Structure, Spectra, and Reaction Energies of the Aluminum−Phosphorus Rings $(HAl-PH)_2$ and $(H_2Al-PH_2)_2$ and the $(HAl-PH)_4$ Cluster

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Recently a six-membered ring consisting of three coordinate aluminum and phosphorus was synthesized, as well as an $R_2AlPR'_2$ compound of three coordinate aluminum and phosphorus. This research was initiated in order to better understanding the bonding in these new compounds, as well as the more common compounds that contain four coordinate aluminum and phosphorus. *Ab initio* investigations of the structure, bonding, vibrational spectra, and reaction energies for the unknown three coordinate ring $(HAl-PH)_2$, the four coordinate ring $(H_2Al-PH_2)_2$, and the four coordinate cluster $(HAl-PH)_4$ are presented. The three coordinate ring has two conformers that are within 3 kcal mol^{-1} in energy. The higher energy conformer is planar and the P−H bonds are *trans*, while the other is puckered and the P−H bonds are *cis*. The theoretical Al−P bond lengths are within 0.01 Å of the experimental values for the three coordinate Al−P compounds, despite the size difference between the hydrogen atoms of the model compound and the substituents on the experimentally determined structures. The structures for $(H_2Al-PH_2)_2$ and for the $(HAl-PH)_4$ cube are also in good agreement with analogous known compounds. The theoretical energies of H_2 loss and dimerization to form the cube compound from an initial Lewis acid−base adduct are also reported. The laboratory synthesis of $(RAl-PR')_2$ compounds should be possible.

Introduction

In their synthesis of the cubic cluster $(RAl-PR')_4$ (R = iBu, R′ = Ph_3Si), Cowley, Jones, Mardones, Atwood, and Bott begin with iBu_2AlH and Ph_3SiPH_2.[1] The reaction proceeds through elimination of hydrogen to form a ring of formula $(R_2Al-PHR')_2$. This initial ring undergoes elimination of isobutane and forms the cube. Although a mechanism has not been proposed, it is possible that an intermediate $(RAl-PR')_2$ ring, which has phosphorus and aluminum atoms that are only three coordinate, is formed. Such a ring has not yet been synthesized. Recently a six-membered-ring compound with three coordinate aluminum and phosphorus was synthesized by Wehmschulte and Power.[2] This was only the second compound with a bond between three coordinate aluminum and phosphorus to be structurally characterized. The other was the $(2,4,6\text{-}(iPr)_3C_6H_2)_2$-Al−P(1-adamantyl)($SiPh_3$) compound reported by Wehmschulte, Ruhlandt-Senge, and Power.[3] Although the chemistry of aluminum phosphorus compounds has been reviewed by Haaland as a part of aluminum coordination chemistry,[4] this was prior to synthesis of any three coordinate Al−P compounds. Haaland used the Schomaker−Stevenson rule to predict the Al−P bond length between three coordinate Al and P atoms to be 2.31 Å. The Al−P bonds in the two compounds now known are 2.328(3) Å for the six-membered ring[2] and 2.342 Å for the unassociated compound.[3]

Both of the recently synthesized compounds have of necessity sterically demanding substituents. Theoretical model compounds have the advantage of eliminating the complicating factors of sterically demanding substituents that could alter bond lengths and angles. Trends in bond lengths and angles obtained will ordinarily be due only to underlying bonding considerations. Recently reviews of low-valent phosphorus−boron compounds have been published,[5−7] and low-valent Al−N compounds have been studied.[8,9] To date the only theoretical studies of low-valent Al−P compounds have been those of six-membered rings.[10,11] We have undertaken theoretical studies of low-valent Al−P compounds, both unassociated[12] and now ring and cluster compounds. We report here theoretical structures, energies, and vibrational frequencies for the $(HAl-PH)_2$ ring, which contains three coordinate aluminum and phosphorus, and the $(H_2Al-PH_2)_2$ ring and the $(HAl-PH)_4$ cluster, which contain four coordinate atoms.

