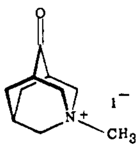
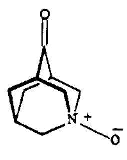
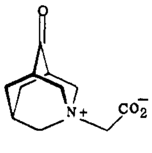


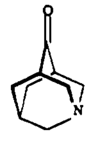
4



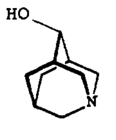
5



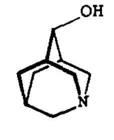
6



7



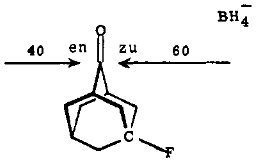
E-8

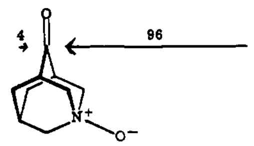


Z-8

The reduction of **4** in methanol gave a product whose NMR spectra suggested that it was a single compound. N-Methylation of the two parent alcohols **8**[7] showed the product to be the *E* epimer. Careful scrutiny of the base line in the NMR spectra revealed the *Z* alcohol to be detectible also, to the extent of 4–5%. Thus, the *E*/*Z* ratio of isomers in this instance was 20–25, an order of magnitude larger than any we had encountered before.

Oxidation of **7** gave amine oxide **5** (isoelectronic with our previously most powerful probe, **1**–F), and treatment of **7** with chloroacetic acid furnished betaine **6**. Both **5** and **6** were subjected to borohydride reduction and product proof and analysis, as was **4**; furthermore, ^{13}C NMR additivity studies supported our assignments of configuration. The *E*/*Z* ratio in all three cases equaled 20–25.





One alternative reason for the large selectivity in **4** is the possibility of an electrostatic interaction bringing the borohydride anion preferentially to the *zu* face. Haberfield[8] has shown convincingly that such preassembly can lead to large rate effects, such as a factor of 10^6 in one such reaction in THF, and also that the effect virtually vanishes (1.2) upon a change of solvent to water. In our case, the ratio with **4** did not change at all with a change of methanol to water or even to saturated aqueous sodium chloride. The results cannot be attributed to unexpected strains or distortions in the cage structure either. In support of this statement, we refer to Galvez's crystal structure of a derivative of protonated *E*-**8** ("Each ring of the adamantone cage system is a nearly perfect chair ...").[9a] A pyramidally distorted carbonyl group is ruled out by known crystal structures of monoprotonated[9b] and -methylated[9c] 5,7-diazaadamantanone, in which the three angles at C_2 add up to 360°. We conclude therefore that the unusually large selectivities reported here are attributable to transition-state hyperconjugation. The effect is so much more visible than before, because the bonds vicinal to the 5-substituent have been so much more powerfully deactivated.

The nucleophilic addition to **7** itself is also of interest, since it seems conceivable that the unshared pair on nitrogen might interact with the C_{1-9} and C_{3-4} bonds so as to promote their donor abilities. It is noteworthy, in this connection, to compare the following carbonyl stretching frequencies (KBr): **4**, 1735.5 cm^{-1}; **5**, 1729.0 cm^{-1}; adamantanone, 1718.2 cm^{-1}; **7**, 1713.4 cm^{-1} (**6** gave only strong OH signals). Indeed, treatment with methyllithium in THF gave a mild excess (55–45) of the *Z* tertiary alcohol *Z*-**9**. Borohydride reduction in methanol produced an excess of *E*-**8** (62/38); possibly a hydrogen-bonded amine center is responsible for this unprecedented reversal of stereochemistry. We also mention here experiments detailed in the supplementary material and aimed at the pH dependence of the carbonyl carbon resonance of **7** and its derivatives. They may vary by more than 100 ppm; carbonyl hydration is responsible.[10,11]

Acknowledgment. We benefited greatly from advice and unpublished data by Professor Paul Haberfield of SUNY (Brooklyn) and from help in X-ray analysis by Professor Joe Lauher of our department. Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research.

Supplementary Material Available: Synthesis and reduction experiments and physical properties of all new compounds mentioned in this report, as well as pertinent NMR spectra (24 pages). Ordering information is given on any current masthead page.

---

[8] Haberfield, P.; Cincotta, J. J. *J. Org. Chem.* **1987**, *52*, 4627; **1990**, *55*, 1334.

