with the fact that Mg^{2+} templates the conversion of **2** to **4** and Ca^{2+} does not. The high value for Pb^{2+} (0.9) suggests this ion should be used as the templating agent for preparation of **4**. The overall log K^f_{av} values for **4** − **2** vary much more (from 0.9 to −2.2) than do the values for **3** − **1** (from 0.7 to 0.1). This fact correlates with the much greater difference in rigidity of ligand organization induced by cyclization of acac units through m-$CH_2C_6H_4CH_2$ vs. $CH_2CH_2OCH_2CH_2$ connecting units. However, CPK models of complexes of the smaller ions indicate **3** or **4** can form two different Macac rings with either square planar or tetrahedral arrangements of oxygens.

Comparisons of log K^f_{av} values for cycles **3** and **4** are particularly interesting. Toward all ions but Cd^{2+}, **3** is a better binder than **4**. However, the more rigid **4** shows more selectivity toward the ions than does **3** (or acac, **1**, or **2**). Thus log K^f_{av} values for **4** complexing the ten ions vary by 9.5, whereas for **3** the values vary by 6.7. Particularly noteworthy are the relatively high log K^f_{av} values that result from encircling with **3** to give neutral complexes of the physiologically important ions Cu^{2+} (12.1), Co^{2+} (9.7), Zn^{2+} (9.5), Ca^{2+} (7.4), and Mg^{2+} (7.2). Since Na^+ was the reference ion, it complexes powers of ten less well than these ions.

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(8) Degassed stock solutions (0.02 M) of the metal nitrates that were 0.02 M in $HClO_4$ and 0.05 M in $NaClO_4$ were used in 25-mL aliquots. Compounds **1–4** (0.60 mmol) in 0.3 mL of dioxane (0.024 M) or 1.20 mmol of acetylacetone were added. The solutions were titrated with 1.00 N aqueous NaOH solutions.

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A Crown Ether NAD(P)H Mimic. Complexation with Cations and Enhanced Hydride Donating Ability toward Sulfonium Salts

Sir:

The ability of crown ethers to associate with a variety of charged and uncharged substrates[1] bears resemblance to the initial step in reactions catalyzed by enzymes. In developing enzyme mimics one may hope that by using correctly designed crown ethers bearing the proper functional groups both a high degree of substrate selectivity and reactivity could be attained. The feasibility of this idea has been illustrated recently by Chao and Cram[2] with a crown ether model capable of mimicking reactions catalyzed by the enzyme trypsin. We describe here the first, to the best of our knowledge, report of the reactions of a NAD(P)H mimic formed from the union of a Hantzsch 1,4-dihydropyridine segment (**1a**) and a polyethylene glycol chain.[3]

The dihydropyridines (**1**) donate hydride only sluggishly or not at all to unactivated carbonyl compounds.[4] Enhanced rates of reaction with **1** can be achieved by activating carbonyl substrates by chelation with a metal ion[5] or by hydrogen bonding;[6] similar effects are probably involved in hydrogenase enzymes.[7] The complexing ability of the crown in **2**, the synthesis of which has been described recently,[8] offers in principle the opportunity to have the hydride donor, a possible catalytic site, and a substrate in a single complex. For activation two types of complexes come to mind: (a) a *ternary* complex consisting of **2**, a (metal) ion, and a substrate and (b) a *binary* complex of **2** with a (positively charged) substrate capable of accepting hydride. We have isolated (unproductive) examples of the former and have obtained evidence for enhanced rates of hydride transfer with examples of the latter.