Theoretical Methods

Ab initio theoretical studies were carried out initially at the Hartree−Fock self-consistent-field (SCF) level, using a double-ζ plus polarization (DZP) basis set. The Huzinaga−Dunning (4s/2s) basis set was used for hydrogen,[13,14] and the Huzinaga−Dunning (11s7p/6s4p) basis set was used for aluminum and phosphorus.[15,16] The exponents for the polarization functions were Al = 0.40, P = 0.80, and H = 0.75. Electron correlation was included via the method of configuration interaction including all single and double excitations (CISD) and the coupled cluster method including all single and double excitations (CCSD). In all correlated methods the orbitals corresponding to the Al and P 1s atomic orbitals were frozen, and the corresponding high-energy virtual orbitals deleted. A larger basis set was also used to assure that no anomalous results were obtained due to small basis set size. Triple-ζ plus double polarization (TZ2P) basis sets consisting of the Huzinaga−Dunning[13,17] (5s/3s) basis set on hydrogen and the McLean−Chandler (12s9p/6s5p) basis set on aluminum and phosphorus were used.[15,18] The exponents of the TZ2P polarization functions were H = (1.50, 0.375), P = (1.20, 0.30), Al = (0.80, 0.20). Geometry optimizations were performed via analytic

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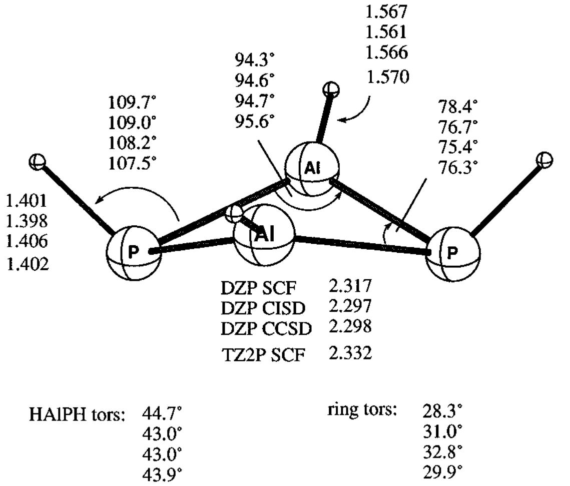

Figure 1. Theoretical geometry of the *cis*-puckered (HAl−PH)$_2$ ring in angstroms and degrees.

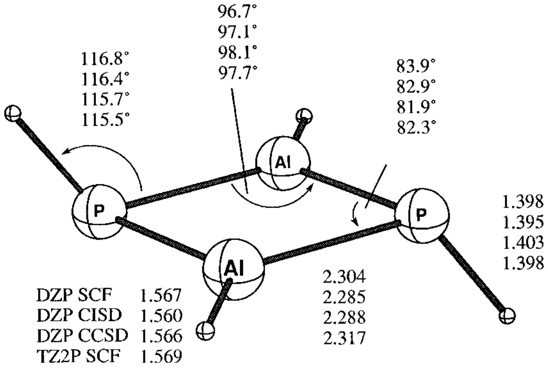

Figure 2. Theoretical geometry of the *trans*-puckered (HAl−PH)$_2$ ring in angstroms and degrees.

first-derivative methods. Harmonic vibrational frequencies were obtained via analytic second derivatives at the Hartree−Fock level. The PSI suite of programs was used throughout.[19]

Results and Discussion

The theoretical geometries of the three-coordinate (HAl−PH)$_2$ ring in different conformations are given in Figures 1 and 2. The harmonic vibrational frequencies are given in Tables 1 and 2. The theoretical geometry of the four-coordinate (H$_2$-Al−PH$_2$)$_2$ ring is given in Figure 3, and the corresponding predicted harmonic vibrational frequencies are given in Table 3. The results for the cube are given in Figure 4 and Table 4. We will discuss first the geometries and harmonic vibrational frequencies of the two rings and the cube in turn, and then we will examine the energies of the reactions that lead to formation of the cube from an initial H$_3$Al−PH$_3$ adduct.