[9] (a) Fernandez, M. J.; Galvez, E.; Lorente, A.; Soler, J. A.; Florencio, F.; Sanz, J. *J. Heterocycl. Chem.* **1989**, *26*, 349. (b) McCabe, P. H.; Milne, N. J.; Sim, G. A. *Acta Crystallogr.* **1989**, *C45*, 114. (c) Goncharov, A. V.; Panov, V. N.; Maleev, A. V.; Potekhin, K. A.; Kurkutova, E. N.; Struchkov, Y. T.; Palyulin, V. A.; Zefirov, N. S. *Dokl. Akad. Nauk USSR* (*Engl. Transl.*) **1991**, *318*, 148.

[10] Schulman, E. M.; Bonner, O. D.; Schulman, D. R.; Laskovics, F. M. *J. Am. Chem. Soc.* **1976**, *98*, S793. Van Luppen, J. J.; Lepoivre, J. A.; Dommisse, R. A.; Alderweireldt, F. C. *Org. Magn. Reson.* **1979**, *12*, 399.

[11] A referee suggested that we consider a recent critique (Frenking, G.; Kohler, K. F.; Reetz, M. T. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1146). In this computational paper, the authors state that the "explanation given by Cieplak ... is based on a rather paradoxical assumption: Stereoelectronic control ... is attributed to electron donation from the occupied orbitals ... into the vacant *antibonding* σ* orbital associated with the incipient bond" (italics theirs). Presumably, the explanation would not be "paradoxical" for a breaking bond yet, by virtue of microscopic reversibility, the transition states for bond formation and cleavage are the same. The explanation is paradoxical only if one attributes too literal a meaning to the term "antibonding". The proposition that electronic energy is lowered by delocalization into a vacant *orbital of higher energy* is a fundamental tenet of quantum chemistry.

Platinum-Mediated Reactions of Hydrosilanes. Isolation of a Complex with Bridging Disilene and Silylene Ligands

Richard H. Heyn and T. Don Tilley*

Department of Chemistry, 0506
University of California at San Diego
9500 Gilman Drive
La Jolla, California 92093-0506

Received October 28, 1991

Palladium and platinum provide the most widely used catalysts for transformations of organosilicon compounds.[1] Recent interest has focused on development of catalysts for the dehydrocoupling of hydrosilanes to polysilanes, which can suffer from competing, metal-catalyzed redistribution of substituents at silicon.[2] Unfortunately, enhancement of selectivity in these systems is complicated by a lack of relevant mechanistic information.[2c] Recent observations that Si-Si bond formation can occur via reductive elimination from Pt and Pd bis(silyl) complexes[2e,f] suggest the possibility that dehydrocoupling may occur simply via oxidative addition/reductive elimination cycles.[2c] Redistribution has most often been attributed to the activity of intermediate silylene complexes (e.g., $(R_3P)Pt({=}SiR'R'')(R''')SiR'R''R'''$),[2e] but oxidative addition/reductive elimination cycles could also account

---

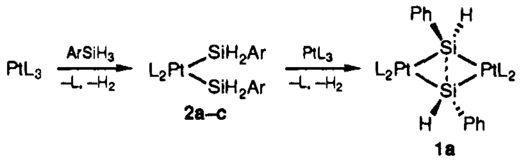
[1] (a) Tilley, T. D. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Chapter 24, p 1415. (b) Ojima, I. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Chapter 25, p 1479. (c) Tilley, T. D. In *The Silicon–Heteroatom Bond*; Patai, S., Rappoport, Z., Eds.; Wiley: New York; Chapter 10, p 309. (d) Curtis, M. D.; Epstein, P. S. *Adv. Organomet. Chem.* **1981**, *19*, 213 and references in the above.

[2] (a) Corey, J. In *Advances in Silicon Chemistry*; Larson, G., Ed.; JAI Press, Inc.: Greenwich, CT, 1991; Vol. 1., p 327. (b) Harrod, J. F.; Mu, Y.; Samuel, E. *Polyhedron* **1991**, *10*, 1239. (c) Tilley, T. D. *Comments Inorg. Chem.* **1990**, *10*, 37. (d) Laine, R. M. In *Aspects of Homogeneous Catalysis*; Ugo, R., Ed.; Kluwer Academic Publishers: Amsterdam, 1990; p 37. (e) Kobayashi, T.; Hayashi, T.; Yamashita, H.; Tanaka, M. *Chem. Lett.* **1988**, 1411. (f) Schubert, U.; Müller, C. *J. Organomet. Chem.* **1989**, *373*, 165.

