Table I. Reduction Potentials of Substituted Benzyl Radicals and Calculated pK_a Values for Substituted Toluenes

substituent	$E_{1/2}^{red}$ (V vs SCE)[a,b]	pK_a (X-$C_6H_4CH_3$)[c]	ΔpK_a[d]
4-OMe	−1.75[e]	55.2	4.1
4-Me	−1.62	53.8	2.7
3-Me	−1.50	52.2	1.1
4-F	−1.50	52.2	1.1
H	−1.43 (−1.45)[f]	51.1	0.0
4-Cl	−1.40	50.8	−0.3
3-CN	−1.11	46.8	−4.3
4-CN	−0.77	41.2	−9.9 (−11)[g]
4-C(O)Me	−0.71	39.8	−11.3

[a] Reduction potential of X-$C_6H_4\dot{C}H_2$ measured by PMV at 53 Hz modulation. All values have an experimental uncertainty of ±50 mV. [b] Radicals were generated by hydrogen atom abstraction, eq 6 and 7 in acetonitrile/di-*tert*-butyl peroxide (9:1) containing TBAP (0.1 M). [c] Calculated with eq 9, uncertainty ±2 pK_a units. Absolute pK_a of toluene is 51 in acetonitrile and 42 in DMSO. [d] Relative to toluene. [e] Radical generated by photolysis of 4-methoxyphenylacetone in acetonitrile/TBAP (0.1 M). [f] Reference 2e. [g] Reference 2d.

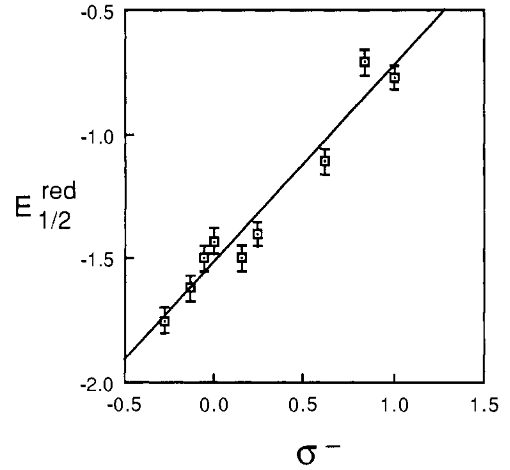

Figure 1. Hammett plot of $E_{1/2}^{red}$ (V vs SCE) versus σ^- for the reduction of substituted toluenes.

peroxide (9:1) solvent containing 0.1 M tetrabutylammonium perchlorate, TBAP) are reported in Table I. A Hammett plot, Figure 1, shows that they correlate with σ^-, and the slope (770 mV, r = 0.97) corresponds to a ρ value of 13. The correlation with σ^- implies that the redox potentials are dominated by the carbanion stability. Extended Hammett treatment of the data using σ^- and $\sigma_\alpha^\bullet$, which reflects the substituent effect on the radical stability,[5] does not improve the correlation.

The linearity of the Hammett plot suggests either that the measured potentials, $E_{1/2}$, are close to the standard potential, $E°$ (which is a thermodynamically significant value[6]), or that they are all irreversible and that the overpotentials vary monotonically with σ^-. In fact, it is easy to differentiate between these possibilities. The measured $E_{1/2}$ value for the reduction of the benzyl radical is indeed close to $E°$ since our value is within 20 mV of that for the reverse process, i.e., the oxidation of the benzyl anion.[3e] The linearity of the Hammett plot, therefore, implies that all of the $E_{1/2}$ values are close to $E°$. This conclusion is further supported by the good agreement between our calculated ΔpK_a value for 4-cyanotoluene and a literature value[2d] (vide infra, Table I).