(HAl−PH)$_2$. One might expect, on the basis of the structure of the six-membered ring of Wehmschulte and Power,[2] that this four-membered Al−P ring would be puckered. Puckering of the ring creates two possible orientations for the hydrogen attached to phosphorus, similar to the axial and equatorial sites of cyclohexane, although the difference between axial and equatorial is smaller in the four-membered ring than in cyclohexane, because the degree of puckering is smaller. There are three possible conformations: axial hydrogens at both phosphorus atoms, equatorial at both, or an axial−equatorial mix. Geometry optimizations at the DZP SCF level were begun from each of these conformations. No stationary point was found for the axial−axial conformation. The optimization that was begun at the axial−axial arrangement underwent ring inversion to the equatorial−equatorial conformation. The optimization begun with an equatorial−axial conformation converges to a minimum on the potential surface for which the ring is planar. We shall refer to it as the *trans*-planar conformation, and it has C_{2h} symmetry and a ^1A_g ground state. The equatorial−equatorial conformation has C_{2v} symmetry and a $^1A_1$ ground state. We will refer to the equatorial−equatorial conformation as *cis*-puckered. The *cis*-puckered ring lies only 0.4 kcal mol^{-1} below the *trans*-planar conformation at the DZP SCF level. Both increase in basis set size and correlated levels of theory favor the *cis*-puckered conformation. The *cis*-puckered ring is lower in energy by 2.2 kcal mol^{-1} at the TZ2P SCF level, and at the DZP CCSD level it is 1.5 kcal mol^{-1} lower in energy. If we assume the effects of basis set and correlation are additive, we estimate that the *cis*-puckered ring is about 3 kcal mol^{-1} lower than the *trans*-planar ring in energy.

TABLE 1: SCF Vibrational Frequencies in cm^{-1} and Infrared Intensities in km mol^{-1} (in Parentheses) for the *cis*-Puckered Conformation of the (HAl−PH)$_2$ Ring[a]

mode (intensity)	DZP	TZ2P
A_1		
P−H str. (6)	2578	2529
Al−H str. (47)	2046	2033
P−H wag (28)	609	598
Al−H wag (141)	466	462
Al−P str. (3)	454	454
ring angle def (216)	216	224
ring pucker (0)	146	139
A_2		
Al−P−H bend (0)	639	616
P−Al−H bend (0)	560	545
Al−P str. (0)	395	374
B_1		
P−H str. (57)	2578	2529
P−Al−H bend (414)	686	677
P−Al−H + P−H wag (3)	478	463
P inversion (113)	191	193
B_2		
Al−H str. (462)	2041	2027
Al−P−H bend (0)	764	737
Al−H wag (92)	448	447
Al−P str. (2)	414	392

[a] Intensities were obtained at the DZP SCF level.

TABLE 2: SCF Vibrational Frequencies in cm^{-1} and Infrared Intensities in km mol^{-1} (in Parentheses) for the *trans*-Planar Conformation of the (HAl−PH)$_2$ Ring[a]

mode (intensity)	DZP	TZ2P
A_g		
P−H str. (0)	2599	2551
Al−H str. (0)	2050	2033
P−H wag (0)	576	547
Al−P str. (0)	440	425
ring angle def. (0)	210	197
A_u		
Al−H str. (519)	2045	2027
Al−P−H bend (7)	711	694
Al−P str. (67)	443	427
B_g		
Al−P−H bend (0)	729	712
P−Al−H bend (0)	584	581
Al−H wag (0)	465	455
Al−P str. (0)	413	395
B_u		
P−H str. (75)	2599	2551
P−Al−H bend (405)	699	679
Al−H wag (139)	505	498
P−H, Al−H bend comb. (139)	447	441
P inversion (48)	210	232
ring pucker (24)	99	55

[a] Intensities were obtained at the DZP SCF level.

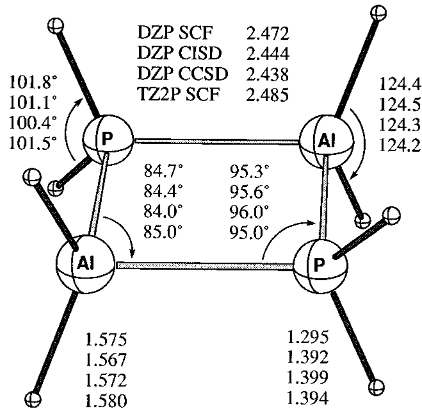

Figure 3. Theoretical geometry of the $(H_2Al-PH_2)_2$ ring in angstroms and degrees.