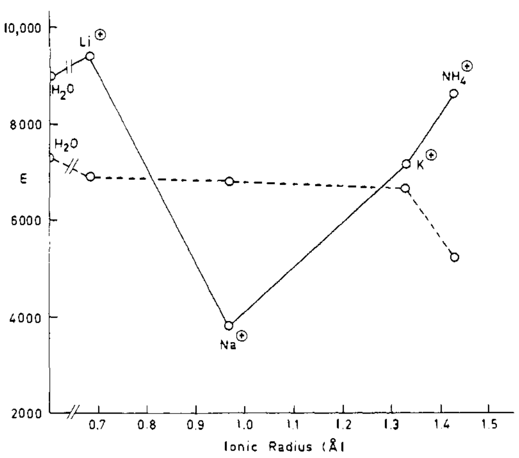
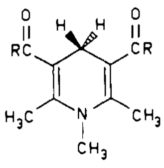
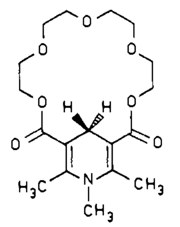


Figure 1. UV maxima for **2** (solid lines) at 270 nm and **1b** (dashed line) at 268 nm in 1.6 M aqueous M^+, Cl^- solution.



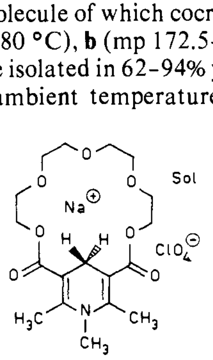
1

a) R = −O−
b) R = $-OC_2H_5$



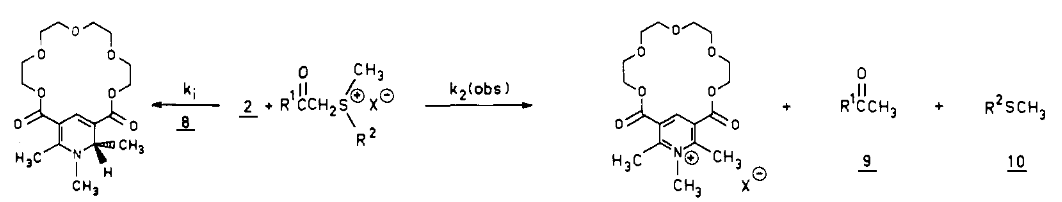
2

Spectroscopic (UV, and ^1H and ^{13}C NMR) measurements gave evidence that **2** associates with positive ions. For example in the UV spectrum of **2** in 1.6 M aqueous M^+, Cl^- solution the intensity of absorption at 270 nm depends strongly on the radius of M^+; this effect is absent with **1b** (Figure 1).[9] Na^+ ions give the strongest effect. When **2** (mp 90-92 °C) and $NaClO_4$ are mixed in the appropriate solvent (indicated in the formulation by Sol, one molecule of which cocrystallized) the complexes **3a** (mp 176-180 °C), **b** (mp 172.5-175 °C), and **c** (mp 169.5-171.5 °C) are isolated in 62-94% yield.[10] These materials are stable at ambient temperature but decompose in



3

a) Sol = H_3CCN
b) Sol = H_3CCOCH_3
c) Sol = $H_3CCO_2CH_3$



11^{15} 8 9 10 (1)

11		8	9	10
43% (86%)	4 $R^1 = C_6H_5, R^2 = C_6H_5, X = BF_4^{\ominus}$	43% (15%)	43% (10%)	49% (12%)
33 (0)	5 $R^1 = C_6H_5, R^2 = CH_3, X = ClO_4^{\ominus}$	50 (4)	50 (2)	50 (2)
40 (12)	6 $R^1 = CH_3, R^2 = C_6H_5, X = ClO_4^{\ominus}$	26 (11)	—[14] (—)[14]	27 (14)
79 (38)	7 $R^1 = OCH_3, R^2 = C_6H_5, X = BF_4^{\ominus}$	12 (14)	19 (14)	14 (14)

chloroform solution with deposition of $NaClO_4$ and regeneration of **2** and Sol. No evidence is available for hydride transfer within these ternary complexes.[11]