0002-7863/92/1514-1917$03.00/0 © 1992 American Chemical Society

for this chemistry.[1d] More complex mechanisms for these reactions are suggested by the discovery of diplatinum disilene complexes, $(Et_3P)_2Pt(\eta^2,\eta^2\text{-}PhXSiSiX'Ph)Pt(PEt_3)_2$ (X, X' = H, Cl).[3] To gain more insight into possible reaction pathways, we have examined the interaction of Pt(0) complexes with primary silanes. Initial investigations have resulted in the discovery of new structures for possible intermediates in dehydrocoupling and redistribution processes, including a new diplatinum complex that results from Si–Si bond formation.

The products from reactions of $Pt(PEt_3)_3$ with arylsilanes $ArSiH_3$ (Ar = Ph, *p*-Tol, Mes) are determined by the ratio of reactants. At one extreme, reaction of 1 equiv of $ArSiH_3$ with 2 equiv of $Pt(PEt_3)_3$ gives near-quantitative formation of the Tessier–Youngs dimers $(Et_3P)_2Pt(\eta^2,\eta^2\text{-}Ar(H)SiSi(H)Ar)Pt(PEt_3)_2$ (**1a**, Ar = Ph; **1b**, Ar = *p*-Tol; **1c**, Ar = Mes) as crystalline products from pentane. If the $ArSiH_3{:}Pt(PEt_3)_3$ ratio is increased to 3:1, the new compounds *cis*-$(Et_3P)_2Pt(SiH_2Ar)_2$ (**2a**, Ar = Ph; **2b**, Ar = *p*-Tol; **2c**, Ar = Mes) are isolated. The kinetic cis products isomerize in solution to form mixtures of the cis and trans isomers.[4] Compounds **2a–c** are moderately air-stable as solids, but decompose in solution over several days to produce the dimers **1a–c**, $ArSiH_3$, and H_2, and at longer times the redistribution products Ar_2SiH_2. No disilane or higher oligomers were observed as final products in these decompositions, but in the case of more slowly decomposing **2c**, it was possible to observe $MesH_2SiSiH_2Mes$ *as an intermediate*. Insight into the mechanism of formation of **1a–c** is perhaps provided by the observed reaction of **2a** with $Pt(PEt_3)_3$, which cleanly gives **1a**, H_2, and PEt_3 (eq 1, L = PEt_3).[5]



(1)

The chelating phosphine $Me_2PCH_2CH_2PMe_2$ (dmpe) was introduced in attempts to obtain stereochemically rigid bis(silyl) complexes. Reaction of **2c** with dmpe afforded the expected product $(dmpe)Pt(SiH_2Mes)_2$ (**3**), but with the less sterically demanding silyl ligands, dimeric species $[(dmpe)Pt(SiH_2Ar)_2]_2(\mu\text{-dmpe})$ (**4a**, Ar = Ph; **4b**, Ar = *p*-Tol) were isolated. In solution, **4a,b** are in equilibrium with the corresponding monomers $(dmpe)Pt(SiH_2Ar)_2$. An X-ray structure determination revealed a square-pyramidal coordination geometry for the Pt atom in centrosymmetric **4a** with the phosphorous atoms of the bridging dmpe ligand occupying apical positions.[6]

