Inorganic Inclusion Chemistry: A Novel Anion Inclusion System

Wei Xu, Jadagese J. Vittal, and Richard J. Puddephatt*

Contribution from the Department of Chemistry, University of Western Ontario, London, Ontario, Canada N6A 5B7

Received January 25, 1995[®]

Abstract: A bowl-shaped calixresorcinarene, **1**, has been derivatized to incorporate four phosphonite units to give a phosphonitocavitand, **2**, which can act as a tetradentate ligand. Thus, **2** has been used in the synthesis of several tetracopper(I) and tetrasilver(I) complexes, such as $[PyH]^+[\mathbf{2}\cdot Cu_4(\mu\text{-}Cl)_4(\mu_3\text{-}Cl)]^-$ (**4**) and $[PyH]^+[\mathbf{2}\cdot Ag_4(\mu\text{-}Cl)_4(\mu_4\text{-}Cl)]^-$ (**5**). The tetracopper(I) complex, **4**, and tetrasilver(I) complex, **5**, have been shown to act as size-selective hosts for halide inclusion. Iodide is preferred over chloride as guest in **4** since it is large enough to coordinate to all four copper atoms in an unusual μ_4-face-bridging bonding mode. The anion inclusions found for the transition metal rimmed bowl complexes are unique in supramolecular chemistry. The anion occluded complex **5a** can act as a nucleophile to convert RI to RCl; the reaction occurs in high yield, follows the reactivity sequence *t*-BuI > *i*-PrI > MeI, and occurs with predominant retention of stereochemistry in the reaction of (*S*)-(+)-2-iodooctane. The overall reaction leads to the favorable replacement of the occluded μ_3-Cl ligand in **5a** by μ_4-I.

Introduction

Virtually all of the known macrocyclic compounds used in inclusion chemistry are polybasic hosts such as polyethers, amines, sulphides, and carbonyl compounds, and they act as hosts for neutral or positively charged guests such as toluene, acetone, chloroform, metal cations, and ammonium salts. As a result, anion complexation has received very little attention compared to cation complexation, although selective anion complexation and transport can play important roles in organic, inorganic, and biological chemistry[1] and could be useful in anion separation and recovery technologies. In biology, it is thought that anionic substrates participate in approximately 70% of all enzymatic reactions.[2] In chemistry, anions play many roles as nucleophiles, bases, and redox agents in phase-transfer catalysis and others.[2] Inclusion of anions can cause changes in chemical reactivity of the anions in a way similar to how cation complexation affects cation reactivity. Furthermore, once anions are captured, a "naked cation" will be formed and its chemistry will also be of interest.

The first model system for anion inclusion was derived from the class of cation complexing agents known as aza crown ethers.[3,4] When polyprotonated, these macrocyclic polyamines form cavities lined with positive charges. In such hosts, the distance between charged sites, the cavity size, and the potential for hydrogen bonding all play a role in determining the binding of anionic guests. A second approach to anion fixation is by the polycyclic quaternary ammonium salts, and anion inclusion by these hosts is dominated by direct electrostatic interactions and hydrogen bonding.[5,6] In such anion receptors, the anion may form either an endo complex in which it is fully incorporated into the cavity, or, more often, it can bind outside the cavity and the ionic and nucleophilic properties of the captured anions are then changed only slightly.[7,8]

It is well-known that a rim of nucleophilic atoms such as oxygen, nitrogen, and sulfur in crown ethers or cryptands can bind cations strongly by multiple coordination. It was of interest to determine whether a rim of electron-deficient transition metals incorporated into a macrocyclic framework can create a suitable environment to include an anion by analogous multiple coordination.

The macrocyclic system chosen was based on the calixresorcinarenes, **1**, which are bowl shaped molecules with a remarkable ability to contain either neutral or cationic guests.[9–11] However, owing to the poor electrophilicity of calixresorcinarenes, there is little anion inclusion chemistry and no halide inclusion.[12] Most known metal derivatives of calixarenes are with oxophilic metal ions, which cannot easily be used for anion inclusion. Therefore, in these complexes, inclusion of neutral molecules is still preferred.[13–16] It has been shown that the phosphonitocalixresorcinarene, **2**, can act as a tetradentate ligand

---

[®] Abstract published in *Advance ACS Abstracts,* July 15, 1995.

(1) Katz, H. E. *Inclusion Compounds*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds.; Oxford University Press: New York, 1991; Vol. 4, Chapter 9.

(2) Schmidtchen, F. P. *Nachr. Chem., Tech. Lab.* **1988**, *36*, 8.

(3) Frauste da Silva, J. J. R.; Williams, R. J. P. *Struct. Bonding (Berlin)* **1976**, *29*, 67.

(4) Simmons, H. E.; Park, C. H. *J. Am. Chem. Soc.* **1968**, *90*, 2428.

(5) Lehn, J.-M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 89.

(6) Schneider, H.-J.; Theis, I. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 753.

(7) Wilkinson, G.; Gillard, R. D.; McCleverty, J. A. *Comprehensive Coordination Chemistry*; Pergamon: Oxford, U.K., 1987; Vol. 2, p 948.

(8) (a) Graf, E.; Lehn, J.-M. *J. Am. Chem. Soc.* **1978**, *98*, 6405. (b) Arimura, E.; Edamitsu, S.; Shinkai, S.; Maramatsu, T.; Tashiro, M. *Chem. Lett.* **1987**, 2269.

(9) Cram, D. J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1009.

(10) Atwood, J. L.; Davies, J. E. D.; MacNicol, D. D. *Inclusion Compounds*; Academic Press: Orlando, FL, 1991.

(11) Gutsche, C. D. *Calixarenes*; Monographs in Supramolecular Chemistry; The Royal Society of Chemistry: Cambridge, U.K., 1989.

(12) (a) Asfari, Z.; Harrowfield, J. M.; Ogden, M. I.; Vicens, J.; White, A. H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 854. (b) Asfari, Z.; Weiss, J.; Pappalardo, S.; Vicens, J. *Pure Appl. Chem.* **1993**, *65*, 585. (c) Beer, P. D.; Chen, Z.; Goulden, A. J.; Grieve, A.; Hesek, D.; Szemes, F.; Wear, T. *J. Chem. Soc., Chem. Commun.* **1994**, 1269.

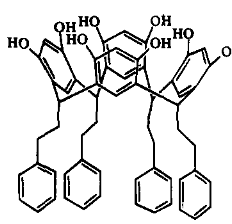
(13) Power, P. *J. Am. Chem. Soc.* **1985**, *107*, 8087.

(14) (a) Corazza, F.; Floriani, C.; Chiesi-Villa, A.; Gaustini, C. *J. Chem. Soc., Chem. Commun.* **1990**, 640. (b) Corazza, F.; Floriani, C.; Chiesi-Villa, A.; Guastini, C.; Rizzoli, C. *Inorg. Chem.* **1991**, *30*, 4465. (c) Corazza, F.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.* **1990**, 1083. (d) Calestani, G.; Ugozzoli, F.; Arduini, A.; Ghidini, E.; Ungaro, R. *J. Chem. Soc., Chem. Commun.* **1990**, 344.

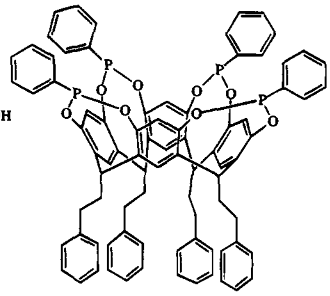
(15) (a) Atwood, J. L.; Orr, G. W.; Means, N. C.; Hamada, F.; Zhang, H.; Bott, S. G.; Robinson, K. D. *Inorg. Chem.* **1992**, *31*, 603. (b) Atwood, J. L.; Bott, S. G.; Jones, C.; Raston, C. L. *J. Chem. Soc., Chem. Commun.* **1992**, 1349. (c) Atwood, J. L.; Orr, G. W.; Bott, S. G.; Robinson, K. D. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1093.

0002-7863/95/1517-8362$09.00/0

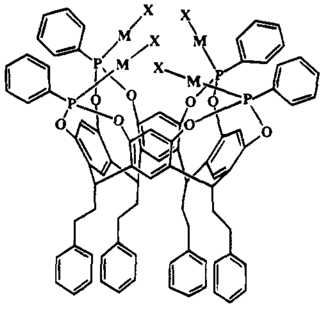
in forming the tetragold(I) derivative **3**,in which there is a metal "picket fence" around the upper rim of the bowl with one AuCl unit tilting to the center of the bowl.[17] Although the gold(I) rimmed calixresorcinarene **3** derivative did not show anion inclusion properties, it did show that anion inclusion might be possible if more electron-deficient metal centers than gold(I) could be introduced.[18] The successful introduction of copper(I) and silver(I) centers around the upper rim of a calixresorcinarene and the unique anion inclusion properties of these compounds are the subjects of the present report. Preliminary results of parts of this work have been communicated.[18]



1



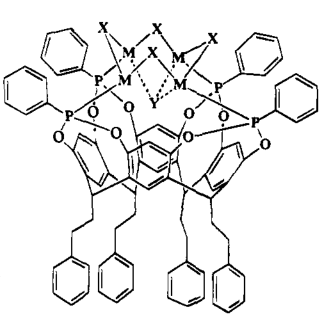
2



3, M = Au, X = Cl

Results and Discussion

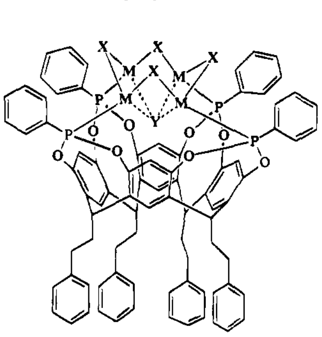
Copper(I) Rimmed Calixresorcinarenes. The phosphorus(III) derivative **2** of a calixresorcinarene, in which the lone pair electrons on the phosphorus atoms are directed inward can be obtained from reaction of the calix[4]resorcinarene **1** and $PhPCl_2$ in the presence of pyridine as base.[17] Treatment of the ligand **2** with $(CuCCPh)_n$ in the presence of pyridinium chloride, gave $[C_5H_5NH]^+[2{\cdot}Cu_4(\mu\text{-}Cl)_4(\mu_3\text{-}Cl)]^-$ (**4a**) in high yield (76%) with release of HCCPh. The ligand **2** failed to react with $(CuCCPh)_n$ in the absence of pyridinium chloride.