The pK_a values were calculated, eq 9, by combining the measured reduction potentials, eq 2, with the free energy for homolytic bond dissociation, eq 1,[7–9] and by introducing the free energies for reactions 3 ($\Delta G_3°$ = 48.6 kcal mol^{-1}) and 4 ($E_4°$ = 0.254 V vs SCE).[12] The energies for the homolytic cleavages are barely affected by the substituents,[7,8] the maximum variation being 2–3 kcal mol^{-1}. In fact, the contributions from the reduction potentials dominate the changes in acidities and $\Delta pK_a \approx F\Delta E_2°/2.3RT$.

$$pK_a = (\Delta G_1° - F(E_2° - E_4°) - \Delta G_3°)/2.3RT \qquad (9)$$

It is interesting to compare the pK_a's in acetonitrile with those reported by Bordwell with the titration method in dimethyl sulfoxide.[2d] For toluene and 4-cyanotoluene, $pK_a^{CH_3CN} - pK_a^{DMSO}$ is completely accounted for by only considering the change in solvation of the proton indicating that the free energy change for the transfer of the carbanion between the two solvents, $\Delta G_{tr}°(R^-)$, is small.[4c] The implication of this result is that $\Delta G_{tr}°(R^-)$ for all of the substituted benzylic carbanions is small (i.e., less than 2 kcal mol^{-1}).

Acknowledgment. We thank Dr. Larkin Kerwin for a "President's Award" that made this work possible.

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Structure and Binding for Rebek's Diacid in Chloroform. A Demure Host for Pyrazine

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A major, current activity in bioorganic chemistry is the development of synthetic receptors[1] that selectively bind neutral organic molecules in organic solvents[2] or water.[3] Rebek has actively studied a class of hosts that feature a binding cleft with convergent functional groups.[2a] Both binding and catalysis have been demonstrated for **1**.[4,5] In particular, this host is postulated to sequester pyrazine **2** via the "two-point binding" shown below.[4] However, it is not obvious that the ratio of observed[4] K_a's of only

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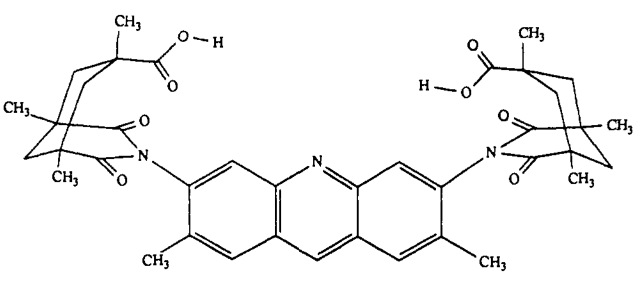

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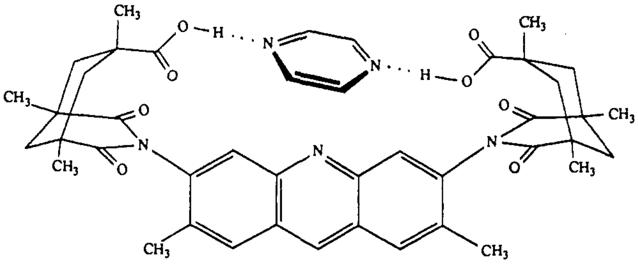

12 for pyrazine over pyridine (**3**) in chloroform is consistent with the loss of an N···HO hydrogen bond. As summarized here, the structural question and binding characteristics of **1** have now been pursued through fluid simulations. The results illustrate the benefits of complementary experimental and theoretical studies of molecular recognition.

Monte Carlo statistical mechanics simulations were carried out to compute the structures and relative free energy of binding (ΔΔG) for **1**:**2** and **1**:**3** in chloroform. Statistical perturbation theory[6] was used to compute ΔG for the mutations **2** → **3** and **1**:**2** → **1**:**3** which give $\Delta\Delta G = \Delta G_3 - \Delta G_2 = \Delta G_b - \Delta G_u$ from the

$$\begin{tikzcd}
1 + 2 \arrow[r, "\Delta G_2"] \arrow[d, "\Delta G_u"'] & 1:2 \arrow[d, "\Delta G_b"] \\
1 + 3 \arrow[r, "\Delta G_3"] & 1:3
\end{tikzcd}$$