Complex **3** thermally decomposes (150 °C) in a manner analogous to **2a–c** (by NMR spectroscopy). This reaction does not proceed according to any simple rate law, as might be expected for a rate-limiting oxidative addition or α-migration. In contrast, **4a** and **4b** undergo thermolysis at 60 °C to the unusual products $(dmpe)(H)Pt(\mu\text{-}SiHAr)_2[\mu\text{-}\eta^1,\eta^1\text{-}ArHSiSiHAr]Pt(H)(dmpe)$ (**5a,b**), which possess an η^1,η^1-disilene ligand and two bridging silylene ligands. The molecular structure of **5a**·OEt_2 (Figure 1) shows that the disilene bridges the two Pt(IV) centers along the Pt–Pt vector and possesses a Si–Si single bond distance of 2.385 (6) Å. Whereas **1a** has a planar Pt_2Si_2 core, the corresponding PtSiPtSi ring of **5a** is slightly puckered by 10.8° to accommodate the μ-disilene ligand. Also, the cross-ring Si–Si distance of 2.882 (6) Å is longer and the Pt–Pt distance of 3.787 Å is shorter than related distances in **1a** (2.58–2.60 Å and 3.97–4.00 Å, respectively). Despite the structural similarities between **1a,b** and **5a,b**, we have not been able to produce **5a,b** via reaction of **1a,b** with either $ArSiH_3$ or ArH_2SiSiH_2Ar. Details concerning the formation of **5a,b** are unavailable at this time, but mechanisms based on addition/elimination cycles or α-migrations to generate silylene ligands both seem possible.

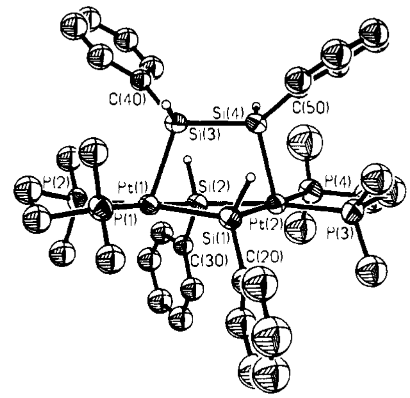


Figure 1. ORTEP view of **5a**·OEt_2. Important bond distances (angstroms) and angles (degrees): Pt(1)–Si(1) 2.382 (4), Pt(1)–Si(2) 2.379 (4), Pt(1)–Si(3) 2.426 (4), Pt(1)–P(1) 2.340 (5), Pt(1)–P(2) 2.341 (4), Pt(2)–Si(1) 2.392 (5), Pt(2)–Si(2) 2.391 (4), Pt(2)–Si(4) 2.439 (4), Pt(2)–P(3) 2.335 (5), Pt(2)–P(4) 2.336 (5), Si(3)–Si(4) 2.385 (6); Si(1)–Pt(1)–Si(2) 74.5 (1), Si(1)–Pt(1)–Si(3) 80.7 (1), Si(2)–Pt(1)–Si(3) 81.0 (1), Si(1)–Pt(1)–P(1) 102.0 (2), Si(3)–Pt(1)–P(1) 99.3 (1), Si(2)–Pt(1)–P(2) 98.1 (2), Si(3)–Pt(1)–P(2) 104.1 (1), Si(1)–Pt(2)–Si(2) 74.1 (1), Si(1)–Pt(2)–Si(4) 81.5 (1), Si(2)–Pt(2)–Si(4) 80.6 (1), Si(1)–Pt(2)–P(3) 99.5 (2), Si(4)–Pt(2)–P(3) 102.8 (1), Si(2)–Pt(2)–P(4) 101.2 (2), Si(4)–Pt(2)–P(4) 97.7 (2), Pt(1)–Si(1)–Pt(2) 105.0 (2), C(20)–Si(1)–H(1) 99 (4), Pt(1)–Si(2)–Pt(2) 105.1 (2), C(30)–Si(2)–H(2) 102 (4), Pt(1)–Si(3)–Si(4) 107.2 (2), Si(4)–Si(3)–C(40) 111.0 (5), Si(4)–Si(3)–H(3) 116 (3), C(40)–Si(3)–H(3) 102 (4), Pt(2)–Si(4)–Si(3) 106.2 (2), Si(3)–Si(4)–C(50) 112.7 (5), Si(3)–Si(4)–H(4) 110 (6), C(50)–Si(4)–H(4) 111 (6).