The possibility of forming reactive binary complexes is opened by providing (carbonyl) substrates with a functionality capable of complexing with the crown. Phenacyl ammonium perchlorate associates strongly with **2** but the complex undergoes little reaction.[9] We have, however, previously demonstrated that properly substituted phenacyl (and other) sulfonium salts are reduced at sp^3 carbon by **1b.**[12] The sulfonium salts **4–7** react smoothly also with **2;** the stoichiometic reaction scheme applicable (also to **1b** as described previously in detail)[12,13] is shown in eq 1. The yields indicated are those obtained in $(CD_3)_2CO$ at ambient temperature at near consumption of **2**, The yields in parentheses are those obtained under the same conditions with **1b** after the same time interval as for **2**.

The second-order rate constant k_2(obsd) for hydride transfer from **2** to **4** was measured in the temperature range 33.5–44,5 °C and for **1b** with the same substrate from 70.0 to 89,5 °C. For the reaction of **1b** with **4** $\Delta G^{\ddagger}_{25°} = 26.0$ kcal/mol, $\Delta H^{\ddagger}_{25°} = 17.7$ kcal/mol, and $T\Delta S^{\ddagger}_{25°} = -8.3$ kcal/mol, whereas for the reaction of **2** with **4** $\Delta G^{\ddagger}_{25°} = 23.0$ kcal/mol, $\Delta H^{\ddagger}_{25°} = 31.6$ kcal/mol, and $T\Delta S^{\ddagger}_{25°} = +8.6$ kcal/mol.[14] Extrapolated to 75 °C k_2 (obsd) for **2** is 3.16×10^{-1} L mol^{-1} s^{-1} whereas at the same temperature for **1b** k_2 (obsd) is 1.18×10^{-4} L mol^{-1} s^{-1}. At 75 °C crown ether **2** would transfer hydride 2700 times faster than **1b** to sulfonium salt **4.** Although not yet measured accurately, a similar order of reactivity obtains for **5;** substrate **6** is much less discriminate although it does react somewhat faster with **2**. For the case of **7** no (qualitative) difference can be discerned in the rate of reaction with **1b** and **2.**

Addition of 1 equiv of 18-crown-6 fails to produce a measurable effect on the rate of reaction of **1b** and **4** ruling out an external crown ether effect. However, association is suggested by the fact that the solubility of **4** in acetone is increased about 33% on adding 18-crown-6.

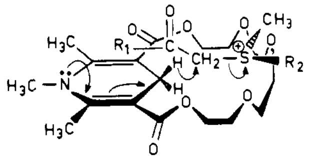
The rate of hydride transfer from **2** to **4** is retarded by $NaClO_4$ whereas this salt has no effect on the rate of hydride transfer from **1b.** In the presence of 0.22 equiv of $NaClO_4$ k_2 (obsd) for **2** is 0.35 times that in the absence of this salt; addition of 1 equiv of $NaClO_4$ completely inhibits hydride transfer. The product pyridinium salt **8** also inhibits the rate of hydride transfer and causes deviation from second-order kinetics at extended reaction times.

We submit that these observations indicate that **2** associates with **4** to form a binary complex.[16] The better complexing agent $NaClO_4$ (see above) acts as a competitive and reversible inhibitor by occupying the complexation site in **2.** If the structures of the sulfonium salt and crown ether are compatible with stereoelectronic necessities for hydride transfer, then reduction will occur in the complex. The activation parameters measured from k_2 (obsd) for **1b** and **2** differ enormously; despite a significant increase in activation enthalpy relative to **1b** the crown ether still reacts faster. The rate enhancement is caused in fact by the great increase in entropy of activation as reflected in the $T\Delta S^{\ddagger}$ contributions to $\Delta G^{\ddagger}$. If the mechanism with **2** involves the complexation indicated in eq 2 then k_2 (obsd) will include the equilibrium constant for complexation and one can imagine that much of the orientation needed for activation is achieved in this non-rate-determining step.

$$\mathbf{2} + \text{sulfonium salt} \underset{k_r}{\overset{k_f}{\rightleftarrows}}$$

$$[\mathbf{2}, \text{sulfonium salt}] \xrightarrow{k_2} \text{products} \quad (2)$$

Inspection of models indicates that a sulfonium salt fits remarkably well into the cavity of **2**. A possible model for this complex is that shown in **12** in which the components are well lined up for a displacement of sulfide.



