

**Table I.** Selected Molecular Parameters for the Cubane-Like  $(\text{Ph}_3\text{P})_4\text{Ag}_4\text{X}_4$  Clusters (Distances in Å, Angles in Degree)

Parameter	X = Cl	X = I
Ag...Ag (av)	3.633	3.483
(min)	3.408 (2)	3.115 (2)
(max)	3.797 (2)	3.769 (3)
X...X (av)	3.838	4.583
(min)	3.652 (6)	4.400 (2)
(max)	4.033 (4)	4.803 (3)
Ag-X (av)	2.654	2.911
(min)	2.532 (3)	2.837 (2)
(max)	2.761 (3)	3.038 (3)
Ag-P (av)	2.379	2.461
(min)	2.372 (3)	2.455 (5)
(max)	2.386 (3)	2.466 (5)
Ag-X-Åg (av)	86.46	73.55
(min)	79.25 (8)	64.46 (6)
(max)	92.63 (9)	81.08 (6)
X-Ag-X (av)	92.73	104.08
(min)	87.21 (9)	97.38 (7)
(max)	101.22 (9)	115.42 (6)
P-Ag-X (av)	122.3	114.1
(min)	109.9 (1)	103.9 (1)
(max)	138.7 (1)	123.6 (2)

of the Ag...Ag distances and the Ag-X distances are consistent with a bonding model<sup>1,10</sup> in which both the bonding ( $a_1 + e + t_2$ ) and the antibonding ( $t_1 + t_2$ ) tetrametal symmetry orbitals and the *partially* antibonding Ag-X ( $e + t_1 + t_2$ ) orbitals are fully occupied. However, electronic factors alone cannot account for the severe distortions of **1** and **2a** from  $T_d$  geometry, or for the *cubane-chair* isomerism of  $(\text{Ph}_3\text{P})_4\text{Ag}_4\text{I}_4$ . We believe that these effects, as well as the occurrence of *both* cubane and chair-type geometries in the  $(\text{R}_3\text{Y})_4\text{Cu}_4\text{X}_4$  series,<sup>4,5</sup> is a consequence of *weak* van der Waals interactions. The latter are evidenced by a wide spectrum of nonbonding intramolecular separations including close (Ph)H...H(Ph) and (Ph)H...X contacts in both **1** and **2a**.

The observed structural variations of the known members of the series  $(\text{R}_3\text{Y})_4\text{M}_4\text{X}_4$  can now be rationalized as follows. First, the replacement of the chlorine atoms in **1** by the much larger iodine atoms in **2a** increases the intracuster nonbonding repulsions (I...I, Ag...Ag) as well as other van der Waals interactions (H...I, H...H). As a result, the iodine atoms move outwards, which, in order to maintain reasonable Ag-I bond lengths, causes the silver atoms to move inward toward the centroid of the  $\text{Ag}_4\text{I}_4$  core; the Ag-P bonds are concomitantly lengthened by 0.08 Å to relieve intensified H...H and H...I interactions. By the same token, a formal transmutation of **1** into the copper analog  $(\text{Ph}_3\text{P})_4\text{Cu}_4\text{Cl}_4$ <sup>4a</sup> through a replacement of the larger silver atoms with smaller copper atoms also enhances the van der Waals repulsive constraints producing a highly distorted cubane core. Further, substitution of chlorine atoms in  $(\text{Ph}_3\text{P})_4\text{Cu}_4\text{Cl}_4$  by larger bromine<sup>4a</sup> or iodine<sup>4b</sup> atoms changes the solid state structure to the chair form, presumably due to even more severe overcrowding. With less bulky terminal ligands such as triethylphosphine and triethylarsine, however, a cubane-like structure is observed in  $(\text{Et}_3\text{P})_4\text{Cu}_4\text{I}_4$  and  $(\text{Et}_3\text{As})_4\text{Cu}_4\text{I}_4$ .<sup>4a</sup>

The fact that  $(\text{Ph}_3\text{P})_4\text{Ag}_4\text{I}_4$  is the first determined member of the series which can exist in both cubane and chair-like forms in the solid state suggests that these forms are fairly close in energy with the difference being comparable to van der Waals interactions.

