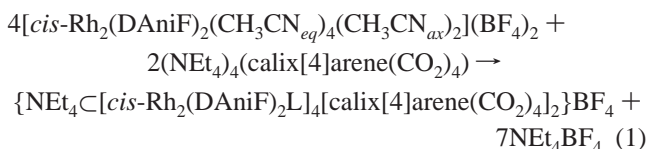
(24) Cotton, F. A.; Walton, R. A. *Multiple Bonds between Metal Atoms*, 2nd ed.; Oxford University Press: Oxford, 1993.

Table 4. Selected Bond Lengths [Å] and Angles [deg] for **1b'** and **1b''**

Rh(1)–Rh(2)	2.417(2)	Rh(6)–N(62)	2.08(1)
Rh(3)–Rh(4)	2.410(2)	Rh(7)–N(71)	2.07(1)
Rh(5)–Rh(6)	2.428(2)	Rh(7)–N(72)	2.02(1)
Rh(7)–Rh(8)	2.413(4)	Rh(8)–N(81)	2.009(9)
Rh(7B)–Rh(8B)	2.412(4)	Rh(8)–N(82)	2.005(9)
Rh(1)–N(11)	2.04(1)	Rh(1)–O(10)	2.316(8)
Rh(1)–N(12)	2.024(9)	Rh(1)–O(12)	2.053(7)
Rh(2)–N(21)	2.020(9)	Rh(2)–O(22)	2.086(7)
Rh(2)–N(22)	2.030(9)	Rh(3)–O(32)	2.094(8)
Rh(3)–N(3)	2.16(1)	Rh(4)–O(42)	2.087(8)
Rh(3)–N(31)	2.03(1)	Rh(5)–O(52)	2.054(8)
Rh(3)–N(32)	2.03(1)	Rh(6)–O(62)	2.072(8)
Rh(4)–N(41)	2.05(1)	Rh(7)–O(71)	2.06(1)
Rh(4)–N(42)	2.02(1)	Rh(7)–O(72)	2.050(9)
Rh(5)–N(5)	2.20(1)	Rh(7B)–O(8B)	2.20(1)
Rh(5)–N(51)	2.02(1)	Rh(8)–O(80)	2.34(2)
Rh(5)–N(52)	2.03(1)	Rh(8)–O(81)	2.103(7)
Rh(6)–N(61)	2.01(1)	Rh(8)–O(82)	2.105(7)
N(12)–Rh(1)–N(11)	87.3(4)	N(22)–Rh(2)–O(22)	86.9(3)
N(12)–Rh(1)–O(12)	93.0(3)	N(21)–Rh(2)–Rh(1)	87.0(3)
N(11)–Rh(1)–O(12)	175.9(4)	N(22)–Rh(2)–Rh(1)	87.4(3)
N(12)–Rh(1)–O(10)	96.5(3)	O(22)–Rh(2)–Rh(1)	88.3(2)
N(11)–Rh(1)–O(10)	102.7(4)	N(31)–Rh(3)–N(32)	92.0(5)
O(12)–Rh(1)–O(10)	81.4(3)	N(31)–Rh(3)–O(32)	173.6(4)
N(12)–Rh(1)–Rh(2)	88.9(3)	N(32)–Rh(3)–O(32)	88.2(4)
N(21)–Rh(2)–N(22)	91.0(4)	N(31)–Rh(3)–N(3)	93.8(4)
N(21)–Rh(2)–O(22)	175.0(3)	N(32)–Rh(3)–N(3)	97.0(4)
N(52)–Rh(5)–O(52)	87.9(4)	O(32)–Rh(3)–N(3)	92.5(3)
N(52)–Rh(5)–Rh(6)	87.6(3)	N(11)–Rh(1)–Rh(2)	89.6(3)

The cores of these molecular cages or capsules resemble those of compounds with cavitant tetracarboxylic acids in which the two units are joined by four 2-aminopyrimidine molecules.^{9a} However, in the latter arrangement, the “molecular glue” is provided by hydrogen bonds, not covalent interactions such as those between the dirhodium units and carboxylate groups in the cores of molecules **1**.

Reactivity and Synthetic Considerations. The assemblage reaction for cage compound **1b** is carried out in CH_3CN and is represented by eq 1.