thermodynamic cycle. Similar calculations have been performed previously for enzyme-substrate complexes.[7,8] The geometrical parameters for **1** were adopted from an X-ray structure[9] and are nearly the same as ones obtained from prior MM2 calculations[10] with MacroModel.[11] The sampling for **1** included the six torsional degrees of freedom about the C—N(C=O)$_2$, C-COOH, and C-OH bonds, while the remaining internal degrees of freedom were kept fixed. This approximation follows from the rigidity of **1** and the observed binding which is not strong enough to provide expectations of substantial shifts from the average structure. The requisite torsional potential functions were derived from MM2 calculations. Experimental structures were used for **2**, **3**, and the $CHCl_3$ molecules and were kept fixed.[12] The simulations were carried out in the NPT ensemble at 25 °C and 1 atm for the complexes plus 250 or 380 chloroform molecules in a periodic box. Each mutation was performed as in previous studies[13] over a series of three or four separate simulations. **2** was originally oriented for the two point binding. Each simulation then involved equilibration for at least 5×10^5 configurations followed by averaging for 2.0×10^6 or 2.5×10^6 configurations. Interactions were included between molecules with any interatomic distance below ca. 11 Å. The OPLS potential functions[14] were used to describe the intermolecular interactions, and all calculations were performed with the BOSS program.

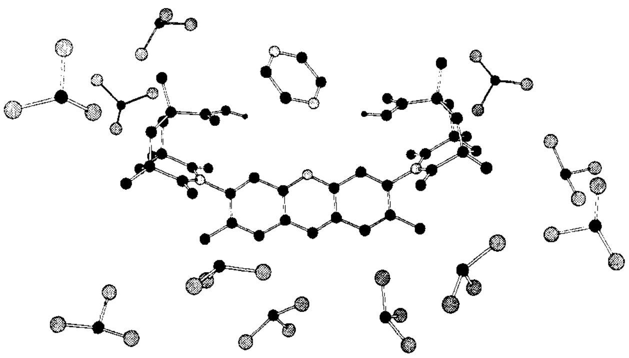

Figure 1. A typical structure for the complex of **1** with pyrazine in chloroform from the Monte Carlo simulations. Some of the nearby chloroform molecules are shown with hydrogens implicit. The corresponding complex with pyridine has the guest tipped up more on average.

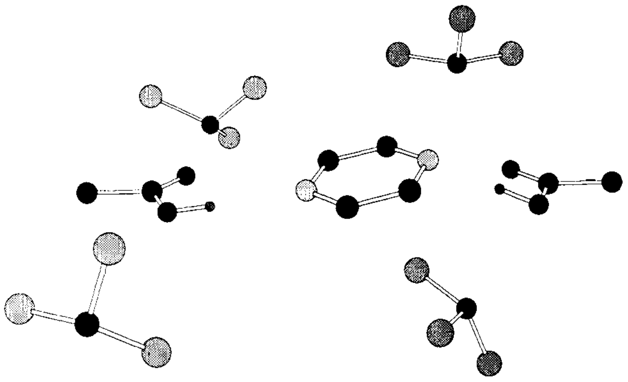

Figure 2. A typical structure for the complex of pyrazine with a model host consisting of two acetic acid molecules with a fixed O_H–O_H separation of 8.4 Å.

Simulations were run for **1** with the acid groups both in a syn, as in the crystal,[9] and anti orientation. The dihedral angles of **1** sampled 30°–60° ranges in the simulations with the largest variations for the acid hydrogens. The key energetic results are $\Delta G_u = 0.34 \pm 0.04$ kcal/mol, and for both syn and anti **1**, $\Delta G_b = 1.5 \pm 0.1$ kcal/mol. Combination gives binding preferences of 1.2 ± 0.1 kcal/mol for pyrazine which compare well with the observed 1.45 kcal/mol. However, the computed structure for **1**:**2** in chloroform does not show the two point binding. There is one strong N···H_O hydrogen bond with an average length of 2.4 Å (syn) or 2.3 Å (anti), but the other N···H_O distance averages 4.2 Å (syn) and 3.8 Å (anti). The latter interaction does provide some electrostatic stabilization that can account for the small preference for binding pyrazine. A typical structure for the anti-**1**:**2** complex is shown in Figure 1. The guest floats above the acids groups; the cleft is too small for two point binding, which is also disfavored on entropic grounds. The averge O_H···O_H separation of 7–8 Å in **1** needs to expand to ca. 8.4 and 9.2 Å for the syn and anti forms for optimal two point binding according to model calculations. This notion was pursued by analogous simulations for the **2** → **3** mutation in a cleft formed by two acetic acid molecules. They were oriented syn and fixed to be coplanar with an O_H···O_H separation of 8.4 Å. The two point binding was found to be maintained for **2** (Figure 2). The computed ΔΔG