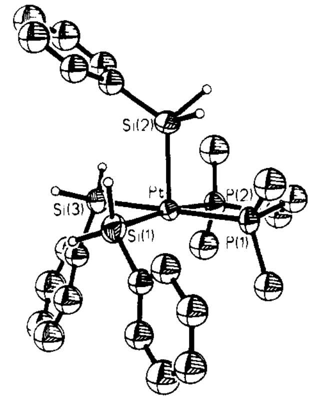


Figure 2. ORTEP view of **6a**. Important bond distances (angstroms) and angles (degrees): Pt–Si(1) 2.385 (5), Pt–Si(2) 2.406 (5), Pt–Si(3) 2.362 (5), Pt–P(1) 2.365 (4), Pt–P(2) 2.340 (4); P(1)–Pt–P(2) 84.9 (2), P(1)–Pt–Si(1) 97.6 (2), P(1)–Pt–Si(2) 90.9 (2), P(2)–Pt–Si(2) 98.1 (2), Si(1)–Pt–Si(2) 89.2 (2), P(2)–Pt–Si(3) 90.7 (2), Si(1)–Pt–Si(3) 86.7 (2), Si(2)–Pt–Si(3) 90.5 (2).

Compound **5a** reacted with 4 equiv of $PhSiH_3$ to give the disilane PhH_2SiSiH_2Ph, followed by slow quantitative formation of the Pt(IV) silyl *fac*-$(dmpe)Pt(H)(SiH_2Ph)_3$ (**6a**).[7] Given the interest in Pt(IV) silyl species as possible reaction intermediates and the lack of isolable examples,[8] the structure of **6a** was de-

---

(3) (a) Zarate, E. A.; Tessier-Youngs, C. A.; Youngs, W. J. *J. Am. Chem. Soc.* **1988**, *110*, 4068. (b) Zarate, E. A.; Tessier-Youngs, C. A.; Youngs, W. J. *J. Chem. Soc., Chem. Commun.* **1989**, 577. (c) Anderson, A. B.; Shiller, P.; Zarate, E. A.; Tessier-Youngs, C. A.; Youngs, W. J. *Organometallics* **1989**, *8*, 2320. (d) Tessier, C. A.; Kennedy, V. O.; Zarate, E. A. In *Inorganic and Organometallic Oligomers and Polymers*; Harrod, J. F., Laine, R. M., Eds.; Kluwer Academic Publishers: Amsterdam, 1991; p 13.

(4) For example, freshly prepared, pure *cis*-**2a** isomerizes within 0.5 h at 25 °C in benzene-d_6 solution to give a 70:30 mixture of cis and trans isomers.

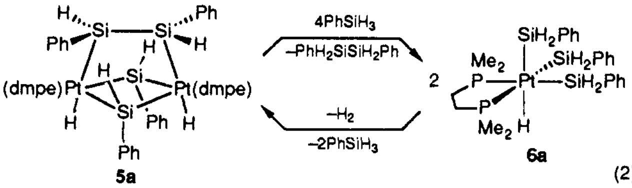
(5) Pham and West (Pham, E. K.; West, R. *Organometallics* **1990**, *9*, 1517) have reported mononuclear disilene complexes $L_2Pt(\eta^2\text{-}R_2Si{=}SiR_2)$, which suggests the possibility that **1a–c** might form via coordination of $Pt(PEt_3)_2$ to a $(PEt_3)_2Pt(\eta^2\text{-}ArHSi{=}SiHAr)$ complex. However, this expected reactivity mode has not yet been observed. Also, in contrast to West's observation that Pt(0) species react with more substituted disilanes $R_2HSiSiHR_2$ to give η^2-disilene complexes, $Pt(PEt_3)_3$ reacts with PhH_2SiSiH_2Ph to give $(PEt_3)_2Pt(SiH_2Ph)_2$ as the only observed Pt-containing product.[6]

(6) Heyn, R. H.; Tilley, T. D. Unpublished results.

(7) Compound **6a** is more conveniently prepared via the reaction of **4a** with $PhSiH_3$.

(8) Grundy, S. L.; Holmes-Smith, R. D.; Stobart, S. R.; Williams, M. A. *Inorg. Chem.* **1991**, *30*, 3333 and references therein.

termined (Figure 2). Complex **6a** thermally decomposes at 60 °C with loss of H_2 and $PhSiH_3$ (but not PhH_2SiSiH_2Ph) to regenerate **5a** (eq 2).