12

These results encourage us to believe that better-structured dihydropyridine containing crown ethers can be prepared that will have an even greater complexing power and concomitant hydride donating ability toward not only sulfonium salts but also other potential substrates that can form ternary complexes like **3a–c** but in which the stereoelectronic situation is more favorable for hydride transfer. We hope in due course to report on such reactions.

Acknowledgment. We are indebted to Professor D. J. Cram for a free and valuable exchange of information. Technical assistance was provided by W. H. Kruizinga and R. A. Slagter.

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(9) For **2** UV_{max} (H_2O) 238 nm (ϵ 14 450), 270 nm (ϵ 9000), and 370 nm (ϵ 6500). The intensities of the 238 and 370 nm bonds are only weakly affected. Full details of this and other spectroscopic measurements will be deferred to a full publication.

(10) Acceptable elemental analyses (within 0.3% of theory) have been obtained for all new compounds. Spectral data are in accord with the proposed structures.

(11) An x-ray crystallographic structure determination is being undertaken to examine the orientation of Sol relative to the hydride donor.

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(14) The rate of disappearance of **2** (0.14 M in **2** and **4**) and **1b** (0.33 M in **1b** and **4**) in C_3D_6O was measured by ^1H NMR spectroscopy. Complete material balances were obtained for all reactions except that of **6**, which was not entirely clean; very likely some H/D exchange and alkylation of the dihydropyridine occurs;[12] the yield of acetone cannot be determined. Good plots of k_2 (obsd) against T^{-1} were obtained.

(15) The sum of isomerization product **11**[13] and unreacted **2** accounts for the balance of the pyridine. As expected the amount of **11** corresponds to the amount of unreacted sulfonium salt.[12]

(16) To the best of our knowledge no examples of sulfonium salt–crown ether complexes have hitherto been reported.

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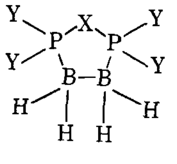
Phosphorus–Nitrogen–Boron Heteroring Systems. Preparation of Methylaminobis(difluorophosphine)diborane(4)

Sir:

Despite the many successes in preparing phosphazene and phosphazane ring systems[1] and phosphorus–oxygen and phosphorus–sulfur clusters,[2] there has been little progress made in preparing inorganic ring or cluster backbones containing phosphorus and two other nonmetal elements. It has been demonstrated that several fluoro-,[3] alkyl-,[4] and aryldiphosphine[4] ligands do act as bidentate ligands toward classical and metal carbonyl Lewis acid sites, and interest in these coordination complexes is keen because of the potential for forming extensive π-electron delocalized networks and establishing synthetic routes to new multielement cluster systems. We have prepared the first in a possible series of diphosphinediborane(4) ring complexes having the proposed structure type I where X = $N(CH_3)$ and Y = F. Bis(trifluorophosphine)diborane(4)[5] (2.4 mmol) is treated with an equimolar amount of methylaminobis(difluorophosphine)[6] at −23 °C for 24 h. The product is separated by fractional distillation through U-traps cooled to −45, −96, and −196 °C. The pure base displacement product is retained at −45 °C in 100% yield.