4a, M = Cu, X = Y = Cl

Charges:

4, 5	-1
6	0
7	-2



4b, M = Cu, X = Y = Br
4c, M = Cu, X = Y = I
4d, M = Cu, X = Cl, Y = I
5a, M = Ag, X = Y = Cl
5b, M = Ag, X = Y = Br
5c, M = Ag, X = Y = I
5d, M = Ag, X = Cl, Y = I
6, M = Ag, X = Cl, Y abs.
7, M = Ag, X = Cl, Y = S

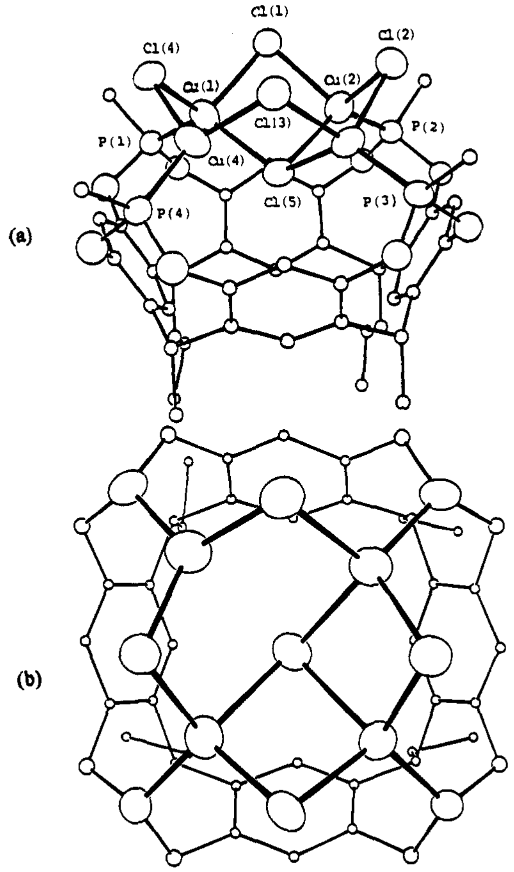


Figure 1. (a) Side view and (b) front view of the molecular structure of the anion **4a**. The phenyl rings on both PhP and CH_2CH_2Ph groups and hydrogens have been omitted for clarity.

The ^{31}P NMR spectrum of complex **4a** in CD_2Cl_2 contained a single resonance, indicating effective C_4 symmetry, and the ^1H NMR spectrum clearly indicated that the complex still contained the calixarene in the cone conformation. The ^1H NMR spectrum of **4a** also showed the presence of the pyridinium cation, perhaps indicating anion inclusion. The anion occluded structure of **4a** was finally established by an X-ray structure determination, and the structure of the complex anion is shown in Figure 1. The main structural features are summarized as follows:

(1) The tetraphosphonitocalixarene unit is present in the cone conformation with each phosphorus coordinated to a copper(I) center.

(2) There is a $Cu_4(\mu\text{-}Cl_4)$ unit arranged in a crown shape around the bowl rim, thus closing the bowl, in which the Cu−Cl bond distances are in the range 2.306(6)−2.410(5) Å, which is normal for Cu−Cl bonds.[19] This unit effectively seals the top of the calixarene bowl.

(3) A chloride ion is trapped inside the bowl and is more weakly bound to three of the copper atoms with Cu−μ_3-Cl distances in the range 2.467(5)−2.548(6) Å. These distances are significantly longer than the Cu−μ_2-Cl distances within the crown structure, apparently indicating weaker Cu−Cl bonding. The distance Cu(4)−Cl(5) is 2.983(5) Å, which is considered too long for a Cu−Cl bond.[19]

---

(16) Floriani, C.; Jacoby, D.; Chiesi-Villa, A.; Guastini, C. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1376.

(17) Xu, W.; Rourke, J. P.; Vittal, J. J.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* **1993**, 145.

(18) Xu, W.; Vittal, J. J.; Puddephatt, R. J. *J. Am. Chem. Soc.* **1993**, *115*, 6456.

(19) (a) Andersson, S.; Jagner, S. *Acta Chem. Scand.* **1985**, *A40*, 177. (b) Asplund, M.; Jagner, S.; Nilsson, M. *Acta Chem. Scand.* **1985**, *A39*, 447. (c) Asplund, M.; Jagner, S. *Acta Chem. Scand.* **1984**, *A38*, 129.

Table 1. Selected Bond Distances (Å) and Angles (deg) in the Anions **4a**,**d** and **5a**

	4a (M = Cu, X = Cl)	**4d** (M = Cu, X = I/Cl)	**5a** (M = Ag, X = Cl)
M(1)−X(1)	2.374(5)	2.630(2)	2.56(1)
M(1)−X(4)	2.405(5)	2.664(2)	2.57(1)
M(1)−X(5)	2.512(5)	2.758(2)	2.72(1)
M(2)−X(1)	2.348(5)	2.649(2)	2.59(1)
M(2)−X(2)	2.386(5)	2.673(2)	2.58(1)
M(2)−X(5)	2.548(6)	2.752(2)	2.76(1)
M(3)−X(2)	2.410(5)	2.645(2)	2.60(1)
M(3)−X(3)	2.369(5)	2.519(2)	2.62(1)
M(3)−X(5)	2.467(5)	2.845(2)	2.69(1)
M(4)−X(3)	2.294(6)	2.560(2)	2.59(1)
M(4)−X(4)	2.306(6)	2.631(2)	2.61(1)
M(4)−X(5)	2.983(5)	2.813(2)	2.69(1)
M(1)−P(1)	2.177(6)	2.215(3)	2.41(1)
M(2)−P(2)	2.177(5)	2.216(3)	2.40(1)
M(3)−P(3)	2.181(5)	2.209(3)	2.39(1)
M(4)−P(4)	2.168(6)	2.206(3)	2.37(1)
P···P[a]	6.04(1)	6.09(1)	6.29(1)
M···M[a]	3.33(1)	3.37(1)	3.48(2)
X···X[a]	3.74(1)	4.23(2)	4.24(2)
X(4)−M(1)−X(1)	107.5(2)	108.07(7)	108.5(4)
X(5)−M(1)−X(1)	95.4(2)	103.33(6)	96.4(4)
X(5)−M(1)−X(4)	100.6(2)	105.89(6)	98.4(4)
P(1)−M(1)−X(1)	114.7(2)	109.6(1)	114.6(4)
P(1)−M(1)−X(4)	109.7(2)	109.6(1)	114.3(4)
P(1)−M(1)−X(5)	126.7(2)	119.7(1)	122.1(3)
X(2)−M(2)−X(1)	105.5(2)	107.50(6)	111.8(4)
X(5)−M(2)−X(1)	95.1(2)	102.98(6)	94.9(3)
X(5)−M(2)−X(2)	95.1(2)	103.76(6)	96.2(4)
P(2)−M(2)−X(1)	117.6(2)	112.5(1)	115.8(4)
P(2)−M(2)−X(2)	114.0(2)	109.5(1)	115.7(4)
P(2)−M(2)−X(5)	125.6(2)	119.6(1)	119.3(3)
X(3)−M(3)−X(2)	106.6(2)	107.20(7)	108.8(5)
X(5)−M(3)−X(2)	96.7(2)	101.99(6)	97.6(4)
X(5)−M(3)−X(3)	96.9(2)	98.75(7)	96.7(4)
P(3)−M(3)−X(2)	110.7(2)	113.0(1)	114.2(4)
P(3)−M(3)−X(3)	114.0(2)	115.9(1)	114.7(4)
P(3)−M(3)−X(5)	129.2(2)	118.0(1)	122.5(3)
X(4)−M(4)−X(3)	110.0(2)	108.61(7)	110.9(4)
X(5)−M(4)−X(3)		98.62(7)	97.2(4)
X(5)−M(4)−X(4)		105.26(7)	98.3(3)
P(4)−M(4)−X(3)	121.1(2)	115.1(1)	113.8(5)
P(4)−M(4)−X(4)	120.3(2)	109.3(1)	113.6(4)
P(4)−M(4)−X(5)		119.0(1)	121.1(3)

[a] Mean of four values.

(4) As a result, the stereochemistry of atoms Cu(1)−Cu(3) is best described as distorted tetrahedral while Cu(4) has distorted trigonal planar geometry. For example, the angles Cl−Cu−Cl and Cl−Cu−P range from 95.4(2) to 107.5(2)° and 109.7(2) to 126.7(2)°, respectively, for Cu(1) and are 110.0(2)° and 120.3(2)−121.1(2)°, respectively, for Cu(4).

The crown structure observed in **4a** is rare in tetranuclear copper(I) halide derivatives, for which cubane or ladder structures are typical.[20] The pyridinium cation was found to be disordered, with partial occupation of two positions outside the upper rim of the bowl. Selected bond distances and angles for **4a** are listed in Table 1.

The structure of **4a** has approximate C_s symmetry, with the mirror plane containing the atoms P(2)Cu(2)Cl(5)Cu(4)P(4) (Figure 1b). Hence, if the structure is maintained in solution, the ^{31}P NMR spectrum should contain three resonances in a 2:1:1 ratio, whereas the spectrum even at −90 °C actually contained only one resonance. This indicates that the anion **4a** is fluxional in solution, with the trapped μ_3-Cl$^-$ migrating rapidly between the four copper atoms to give effective 4-fold symmetry. Given that the Cu−μ_3-Cl bonds appear to be weak and that only a small motion of the μ_3-Cl ligand is required, this fluxionality might be expected to occur very easily and, indeed, the trapped chloride appears to be free to move around within the bowl structure.

The type of anion inclusion demonstrated here for compound **4a** appears to be unique in both calixarene chemistry and supramolecular chemistry and is made possible by the presence of the electrophilic copper(I) centers around the top of the bowl. It was of interest to determine if other anions could replace either the μ_2-Cl or the μ_3-Cl ligands within the structure of **4a**. The other halide derivatives of **4** (**4b**, X = Br; **4c**, X = I) could be obtained either from **3a** by halide exchange using excess LiBr and NaI, respectively, or by direct reaction of ligand **2** with $(CuCCPh)_n$ in the presence of $[C_5H_5NH]Cl$ and LiBr or NaI. In the reactions of **4a**, the occluded μ_3-Cl as well as the more exposed μ_2-Cl ligands of **4a** are readily replaced by bromide or iodide. Attempts to trap anions such as BF_4^- or PF_6^- inside the bowl were unsuccessful, probably because the cavity formed by ligand **2** and the Cu_4Cl_4 aggregate is too small to accommodate the larger anions and because these ligands cannot mimic the ability of the occluded halide to bind weakly to the copper centers.

The difference in the preferred stereochemistries of gold(I) and copper(I) clearly has a profound effect on the ability of the bowl complexes to occlude a halide ion. The gold complex does not bind halide ions strongly whereas the copper complex does. Clearly, by modifying the metal substituents, there is the potential to tune the halide binding ability.