The reaction conditions are very important for the success of the reaction and thus worthy of discussion. The reaction temperature must be kept above room temperature at 35–40 °C. Furthermore, a long reaction time appears to be necessary. Under these conditions, the reaction is highly reproducible. When the reaction is done under an inert atmosphere, the compound is isolated as red crystals with $\text{L} = \text{CH}_3\text{CN}$. When water molecules replace two of the four axial CH_3CN molecules, the color of the crystals changes from red to green. This is consistent with the well-established fact that the colors of paddlewheel compounds having the dirhodium unit are highly dependent on the nature of the axial ligands.²⁵ We found by structural studies and mass spectroscopy (vide infra) that the

(25) (a) Cotton, F. A.; Hillard, E. A.; Murillo, C. A. *J. Am. Chem. Soc.* **2002**, *124*, 5658. (b) Johnson, S. A.; Hunt, H. R.; Neumann, H. M. *Inorg. Chem.* **1963**, *2*, 960. (c) Trexler, J. W., Jr.; Schreiner, A. F.; Cotton, F. A. *Inorg. Chem.* **1988**, *27*, 3265. (d) Miskowski, V. M.; Schaefer, W. P.; Sadeghi, B.; Santarsiero, B. D.; Gray, H. B. *Inorg. Chem.* **1984**, *23*, 1154. (e) Lichtenberger, D. L.; Pollard, J. R.; Lynn, M. A.; Cotton, F. A.; Feng, X. *J. Am. Chem. Soc.* **2000**, *122*, 3182.

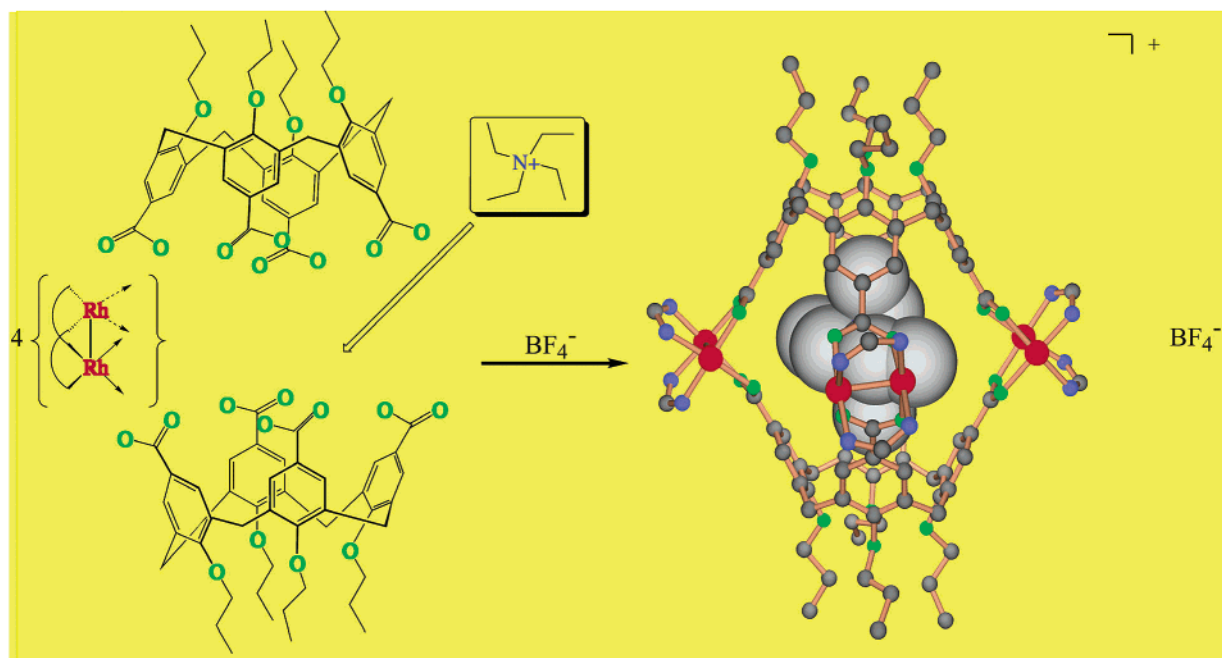


Figure 3. A schematic drawing showing the formation of the carceplex **1b**. The drawing on the right has a space filling diagram of one orientation of the encapsulated tetraethylammonium ion in one of the two crystallographically independent molecules. The anisyl groups of all formamidinate ligands and the axial ligands (two water and two acetonitrile molecules which occupy one axial position of each of the four Rh₂⁴⁺ units) have been removed for clarity. For a balanced equation for the process, see eq 1.