I

The following characterization results provide unequivocal composition and tentative structural assignments.[7] The mass spectrum (70 eV) displays the following peaks all of which are assignable to $F_2PN(CH_3)PF_2(B_2H_4)$ (relative intensities and assignments enclosed in parentheses): *m/e* 193–189 (total 1, $F_2PN(CH_3)PF_2B_2H_{4-x}{}^+$)[8], 180–178 (total 2, $F_2PN(CH_3)PF_2BH_{2-x}$)[8], 167 (16, $F_2PN(CH_3)PF_2{}^+$), 152 (7, $F_2PNPF_2{}^+$), 148 (9, $F_2PN(CH_3)PF^+$), 133 (1, F_2PNPF^+), 114 (1, $FPNPF^+$), 98–95 (total 6, $F_2PN(CH_{3-x})^+$, $PNPF^+$), 79 (43, $FPN(CH_3)^+$), 78 (82, $FPN(CH_2)^+$), 77 (3, $FPN(CH)^+$), 76 (2, $FPNC^+$), 60 (31, $PN(CH_3)^+$), 59 (3, $PN(CH_2)^+$), 58 (2, $PN(CH)^+$), 50 (27, PF^+), 45 (15, PN^+), 31 (9, P^+). The infrared spectrum of a gaseous sample shows absorptions at 2964 (m), 2910 (w), 2438 (s), 2350 (s), 1210 (m), 1105 (m), 1095 (s), 1050 (s), 937 (s), 894 (s), 825 (vs), 730 (s), 675 (m), 590 (m), 572 (m), 485 (s), 440 (m), and 373 (s) cm^{-1}. The band at 590 cm^{-1} is tentatively assigned to the P–B stretch and the bands at 2438, 2350, and 1105 cm^{-1} are assigned to BH_2 stretching and bending modes. The remaining bands correlate with the infrared spectrum of the free ligand.

The NMR spectra of the free ligand are complex, and they have been interpreted in terms of a XX′AA′X″X‴ spin system.[6] The proton spectrum (100 MHz, −10 °C, neat) of the ring coordination complex consists of a broadened multiplet centered at +2.9 ppm (TMS external reference) and a very broad, low intensity resonance at ~1 ppm. The free ligand ^1H spectrum shows a triplet (J_{PH}) of quintets (J_{PF}) centered at +2.34 ppm.[6] A proton chemical shift for the hydrogens attached to diborane(4) in related complexes has not been reported.[5,9] The fluorine spectrum (94.1 MHz, −15 °C, neat) of the complex consists of a doublet (J_{PF} = 1207 Hz) centered at +77.3 ppm (upfield of $CFCl_3$ external reference). Each member of the doublet is further split into a triplet (J_{HBPF} = 14 Hz). This observation is consistent with the equivalence of both base sites and a direct P–B bond. The ^{19}F spectrum of the free ligand is second order and it is centered at +75.8 ppm. The boron spectrum (32.1 MHz, −10 °C, neat) of the complex consists of a single broad resonance centered at +44.8 ppm (upfield of BF_3OEt_2 external reference). This featureless ^{11}B peak appears to be characteristic of diborane(4) complexes.[5,9]

The ^{19}F and ^1H NMR spectra of the complex are similar to spectra recorded for the related bis borane(3) complex $F_2PN(CH_3)PF_2(BH_3)_2$.[10] The ^{11}B NMR spectrum distinguishes these complexes since a doublet of quartets is observed at +43.3 ppm for the borane(3) complex. The pattern in the ^{19}F spectrum is a doublet of quartets.

Further proof of the stoichiometry of the ring complex is given by the quantitative recovery of the displaced PF_3 of the reactant diborane(4) complex. The characterization data, therefore, fully support the stoichiometry and structure represented in I. Crystals of the ring complex have been isolated and an x-ray diffraction structure determination will be initiated shortly. A study of the structure and synthesis of related ring complexes using other bidentate phosphine ligands will be the subject of a future paper. It is appropriate to point out that King and coworkers[11] have recently prepared several interesting metal carbonyl complexes of the $(F_2P)_2N(CH_3)$ ligand, and comparison of the coordination chemistry and structures should prove to be interesting.

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