Anion Recognition by Copper(I) Rimmed Calixresorcinarenes. Since selective anion inclusion is important in both biochemistry and chemistry, it was interesting to ask if **4** could display **selectivity** in halide inclusion. Indications that this might be possible were first obtained in attempts to prepare the iodide complex **4c**. Reactions between **2** and CuI in the presence of pyridinium chloride or between **4a** and *n*-Bu$_4$NI were carried out and, in each case, the product analyzed as $[C_5H_5NH]^+[\mathbf{2}{\cdot}Cu_4I_{3.3}Cl_{1.7}]^-$ (**4d**), showing that complete replacement of chloride by iodide is difficult. This was unexpected since copper(I) is a soft metal ion with a strong preference for iodide. The first priority was to determine if the occluded anion in **4d** was chloride or iodide. The ^{31}P NMR spectrum of **4d** showed three broad peaks, and its ^{1}H NMR spectrum indicated the presence of the pyridinium cation. These observations suggested that **4d** has structure similar to that of **4a** but did not define the positions of the iodide and chloride ligands. Therefore, an X-ray structure determination was carried out. The structure of the anion is shown in Figure 2 and reveals that *iodide* is selectively included in the middle of the bowl by weakly bonding to *four* copper(I) atoms, while chloride and iodide ions in a ratio of 1.75:2.25 occupy the μ_2-bridging sites in a disordered way.

The occupancy factors for the halogen atoms were obtained from peak heights in the SHELXS-86 solution and later refined in the least-squares refinements. Refinement of occupancy factors gave the following ratios of I/Cl: X(1) and (X)2, 0.625/0.375; X(3), 0.40/0.60; X(4), 0.60/0.40; giving the overall partial formula $[Cu_4I_{3.25}Cl_{1.75}]$, in good agreement with analytical data. The Cu−I(5) distances are 2.752(2)−2.845(2) Å, which are longer than that of a normal Cu−I bond (~2.5 Å),[19] and adjacent nonbonding Cu···Cu distances are 3.275−3.461 Å. The bond distances and angles are listed in Table 1.

The complexes $[C_5H_5NH]^+[\mathbf{2}{\cdot}Cu_4Cl_5]^-{\cdot}2MeCN$ and $[C_5H_5NH]^+[\mathbf{2}{\cdot}Cu_4Cl_{1.75}I_{3.25}]^-{\cdot}2MeCN$ can be considered as isostruc-

---

(20) Bowmaker, G. A.; Camp, D.; Hart, R. D.; Healy, P. C.; Skelton, B. W.; White, A. H. *Aust. J. Chem.* **1992**, *45*, 1155.

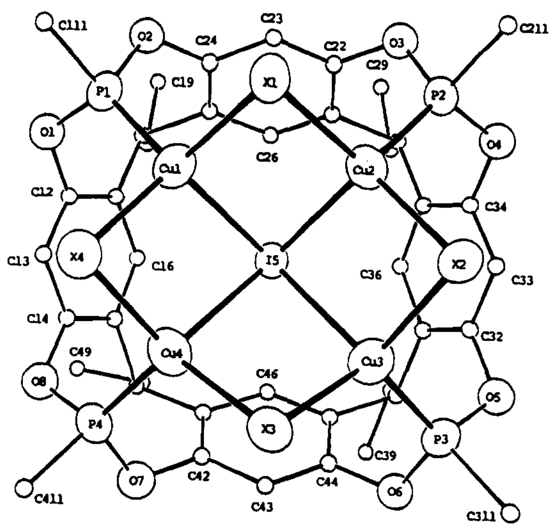


Figure 2. Front view of the molecular structure of the anion **4d**. The phenyl rings have been omitted for clarity.

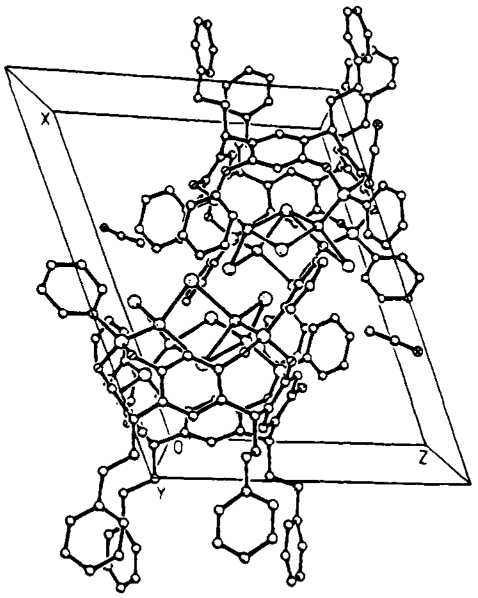


Figure 3. Unit cell packing of the complex pyH[**4d**]·2MeCN.

tural or close to isostructural. In contrast to most calixresorcinarene derivatives, the cavity of **4**, which is normally available to a guest, is occupied by an anion and hence the solvent molecules are not included in the cavity of the bowl but occupy holes in the lattice formed by the calixresorcinarene molecules as illustrated in Figure 3. As in complex **4a**, the nitrogen atom of the pyridinium ring in **4d** could not be distinguished from the carbon atoms and hence a disorder of the nitrogen atom over all six sites was assumed. The structure determination shows that the anion inclusion is selective and that the geometry imposed by the calixresorcinarene host can stabilize an unusual μ_4-face-bridging binding mode of the guest halide.

The face-bridging μ_4-I binding mode for the included iodide in **4d** is rare in tetranuclear Cu(I) halide derivatives, although face-bridging μ_4-Cl binding has been observed in some polynuclear complexes.[19] Why is it formed? We suggest that copper(I) has a thermodynamic preference for tetrahedral rather than trigonal planar stereochemistry and this can only be accommodated, given the ligand geometry, by the μ_4-halide binding in **4**. The chloride ligand is too small to bridge between all four copper(I) atoms for which the internuclear distances are controlled by the relatively rigid geometry of **2**, but it can bridge between three of them as in **4a**. On the other hand, iodide is large enough to bridge between all four copper atoms. Hence, in a mixed chloride–iodide complex, the iodide will bind selectively in the center as in **4d,e** to form the more effective μ_4-face-bridging bonds. It is less obvious why it is difficult to replace all the μ-Cl groups. The cavity size is determined by the $Cu_4(\mu\text{-}X)_4$ crown structure, and this may be optimized for iodide inclusion or the formation of μ_4-face-bridged binding when a mixture of μ-I and μ-Cl ligands is present. The three resonances in the ^{31}P NMR spectrum of **4d** are then interpreted in terms of each of the three possible coordination types $P(\mu_4\text{-}I)Cu(\mu\text{-}Cl)_2$, $P(\mu_4\text{-}I)Cu(\mu\text{-}I)_2$, and $P(\mu_4\text{-}I)Cu(\mu\text{-}Cl)(\mu\text{-}I)$, giving rise to a singlet resonance.

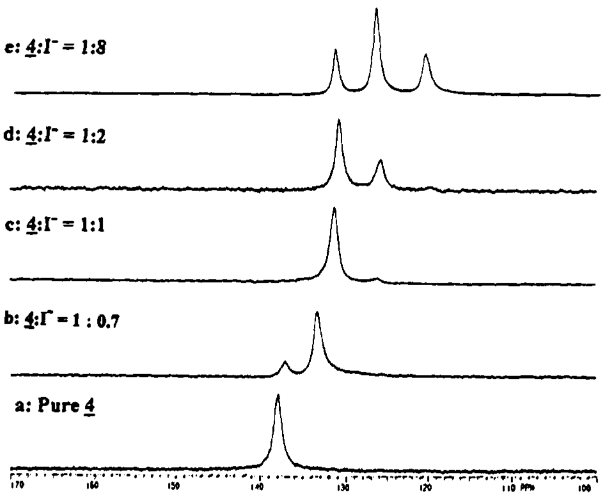


Figure 4. ^{31}P NMR spectra of complex **4a** with added Bu_4NI in CD_2Cl_2.

From the discussion above, it was concluded that I^- gives effective μ_4-face-bridged binding with four copper(I) centers. Will this effect lead to selective recognition of I^- over other anions by the complex **4a**? To test the selectivity of the anion inclusion, the complex **4a** and Bu_4NX (X = Br, I, CN, or NO_3) were reacted in a 1:1 stoichiometric ratio in CD_2Cl_2. The occluded Cl^- or **4a** can be replaced selectively by Br^- or I^- as indicated by the presence of only a single resonance in the ^{31}P NMR spectrum (Figure 4). Thus only the replacement of the occluded Cl^- with Br^- or I^- will keep the geometry of the molecule in C_4 symmetry. Any replacement of chloride ligands on the rim will lead to lower symmetry and so to more resonances in the ^{31}P NMR spectra. The CN^- and NO_3^- ions cannot replace the occluded Cl^-. Instead, excess CN^- decomposed **4a**. These results can easily be explained, since the size of the cavity in **4** can accommodate Br^- and I^- and form the favored μ_4-face-bridged binding. When excess Bu_4NX (X = Br, I) was added to the solution of **4a**, partial replacement of the chloride ligands on the rim is also possible and does indeed give rise to extra resonances in the ^{31}P NMR, as indicated in Figure 4.

Silver(I) Rimmed Calixresorcinarenes. If the cavity size in **4** is determined by the $Cu_4(\mu\text{-}X)_4$ crown structure, it should be possible to optimize selectivity for anions of different sizes by using different transition metals. Furthermore, if the interpretation that the trapped μ_3-Cl migrates rapidly between the four copper atoms to give effective 4-fold symmetry is correct, then a μ_4-Cl group should be possible even in the solution if copper(I) is replaced by a large metal ion such as Ag(I). Reaction of **2** with $(AgCCPh)_n$ in the presence of pyridinium chloride gave a new complex $[C_5H_5NH]^+[\mathbf{2}\cdot Ag_4(\mu\text{-}Cl)_4(\mu_4\text{-}Cl)]^-$ (**5a**). As an alternative route to the preparation of **5a**, the reaction of $AgNO_3$ with **2** followed by addition of pyridinium chloride also gave **5a**, although in lower yield. The

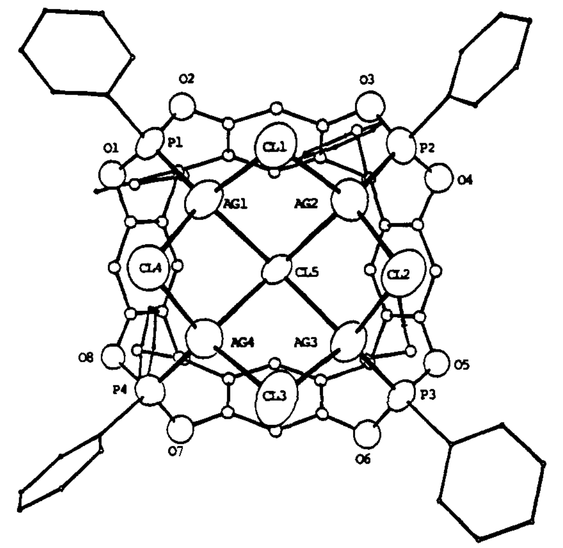


Figure 5. Front view of the molecular structure of the anion **5a**. The phenyl rings on the CH_2CH_2Ph groups and hydrogen atoms have been omitted for clarity.