core of the cage remained unchanged upon substitution of the axial ligands. Furthermore, when single crystals of the corresponding acetonitrile cage with the encapsulated NEt₄⁺ cation are exposed to moist air over a period of many days, or rinsed with distilled water, the diffraction pattern remains essentially unchanged even though the color of the crystals changes. This indicates that the cage is quite sturdy and persists. Although exposure of the aqua complex to an atmosphere of acetonitrile did not reverse the process, water can be removed under vacuum and then replaced by placing the solid in contact with acetonitrile. We found that the cage in its green form having some axially coordinated water molecules is more stable and easier to handle than the corresponding compound with acetonitrile molecules in all axial positions.

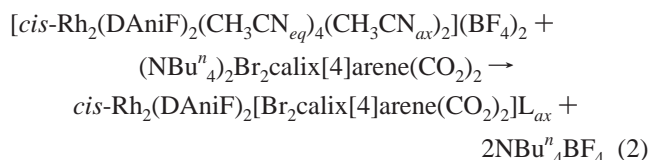
The complex with encapsulated diethyl ether, **1a**, is significantly less stable, and the crystals appear to lose crystallinity very rapidly upon exposure to air. This crystalline form was obtained in very low yield from a reaction carried out at 22 °C over a 2 day period.²⁶

Also important for the isolation of a pure crystalline product with an encapsulated NEt₄⁺ cation is the purification by column chromatography over silica gel, although this has some unwelcome consequences too. The progress of the reaction mixture was monitored by thin-layer chromatography which showed that the cage compound was the major product with a small amount of unreacted starting material also present. However, the use of column chromatography produced a third band (blue in color) that trailed the green band of the product and a tan band containing the Rh₂ starting material. This blue band is due to decomposition of the product upon prolonged contact with the

chromatographic support. Nevertheless, the green band produced a very pure sample of the cage compound as shown below.

Attempts to prepare the cage species using (NBuⁿ)₄(calix[4]arene(CO₂)₄) instead of the NEt₄⁺ analogue were unsuccessful, which is a good indication that the stability of the cage is adversely affected by the presence of the much larger cation which does not fit into the cavity. We also tried the crystallization process in the presence of adamantane, but again no inclusion of this hydrocarbon was observed. Thus, encapsulation of the NEt₄⁺ cation seems to be favored and appears to be quite selective.

The synthesis of the simple molecule **2** was accomplished in very high yield in acetonitrile at 22 °C upon reaction of the corner piece and the calix[4]arenedicarboxylate, as shown in eq 2. The crystalline compound with one axial ligand, L_{ax} = CH₃OH, can be isolated upon recrystallization from a methanol solution:

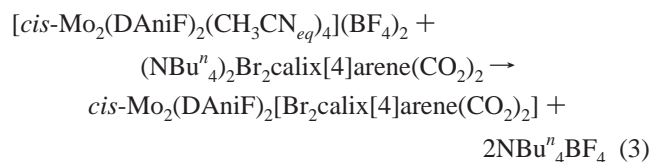


The red crystalline compound **2** thus obtained is spectroscopically pure as shown by the ¹H NMR spectrum, and there is no need to purify it further by column chromatography. While it is possible that an analogue of this type might occur during the assemblage reaction of **1**, no such compounds were isolated from the preparations of **1**. The higher temperatures and longer periods of time used for the preparation of the cage compounds might be attributed to the need to rearrange such intermediates into the cage products. A rearrangement would be necessary because in the dinuclear species the two carboxylate groups are

(26) The reproducibility of this reaction is not very good. Because of this, the molecule with an encapsulated Et₂O was characterized only by X-ray crystallography and ¹H NMR spectroscopy, and no further efforts to make it again have been made. Higher crystallization temperatures give exclusively, and reproducibly, the complex with an encapsulated NEt₄⁺ cation, for which extensive characterization was done.

provided by only one calixarene ligand, while in the cage each carboxylate group is attached to a different dirhodium unit.