**Acknowledgments.** We thank Dr. A. P. Ginsberg, Dr. J. W. Koepke, and Dr. D. W. Murphy at Bell Laboratories (Murray Hill) and Professor L. F. Dahl at the University of Wisconsin (Madison) for helpful discussions.

## References and Notes

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- (a) M. R. Churchill and K. L. Kalra, *Inorg. Chem.*, **13**, 1065, 1427, 1899 (1974), and references cited therein; (b) M. R. Churchill, B. G. DeBoer, and D. J. Donovan, *ibid.*, in press.
- (a) N. Marsich, G. Nardin, and L. Randaccio, *J. Am. Chem. Soc.*, **95**, 4053 (1973); (b) W. R. Clayton and S. G. Shore, *Cryst. Struct. Commun.*, **2**, 605 (1973); (c) I. D. Brown and J. D. Dunitz, *Acta Crystallogr.*, **13**, 28 (1960); (d) A. F. Wells, *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.*, **94**, 447 (1936); (e) F. G. Mann, D. Purdie, and A. F. Wells, *J. Chem. Soc.*, 1503 (1936).
- For the first indication of a "cubane-like" structure for  $(\text{R}_3\text{Y})_4\text{Ag}_4\text{L}_4$  tetramers (where R = alkyl, L = P, As) see F. G. Mann, A. F. Wells, and D. Purdie, *J. Chem. Soc.*, 1828 (1937). However, no full structural study was reported.
- (a)  $(\text{Ph}_3\text{P})_4\text{Ag}_4\text{Cl}_4$  (**1**): orthorhombic *Pbcn*;  $a = 17.925$  (4),  $b = 20.778$  (15),  $c = 18.299$  (3) Å;  $V = 6815$  (5) Å<sup>3</sup>; and  $Z = 4$ . Anisotropic least-squares refinement<sup>8</sup> gave  $R_1 = 4.11\%$  and  $R_2 = 4.57\%$  for 2059 independent reflections. (b)  $(\text{Ph}_3\text{P})_4\text{Ag}_4\text{I}_4$  (**2a**): monoclinic *P2<sub>1</sub>/c*;  $a = 24.991$  (5),  $b = 12.402$  (3),  $c = 25.074$  (6) Å,  $\beta = 113.30$  (2)°;  $V = 7137$  (3) Å<sup>3</sup>, and  $Z = 4$ . Anisotropic least-squares refinement<sup>8</sup> gave  $R_1 = 4.94\%$  and  $R_2 = 5.03\%$  for 3782 independent reflections. (c)  $(\text{Ph}_3\text{P})_4\text{Ag}_4\text{I}_4 \cdot x\text{CH}_2\text{Cl}_2$  (**2b**): triclinic *P1*;  $a = 12.126$  (7),  $b = 15.107$  (7),  $c = 11.977$  (7) Å;  $\alpha = 110.47$  (4),  $\beta = 96.42$  (4),  $\gamma = 71.67$  (4)°;  $V = 1951$  (2) Å<sup>3</sup>; and  $Z = 1$ ; least-squares refinement in progress.
- Hydrogen atoms were calculated at C-H distance of 1.00 Å and assigned constant isotropic thermal parameters of 7.00 Å<sup>2</sup>. For other crystallographic details, see T. H. Whitesides, R. W. Slaven, and J. C. Calabrese, *Inorg. Chem.*, **13**, 1895 (1974).
- Nonsystematic variations of 0.1–0.3 Å in metal-metal distances are not uncommon for other cubane-like clusters with no metal-metal bonds.
- This bonding scheme is consistent with a preliminary MO calculation on  $(\text{H}_3\text{P})_4\text{Cu}_4\text{Cl}_4$  utilizing Fenske's model (M. B. Hall and R. F. Fenske, *Inorg. Chem.*, **11**, 768 (1972)).