tendency to form **5a** was so strong that reaction of **3** with $Ag_2(\mu\text{-dppm})(NO_3)_2$ (dppm = $Ph_2PCH_2PPh_2$) in the presence of pyridinium chloride also gave **5a** and $Ag_2(\mu\text{-dppm})_2(NO_3)_2$.[21]

The structure of **5a** is proposed to be the same as **4a** but with a μ_4-Cl ligand in place of the μ_3-Cl ligand in **4a**. The anion inclusion was readily proved by the presence of the cation, $[C_5H_5NH]^+$, and by the observation of cation exchange reactions. The cation, $[C_5H_5NH]^+$, in $[C_5H_5NH]^+$[**5a**]$^-$ can be replaced by other bulky cations such as Me_4N^+ and $n\text{-}Bu_4N^+$ to give $[Me_4N]^+$[**5a**]$^-$ and $[n\text{-}Bu_4N]^+$[**5c**]$^-$. The isolation of complex **5** with different cations can also be achieved easily by carrying out the reaction of **2** with AgCCPh in the presence of the corresponding tetraalkylammonium chlorides, such as $n\text{-}Bu_4NCl$ and Me_4NCl. In addition, it was easier to replace all chlorides in **5a** with bromide or iodide to give the corresponding anions $[2\cdot Ag_4(\mu\text{-}X)_4(\mu_4\text{-}X)]^-$, [**5b**, X = Br; **5c**, X = I; for example, $[n\text{-}Bu_4N]^+$[**5c**], $[C_5H_5NH]^+$[**5b**], and $[C_5H_5NH]^+$[**5c**]) than in **4a**. Each complex **5** gave one resonance in the ^{31}P NMR spectrum, appearing as two doublets due to the couplings $^1J(^{107}AgP)$ and $^1J(^{109}AgP)$, consistent with effective C_4 symmetry.

The structure of **5** was eventually proved by an X-ray structure analysis on complex $Me_4N[2\cdot Ag_4(\mu\text{-}Cl)_4(\mu_4\text{-}Cl)]^-$ (Me_4N[**5a**]). As expected, a μ_4-Cl unit is indeed present as is illustrated in Figure 5. The distances Ag$-\mu$-Cl (2.56(1)−2.62(1) Å) are significantly shorter than Ag$-\mu_4$-Cl (2.69(1)−2.76(1) Å), and hence, the Ag$-\mu$-Cl bonds are presumably stronger than the Ag$-\mu_4$-Cl bonds.[22] The bond distances and angles for **5a** are listed in Table 1.

Although the geometry of **2** is relatively rigid, the cavity size is still flexible and can be adjusted by moving the phosphorus atoms outward or inward. When Cu(I) atoms are replaced by larger Ag(I) atoms, the P···P distances increase to fit the larger metal atoms, while still allowing the effective μ_4-X-face-bridged bonding (Table 1). When μ_4-bridging chloride ligands are replaced by larger anions such as iodide, the M···M distance increases to leave more space for the larger anion inclusion. A number of angles, including O−P−M, P−O−C, and O−P−O angles, appear to change to allow flexing of the bowl structure.

Anion Recognition Driven by the μ_4-Face-Bridged Binding. From the supramolecular chemistry point of view, it is crucial to know whether the anion inclusions are reversible and selective. Two experiments have been designed to test the reversibility and selectivity of anion inclusion in complex **5a**. When complex **5a** was treated with silver(I) nitrate salt in 1:1 ratio, the occluded chloride anion could be removed selectively to give **6**, and **6** reacted quantitatively with Cl^- to regenerate **5a** (Figure 6). Complex **6** was isolated in pure form, but crystals suitable for an X-ray structure determination could not be grown. Complex **6** contains no pyridinium cation (NMR) and no nitrate (IR) and so must have the structure shown in Figure 6. The ^{31}P NMR spectrum contains a single resonance but the chemical shift and $^1J(AgP)$ coupling constants are significantly different from those for **5a**. A comparison of the ^1H and ^{31}P NMR spectra of **5a** and **6** is shown in Figure 7. It is interesting to note that a different reaction occurred when the copper(I) derivative **4a** was treated with $AgNO_3$ in acetonitrile. The silver(I) did not remove the occluded chloride to give a precipitate of AgCl, but silver(I) replaced copper(I) to form **5a**. This experiment gives further evidence that the μ_4-face-bridged binding, which is present in **5a** but not in **4a**, is favored in this particular cluster system.

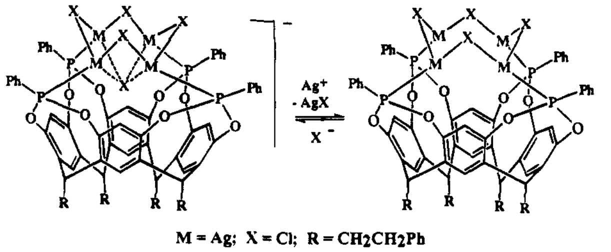


Figure 6. Reversibility of anion inclusion of **5a**.

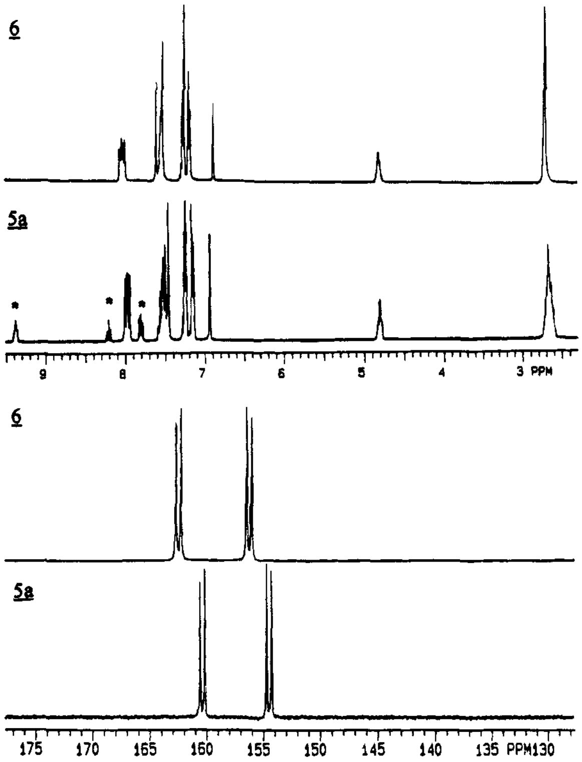


Figure 7. ^1H and ^{31}P NMR spectra of pyH[**5a**] and **6** showing the differences between complexes with and without anion inclusion. Note that pyridinium resonances, which are marked with an asterisk in the ^1H spectrum of pyH[**5a**], are absent in the spectrum of **6**.

As with **4a**, complex **5a** can also recognize different anions and selectively include them in its cavity. When Bu_4NX (X = Cl, I, CN, NO_3) were reacted with **5a** in a 1:1 stoichiometric ratio, only I^- could replace Cl^- and was selectively included.

---

[21] Obendorf, D.; Probst, M.; Peringer, P. *J. Chem. Soc., Dalton Trans.* **1988**, 1709.

[22] Helgesson, G.; Jagner, S. *Acta Crystallogr.* **1988**, *C44*, 2059.

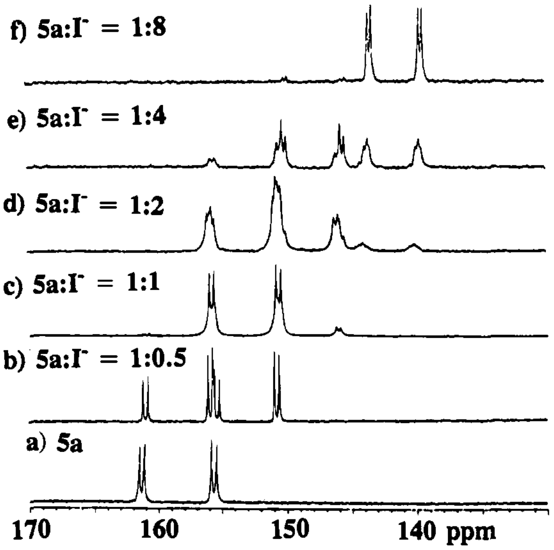


Figure 8. ^{31}P NMR spectra of complex **5a** and Bu_4NI in CD_2Cl_2 in different ratios at 25 °C showing the selective iodide inclusion.

Table 2. ^{31}P NMR Chemical Shifts and Coupling Constants of **6**, **5a**, **5d**, **7**, and **8** in $CDCl_3$ at Room Temperature

complex	6	5a	5d	7	8
included anion		Cl^-	I^-	S^{2-}	CN^-
δ (ppm)	161.9	157.0	153.4	153.9	158.9
$J(^{109}Ag-^{31}P)$ (Hz)	822.5	766.3	667.2	673.3	723.4
$J(^{107}Ag-^{31}P)$ (Hz)	712.5	664.1	578.6	584.7	627.2

The priority of iodide inclusion is clearly indicated by the ^{31}P NMR spectra illustrated in Figure 8. When **5a** and I^- were mixed in a 1:1 ratio, only the occluded Cl^- was replaced by I^-, thus giving rise to a single resonance since all silver atoms have the $P(\mu_4\text{-}I)Ag(\mu\text{-}Cl)_2$ coordination. When more iodide is added, extra peaks arise due to the formation of compounds with $P(\mu_4\text{-}I)Ag(\mu\text{-}Cl)(\mu\text{-}I)$ and then $P(\mu_4\text{-}I)Ag(\mu\text{-}I)_2$ coordination as replacement of chloride ligands on the rim then occurs also.

Model System for Anion Inclusion. When the occluded anion in complex **5a** is removed by $AgNO_3$, compound **6** is formed with an empty cavity defined by a set of electron-deficient transition metals on the upper rim of the calixresorcinarene bowl. Does **6** act as an anion receptor? Treatment of **6** with Bu_4NI in a 1:1 ratio gave the I^- inclusion complex **5d**, identical to the compound obtained by the anion exchange reaction of **5a** with I^- (Figure 8). The structure of **5d** is expected to be the same as for **5a**, that is with C_4 symmetry but with an iodide anion encapsulated in the cavity. When complex **6** was treated with $(Me_3Sn)_2S$ in a 1:1 ratio in $CHCl_3$, complex **7** was formed. The ^{31}P NMR spectrum of **7** showed only one resonance, which appeared as two doublets due to ^{109}Ag and ^{107}Ag coupling, suggesting that S^{2-} was included selectively in the cavity without any replacement of the rim chloride ligands, since that would lead to a product with lower symmetry and hence to a more complex spectrum. It is well-known that, in silver(I) complexes with the same phosphorus donor, the coupling constant $^1J(Ag-P)$ decreases as the coordination number at silver(I) increases. The coupling constant of complex **7** decreased significantly from $^1J(^{109}Ag^{31}P) = 823$ Hz in the anion receptor **6** to $^1J(^{109}Ag^{31}P) = 673$ Hz in complex **7**, which is consistent with the conclusion that the S^{2-} anion was included selectively by interaction with all four Ag(I) centers. Details of chemical shift and coupling constant changes are listed in Table 2. In terms of relative binding ability, it was found that the S^{2-} anion does not replace I^- in **5d** whereas it partly replaces occluded Cl^- in **5a** to give **7**, although the equilibrium lies toward **5a**. Clearly, the binding of I^- with four Ag(I) atoms is much stronger than that of either S^{2-} or Cl^-.