5a **6a** (2)

These results emphasize the potential importance of Pt(IV) intermediates in catalytic reactions of hydrosilanes. It is perhaps significant that in the reactions above stoichiometric Si–Si bond formation is observed only upon production of bimetallic complexes **1a–c** or the "basket" molecules **5a,b**, which represent a new structure resulting from Pt-mediated dehydrocouplings. The observed interconversion of **5a** and **6a** (eq 2) suggests that dehydrocoupling mechanisms might be more complicated than those originally considered and lends further credence to the notion that Si–Si bond formation may require two platinum centers acting cooperatively.[1d,3c] The cycle of eq 2 may in fact be catalytic, since both **5a** and **6a** act as a catalysts for the slow dehydrocoupling of $PhSiH_3$ to PhH_2SiSiH_2Ph.[9]

Acknowledgment is made to the National Science Foundation for their generous support. We thank Johnson-Matthey Inc. for a loan of platinum, and T.D.T. thanks the Alfred P. Sloan Foundation for a research fellowship (1988–1992).

Supplementary Material Available: Experimental procedures and characterization data for **1–6** and tables of crystal, data collection, and refinement parameters, bond distances and angles, anisotropic displacement parameters, and hydrogen atom coordinates for **5a**·OEt_2 and **6a** (24 pages); listings of observed and calculated structure factors for **5a**·OEt_2 and **6a** (31 pages). Ordering information is given on any current masthead page.

---

(9) For example, thermolysis of **6a** at 95 °C with an 80-fold excess of $PhSiH_3$ produced 4.5 equiv PhH_2SiSiH_2Ph/**6a** after 2 weeks. Of course, the complexes in eq 2 may be merely "resting states" for true catalytic intermediates. For example, it seems possible that **6a** might serve as a precursor to $(dmpe)Pt(SiH_2Ph)_2$, which actually participates in the catalytic cycle.

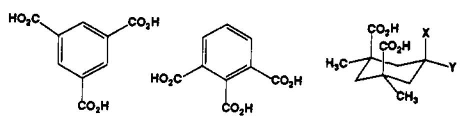
Remarkable Shape Selectivity in the Molecular Recognition of Carboxylate Anions in Aqueous Solution

Andrea Bencini,[†] Antonio Bianchi,*[,†] M. Isabel Burguete,[‡] Enrique García-España,*[,§] Santiago V. Luis,*[,‡] and José A. Ramírez[§]

Department of Chemistry
University of Florence, Via Maragliano 75/77
50144 Firenze, Italy
Department of Chemistry, University Jaume I
E-12080 Castellón, Spain
Department of Inorganic Chemistry
University of Valencia, C/Dr. Moliner 50
46100 Burjassot, Valencia, Spain

Received October 3, 1991
Revised Manuscript Received December 30, 1991

Scheme I



1 2

3 : X = CO_2H, Y = CH_3
4 : X = CH_3, Y = CO_2H

Table I. Logarithm of the Stepwise Basicity[a] and Stability[b] Constants (log *K* (±0.1)) for the Interaction between [21]andN_7 and Tricarboxylate Anions Determined at 298.15 K in 0.15 mol dm^{-3} $NaClO_4$ in Aqueous Solution

reaction	A **1**	 **2**	 **3**	 **4**	 **5**
A + H	4.4	5.4	7.3	6.9	5.4
AH + H	3.7	3.9	6.2	4.7	4.2
AH_2 + H	3.0	2.7	3.6	3.8	2.7
A + H_3L	3.1	3.2	3.4	2.5	
A + H_4L	4.6	5.2	5.2	4.0	2.7
A + H_5L	6.2	8.2	8.6	6.6	4.6
A + H_6L	8.0	11.0	12.9	9.7	6.6
A + H_7L	10.0	12.7	15.7	11.7	8.1

[a] As defined by the equation: $AH_n + H \rightleftarrows AH_{n+1}$. [b] As defined by the equation: $A + LH_n \rightleftarrows ALH_n$. In both equations, charges have been omitted for clarity.