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Received October 25, 1974

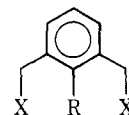
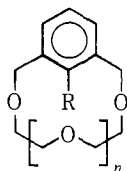
## Effect of Centered Functional Groups on Complexing Properties of Cyclic Polyether Hosts<sup>1</sup>

Sir:

Carboxylic acid and ester groups frequently act as binding sites for complexation by enzymes and antibiotics. Shaping and binding units that control association constants between synthetic multiheteromacrocyclic host and alkylammonium guest compounds have been studied.<sup>2</sup> We report here the syntheses<sup>3</sup> and binding properties toward cations of macrocyclic polyethers whose incorporated 1,3-xylyl unit directs toward the center of the ring, carboxyl, carbomethoxy, or other groups attached to the 2-position.

Cycles **1–4** and **11** were prepared by adding under nitrogen equimolar mixtures of the appropriate dibromide (**16** or 1,3-bis(bromomethyl)benzene) and polyethylene glycol in dry THF over a 3-hr period to a refluxing mixture of THF containing a 3 *M* excess of sodium hydride.<sup>8</sup> For **12–14**, **17–19** were added to the already prepared alkoxides.<sup>8</sup>

The  $pK_a$ 's ( $\pm 0.2$ ) of the four cyclic carboxylic acids (**5–8**) and of their open-chain model (**20**) were determined in water at 22°<sup>9</sup> (**5**, 4.8; **6**, 4.8; **7**, 3.8; **8**, 3.4; **20**, 3.3). Thus in acid strength, the five compounds are arranged: zero-membered ring  $\approx$  30-membered ring  $>$  21-membered ring  $>$  18-membered ring  $\sim$  15-membered ring. Two effects explain the acidity order. (1) Molecular models (Corey, Pauling, Koltun or CPK) of the five acids reveal that **5** and **6** are relatively rigid, and their carboxyl groups comfortably hy-



	<i>n</i>	R	Yld (%)		<i>n</i>	R	Yld (%)		R	X	Yld (%)
1 <sup>3</sup>	2	CO <sub>2</sub> CH <sub>3</sub>	34	8 <sup>3</sup>	7	CO <sub>2</sub> H	~98	15 <sup>5</sup>	CO <sub>2</sub> CH <sub>3</sub>	H	~100
2 <sup>3</sup>	3	CO <sub>2</sub> CH <sub>3</sub>	82	9 <sup>3c</sup>	3	CH <sub>2</sub> OH	80	16 <sup>3,6</sup>	CO <sub>2</sub> CH <sub>3</sub>	Br	46
3 <sup>3</sup>	4	CO <sub>2</sub> CH <sub>3</sub>	68	10 <sup>3a,c</sup>	3	CH <sub>2</sub> OCH <sub>3</sub>	50	17 <sup>7a</sup>	Cl	Br	22
4 <sup>3</sup>	7	CO <sub>2</sub> CH <sub>3</sub>	34	11 <sup>3,4</sup>	3	H	60	18 <sup>7a</sup>	Br	Br	55
5 <sup>3</sup>	2	CO <sub>2</sub> H	~98	12 <sup>3,4</sup>	3	Br	7	19 <sup>7b</sup>	CN	Br	30
6 <sup>3</sup>	3	CO <sub>2</sub> H	~98	13 <sup>3</sup>	3	Cl	53	20 <sup>3</sup>	CO <sub>2</sub> H	OCH <sub>3</sub>	50
7 <sup>3</sup>	4	CO <sub>2</sub> H	~98	14 <sup>3</sup>	3	CN	10				

drogen-bond transannularly located ether oxygens.<sup>10a</sup> Although intramolecular hydrogen bonds can form in models of **7** and **8**, many more conformations have to be frozen out in the resulting structures. No such hydrogen bonds are possible in **20**. Carboxyl to benzyl-oxygen hydrogen bonds appear more strained than those to more remote oxygens. (2) Molecular models of the corresponding carboxylate anions indicate those from **5** and **6** to be more rigidly pointing toward the center of the macrocycles than those from **7** and **8**. Thus steric inhibition of solvation of the anion in the smaller rings should be more pronounced than in the larger rings or in **20**.