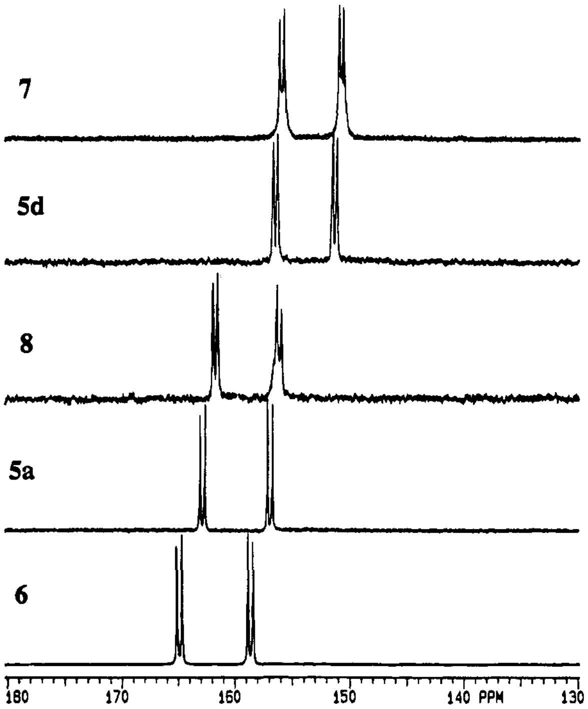


Figure 9. ^{31}P NMR spectra of **6**, **5a**,**d**, **7**, and **8** showing the anion inclusion.

Furthermore, if **6** and Bu_4 NCN were mixed in a 1:1 ratio in $CHCl_3$ solution, complex **8** was formed and, in the ^{31}P NMR spectrum, a similar decrease in $^1J(Ag-P)$ values was observed as in the formation of **8** (Figure 9). The CN^- anion is also expected to be included in the cavity by interaction with Ag(I) atoms, but since there is no precedent for a quadruply bridging cyanide, it is probable that **8** has symmetry lower than C_4 but with a fluxional cyanide ligand. Therefore, it could be concluded that compound **6** acted as a powerful anion receptor toward small guests such as CN^-, Cl^-, Br^-, I^-, or S^{2-} in solution.

Nature of the Unusual μ_4-Face-Bridged Binding. It is clear from the above discussion that anion inclusion is favored by formation of the unusual μ_4-face-bridged binding. The nature of the unusual $M_4(\mu_4\text{-}X)$ bond in **4** and **5** was studied by carrying out extended Huckel MO calculations.[23] The model complex $[Ag_4(\mu\text{-}Cl)_4(\mu_4\text{-}Cl)(PH_3)_4]^-$ (**A**) was considered to be formed from the fragment $[Ag_4(\mu\text{-}Cl)_4(PH_3)_4]$ (**B**) by coordination of Cl^-. Both **A** and **B** were build up with ideal C_{4v} symmetry by using average distances and angles based on the X-ray structure determination. Bonding interactions are readily identified by overlap of filled orbitals of Cl^- with acceptor orbitals on silver. There are only three net σ-bonding interactions ($a_1 + 2e$). Since one of the four sets of acceptor orbitals (b_{1u}, LUMO in **A**) is nonbonding (Figure 10), the maximum $Ag_4(\mu_4\text{-}Cl)$ total bond order is 3 rather than 4, consistent with the longer $Ag-\mu_4\text{-}Cl$ distance (average 2.718 Å) compared to the single-bond $Ag-\mu\text{-}Cl$ distance (average 2.585 Å).[22] The calculated charge on the μ_4-Cl ligand in **A** is −0.5 e, indicating that the $\mu_4\text{-}Cl^-$ ligand is not simply a guest anion but is covalently bonded to the silver(I) centers.[23]

Aliphatic Nucleophilic Substitution Involving the Occluded Cl^-. It is well established that halide exchange, a type of aliphatic nucleophilic substitution, in aprotic solvents follows the S_N2 mechanism with inversion of configuration at carbon

---

[23] Subramanian, L.; Hoffmann, R. *Inorg. Chem.* **1992**, *31*, 1021.

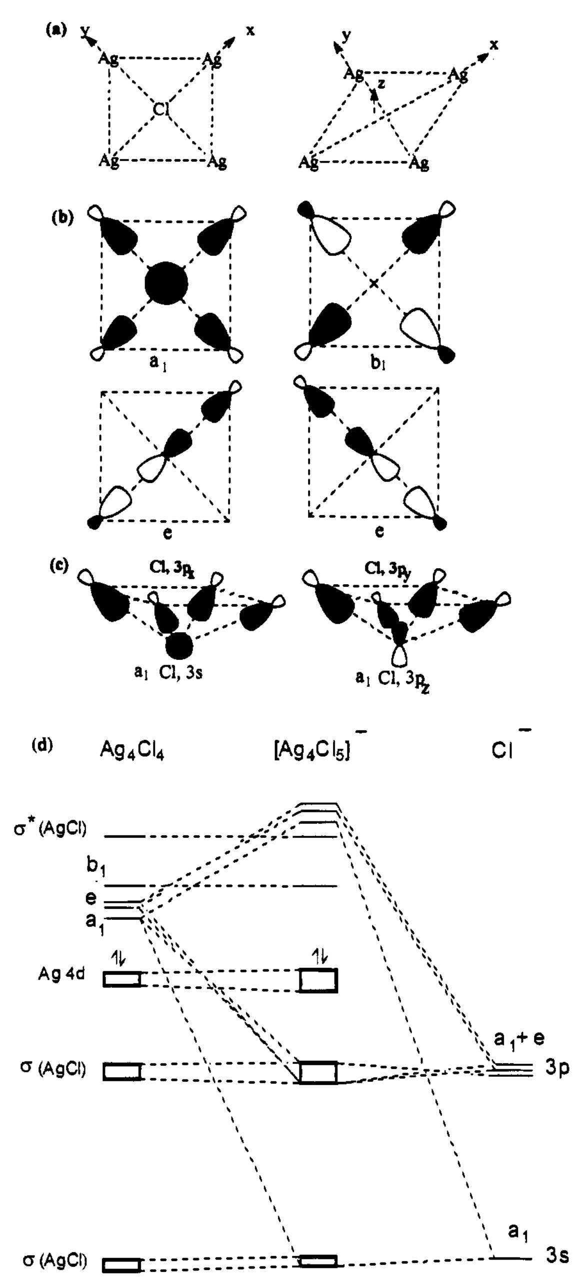


Figure 10. Schematic view of the overlap between the symmetry adapted acceptor orbitals on the $L_4Ag(\mu\text{-}Cl)_4$ unit with the donor orbitals of the included Cl^- ligand: (a) the axes used (PH_3 ligands omitted for clarity); (b) the orbital overlaps; (c) the two main components of the a_1 bonding MO; (d) the energy correlation diagram. The b_{1u} acceptor orbital is the LUMO in the model complex **A**.

center.[24] The reactivity of the alkyl halides follows the order primary > secondary ≫ tertiary, and the halide exchange is an equilibrium process, which may limit its applications. In previous sections, it was demonstrated that a halide anion can be included in the cavity defined by a set of transition metal atoms on the upper rim of a calixresorcinarene bowl and that I^- has precedence over other halide ions for inclusion in the cavity. This strong preference for iodide inclusion should favor the reaction of Cl^- with RI to give RCl and I^-, although the rate of reaction is less easy to predict. Thus the aliphatic nucleophilic substitution of alkyl iodides was investigated, using the chloride of **5a** as a nucleophile. The initial reactions were carried out in CD_2Cl_2 solution at 20 °C and were monitored by ^1H and ^{31}P NMR.

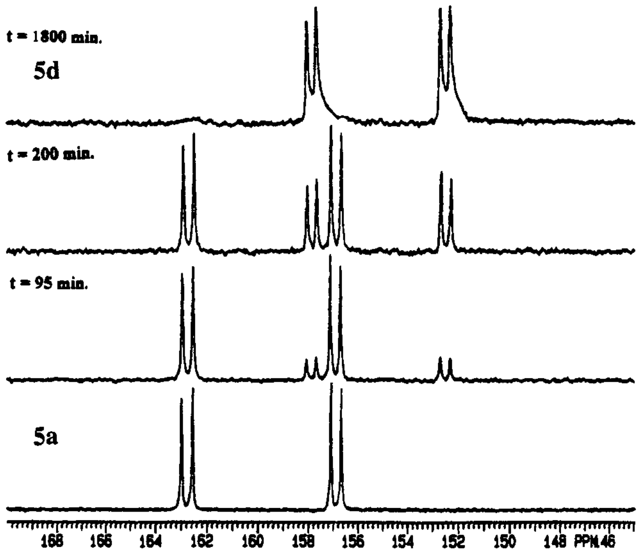


Figure 11. Reaction of pyH[**5a**] with Me_2CHI in a 1:25 stoichiometric ratio and the ^{31}P NMR spectral changes against time at 30 °C in CD_2Cl_2.

The reaction of *t*-BuI with **5a** in a 1:1 ratio gave **5d** and *t*-BuCl quantitatively within 5 min. The similar reaction of *i*-PrI and **5a** in a 1:1 ratio proceeded much more slowly to give **5d** and *i*-PrCl, reaching completion in about 10 days, and the similar reactions with *n*-BuI and MeI were too slow to monitor to completion. For example, the reaction with MeI reached 1% conversion after 3 days. The relative rates are the opposite of those expected for an S_N2 mechanism and are consistent with an S_N1-like mechanism with reaction initiated by iodide abstraction by silver(I). The reaction of **5a** with *i*-PrI at 30 °C in a 1;25 molar ratio occurred at a rate suitable for kinetic measurements using ^{31}P NMR to monitor conversion of **5a** to **5d**, and typical spectra are shown in Figure 11. Conversion of **5a** to **5d** is quantitative. In contrast, the equilibrium constant (K) for reaction between [PPN]Cl (PPN = $(Ph_3P)_2N$) and *i*-PrI to give [PPN]I and *i*-PrCl in $CDCl_3$ was determined as $K = 0.30$. Clearly the strong preference for I^- over Cl^- inclusion, due to stronger μ_4-face-bridged bonding with the μ_4-I ligand, accounts for the much more favorable equilibrium with **5a** as reagent. One possible mechanism for the reaction is illustrated in Figure 12. The reagent RI undergoes iodide abstraction by silver(I), perhaps involving two Ag(I) centers to give an $Ag_2(\mu\text{-}I)$ unit with fast attack by a neighboring $Ag_2(\mu\text{-}Cl)$ ligand on the forming carbocation to give RCl. Finally, the μ_2-I ligand migrates to the bowl center to form the strong $Ag_4(\mu_4\text{-}I)$ unit while the μ_4-Cl ligand moves to the rim and becomes a μ_2-Cl ligand. Note that the nucleophile is then a rim-bound chloride though the overall reaction leads to substitution of the occluded chloride. Since the iodide abstraction step is rate determining (it has already been established that iodide reacts very rapidly with **5a** to give **5d**, presumably by initial coordination at the rim followed by migration to the bowl center), the reaction should follow second-order kinetics with reactivity of RI following the sequence tertiary > secondary > primary as observed.