The molybdenum analogue **3** was prepared similarly in very high yield and excellent purity according to eq 3:



Like other compounds described here, it is diamagnetic because of the closed shell structure of the metal–metal bonded M_2^{4+} species.

Other Spectroscopic Observations. The high purity of all crystalline products was assessed by elemental analyses and 1H NMR spectroscopy. The latter, as well as mass spectrometric studies, provide evidence that the solid-state structures remain unchanged in solution and in the gas phase.

The 1H NMR spectra of **2** and **3** show that the molecule is highly symmetrical having only one signal for the methine proton of the formamidinate group at 7.36 ppm for **2** and at the lower field of 8.46 ppm for **3**. This shift is consistent with the higher magnetic anisotropy of the quadruple bond in the Mo_2^{4+} species.²⁷ All other signals are consistent also with a highly symmetrical species such as that found in the solid state.

The proton NMR spectrum of **2** is very helpful in assigning that of the cage **1b** as there are only small shifts (in ppm referenced to CH_2Cl_2) because of the similarity of the chemical environment of the singly bonded Rh_2^{4+} units in these compounds. The singlet at 7.766 ppm corresponds to the 16 aromatic protons in the calix[4]arene ligand, while those on the 8 methylene groups appear as expected as a pair of doublets at 4.508 and 3.353 ppm. By analogy to those of the corresponding acid, the axial doublet is at lower field than the equatorial one.^{14a} More importantly, there are signals at very high field that correspond to the encapsulated NEt_4^+ cation (broad signals at 0.791 and -1.560 ppm). These have been assigned by analogy to those in other carceplexes and related species containing trapped organic entities which show strong shielding and signals at higher fields relative to those of the same molecules in ordinary solutions. Prior examples are provided by encapsulated NEt_4^+ cations²⁸ and a variety of species.²⁹ The broadening of the tetraethylammonium bands in the NMR spectrum is consistent with some motion of the cation within the cage which might be due to an interconversion between the two disordered positions which exist in the solid state. Other spectral assignments are shown in the Experimental Section.

Table 5. Selected Bond Lengths [Å] and Angles [deg] for **3**

Mo(1)–Mo(2)	2.0931(4)	Mo(1)–O(5)	2.124(2)
Mo(1)–N(1)	2.132(3)	Mo(1)–O(7)	2.134(2)
Mo(1)–N(3)	2.116(3)	Mo(2)–O(6)	2.155(2)
Mo(2)–N(2)	2.104(3)	Mo(2)–O(8)	2.133(2)
Mo(2)–N(4)	2.126(3)		
Mo(2)–Mo(1)–N(3)	93.04(8)	O(5)–Mo(1)–O(7)	80.04(9)
Mo(2)–Mo(1)–O(5)	92.27(6)	N(1)–Mo(1)–O(7)	91.1(1)
N(3)–Mo(1)–O(5)	92.5(1)	Mo(1)–Mo(2)–N(2)	92.83(8)
Mo(2)–Mo(1)–N(1)	92.63(8)	Mo(1)–Mo(2)–N(4)	92.39(8)
N(3)–Mo(1)–N(1)	96.0(1)	N(2)–Mo(2)–N(4)	95.2(1)
O(5)–Mo(1)–N(1)	170.0(1)	Mo(1)–Mo(2)–O(8)	92.01(7)
Mo(2)–Mo(1)–O(7)	91.52(6)	N(2)–Mo(2)–O(8)	89.7(1)
N(3)–Mo(1)–O(7)	171.4(1)	N(4)–Mo(2)–O(8)	173.2(1)
N(2)–Mo(2)–O(6)	168.7(1)	Mo(1)–Mo(2)–O(6)	91.14(6)

Accompanying the trapped NEt_4^+ cation in $\{NEt_4\text{Cage}\}$ is a BF_4^- counterion which is found outside the cage. Spectroscopic evidence for this is provided by the appearance of bands in the infrared spectrum at 1083 and 531 cm^{-1} which are similar to those reported by Nakamoto³⁰ for the BF_4^- anion and those in $cis-[Rh_2(DAniF)_2(CH_3CN_{ax})_4(CH_3CN_{eq})_2](BF_4)_2$ ¹¹ and $[Mo_2(DAniF)_2(CH_3CN)_4](BF_4)_2$,¹² and absent in $(NEt_4)_2\text{-}(calix[4]arene(CO_2)_4)$. Elemental analysis also supports this formulation.