Association constants ( $K_a$ ) for complexation of *tert*-butylammonium thiocyanate with nine of the cycles in chloroform at 22° were determined:<sup>11</sup> **1**,  $\approx 150$ ; **2**, 17,000; **3**, 930; **4**, 240; **6**, 380; **9**, 710; **10**, 760; **11**,<sup>12</sup> 1000; **14**, 350. For the R groups in the 18-membered ring hosts, CO<sub>2</sub>CH<sub>3</sub>  $\gg$  H  $>$  CH<sub>2</sub>OCH<sub>3</sub>  $\sim$  CH<sub>2</sub>OH  $>$  CO<sub>2</sub>H  $>$  CN in their ability to stabilize the complexes. When R = CO<sub>2</sub>CH<sub>3</sub>, the hosts change in complexing power as follows: 18-membered  $\gg$  21-membered  $>$  30-membered  $>$  15-membered ring. Molecular models (CPK) of the complexes indicate that those containing the 18-membered rings provide the most ideal fits of host to guest. Only in the models of these sized cycles do the ring oxygens almost perfectly encircle (300° out of 360°) the NH<sub>3</sub><sup>+</sup> group. In these models, the plane of the aryl is tilted out of the best plane of the ether oxygens by about 30–60°. The angle decreases with R group changes in the order CH<sub>2</sub>OCH<sub>3</sub>  $\sim$  CH<sub>2</sub>OH  $\sim$  CN  $>$  CO<sub>2</sub>CH<sub>3</sub>  $\sim$  CO<sub>2</sub>H  $>$  H. Sterically all of the R groups probably destabilize the complexes, but some of the groups (e.g., CO<sub>2</sub>CH<sub>3</sub> and CH<sub>2</sub>OCH<sub>3</sub>) compensate by providing an additional ligand as in the linear part structure, R–N<sup>+</sup>...:O. The electron pair of the space-consuming cyano group is mislocated to act as a ligand, and  $K_a$  where R is C $\equiv$ N: is lower than where R is H. Where R is CO<sub>2</sub>H, the uncomplexed host probably is stabilized by CO<sub>2</sub>H...:O which CPK models indicate is inhibited in the complex. Structure **21** seems probable for the complex of **2**, which is  $\approx 1.7$  kcal more stable than the other complexes.

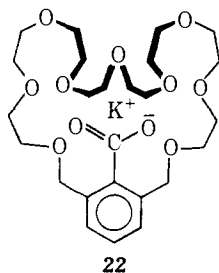
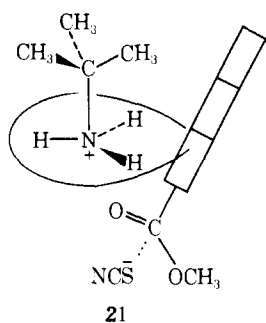
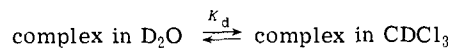


Table I

Salt of	% salt in CH <sub>2</sub> Cl <sub>2</sub> layer			
	Li <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>
5	1.4	1.5	1.4	1.1
6	7.2	7.9	6.7	4.8
7	6.1	8.7	6.8	1.8
8	3.4	5.2	8.0	2.9
20	3.3	3.2	2.8	3.4