To confirm the kinetic order of the reaction, a series of kinetic measurements were made in which the ratio of reagents **5a**:*i*-PrI was varied from 1:25 to 1:100. In each case, the reaction at 30 °C in CD_2Cl_2 followed first-order kinetics in [**5a**], as shown in Figure 13, and a plot of the first-order rate constants versus [*i*-PrI] was linear and passed through the origin as illustrated in Figure 14. Hence the reaction rate is first order in both [**5a**] and [*i*-PrI], as expected for the proposed mechanism.

---

(24) March, J. *Advanced Organic Chemistry*, 4th ed.; Wiley: New York, 1992; p 430.

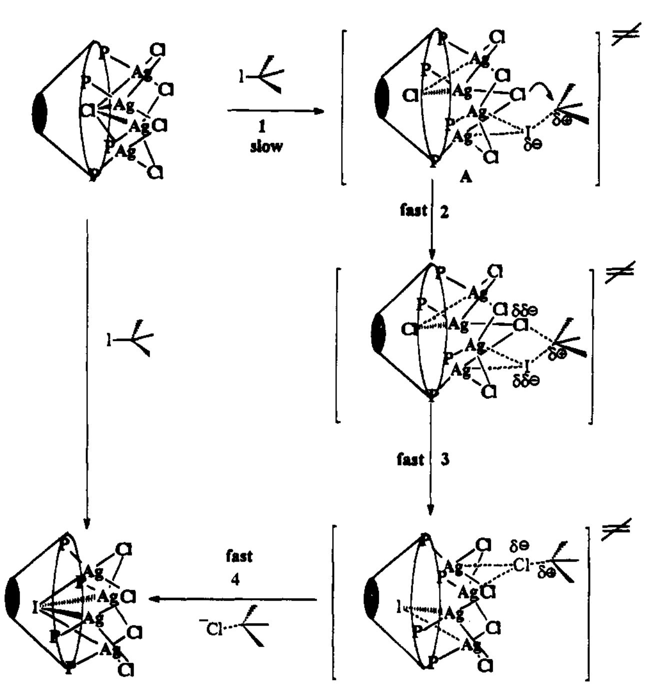


Figure 12. Possible mechanism for the nucleophilic substitution reaction.

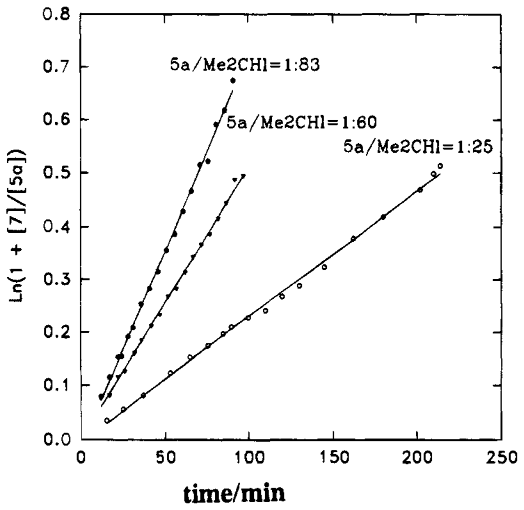


Figure 13. First-order plots for the reaction of pyH[**5a**] with excess *i*-PrI in CD_2Cl_2 at 30 °C.

The second-order rate constant at 30 °C was $k_2 = 8 \times 10^{-3}$ L mol^{-1} min^{-1}.

The mechanism of Figure 12 predicts overall retention of configuration when substitution occurs at a chiral carbon and, in order to check this, the reaction of **5a** with the secondary alkyl iodide (*S*)-(+)-2-iodooctane[25] ($[\alpha]_{589}^{20}$ 37.0°, lit.[26] 36.9°) was carried out in a 1:1 ratio. The reaction in CH_2Cl_2 at 40 °C was complete in 48 h and gave **5d** and (*S*)-(+)-2-chlorooctane ($[\alpha]_{589}^{20}$ 28.8°, lit.[26] 33.7°), corresponding to reaction with 86% overall retention of configuration. This result strongly supports the proposed mechanism of reaction. The partial racemization observed could be caused by some competition with the S_N2 mechanism or by some intermediate formation of a free carbocation.

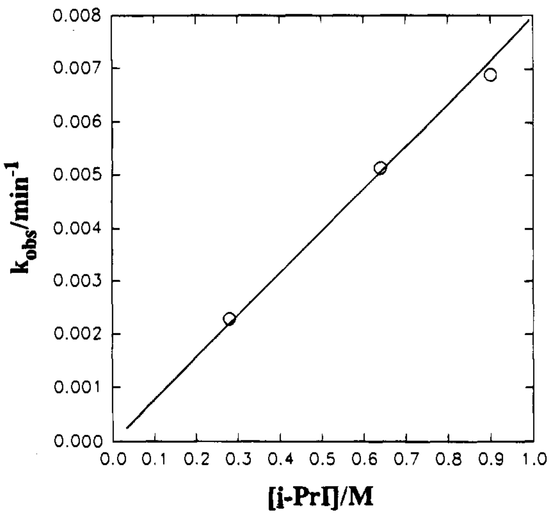


Figure 14. Graph of first-order rate constants for reaction of pyH[**5a**] with *i*-PrI in CD_2Cl_2 at 30 °C, *k*(obs) in min^{-1}, versus the concentration of *i*-PrI.

Conclusions

The multidentate complexation of an anion by a neutral host containing transition metal substituents at the rim of a macrocyclic ligand opens up a realm of new chemistry. This work has demonstrated how transition metal rimmed complexes of a phosphonitocalixresorcinarene can provide a host for the *size-selective* inclusion of anions which are stabilized by a unique μ_4-face-bridged binding mode. The nucleophilic properties of the imprisoned anion are shown to be dramatically changed compared to the free anion, for example, in nucleophilic aliphatic substitution reactions where the position of equilibrium is influenced strongly by the anion inclusion. This suggests wider potential applications of anion inclusion complexes in chemistry.

Should the chemistry described above be considered an area of supramolecular chemistry or is it a form of polynuclear coordination chemistry? We suggest that it is both, in just the same way that the inclusion of cations in polyether or polyamine hosts is.[10] In both cases it is important to have a natural cavity and multiple binding sites in order for novel chemistry to be observed. It is perfectly normal to design hosts for specific guests by incorporating functional groups which can give multiple, weak binding interactions with the guest.[10] These are commonly donor−acceptor (host to guest), hydrogen bonding, or π-stacking;[10] this work simply uses a variety of the multiple donor−acceptor binding with guest to host donation.

Experimental Section

The compounds calixresorcinarene,[27] $[CuCCPh]_n$,[28] and $[AgCCPh]_n$,[28] were prepared by literature methods and the tetraphosphonitocalixresorcinarene **2** was prepared as described in the previous paper.[17,18] All the experiments were carried out by using standard Schlenk techniques. NMR spectra were recorded by using a Varian Gemini 300 MHz spectrometer. ^1H NMR chemical shifts were measured relative to deuterated solvent peaks but are reported relative to tetramethylsilane. ^{31}P NMR chemical shifts were determined relative to 85% H_3PO_4 as the external standard. IR spectra were recorded on a Bruker IFS32 FTIR spectrometer with Nujol mulls.

Complex 4a. A mixture of $[CuCCPh]_n$ (0.61 mmol), pyridinium chloride (0.07 g, 0.6 mmol), and tetraphosphonitocalix[4]resorcinarene, **2** (0.20 g, 0.15 mmol), in CH_2Cl_2 was stirred at room temperature for 15 h to give a clear solution. The CH_2Cl_2 and HCCPh groups were removed completely under vacuum. The residue was redissolved in CH_2Cl_2 (4 mL). After filtration, the solution was crystallized by

---

[25] Place, P.; Roumestant, M.-L.; Gore, J. *Bull. Soc. Chim. Fr.* **1976**, 169.

[26] *Dictionary of Organic Compounds*, 5th ed.; Chapman and Hall: New York, 1982; pp 1182, 3353.

[27] Tunstad, L. M.; Tucker, J. A.; Dalcanale, E.; Weiser, J.; Bryant, J. A.; Sherman, J. C.; Helgeson, R. C.; Knobler, C. B.; Cram, D. J. *J. Org. Chem.* **1989**, *54*, 1305.

[28] Abu-Salah, O. M.; Al-Ohaly, A. R. *J. Chem. Soc., Dalton Trans.* **1988**, 2297.

diffusion with MeCN (10 mL). A white solid **4a** was obtained, which was washed with MeCN and dried under vacuum. Yield: 0.21 g, 76%. Anal. Calcd for **4a** ($C_{89}H_{74}Cl_5Cu_4N_1O_8P_4$): C, 58.2; H, 4.1. Found: C, 58.3; H, 4.4. NMR (CD_2Cl_2): $\delta(^{31}P)$ 134.9 (s, br); $\delta(^1H)$ 2.75 (br, 16H, CH_2CH_2Ph), 4.85 (br, 4H, $CH(CH_2)_2Ph$), 7.01 (t, $^4J_{PH} = 2.0$ Hz, 4H, Ar*H*, ortho to O), 7.20−7.34 (m, 20H, C_6H_5), 7.52 (s, 4H, Ar*H*, meta to O), 7.53−7.67 (m, 12H, PC_6H_5, para and meta to P), 8.02−8.14 (m, 8H, PC_6H_5, ortho to P), 8.28 (t, 2H, $C_5H_5NH^+$, ortho to N), 7.67−7.80 (m, 3H, $C_5H_5NH^+$, meta and para to N), 9.25 (s, br, 1H, $C_5H_5N{\cdot}H^+$).