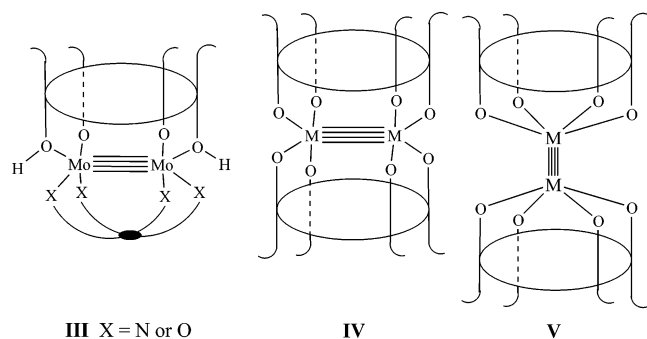
Further evidence for the stability of the $\{NEt_4\text{Cage}\}BF_4$ species is provided by mass spectroscopic studies. The MALDI-TOF spectrum shows a series of peaks distributed about the most intense signal at 4523.7. The signals are consistent with the isotopic distribution for $[NEt_4\text{Cage}]^+$ devoid of axial ligands which are known to be easily lost. There is another signal at 14 mass units lower having significantly lower intensity which can be assigned to the same ion but with a methoxy group from an anisyl moiety replaced by a hydrogen atom. Because of this, the mass spectra of the red form (axial acetonitrile) and the green form (axial water or a mixture of acetonitrile/water) are indistinguishable. Very little else appears in the spectrum, and it is very notable that there are no signals in the region corresponding to the mass of the cationic cage without the NEt_4^+ fragment. This is evidence that the entire crystalline sample contains only species with the encapsulated cation and that these cations remain inside the cage even in the gas phase. This is one of only a few examples in which gas-phase interactions of calixarene cavitands with molecular guests have been observed by mass spectrometry.³¹

Comparison with Other Calix[4]arene Compounds Having Dimetal Units. There is a small number of dinuclear compounds having one metal–metal bonded unit and calix[4]arene ligands.³² It should be noted that there are only two complexes with the quadruply bonded Mo_2^{4+} unit.^{32,33} Like **3**, these have two cisoid ligands, either acetate or formamidinate groups, and a capping calixarene, as shown in **III**. Unlike **2** and **3**, however, the calixarene is bonded to the dimetal units through the oxygen atoms of alkoxy or phenolic components of the calixarene. Interestingly, the Mo–Mo distances differ significantly, with those in **3** being 2.0931(4) Å (Table 5) while

- (27) See, for example: Cotton, F. A.; Daniels, L. M.; Lei, P.; Murillo, C. A.; Wang, X. *Inorg. Chem.* **2001**, *40*, 2778 and references therein.
 (28) (a) Caulder, D. L.; Brückner, C.; Powers, R. E.; König, S.; Parac, T. N.; Leary, J. A.; Raymond, K. N. *J. Am. Chem. Soc.* **2001**, *123*, 8923. (b) Parac, T. N.; Caulder, D. L.; Raymond, K. N. *J. Am. Chem. Soc.* **1998**, *120*, 8003. (c) Vysotsky, M. O.; Pop, A.; Broda, F.; Thondorf, I.; Böhmer, V. *Chem.-Eur. J.* **2001**, *7*, 4403.
 (29) (a) Aoki, S.; Shiro, M.; Kimura, E. *Chem.-Eur. J.* **2002**, *8*, 929. (b) Chopra, N.; Sherman, J. C. *Angew. Chem., Int. Ed.* **1999**, *38*, 1955. (c) Chapman, R. G.; Sherman, J. C. *J. Org. Chem.* **2000**, *65*, 513. (d) Fox, O. D.; Leung, J. F.-Y.; Hunter, J. M.; Dalley, N. K.; Harrison, R. G. *Inorg. Chem.* **2000**, *39*, 783. (e) Atwood, J. L.; Szumna, A. *J. Am. Chem. Soc.* **2002**, *124*, 10646. (f) Tucci, F. C.; Rudkevich, D. M.; Rebek, J., Jr. *J. Am. Chem. Soc.* **1999**, *121*, 4928. (g) Ikeda, A.; Yoshimura, M.; Udzo, H.; Fukuhara, C.; Shinkai, S. *J. Am. Chem. Soc.* **1999**, *121*, 4296. (h) Park, S. J.; Hong, J.-I. *Chem. Commun.* **2001**, 1554. (i) Zhong, Z.; Ikeda, A.; Ayabe, M.; Shinkai, S.; Sakamoto, S.; Yamaguchi, K. *J. Org. Chem.* **2001**, *66*, 1002.