TABLE 3: SCF Vibrational Frequencies in cm^{-1} and Infrared Intensities in km mol^{-1} (in Parentheses) for the $(H_2Al-PH_2)_2$ Ring[a]

mode (intensity)	DZP	TZ2P
A_g		
P−H str. (0)	2618	2587
Al−H str. (0)	2011	1981
H−P−H bend (0)	1183	1193
H−Al−H bend (0)	797	786
Al−P str. (0)	355	352
ring angle def. (0)	226	210
B_{1g}		
AlH_2 wag (0)	659	646
PH_2 wag (0)	595	596
ring angle def. (0)	275	268
B_{2g}		
P−H str. (0)	2627	2594
AlH_2 twist (0)	547	541
PH_2 rock (0)	290	302
B_{3g}		
Al−H str. (0)	2013	1984
PH_2 str. (0)	733	736
AlH_2 rock (0)	289	284
A_u		
PH_2 twist (0)	712	709
AlH_2 twist (0)	422	412
B_{1u}		
P−H str. (20)	2627	2594
Al−H str. (448)	2015	1984
AlH_2 rock (57)	512	512
PH_2 rock (25)	291	301
ring pucker (6)	27	25
B_{2u}		
Al−H str. (303)	2005	1977
H−Al−H bend (689)	792	786
PH_2 wag (110)	658	662
Al−P str. (25)	347	346
B_{3u}		
P−H str. (31)	2616	2584
H−P−H str. (78)	1160	1171
AlH_2 wag (799)	743	729
Al−P str. (26)	319	321

[a] Intensities were obtained at the DZP SCF level.

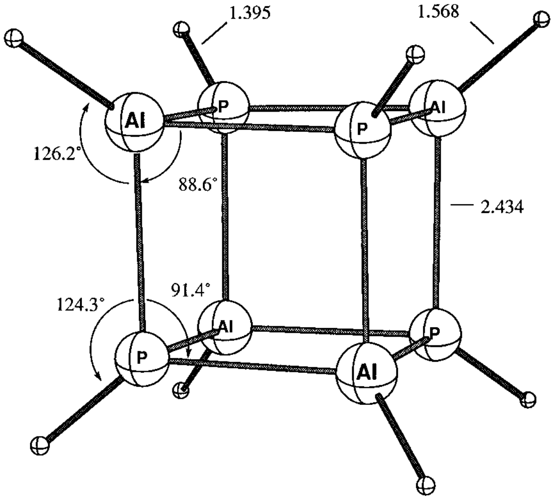

Figure 4. DZP SCF theoretical geometry of the $(HAl-PH)_4$ cube in angstroms and degrees.

TABLE 4: DZP SCF Vibrational Frequencies in cm^{-1} and Infrared Intensities in km mol^{-1} (in Parentheses) for the $(HAl-PH)_4$ Cube[a]

mode (intensity)	frequency
A_1	
P−H str. (0)	2620
Al−H str. (0)	2036
Al−P str. (0)	400
cube angle def. (0)	338
E	
P−H bend (0)	617
Al−H bend (0)	542
Al−P str. (0)	318
cube angle def. (0)	177
T_1	
P−H bend (0)	563
Al−H bend (0)	485
Al−P str. (0)	304
T_2	
P−H str. (37)	2627
Al−H str. (1084)	2031
P−H bend (361)	677
Al−H bend (1104)	631
Al−P str. (90)	396
Al−P str. (33)	360
cube angle def. (1)	174

[a] Intensities were obtained at the DZP SCF level.

The $(HAl-PH)_2$ ring has nondative bonds between three coordinate Al and P. As mentioned above, Haaland used the Schomaker−Stevenson rule to estimate a bond length of 2.31 Å for these bonds,[4] and the Al−P bond length obtianed by X-ray crystallography for the two known compounds are 2.328(3) Å for the six-membered ring[2] and 2.342(2) Å for the unassociated compound.[3] At the DZP CCSD level we obtain at Al−P bond length of 2.298 Å for the *cis*-puckered ring and 2.288 Å for the *trans*-bent. At the SCF level an increase in basis set size from DZP to TZ2P causes a lengthening of the Al−P bond for both conformations. If we assume additivity for changes in bond length due to basis set and correlation effects, the theoretical value that we obtain for the Al−P bond is 2.313 Å for the *cis*-puckered conformation and 2.301 Å for the *trans*-bent. The agreement between model compound and experiment is remarkable if one considers the difference between the hydrogen atom of the model and the sterically demanding groups of the compounds synthesized. The bond length obtained by Matsunaga and Gordon for the six-membered-ring model compound $(HAl-PH)_3$ was 2.315 Å at the SCF level using effective core potentials for Al and P.[11] The Al−P bond in the unassociated model compound H_2Al-PH_2 is 2.309 at the DZP CCSD level, slightly longer than those of the $(HAl-PH)_2$ four-membered-ring conformers at the DZP CCSD level. The Al−P bond length is seen to be very stable with respect to changes in its steric environment. The consistency of the Al−P bond length implies that there is little change in the hybridization of the orbitals on Al and P whether the molecule is the unassociated H_2Al-PH_2, the four-membered ring, or the six-membered ring.