The anionic form of host acids **5–8** and **20** were tested for their abilities to lipophilize Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, and Ca<sup>2+</sup> by distributing their salts at ~22° between dichloromethane and water (Table I).<sup>13</sup> Maximum lipophilization of each ion depends on the ring size of the host: for Li<sup>+</sup>, 18-membered; for Na<sup>+</sup>, 21-membered; for K<sup>+</sup>, 30-membered; for Ca<sup>2+</sup>, 18-membered. For all ions, the 15-membered ring host (**5**) was poorer than the open-chain host (**20**). For the monovalent cations and the restricted series of anions of **6–8**, the maximum lipophilization occurs with different host-guest combinations, the larger rings better lipophilizing the larger ions. The effects are not dramatic, possibly because of cancellation in the large number of parameters that contribute to the distribution coefficients of the salts. Structure **22** is visualized for the potassium salt of **8**.

Acid **6** formed a crystalline one-to-one salt<sup>3a,c,10b</sup> with *tert*-butylamine (mp 117–126° dec) when mixed in cyclohexane-dichloromethane. The <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub> of the salt showed a dramatic broadening of the macrocyclic proton signals as compared to those of **6** itself, and a 0.05 ppm upfield shift of the *tert*-butyl protons as compared to those of a similar mixture of amine and **20**. One complex of **6** in CPK models resembles **21** in geometry. The carboxylate's anionic oxygen is rigidly held in contact with N<sup>+</sup>, and in the center of the macrocyclic ring. One to two methyl protons of the complex are held in (not deeply) the magnetic field of the phenyl. Were not the nine protons averaging, the upfield movement would be larger.<sup>15</sup> Rough distribution constants ( $K_d$ ) for the *tert*-butylamine complexes of **5–8** and **20** between D<sub>2</sub>O and CDCl<sub>3</sub> were determined<sup>14</sup> at 22°: for **5**, ~0.02; for **6**, 0.7; for **7**, 0.36; for **8**, 0.24; for **20**, ~0.06. These results suggest that the salt of **6** is the best or-



ganized of the complexes to bury the hydrophilic sites of both host and guest in a lipophilic skin of C–H bonds. The qualitative result and the order were predicted by examinations of molecular models of the complexes.

These results demonstrate that 2-substituted, 1,3-xylyl units can be incorporated in macrocyclic hosts and that these *inner directed* substituents act as additional binding

sites for anionic guests. The possibility that they can also act as catalytic sites is being explored.