- (30) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds. Part A: Theory and Applications in Inorganic Chemistry*, 5th ed.; John Wiley & Sons: New York, 1997.
 (31) (a) Vincenti, M.; Irico, A. *Int. J. Mass Spectrom.* **2002**, *214*, 23. (b) Schalley, C. A.; Castellano, R. K.; Brody, M. S.; Rudkevich, D. M.; Siuzdak, G.; Rebek, J., Jr. *J. Am. Chem. Soc.* **1999**, *121*, 4568.
 (32) For a review of calixarenes with dimetal units up to the year 2001, see: Cotton, F. A.; Daniels, L. M.; Lin, C.; Murillo, C. A. *Inorg. Chim. Acta* **2003**, *347*, 1.

the others are 2.122(3)³² and 2.1263(6) Å.³³ Other compounds having two calixarene ligands and M₂ units, M = Mo, W, Nb, commonly have the structural motif shown in **IV**, and one has the structure shown in **V**.³⁴ Recently, the compound Rh₂(Br₂-calix[4]arene(CO₂)₂)₂·2toluene was made by reacting Rh₂(O₂-CCH₃)₄L₂ and Br₂calix[4]arene(CO₂H)₂ in refluxing toluene and has been shown to catalyze the intramolecular C–H insertion of α-diazo-β-ketoesters.³⁵ Notably, full substitution of the four labile acetate ligands was accomplished here. This contrasts with the reaction leading to the formation of **2** where the less labile formamidinate ligands remain attached to the Rh₂⁴⁺ unit.



- (33) (a) Acho, J. A.; Lippard, S. J. *Inorg. Chim. Acta* **1995**, 229, 5. (b) Acho, J. A.; Ren, T.; Yun, J. W.; Lippard, S. J. *Inorg. Chem.* **1995**, 34, 5226.
- (34) See, for example: (a) Chisholm, M. H.; Folting, K.; Streib, W. E.; Wu, D.-D. *Inorg. Chem.* **1999**, 38, 5219. (b) Caselli, A.; Solari, A. R.; Scopelliti, L. R.; Floriani, C.; Re, N.; Rizzoli, A. C.; Chiesi-Villa, A. *J. Am. Chem. Soc.* **2000**, 122, 3652.
- (35) Seitz, J.; Maas, G. *Chem. Commun.* **2002**, 338.

Concluding Remarks

A highly reproducible synthesis of a carceplex consisting of two tetracarboxylato-calixarene bowls joined covalently by four singly bonded dirhodium units has been established. The cage molecules encapsulate tetraethylammonium ions selectively over tetrabutylammonium ions to give a very stable species which remains intact in solution, and even under the conditions necessary for mass spectroscopy. Simpler compounds with only one dirhodium or one dimolybdenum unit are also described here. These represent the first known compounds of their class in which there is only one *cis*-[M₂(formamidinate)₂ⁿ⁺] unit attached to carboxylate groups of a calixarene ligand. Efforts to improve the yield of **1b** and study its catalytic activity are in progress.

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Supporting Information Available: X-ray crystallographic data for **1a**, **1b**, **1c**, **2**, and **3** (CIF). Fully labeled plots of the cores of the molecules in **1a** and **1b**, to facilitate the interpretation of the tables of bond distances and angles, and a plot of **3** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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