In contrast to the Al−P bond lengths, the Al−P−Al angles differ sharply between the values found experimentally for the six-membered ring and the theoretical values in the model $(HAl-PH)_2$ four-membered ring. The experimental Al−P−Al angle[2] in the six-membered ring has an average value of

111°, but the Al−P−Al angle in our four-membered ring is 75.4° (*cis*-puckered, CCSD DZP level), a decrease of about 35°. The P−Al−P angle in the six-membered ring has an average experimental value of 112°, compared to the theoretical value of 94.7° (*cis*-puckered, CCSD DZP), a decrease of about 17°. Of course the simple geometric constraint of closing a four-membered ring will cause a decrease in the Al−P−Al and P−Al−P angles, but one wonders why the angle change at phosphorus is double that at aluminum. If, however, we assume that a normal bond angle about a three coordinate phosphorus is about 95° and a normal bond angle about a three coordinate aluminum is 120°, then the angles in the four-membered ring are a reasonable compromise: the angle at phosphorus narrows by about 20°, from a normal angle of 95° to an angle of 75°, and the angle at aluminum narrows by 25°, from a normal angle of 120° to 95°.

The ring stretching vibrational frequencies are in the range 390−450 cm^{-1}. This range brackets the 432 cm^{-1} value predicted theoretically for the H_2Al-PH_2 compound. The ring butterfly motion is the *cis*-puckered conformer has a frequency of 140 cm^{-1} (TZ2P SCF); the same motion has a much smaller frequency, only 55 cm^{-1}, in the *trans*-bent conformer. This is substantially smaller than the value of 233 cm^{-1} obtained for the butterfly motion of the analogous Al−N ring, $(HAl-NH)_2$.[20]

$(H_2Al-PH_2)_2$. The $(H_2Al-PH)_2$ four coordinate ring is planar, but the frequency of the butterfly motion is very low, only 26 cm^{-1} at the DZP SCF level, and 25 cm^{-1} at the TZ2P SCF level. For the analogous Al−N ring, electron correlation had little effect on the frequencies of the butterfly motion, and as correlation does not drastically change the geometry of the ring, we therefore would expect correlation would not dramatically decrease the floppiness of the $(H_2Al-PH_2)_2$ ring. The decrease in the frequency for the butterfly motion from $(HAl-PH)_2$ to $(H_2Al-PH_2)_2$ could be predicted on the basis of the change in the Al−P bonds between the two rings. As Haaland has pointed out,[4] for $(H_2Al-PH_2)_2$ the Al−P bonds can be viewed as half dative and half "normal" (i.e. nondative). Our theoretical estimate of the Al−P bond length in $(H_2Al-PH_2)_2$ is 2.451 Å, on the basis of the DZP CCSD value of 2.438 Å plus $\Delta r = 0.013$ Å, which is the TZ2P SCF − DZP SCF difference. This value is nearly identical to that obtained for the four-membered $(R_2Al-PR'_2)_2$ ring (R = $SiMe_3$, R′ = cyclohexyl) reported experimentally by Janik, Duesler, McNamara, Westerhausen, and Paine.[21] They found Al−P bond lengths of 2.45 Å and Al−P−Al angles of 94°. The Al−P bond length in the six-membered ring composed of four coordinate Al and P, $(Me_2Al-PMe_2)_3$, is 2.43 Å.[22] The value given for half dative/half normal bonds by Haaland[4] was 2.43 Å. Once again the Al−P bond length is very consistent among theoretical predictions and different experimentally determined values.