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of 3.6 ± 0.1 kcal/mol translates to a K_a ratio of 405. This is not the maximal value but indicates the range expected for true two point binding.[15]

Supplementary Material Available: Details on the OPLS parameters for **1**, **2**, **3**, and chloroform are provided (5 pages). Ordering information is given on any current masthead page.

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[15] (15) Gratitude is expressed to the National Institutes of Health for support of this work.

Syntheses and Reactivity of Ruthenium Hydride Complexes Containing Chelating Triphosphines. 1. Characterization of the Molecular Dihydrogen Complex $RuH_2(H_2)(Cyttp)$ (Cyttp = $PhP(CH_2CH_2CH_2P(c\text{-}C_6H_{11})_2)_2$)

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Since the first report of compounds containing a molecular dihydrogen (η^2-H_2) ligand,[1] the number of η^2-H_2 complexes has increased rapidly; in fact, two reviews on this subject have appeared recently.[2] Consequently, many of the previously assigned high-valent metal polyhydrides have been reformulated as lower-valent metal dihydrogen complexes.[2] For example, $RuH_4(PPh_3)_3$[3] is now considered to be $RuH_2(H_2)(PPh_3)_3$.[4a,b] In order to make chemical and structural comparisons between metal hydrides containing monodentate phosphines and those containing chelating polydentate phosphines, we have synthesized several ruthenium hydride compounds that contain chelating triphosphine ligands, one of which is $RuH_2(H_2)(Cytpp)$, Cyttp = $PhP[CH_2CH_2CH_2P(c\text{-}C_6H_{11})_2]_2$, which is the first reported example of a molecular dihydrogen complex containing a chelating triphosphine.

Metathesis reactions of $RuCl_2(Cyttp)$[5] with excess NaH in THF under a dihydrogen atmosphere at 40–50 °C overnight (ca. 10 hours) yield $RuH_4(Cyttp)$. On the basis of proton and $^{31}P\{^1H\}$ NMR evidence[6] and the chemical reactions described below, the compound is best formulated as the ruthenium dihydrogen complex *cis-mer*-$RuH_2(H_2)(Cyttp)$.[6] At room temperature, its ^1H NMR spectrum in the hydride region (Figure 1) shows a broad resonance at ca. −8.2 ppm ($\omega_{1/2}$ = 40 Hz). Integration of the hydride resonance shows that the number of hydrogen atoms per ruthenium ranges from approximately 3.2 to 3.6. Since the compound is diamagnetic, we are formulating it as $RuH_4(Cyttp)$. Low integration values for hydride resonances have been reported previously for similar compounds of monophosphines; for example, the number of hydrides observed for $RuH_4[P(p\text{-tolyl})_3]_3$ was 3.0–3.2, based on integration of the proton NMR spectrum.[3c] It is tempting to attribute the low integration value to partial dissociation of dihydrogen in solution, as was done for $RuH_4[P(p\text{-tolyl})_3]_3$.[3c] Dissociation of the η^2-H_2 ligand in solution would explain the rapid reactions with D_2 and other small molecules; however, solid $RuH_4(Cyttp)$ appears stable to loss of H_2 for a few hours at 0.1 Torr.