Complexes 4b,c. The completely halogen substituted $[C_5H_6N]^+[\mathbf{2}{\cdot}Cu_4X_5]^-$, **4b** (X = Br), and **4c** (X = I) were obtained by stirring the chloride derivative **4a** with an excess of the corresponding potassium halide in CH_2Cl_2 for 24 h followed by filtration and removal of solvent. The products of **4b,c** can be further purified by the crystallization procedure described above. Yield: bromide 88%, iodide 90%. **4b**: Anal. Calcd for **4b** ($C_{89}H_{74}Br_5Cu_4N_1O_8P_4$): C, 52.0; H, 3.6; N, 0.7. Found: C, 52.1; H, 3.9; N, 0.6. NMR (CH_2Cl_2): $\delta(^{31}P)$ 133.0 (s, br); $\delta(^1H)$ 2.74 (br, 16H, CH_2CH_2Ph), 4.86 (br, 4H, $CH(CH_2)_2Ph$), 7.08 (t, $^4J_{PH} = 1.9$ Hz, 4H, Ar*H*, ortho to O), 7.20−7.30 (m, 20H, C_6H_5), 7.54 (s, 4H, Ar*H*, meta to O), 7.52−7.63 (m, 12H, PC_6H_5, para and meta to P), 8.02−8.12 (m, 8H, PC_6H_5, ortho to P), 8.28 (t, 2H, $C_5H_5NH^+$, ortho to N), 7.67−7.80 (m, 3H, $C_5H_5NH^+$, meta and para to N), 8.60 (s, br, 1H, $C_5H_5N{\cdot}H^+$). **4c**: Anal. Calcd for **4c** ($C_{89}H_{74}Cu_4I_5N_1O_8P_4$): C, 46.5; H, 3.3; N, 0.6. Found: C, 46.5; H, 3.2; N, 0.6. NMR (CD_2Cl_2): $\delta(^{31}P)$ 122.6 (s, br); $\delta(^1H)$ 2.73 (br, 16H, CH_2CH_2Ph), 4.86 (br, 4H, $CH(CH_2)_2Ph$), 7.20 (t, $^4J_{PH} = 2.0$ Hz, 4H, Ar*H*, ortho to O), 7.20−7.30 (m, 20H, C_6H_5), 7.51 (s, 4H, Ar*H*, meta to O), 7.52−7.66 (m, 12H, PC_6H_5, para and meta to P), 8.05−8.15 (m, 8H, PC_6H_5, ortho to P), 8.28 (t, 2H, $C_5H_5NH^+$, ortho to N), 7.67−7.77 (m, 3H, $C_5H_5NH^+$, meta and para to N), 9.03 (s, br, 1H, $C_5H_5N{\cdot}H^+$).

Complex 4d. Method 1. A mixture of excess of CuI (0.3 g, 1.6 mmol), pyridinium chloride (0.023 g, 0.2 mmol), and tetraphosphonitocalix[4]resorcinarene, **2** (0.20 g, 0.15 mmol), in THF (20 mL) was stirred at room temperature for 1 week. The excess CuI was removed by filtration. Colorless crystals can be obtained by diffusion of MeCN into the filtrate. The crystals were separated, washed with MeCN (10 mL), and dried under vacuum. A white solid, **4d**, was obtained. Yield: 0.26 g, 81%.

Method 2. A mixture of *n*-Bu_4NI (0.2 g, 0.55 mmol) and **4a** (0.20 g, 0.11 mmol) in CH_2Cl_2 was stirred at room temperature for 1 week. By using the same procedure as mentioned above, the white solid **4d** was obtained. Yield: 0.3 g, 92%. **4d**: Anal. Calcd for **4d** ($C_{89}H_{74}Cl_{1.75}Cu_4I_{3.25}N_1O_8P_4$): C, 50.0; H, 3.5. Found: C, 50.1; H, 3.6. NMR (CD_2Cl_2): $\delta(^{31}P)$ 132.2 (br), 127.1 (br), 120.7 (br), assigned to PCu units with $PCu(\mu_4\text{-}I)Cl_2$, $PCu(\mu_4\text{-}I)ICl$, and $PCu(\mu_4\text{-}I)I_2$ coordination, respectively; $\delta(^1H)$ 2.7 (br, 16H, CH_2CH_2Ph), 4.86 (br, 4H, $CH(CH_2)_2Ph$), 7.08 (m, 4H, Ar*H*, ortho to O), 7.15−7.60 (m, 36H, C_6H_5), 7.97−8.13 (m, 8H, PC_6H_5, ortho to P), 8.28 (t, 2H, $C_5H_5NH^+$, ortho to N), 7.67−7.80 (m, 2H, $C_5H_5NH^+$, meta and para to N), 5.35 (br, 1H, $C_5H_5N^+H$). FAB-MS: *m/e* = 2156.

Complex 5a. A mixture of $[AgCCPh]_n$ (0.13 g, 0.62 mmol), pyridinium chloride (0.07, g, 0.6 mmol), and tetraphosphonitocalix[4]resorcinarene, **2** (0.20 g, 0.15 mmol), in CH_2Cl_2 was stirred at room temperature for 15 h to give a clear solution. By using the same procedure as described for the preparation of **4a**, a white solid **5a** was obtained. Yield: 0.25 g, 83%. Anal. Calcd for **5a** ($C_{89}H_{74}Ag_4Cl_5N_1O_8P_4$): C, 53.1; H, 3.7; N, 0.7. Found: C, 52.7; H, 4.0; N, 0.7. NMR ($CDCl_3$): $\delta(^{31}P)$ 157.0 (2 × d, $^1J_{Ag(109)-P} = 766.3$ Hz, $^1J_{Ag(107)-P} = 664.1$ Hz); $\delta(^1H)$ 2.67 (br, 16H, CH_2CH_2Ph), 4.84 (br, 4H, $CH(CH_2)_2Ph$), 6.97 (t, $^4J_{PH} = 1.6$ Hz, 4H, Ar*H*, ortho to O), 7.15−7.32 (m, 20H, C_6H_5), 7.49 (s, 4H, Ar*H*, meta to O), 7.52−7.59 (m, 12H, PC_6H_5, para and meta to P), 7.95−8.06 (m, 8H, PC_6H_5, ortho to P), 8.18−8.30 (br, 2H, $C_5H_5NH^+$, ortho to N), 7.80−7.90 (br, 3H, $C_5H_5NH^+$, meta and para to N), 9.32 (s, br, 1H, $C_5H_5N{\cdot}H^+$).

Complexes 5b−e. The completely halogen substituted complexes $[C_5H_6N]^+[\mathbf{2}{\cdot}Ag_4X_5]^-$ and $[R_4N]^+[\mathbf{2}{\cdot}Ag_4X_5]^-$ (X = Br, I) were obtained by stirring the chloride derivative **5a** (0.2 g, 0.1 mmol) with an excess of the corresponding R_4NX (R = Me, X = Cl, **5b**; R = *n*-Bu, X = I, **5c**) or MX (M = Li, X = Br, **5d**; M = Na, X = I, **5e**) in CH_2Cl_2 for 24 h. By using the same procedure described in preparation of **4b**, products, **5b,c** can be obtained in crystalline form. Yield: Me_4N[**5a**], 92%; Bu_4N[**5c**], 84%; [pyH][**5b**], 76%; [pyH][**5c**], 83%. Me_4N[**5a**]: Anal. Calcd for $C_{88}H_{80}Ag_4Cl_5N_1O_8P_4$: C, 52.7; H, 4.0. Found: C, 52.4; H, 3.7. NMR ($CDCl_3$): $\delta(^{31}P)$ 155.6 (2 × d, $^1J_{Ag(109)-P} = 745.2$ Hz, $^1J_{Ag(107)-P} = 645.4$ Hz); $\delta(^1H)$ 3.30 (s, 16H, $(CH_3)_4N$), 2.64 (br, 16H, CH_2CH_2Ph), 4.82 (br, 4H, $CH(CH_2)_2Ph$), 6.99 (t, $^4J_{PH} = 1.5$ Hz, 4H, Ar*H*, ortho to O), 7.15−7.30 (m, 20H, C_6H_5), 7.45 (s, 4H, Ar*H*, meta to O), 7.52−7.60 (m, 12H, PC_6H_5, para and meta to P), 7.95−8.05 (m, 8H, PC_6H_5, ortho to P). Bu_4N[**5c**]: Anal. Calcd for $C_{100}H_{104}Ag_4I_5N_1O_8P_4$: C, 45.6; H, 4.0; N, 0.5. Found: C, 45.2; H, 3.9; N, 0.5. NMR (CD_2Cl_2): $\delta(^{31}P)$ 138.6 (2 × d, $^1J_{Ag(109)-P} = 507.0$ Hz, $^1J_{Ag(107)-P} = 439.5$ Hz); $\delta(^1H)$ 0.97 (t, $^3J_{HH} = 7.3$ Hz, 12H, $(CH_3CH_2CH_2CH_2)_4N^+$), 1.40−1.55 (m, 8H, $(CH_3CH_2CH_2CH_2)_4N^+$), 1.65 (br, 4H, $(CH_3CH_2CH_2CH_2)_4N^+)$), 3.19 (t, $^3J_{HH} = 8$ Hz, 4H, $(CH_3CH_2CH_2CH_2)_4N^+$), 2.71 (br, 16H, CH_2CH_2Ph), 4.86 (br, 4H, $CH(CH_2)_2Ph$), 7.19−7.28 (m, 24H, Ar*H*, ortho to O and C_6H_5), 7.45 (s, 4H, Ar*H*, meta to O), 7.55−7.63 (m, 12H, PC_6H_5, para and meta to P), 8.08−8.14 (m, 8H, PC_6H_5, ortho to P). [pyH][**5b**]: Anal. Calcd for $C_{89}H_{74}Ag_4Br_5N_1O_8P_4$: C, 47.9; H, 3.3. Found: C, 47.4; H, 3.1. NMR ($CDCl_3$): $\delta(^{31}P)$ 152.7 (2 × d, $^1J_{Ag(109)-P} = 687.9$ Hz, $^1J_{Ag(107)-P} = 596.3$ Hz); $\delta(^1H)$ 2.69 (br, 16H, CH_2CH_2Ph), 4.84 (br, 4H, $CH(CH_2)_2Ph$), 7.05 (t, $^4J_{PH} = 1.6$ Hz, 4H, Ar*H*, ortho to O), 7.15−7.31 (m, 20H, C_6H_5), 7.47 (s, 4H, Ar*H*, meta to O), 7.51−7.59 (m, 12H, PC_6H_5, para and meta to P), 7.97−8.07 (m, 8H, PC_6H_5, ortho to P), 8.19−8.30 (br, 2H, $C_5H_5NH^+$, ortho to N), 7.80−7.90 (br, 3H, $C_5H_4NH^+$, meta and para to N), 9.31 (s, br, 1H, $C_5H_5N{\cdot}H^+$). [pyH][**5c**]: Anal. Calcd for $C_{89}H_{74}Ag_4I_5N_1O_8P_4$: C, 43.2; H, 3.0; N, 0.6. Found: C, 43.5; H, 3.1; N, 0.6. NMR ($CDCl_3$): $\delta(^{31}P)$ 141.2 (2 × d, $^1J_{Ag(109)-P} = 551.6$ Hz, $^1J_{Ag(107)-P} = 486.8$ Hz); $\delta(^1H)$ 2.71 (br, 16H, CH_2CH_2Ph), 4.84 (br, 4H, $CH(CH_2)_2Ph$), 7.05 (t, $^4J_{PH} = 1.6$ Hz, 4H, Ar*H*, ortho to O), 7.15−7.31 (m, 20H, C_6H_5), 7.47 (s, 4H, Ar*H*, meta to O), 7.51−7.59 (m, 12H, PC_6H_5, para and meta to P), 7.97−8.07 (m, 8H, PC_6H_5, ortho to P), 8.19−8.30 (br, 2H, $C_5H_5NH^+$, ortho to N), 7.80−7.90 (br, 3H, $C_5H_5NH^+$, meta and para to N), 9.31 (s, br, 1H, $C_5H_5N{\cdot}H^+$).

