the equilibrium constants and kinetics for metal ion binding to GaAs.

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Molecular Recognition: Size and Shape Specificity in the Binding of Dicarboxylic Acids

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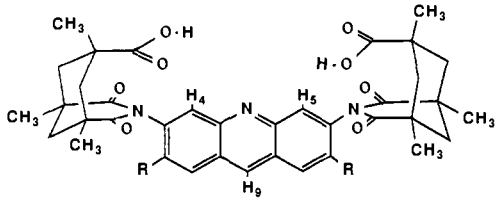
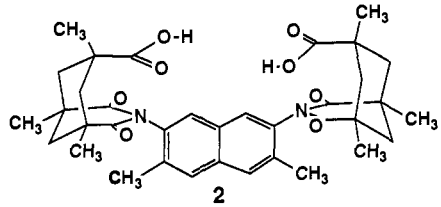
We recently introduced[1] the model receptors **1** and **2** and gave evidence of their unique binding capacities.[2] In these structures



1a R = H
1b R = CH_3



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two carboxyl groups converge on a molecular cleft in a manner similar to the convergence of the carboxyl functions in enzymes such as lysozyme[3] and the aspartic proteinases.[4] This feature accounts for the unusual acid dissociation constants of the diacids[5] and is the crucial element in their ability to recognize smaller molecules of complementary size, shape, and functionality.[6] The aromatic spacer groups in **1** and **2** prevent the formation of intramolecular hydrogen bonds between the opposing carboxyl groups, yet these functions are ideally positioned for intermolecular hydrogen bonding; here we report how these receptors interact with carboxylic acids.

A solution of **1b** in $CDCl_3$ (10^{-3} M) dissolves solid oxalic acid (pK_{a1} = 1.2[8]), a substance otherwise quite insoluble in this medium, and ^{13}C NMR[7] established a 1:1 stoichiometry for the complex.

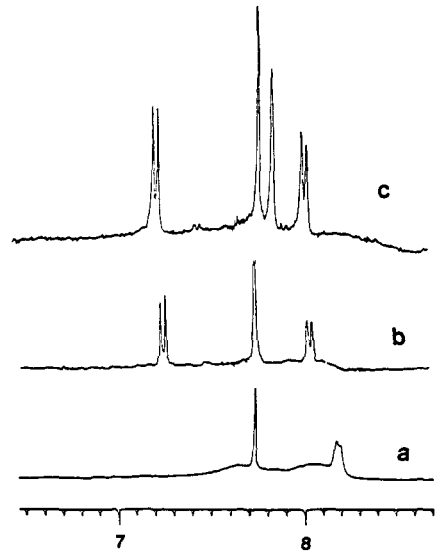

Figure 1. (a) Ambient temperature (297 K) 300-MHz ^1H NMR spectrum of **3** broadened by rotation; (b) spectrum after the addition of 2 equiv of glutaric acid at 297 K; (c) as in (b) but at 210 K.

Similar behavior was observed by proton NMR for malonic acid (pK_{a1} = 2.9), its C-substituted derivatives, and maleic (pK_{a1} = 1.8) or phthalic acids (pK_{a1} = 2.9). Fumaric (pK_{a1} = 3.0), succinic (pK_{a1} = 4.2), or glutaric (pK_{a1} = 4.3) acids were unaffected under these conditions. At first glance, these results appear to establish the pK_a of **1**·H^+ as $\leq$3, since only the stronger acids are complexed. The downfield shift of H_9 (8.7 → 9.2 ppm) seen in the presence of the stronger acids is in accord with partial protonation of the acridine nitrogen; stronger acids such as picric or *p*-toluenesulfonic also cause this proton to shift (9.4 ppm).

Protonation may be a necessary element in the recognition of acids by **1b** but this receptor has more to offer than mere basicity. Specifically, the picrate of **1b** also dissolves oxalic or malonic acid in $CDCl_3$, and this process results in the release of free picric acid (pK_a 0.4). In other experiments the complex of **1b** with malonic acid was treated with excess picric acid in $CDCl_3$. Only after 6 equiv of the stronger acid were added did the weaker malonic acid begin to separate from solution. These experiments establish that **1**·H^+ provides some special stabilization to the conjugate bases of oxalic and malonic acids. That is, these dicarboxylic acids appear stronger than picric acid when **1** is present.

What is the nature of this special stabilization? Two lines of evidence bear on this issue. First, compounds[9] **1a** and **3** provide some dynamic evidence. In these, rotations about the C_{aryl}–N_{imide} bonds are facile at room temperature and result in broadened ^1H NMR spectra. Figure 1a shows the ambient temperature spectrum of **3**; simple salts of **1a** such as the picrate show similar line broadening. At low temperature, complex spectra are observed for **1a** (or its picrate) and for **3** (with or without HOAC) since interconversions between the three possible conformations become slow. However, in the presence of dicarboxylic acids of appropriate size and shape the spectra are sharpened and are no longer temperature dependent.