## References and Notes

- (1) This work was supported by the U.S. Public Health Service Research Grant No. GM12640-10 from the Department of Health, Education and Welfare, and by a grant from the National Science Foundation, GP33533X.
- (2) J. M. Timko, R. C. Helgeson, M. Newcomb, G. W. Gokel, and D. J. Cram, *J. Am. Chem. Soc.*, **96**, 7097 (1974).
- (3) (a) Carbon and hydrogen analyses were within 0.30% of theory; (b) mass spectra exhibited the molecular ion; (c)  $^1\text{H}$  NMR spectra were consistent with the assigned structures.
- (4) The authors are indebted to Dr. Kenji Koga who first prepared these compounds.
- (5) H. L. Goering, T. Rubin, and M. S. Newman, *J. Am. Chem. Soc.*, **76**, 787 (1954).
- (6) Treatment of **15** in carbon tetrachloride with 2.2 equiv of NBS gave **16**.
- (7) (a) F. Vögtle, *Chem. Ber.*, **102**, 1784 (1969); (b) *ibid.*, **105**, 2955 (1972).
- (8) The mixture was stirred at  $25^\circ$  (12 hr). The methyl ester of **20** was prepared similarly. The crude isolated diesters were treated with excess diazomethane. All cycles were purified by chromatography first on silica gel and then by gel permeation (Bio Beads SX-8). Analytical samples were obtained by GLPC. Acids **5**–**8** and **20** were prepared from their esters by hydrolysis with sodium hydroxide–ethanol. Reduction of ester **2** with LAH gave **9**, methylation of which with sodium hydride and methyl iodide in THF gave **10**. Compounds **1**–**20** were oils except for the following: **5**, mp  $106$ – $112^\circ$ ; **6**, mp  $100$ – $101^\circ$ ; **7**, mp  $86$ – $95^\circ$ ; **10**, mp  $70$ – $71^\circ$ ; **11**, mp  $44$ – $46^\circ$ ; **16**, mp  $77$ – $79^\circ$ ; **17**, mp  $84$ – $88^\circ$ ; **18**, mp  $101$ – $103^\circ$ ; **19**, not purified; **20**, mp  $54$ – $62^\circ$ .
- (9) Acid (0.1 mmol) in 20–30 ml of water was neutralized with LiOH and titrated (pH-metric) with 0.10 *N* HCl and 0.10 *N* LiOH.
- (10) (a) An X-ray structure of **6** reveals the carboxyl to be hydrogen-bonded to the oxygen on the  $C_2$  axis of the molecule (I. Goldberg and K. N. Trueblood, private communication). (b) The X-ray structure determination of this complex is being undertaken by I. Goldberg and K. N. Trueblood (private communication).
- (11) Footnote 4 of ref 2 describes the method. Scale C was used.
- (12) Reference 2 erroneously reported the  $K_a$  of **11** at  $22^\circ$  to be 1500. In addition, the  $K_a$  of **11** at  $0^\circ$  is 1800 rather than the 2000 reported in ref 2.
- (13) A mixture was shaken of 2 ml of dichloromethane containing 0.05 mmol of acid and 1 ml of aqueous salt solution of  $\mu = 2.0$  (2.0 *M* LiCl, NaCl, KCl or 0.67 *M* CaCl<sub>2</sub>) and 2 drops of 2 *N* LiOH, NaOH, or KOH (for Ca, solid Ca(OH)<sub>2</sub> was added), respectively. The aqueous phase had pH  $> 11$ . The dichloromethane phase after filtering through glass wool was evaporated. The residue was dissolved in 50  $\mu\text{l}$  of CDCl<sub>3</sub> containing 0.0147 mmol of toluene, the  $^1\text{H}$  NMR spectrum was taken (60 MHz), and the area of the host's methylene or methyl protons was compared ( $\pm 10\%$ ) to that of the toluene's methyl protons.
- (14) A 0.5 *M* solution of the acid host in 0.10 ml of CDCl<sub>3</sub> was made 0.7 *M* in (CH<sub>3</sub>)<sub>3</sub>CNH<sub>2</sub>, and the resulting solution was shaken with 0.10 ml of D<sub>2</sub>O. The layers were separated, and the protons of the host and guest (plus free amine) were counted in their  $^1\text{H}$  NMR spectra in each layer under identical conditions for each complex. Values of  $K_D$  were calculated from the relative amounts of host in each layer. Excess (CH<sub>3</sub>)<sub>3</sub>CNH<sub>2</sub> was observed in each layer.
- (15) NOTE ADDED IN PROOF. A second possible complex locates the (CH<sub>3</sub>)<sub>3</sub>C group on the side of the macroring opposite the tilted benzene ring, whose CO<sub>2</sub><sup>-</sup> group hydrogen bonds one NH, and alternate distant ether oxygens hydrogen bond NH<sub>2</sub> (CPK molecular models).

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Received December 19, 1974

## Chromatographic Optical Resolution through Chiral Complexation of Amino Ester Salts by a Host Covalently Bound to Silica Gel<sup>1</sup>

Sir:

Previous papers demonstrated that optically active host **1** exhibited chiral recognition in complexation in solution of the enantiomers of primary amines and amino ester salts as guests.<sup>2a,b</sup> Total optical resolutions of primary amine salts were realized by liquid–liquid chromatography in which salts in stationary aqueous phases adsorbed on silica gel were eluted fractionally with chloroform solutions of (RR)-**1**.<sup>2c,d</sup> We report here the covalent attachment of (RR)-**1**<sup>2a</sup> to silica gel and use of the designed chiral host