Complex 6. A mixture of $AgNO_3$ (0.017 g, 0.10 mmol) in MeCN (5 mL) and **5a** (0.20 g, 0.10 mmol) in CH_2Cl_2 (5 mL) was stirred at room temperature for 5 h. The AgCl precipitate was removed by filtration. A yellow solid product was obtained by diffusion of MeCN into the solution. Yield: 0.12 g, 63%. Anal. Calcd for **6** ($C_{84}H_{68}Ag_4Cl_4P_4O_8$): C, 53.2; H, 3.6. Found: C, 52.9; H, 3.3. NMR (CD_2Cl_2): $\delta(^{31}P)$ 161.7 (2 × d, $^1J_{Ag(109)-P} = 820.7$ Hz, $^1J_{Ag(107)-P} = 711.4$ Hz); $\delta(^1H)$ 2.69 (br, 16H, CH_2CH_2Ph), 4.80 (br, 4H, $CH(CH_2)_2Ph$), 6.85 (t, $^4J_{PH} = 1.5$ Hz, 4H, Ar*H*, ortho to O), 7.13−7.31 (m, 20H, C_6H_5), 7.50 (s, 4H, Ar*H*, meta to O), 7.52−7.55 (m, 12H, PC_6H_5, para and meta to P), 7.94−8.02 (m, 8H, PC_6H_5, ortho to P).

Complex 5d. A mixture of Bu_4NI (0.041 g, 0.11 mmol) and **6** (0.20 g, 0.11 mmol) in CH_2Cl_2 (5 mL) was stirred at room temperature for 0.5 h. A white solid product was obtained by diffusion of MeCN into the solution. Yield: 0.17 g, 74%. Anal. Calcd for **5d** ($C_{100}H_{104}Ag_4Cl_4I_1N_1O_8P_4$): C, 53.0; H, 4.6. Found: C, 52.7; H, 4.4. NMR ($CDCl_3$): $\delta(^{31}P)$ 153.4 (2 × d, $^1J_{Ag(109)-P} = 667.2$ Hz, $^1J_{Ag(107)-P} = 578.6$ Hz); $\delta(^1H)$ 2.67 (br, 16H, CH_2CH_2Ph), 4.84 (br, 4H, $CH(CH_2)_2Ph$), 6.97 (t, $^4J_{PH} = 1.6$Hz, 4H, Ar*H*, ortho to O), 7.15−7.32 (m, 20H, C_6H_5), 7.49 (s, 4H, Ar*H*, meta to O), 7.52−7.59 (m, 12H, PC_6H_5, para and meta to P), 7.95−8.06 (m, 8H, PC_6H_5, ortho to P), 8.18−8.30 (br, 2H, $C_5H_5NH^+$, ortho to N), 7.80−7.90 (br, 3H, $C_5H_5NH^+$, meta and para to N), 9.32 (s, br, 1H, $C_5H_5N{\cdot}H^+$).

Kinetic Studies. A solution of **5a** (ca. 0.01 M) and *i*-PrI (excess, 0.2−0.9 M) in CD_2Cl_2 (1 mL) was held in the NMR probe at 30 °C. Spectra were recorded at regular intervals until the reaction was effectively complete. Kinetic plots were made using the ratio of concentrations of **5a,d** determined by integration of the ^{31}P NMR spectra.

Qualitative studies of the relative reactivities of different alkyl iodides were carried out in a similar way but with equal amounts of **5a** and RI, to facilitate monitoring by both ^1H and ^{31}P NMR.

Optical Rotation Studies. A mixture of **5a** (0.1 mmol) and (*S*)-(+)-2-iodooctane (0.1 mmol) in CH_2Cl_2 (10 mL) was thermostated at 40 °C, and the optical rotation was measured periodically until no further change occurred. The volatiles were removed under vacuum, and the products were identified as **5d** and 2-chlorooctane by NMR. No **5a** remained.

Table 3. Crystal Data for pyH[**4a**]·2MeCN, pyH[**4d**]·2MeCN, and Me_4N[**5a**]·1.5EtCN·CH_2Cl_2

formula	$C_{89}H_{74}N_1Cu_4Cl_5$-P_4O_8·$2CH_3CN$	$C_{89}H_{74}N_1O_8P_8Cu_4$-$Cl_{1.75}I_{3.25}$·$2CH_3CN$	$C_{88}H_{80}N_1Cl_5O_8P_4Ag_4$·$1.5C_2H_5CN$·$CH_2Cl_2$
fw	1939.08	2220.2	2179.79
cryst syst	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	17.511(4)	17.830(3)	15.532(4)
b (Å)	21.479(4)	21.321(4)	24.421(8)
c (Å)	13.253(2)	13.779(4)	14.049(8)
α (deg)	101.52(1)	103.3(2)	90.98(4)
β (deg)	111.94(1)	112.5(2)	99.10(4)
γ (deg)	82.14(2)	81.03(1)	99.22(3)
V (Å^3)	4519(2)	4695(3)	5289(4)
Z	2	2	2
d(calcd) (g·cm^{-3})	1.42	1.55	1.395
radiatn, λ (Å)	Mo Kα, 0.71073	Mo Kα, 0.71073	Mo Kα, 0.71073
μ (cm^{-1})	11.39	19.4	9.4
R^a	0.0803	0.0576	0.1075
$R_w{}^b$	0.0863	0.0657	0.1188

[a] $R = \Sigma||(F_o)| - |(F_c)||)/(\Sigma|(F_o)|$. [b] $R_w = \Sigma\sqrt{w}||(F_o)| - |(F_c)||/(\Sigma\sqrt{w}|(F_o)|$.

X-ray Structure Determinations. In each case, the crystal was sealed inside a Lindemann capillary with mother liquor to prevent loss and data were collected by using an Enraf-Nonius CAD4F diffractometer.[29] The cell constants and an orientation matrix were obtained from photo and automatic indexing routines, followed by least squares fits of 21−22 accurately centered reflections ($20 \le 2\theta \le 30°$). Intensity data were recorded at 295 K in $\theta-2\theta$ mode (**4a**) or ω-mode (**4d**, **5a**), at variable scan speeds. Corrections were made for Lorentz, monochromator and crystal polarization, background, decay, and absorption. The NRCVAX crystal structure programs[30] were used to process the data, and the structure was solved by a combination of SHELXS-86[31] and difference Fourier techniques. Refinement was by full-matrix least-squares techniques on F, using the SHELX-76 software.[32] Scattering factors for neutral, non-hydrogen atoms were taken from ref 33. Anisotropic thermal parameters were assigned for all the Cu, Ag, Cl, I, and P atoms and were refined. Phenyl rings were treated as regular hexagons (with C−C = 1.392 Å). Experimental details and crystal data are given in Table 3, and descriptions of individual refinements as well as more complete tables of bond distances and angles, atomic coordinates, and calculated H-atom positions are included in the supplementary information.

4a. Disorder was found and resolved for the pyridinium cation, with multiplicities of 0.70 and 0.30, and the nitrogen and carbon atoms could not be distinguished in either **4a** or **4d**. Hence a disorder of the N atom over all six sites was assumed. Individual isotropic thermal parameters were refined for the major disorder component whereas a common isotropic thermal parameter was refined for the minor disorder model in least-squares cycles. The solvent molecules were located in difference Fourier synthesis, and disorder in an acetonitrile molecule was successfully resolved. All the hydrogen atoms excluding the solvent and the pyridinium cations were placed in ideal positions (C−H = 0.95 Å) and were included in the least-squares cycles for the purpose of structure factor calculations only.

4d. The halogen positions were treated in terms of iodine atoms with varied occupancies, which were obtained from peak heights in the SHELXS-86 solution and later refined by least-squares methods. The occupancy factors (ratio of I/Cl) over four bridging sites are 0.625/0.375 for X(1) and X(2), 0.40/0.60 for X(3), and 0.60/0.40 for X(4) and lead to the formula [$Cu_4I_{3.25}Cl_{1.75}$]. Both of the solvent molecules were located, and their positional and the isotropic thermal parameters were refined. High thermal motions for the phenyl carbon atoms C(39) and C(301)−C(306) indicated disorder. Two different orientations of this benzyl group were resolved (occupancy 0.65:0.35), and their positional and common isotropic thermal parameters were refined in the least-squares cycles.

5a. The crystal diffracted weakly and decayed during data collection, so the refinement was difficult. The phenyl rings attached to the phosphorus atoms showed high thermal motions indicating disorder, and since the disorder was not resolved, common isotropic thermal parameters for each rings were assigned and refined in the least-squares cycles. One and a half molecules of ethyl cyanide were found from the difference Fourier techniques. The positional and the isotropic thermal parameters were refined for one molecule, and the other half molecule was refined as a rigid body. The tetramethyl ammonium cation was located with difficulty, and the positional and thermal parameters could not be refined in the least-squares cycles. Owing to this problem, the cation was treated as a regular tetrahedron with N−C = 1.485 Å and the temperature factor was fixed at $U = 0.12$. For the disordered molecule of dichloromethane, the C−Cl distance (1.600 Å) and the Cl−C−Cl angle (109.5°) were fixed.

Acknowledgment. We thank the NSERC (Canada) for financial support and Dr. N. C. Payne for access to X-ray facilities.

Supporting Information Available: Tables of X-ray data (27 pages); tables of structure factors (98 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

JA950251L

---

(29) *CAD4 Diffractometer Manual*; Enraf-Nonius: Delft, The Netherlands, 1988.

(30) Gabe, E. J.; Le Page, Y.; Charland, J.-P.; Lee, F. C. *J. Appl. Crystallogr.* **1989**, *22*, 384.

(31) Sheldrick, G. M. *SHELXS-86, Structure Solving Program*; University of Gottingen: Gottingen, Germany, 1986.

(32) Sheldrick, G. M. *SHELX-76. Program for Crystal Structure Determination*; University of Cambridge: Cambridge, England, 1976.

(33) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.