Molecular recognition of polycarboxylic acids and their anions has received much attention in the last few years.[1–6] Size and shape specificity or chain length selectivity in the binding of dicarboxylic acids has been attained in nonpolar solvents by using preorganized receptors.[4,5] In protic solvents, the situation becomes, however, more complex as solvation can compete with host–guest interactions. Highly charged polyammonium macrocycles have been studied as receptors for carboxylate anions in water,[1,2,6] and moderate chain length selectivities have been described. Mainly, structurally very simple anions derived from linear α,ω-dicarboxylic acids were used in these studies. However, it is generally assumed that preorganization plays an essential role in host–guest chemistry.[7] In order to gain further insight into the factors governing anion coordination chemistry, we have studied the interaction of polyammonium receptors and a series of "preorganized" polycarboxylate anions. Here we report on the interactions between the macrocyclic receptor 1,4,7,10,13,16,19-heptaazacycloheneicosane ([21]aneN_7)[8] and the tricarboxylic acids **1–5**, illustrating how small structural modifications in the rigid substrates greatly affect their interaction.

Carboxylates derived from benzenetricarboxylic acids (**1** and **2**) can be considered as ideal models for rigid anionic substrates having well defined shapes in terms of both charge density and hydrogen bonding. Kemp's triacid **3**[9] and its cis,trans isomer **4**[10]

[†] University of Florence.
[‡] University Jaume I.
[§] University of Valencia.

(1) Dietrich, B.; Hosseini, M. W.; Lehn, J. M.; Sessions, R. B. *J. Am. Chem. Soc.* **1981**, *103*, 1282–1283. Hosseini, M. W.; Lehn, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 3525–3527. Hosseini, M. W.; Lehn, J. M. *Helv. Chim. Acta* **1986**, *69*, 587–603. Hosseini, M. W.; Lehn, J. M. *Helv. Chim. Acta* **1988**, *71*, 749-756. Lehn, J. M.; Mêric, R.; Vigneron, J.-P.; Bkouche-Waksman, I.; Pascard, C. *J. Chem. Soc., Chem. Commun.* **1991**, 62–63.

(2) Kimura, E.; Sakonaka, A.; Yatsunami, T.; Kodama, M. *J. Am. Chem. Soc.* **1981**, *103*, 3041–3045. Kimura, E.; Kuramoto, Y.; Koike, T.; Fujioka, H.; Kodama, M. *J. Org. Chem.* **1990**, *55*, 42–46.

(3) Breslow, R.; Rajagopalan, R.; Schwarz, J. *J. Am. Chem. Soc.* **1981**, *103*, 2905–2907. Vögtle, F.; Puff, H.; Friedrichs, E.; Müller, W. M. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 431. Müller, G.; Rirde, J.; Schmidtchen, F. P. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1516–1518.

(4) Rebek, J., Jr.; Nemeth, D.; Ballester, P.; Lin, F.-T. *J. Am. Chem. Soc.* **1987**, *109*, 3474–3475. Echavarren, A.; Galán, A.; Lehn, J. M.; de Mendoza, J. *J. Am. Chem. Soc.* **1989**, *111*, 4994–4995.

(5) Tanaka, Y.; Kato, Y.; Aoyama, Y. *J. Am. Chem. Soc.* **1990**, *112*, 2807–2808. Kikuchi, Y.; Kato, Y.; Tanaka, Y.; Toi, H.; Aoyama, Y. *J. Am. Chem. Soc.* **1991**, *113*, 1349–1354. Garcia-Tellado, F.; Goswami, S.; Chang, S.-K.; Geib, S. J.; Hamilton, A. D. *J. Am. Chem. Soc.* **1990**, *112*, 7393–7394.

(6) Shinkai, S.; Yoshioka, A.; Nakayama, H.; Manabe, O. *J. Chem. Soc., Perkin Trans. 2* **1990**, 1905–1909.

(7) Cram, D. J. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1039–1057. Lehn, J. M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 89–112.

(8) 1,4,7,10,13,16,19-Heptaazacyclohenicosane ([12]aneN_7]: García-España, E.; Micheloni, M.; Paoletti, P.; Bianchi, A. *Inorg. Chim. Acta* **1985**, *102*, L9–L11. Bianchi, A.; García-España, E.; Mangani, S.; Micheloni, M.; Orioli, P.; Paoletti, P. *J. Chem. Soc., Chem. Commun.* **1987**, 729–731. Bencini, A.; Bianchi, A.; Dapporto, P.; García-España, E.; Micheloni, M.; Paoletti, P. *Inorg. Chem.* **1989**, *28*, 1188–1191.

(9) Kemp, D. S.; Petrakis, K. S. *J. Org. Chem.* **1981**, *46*, 5140–5143.

0002-7863/92/1514-1919$03.00/0