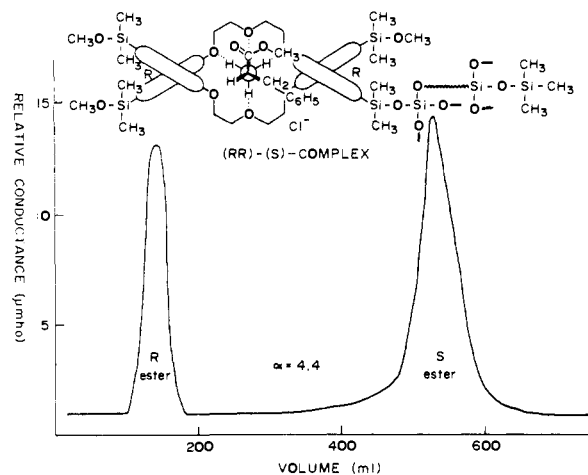
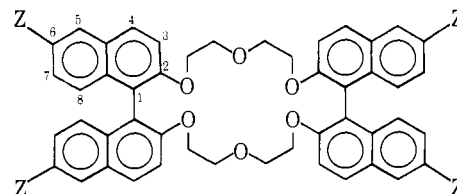


Figure 1. Chromatographic optical resolution by host-bound silica gel of methyl phenylalaninate hydrochloride salt.

sites to totally resolve amine (especially amino ester) salts as guests by solid–liquid chromatography.

Bromination (7 mol of Br<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> added at  $-5^\circ$  over 1 hr) of the isomers of **1** (1 mol) gave **2** whose four bromine



(RR)(SS)-**1**, Z = H;<sup>2a</sup> (RR)-**1**, Z = H;<sup>2a</sup> (RS)-**1**, Z = H<sup>2a</sup>

Compd no.	Z	Mp, °C	Yld, %
(RR)(SS)- <b>2</b> <sup>3a,b</sup>	Br	299–300	80
(RR)- <b>2</b> <sup>3a</sup>	Br	189–191	91
(RS)- <b>2</b> <sup>3</sup>	Br	334–335	90
(RS)- <b>3</b> <sup>3a,c</sup>	Si(CH <sub>3</sub> ) <sub>2</sub> OCH <sub>3</sub>	95–96	84

atoms were substituted in the 6-positions.<sup>4</sup> Addition of (RS)-**2** to butyllithium in dry glyme under nitrogen at  $-75^\circ$  followed by dichlorodimethylsilane at  $-75^\circ$  (mixture then refluxed) followed (after evaporation) by dry methanol gave (RS)-**3**. Treatment of the tetrakis(dimethylchlorosilyl) compound (similarly prepared from optically pure (RR)-**2**)<sup>5</sup> with dry carbon-free silica gel followed by methanol gave after washing and drying, host-bound silica gel, 3.94% by weight carbon by combustion. If each cycle is covalently bound at only one site, and the other three are capped with CH<sub>3</sub>O groups, the silica gel is 0.059 mmol per gram in host residues, or each host site has an average molecular weight of 17,000. Further treatment of this silica gel with excess trimethylsilyl chloride to cap the more hindered SiOH groups gave (RR)-**4**<sup>5</sup> (H), 4.65% by weight carbon by combustion, or 0.20 mmol/g in (CH<sub>3</sub>)<sub>3</sub>Si groups.

Table I reports the results of chromatograms run<sup>6</sup> on racemic  $\alpha$ -phenylethylammonium hexafluorophosphate, the methyl or isopropyl esters of phenylglycine hexafluorophosphate or hydrochloride salts, and the methyl esters of the hydrochloride salts of valine, phenylalanine, and tryptophan. The configurational identities of the enantiomers in the bands eluted were established by their signs of rotation (e.g., in runs 1, 3, 4, and 6) or by comparisons of their retention volumes with those of pure enantiomers put through the same column under the same conditions as their racemates (runs 7, 8, and 9). Plots of the relative conductance vs. milliliters of eluate gave curves for each run from which the