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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.

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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.

T. J. van Bergen, Richard M. Kellogg*
Department of Organic Chemistry, University of Groningen
Zernikelaan, Groningen, The Netherlands

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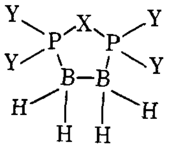
Phosphorus-Nitrogen-Boron Heteroring Systems. Preparation of Methylaminobis(difluorophosphine)diborane(4)

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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R. T. Paine*
Department of Chemistry, The University of New Mexico
Albuquerque, New Mexico 87131

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A Novel Class of Molecular Complexes: Li-NH_3, Li-H_2O, Li-HF, Li-H_2S, Na-H_2O, and Na-HF

Sir:

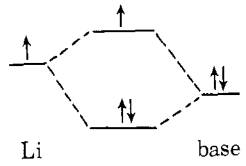
In recent years theoretical chemists have made considerable progress in understanding the gas phase hydration[1-4] of simple cations and anions. For example, theory and experiment agree that Li^+ and F^- bind a single water molecule by 35 and 24 kcal/mol, respectively. In addition, ab initio calculations have been reported for systems as large as $Li(H_2O)_6{}^+$, leading to the conclusion[4] that Li^+ prefers a tetrahedral (rather than octahedral) coordination. There seems to be agreement[4] that much of the strength and directionality of these interactions can be qualitatively understood in terms of classical electrostatics.[5]

However, the analogous neutral systems (e.g., Li-H_2O and F-H_2O) have, for the most part, remained unexplored. This is in part due to the lack of charge, suggesting that such systems might not be significantly bound. In addition the unpaired electron makes standard closed-shell self-consistent-field theory[6] inapplicable. Nevertheless, there is at least one indication in the literature that such molecular complexes may be strongly bound. This is the work on Li-NH_3 by Nicely and Dye,[7] who used SCF theory to predict a binding energy of ~20 kcal/mol. In the present communication we report SCF studies on a family of molecular complexes involving neutral alkali and halogen atoms and dipolar molecules. In particular, we have studied interactions between Li, Na, and F atoms and the dipolar molecules NH_3, H_2O, HF, PH_3, H_2S, and HCl.[8] The results of these calculations are summarized in Table I.

The minimum energy structure for alkali atom (M)-hydride (BH_n) interactions is M···BH_n, where the negatively charged end of the hydride approaches the neutral atom. There is charge transfer from the hydride to the metal and this leads to a rather substantial dipole moment for the complex. Comparing the Li atom interaction energies with different hydrides, we see that they qualitatively follow the order expected on the basis of the electrostatic potential model we developed[9] ($NH_3 > H_2O > HF > PH_3 > H_2S > HCl$), with the exception that H_2S is more strongly bound than PH_3. The reason for this discrepancy is not completely clear at this point. Another interesting feature of the calculations, which could have been predicted on the basis of the electrostatic potential of the hydrides,[9] is that the minimum energy θ, the angle between the Li···B vector and the dipole vector of the base is ~0 for H_2O and ~70–80° for H_2S and HCl. This is another demonstration that there is much greater "lone pair directionality" in the hydrides of the second row than in the hydrides of the first row (H_2O, HF).[10]

The Na···hydride interactions appear to have the same relative strength as the Li···hydride for NH_3, H_2O, and HF, although the interaction energies are smaller. Na is at least as polarizable as Li,[11] but the greater Na···hydride distances would be expected to decrease the interaction energies compared to those found for Li···hydride. If the Li···base interactions are analogous to Li_2···base interactions,[12] we expect electrostatic and polarization energies (especially the latter) to dominate these alkali metal-hydride interaction potentials.

A simple orbital picture which describes these interactions and is consistent with the Mulliken populations changes[13] showing base → atom charge transfer is shown below. This



type of an orbital interaction would be net stabilizing. The less tightly bound the orbital of the base, the more strongly it would interact with that of Li, and this is consistent with the strength

Table I. Interaction Energies Geometries and Charge Redistribution in Complexes Studied

Complex	$-\Delta E$ (kcal/mol)	R (Å)[a]	θ (deg)[b]	Charge transfer[c]	Dipole moment enhancement[d]
Li···NH_3	14.5	2.07	(0)	0.059	4.05
Li···OH_2	12.8	1.93	0	0.046	3.69
Li···FH	4.2	1.94	(0)	0.036	3.61
Li···PH_3	0.5	3.03	(0)	0.054	3.51
Li···SH_2	1.8	2.78	78°	0.081	3.32
Li···ClH	<0.1	(3.18)	71°	0.035	1.58
Na···NH_3	6.0	2.75	(0)	0.030	3.33
Na···OH_2	5.2	2.38	(0)	0.024	3.28
Na···FH	1.2	2.46	(0)	0.019	2.93
F···$NH_3(^2E)$	−3.0	(2.80)	(0)	−0.002	0.37
F···$NH_3(^2A)$	1.8	2.80	(0)	0.006	0.53

[a] Distance between atom and electronegative atom on the polar molecule; values in parentheses are nonoptimized values. [b] Angle between the R vector and the dipolar axis of the neutral molecule; values in parentheses are nonoptimized values. [c] Net Mulliken charge transfer from molecule to atom. [d] Dipole moment of complex minus dipole moment of isolated molecules (in Debyes).