Figure 1b shows the room temperature spectrum of **3** in contact with glutaric acid and Figure 1c shows the same system at 210 K. Similar behavior is seen in the spectra of **1a** in the presence of 1 equiv of oxalic or malonic acids.[10] Binding to diacids of appropriate size, shape, and pK_a restricts **1a** or **3** to the conformations featuring convergent carboxyls as shown in **4**. Only these

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(5) Rebek, J., Jr.; Duff, R. J.; Gordon, W. E.; Parris, K. *J. Am. Chem. Soc.* **1986**, *108*, 6068-6069.
(6) Rebek, J., Jr.; Askew, B.; Nemeth, D.; Parris, K. *J. Am. Chem. Soc.* **1987**, *109*, 2432-2434.
(7) The ^{13}C oxalate resonance appears at 161.5 ppm in the complex (Me_2SO–$CDCl_3$ at 77.09 ppm) where free oxalic acid appears at 159.5 ppm in the same medium.
(8) Acid dissociation constants are from: Bonhomme, G.; Juillard, J. *J. Chim. Phys.* **1974**, *71*, 1097-1100. *CRC Handbook of Chemistry and Physics*, 60th ed.; CRC Press: Boca Raton, FL, 1979.
(9) Rebek, J., Jr.; Nemeth, D. *J. Am. Chem. Soc.* **1985**, *107*, 6738.
(10) For **1a**–oxalate in $CDCl_3$ signals were at 7.35, d; 8.15, d; 8.6, s; and 9.3 ppm, s, and for **1a**–malonate at 7.35, d; 8.1, d; 8.45, s; and 9.3 ppm, s.

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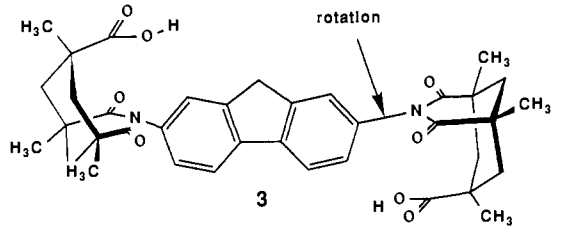

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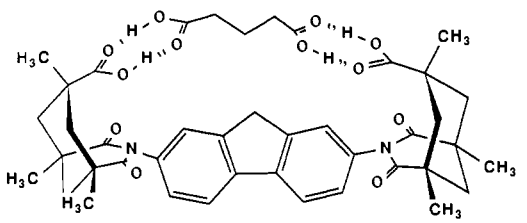

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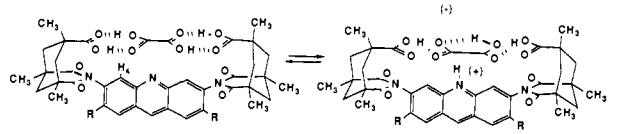
conformations can provide specific stabilization of the substrates by involving both carboxyls of the receptor in hydrogen bonding so that rotation is stopped. For the acridines, some protonation also occurs; this is accommodated in the tautomeric structures **5a** ⇌ **5b** proposed for these complexes. Similar structures can



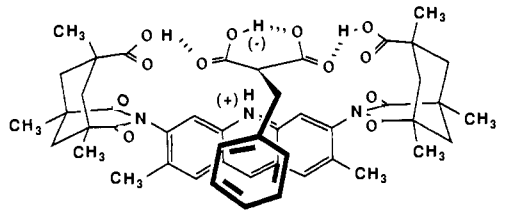
5a 5b

be envisioned for the complexes of malonate, maleate, and other anions that can be chelated between the convergent carboxyls.

Second, intermolecular NOE experiments[11] revealed an 18% enhancement of the ^{13}C oxalate signal when H_4 of the receptor **1b** was irradiated in the 1:1 complex. These establish a propinquity between these nuclei that is consistent with the proposed structures **5**.

Finally, a highly specific means of stabilization can be observed with substrates bearing suitably placed aromatic functions. These are *stacking interactions* between the pendant aryl and the large π surface presented by **1**. For example, benzylmalonic acid forms complexes with **1a** or **1b** in which large upfield shiftsd of the phenyl protons are observed in the NMR.[12] In addition, homonuclear intermolecular NOE was observed between the ortho protons of the substrate and those lining the cleft of **1**. These are similar to those observed in phenylalanine[9] and heterocyclic diamines[6] when these substrates are in contact with **1** in organic solvents.