The broad hydride resonance of $RuH_2(\eta^2\text{-}H_2)(Cyttp)$ at ca. −8.2 ppm is separated into two broad signals when the temperature is lowered below 240 K; one signal is at ca. −6.5 ppm and the other is at ca. −9.5 ppm with an intensity ratio of ca. 1:1. In contrast to the two peaks observed for our $RuH_4(Cyttp)$ complex, both $RuH_4(PPh_3)_3$[4a] and $RuH_4(PCy_3)_3$[8g] show only one resonance in the hydride region. To confirm the presence of the nonclassical hydride $Ru(H_2)$ unit, we have used the T_1 criterion reported by Crabtree[4] and others.[8] The T_1 value was measured by the inverse-recovery method. At room temperature in toluene-d_8, the T_1 value for the broad hydride resonance signal is 38 ms; it decreases to 18 ms at 260 K. At 230 K, the T_1 for the resonance at −6.5 ppm is 16 ms, while that for the −9.5 ppm resonance is 18 ms. As the temperature is decreased further, the T_1 values for both resonances increased, but at a different rate, as shown in Figure 1. All the T_1 values observed for our $RuH_2(\eta^2\text{-}H_2)(Cyttp)$ are in the range for molecular dihydrogen complexes (usually < 100 ms). Considering that the molecule is highly fluxional and that the T_1 value for the −9.5 ppm resonance increased much faster than that at −6.5 ppm, we suggest that the actual T_1 values for the −9.5 ppm resonance probably are much larger than the measured ones.[9] The resonance at −9.5 ppm is, therefore, assigned to classical Ru–H bonds, while that at −6.5 ppm is assigned to the nonclassical $Ru(H_2)$. The behavior of these two resonances is very similar to that observed for $[IrH(H_2)(bq)(PPh_3)_2]^+$.[4b]

The line widths of the hydride resonances changed with temperature; for example, at 303 K the $\omega_{1/2}$ is ca. 40 Hz and ca. 260 Hz at 250 K. Below 240 K, the line widths of the two resonances changed in a different manner. The line width for the resonance at δ −9.5 decreased as the temperature was lowered,[10] whereas, the line width for the resonance at δ −6.5 first decreased, and then it increased.[10] The line width behavior is consistent with several other $M(H_2)$ complexes.[8b,c]

Several factors have been suggested to be responsible for the broad lines (small T_2) observed for $M(\eta^2\text{-}H_2)$ signals, such as exchange of free and coordinated H_2, molecular motion (e.g., rotation) of the H_2 ligand, and dipolar interaction between the two hydrogen atoms of η^2-H_2.[8c] The values of T_2 decrease monotonically with increasing τ_c and approach a limiting value that is characteristic of a completely rigid solid. As the temperature is lowered, the molecular motions, including rotation of the η^2-H_2 ligand, are slowed and τ_c increases; thus T_2 is smaller at lower temperatures. The slowing rotation of the η^2-H_2 ligands

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† Deceased December 7, 1988.

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[6] (6) The ^{31}P NMR spectrum of $RuH_2(H_2)(Cyttp)$ showed a triplet at 28.3 ppm for the central phosphorus atom and a doublet (J_{PP} = 31 Hz) at 52.4 ppm for the two terminal phosphorus atoms at room temperature in toluene-d_8. The ^{31}P NMR data indicate a structure in which the triphosphine Cyttp is bonded meridional around ruthenium. The meridional arrangement of Cyttp is confirmed by its ^{13}C NMR spectrum; i.e., virtual triplets for the ipso carbon of the cyclohexyl groups were observed at ca. δ 39.5.[7]

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[10] (10) The −9.5 ppm resonance had the following line widths: at 230 K, $\omega_{1/2}$ = 190 Hz; 220 K, $\omega_{1/2}$ = 115 Hz; 210 K, $\omega_{1/2}$ = 80 Hz; 200 K, $\omega_{1/2}$ = 60 Hz; 190 K, $\omega_{1/2}$ = 65 Hz; 183 K, $\omega_{1/2}$ = 70 Hz. The −6.5 ppm resonance had the following line widths: at 230 K, 280 Hz; 220 K, 180 Hz; 210 K, 160 Hz; 200 K, 300 Hz.

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