The structural details of these complexes must await crystallographic analysis, but the facts are in accord with structure 6 for the benzylmalonic acid complex. In the meantime, we note



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that the reversal of acidities resulting from the specific stabilization of conjugate bases has also been observed by Kimura[13] in the chemistry of carboxylic acids in contact with macrocyclic polyamines.

Acknowledgment. We are grateful to the National Science Foundation and the National Institutes of Health for support of this research.

(11) The program described by Cativiela and Sanchez-Ferrando (Cativiela, C.; Sanchez-Ferrando, F. *Magn. Reson. Chem.* **1985**, 1072-1075) was used on an IBM 300-MHz instrument; 90% enriched ^{13}C oxalic acid was dissolved in $CDCl_3$ using the receptor **1b** and selective irradiation of H_4 led to the difference spectra for the ^{13}C resonance of the bound oxalate at 162.84 ppm.

(12) Chemical shifts ($CDCl_3$) observed for the phenyl group of **6** were 6.85, t (para); 7.02, t (meta); and 7.25 ppm, d (ortho). The difference NOE experiment was similar to that recently described: Pirkle, W. H.; Pochapsky, T. C. *J. Am. Chem. Soc.* **1986**, *108*, 5627-5628. Nehaus, D. *J. Magn. Reson.* **1983**, *53*, 109-114. A 5% enhancement of the H_4 signal was observed.

(13) Kimura, E.; Sakonaka, A. *J. Am. Chem. Soc.* **1982**, *104*, 4984-4985. For other studies of selective binding of carboxylic acids, see: Breslow, R.; Rajagopalan, R.; Schwartz, J. *J. Am. Chem. Soc.* **1981**, *103*, 2905-2907. Kimura, E.; Sakonaka, A.; Yatsunami, T.; Kodama, M. *Ibid.* **1981**, *103*, 3041-3045. Hosseini, M. W.; Lehn, J. M. *Ibid.* **1982**, *104*, 3525-3527.

Synthesis and X-ray Crystal Structure Analysis of a η^4-1-Phosphabutadiene Tetracarbonyltungsten Complex

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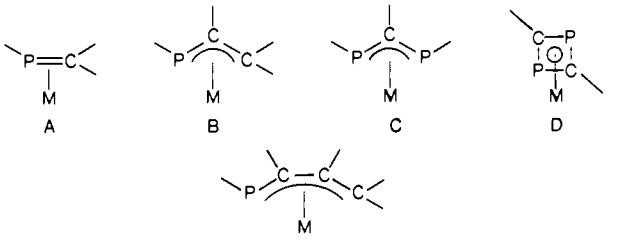
The formal replacement of a carbon by a phosphorus unit in the skeleton of each known type of alkene and cyclic or acyclic polyalkene π-complex (η^2-η^8) suggests a wide range of interesting new structures. Until recently, these new structures were either unknown or very poorly investigated. However, during the last 4 years, it has become increasingly evident that such a formal replacement is possible in almost every conceivable case.[2] For example, η^2-phosphaalkene (A),[3] η^3-phosphaallyl (B[4] and C[5]), and η^4-diphosphacyclobutadiene (D)[6] complexes have all been described recently. At the moment, the most obvious gap in this series concerns the open η^4-phosphabutadiene structure (E). We wish to report here on the first known complexes of this type. Our



A B C D

E

(1) (a) Ecole Polytechnique. (b) Institut Le Bel.

(2) This topic has been reviewed very recently: Mathey, F. *Nouv. J. Chim.*, in press.

(3) (a) van der Knaap, Th. A.; Jenneskens, L. W.; Meeuwissen, H. J.; Bickelhaupt, F. *J. Organomet. Chem.* **1983**, *254*, C33. (b) Cowley, A. H.; Jones, R. A.; Stewart, C. A.; Stuart, A. L. *J. Am. Chem. Soc.* **1983**, *105*, 3737. (c) Cowley, A. H.; Jones, R. A.; Lasch, J. G.; Norman, N. C.; Stewart, C. A.; Stuart, A. L.; Atwood, J. L.; Hunter, W. E.; Zhang, H.-M. *J. Am. Chem. Soc.* **1984**, *106*, 7015. (d) Al-Resayes, S. I.; Klein, S. I.; Kroto, H. W.; Meidine, M. F.; Nixon, J. F. *J. Chem. Soc., Chem. Commun.* **1983**, 930. (e) Werner, H.; Paul, W.; Zolk, R. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 626. (f) Appel, R.; Casser, C.; Knoch, F. *J. Organomet. Chem.* **1985**, *293*, 213. (g) Deschamps, B.; Mathey, F. *J. Chem. Soc., Chem. Commun.* **1985**, 1010.

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