At first glance the bond angles in the four-membered $(H_2Al-PH_2)_2$ ring might be puzzling. In contrast to the $(HAl-PH)_2$ ring, the angle at phosphorus in $(H_2Al-PH_2)_2$ is wider than the angle at aluminum. The Al−P−Al angle is 96.0° at the DZP CCSD level, and the P−Al−P angle is 84.0°. This result is consistent with experiment. In the $(R_2Al-PR'_2)_2$ ring reported by Janik *et al.*[21] the Al−P−Al angle is 94°, while the P−Al−P angle is 86°. To understand why the angle at phosphorus opens in $(H_2Al-PH_2)_2$ compared to $(HAl-PH)_2$, we again consider the orbitals used for ring bonding. As shown in Figure 5b, the saturated ring has a mixture of dative and nondative bonds. For aluminum, the orbitals used in ring bonding are an sp^2 hybrid and the empty p orbital, and the angle between them is 90°. For phosphorus the orbitals used in ring bonding are a weakly hybridized s lone pair and p bonding orbitals. (There is some s−p hybridization in $(H_2Al-PH_2)_2$, because the H−P−H angles are 100.4° at the DZP CCSD level, rather than 90°.) The angle between the lone pair and the p orbital is approximately 120°. If the phosphorus angle remained unchanged, the angle at Al would have to be 60° in a planar four-membered ring; if the angle at Al remained unchanged, the angle at P would have to drop from 120° to 90°. The ring angles are therefore again a compromise, but in $(H_2Al-PH_2)_2$ the compromise is achieved by a decrease in the angle at phosphorus from ∼120° to 96° and a decrease at aluminum from 90° to 84°. Experimental results on the nonplanar six-membered $(Me_2Al-PMe_2)_3$ ring, for which there is less angle constraint, find the Al−P−Al angle to be 120.4° and the P−Al−P angle to be only 99°.[22]

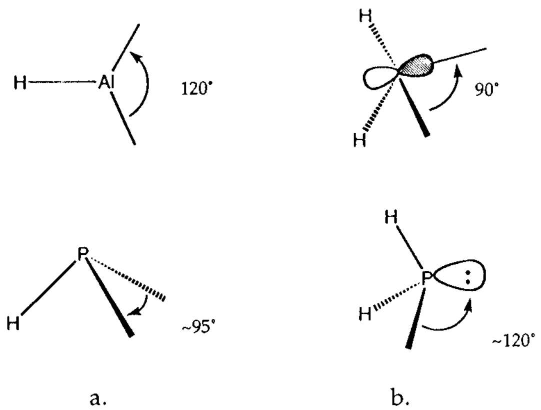

Figure 5. Bond angles between (a) two normal covalent bonds and (b) a dative bond and a normal covalent bond.

$(HAl-PH)_4$. This cubic cluster was studied at the DZP SCF level. We may compare the results obtained at the DZP SCF level with the results at higher levels of theory for $(HAl-PH)_2$ and $(H_2Al-PH_2)_2$ to estimate the reliability of the DZP SCF results. For the $(H_2Al-PH_2)_2$ ring, we find that the Al−P bond length is overestimated by about 0.02 Å at the DZP SCF level compared to our best estimates. The other geometrical parameters have smaller errors. For the cubic cluster the Al−P bond length is 2.434 Å, and we would assume on the basis of earlier results that this is an upper limit to the bondlength that would be obtained at higher levels of theory, which are likely to be 0.01 to 0.02 Å shorter. The Al−P bond length determined by X-ray crystallography for the substituted cube synthesized by Cowley *et al.* is 2.414(4) Å (av).[1] The steric demands of the bulky groups on Al and P do not appear to affect the Al−P bond length. As was the case for Al−N compounds, the bonds in the cube are shorter than those of the saturated four-membered ring, but longer than the unsaturated four-membered ring.[20] This is consistent with Haaland's analysis[4] that in the $(HAl-PH)_2$ ring the Al−P bonds are not dative, in the cube they can be seen as one-third dative, two-thirds normal, and in the $(H_2Al-PH_2)_2$ ring, they can be seen as half normal and half dative.

For the $(HAl-PH)_4$ cube the Al−P−Al angle is 91.4° and the P−Al−P angle is 88.6° at the DZP SCF level. This is opposite the experimental results. The crystal structure of the cube has an angle at P of 88.2° and an angle at Al of 91.8°. However, this reversal is only a difference of about 2.5° and could be due to the presence of substituents in the structure determined by crystallography.

The lowest frequency vibration is the cube angle deformation at 147 cm^{-1}. The Al−P stretching modes in the cube are clustered around 400 cm^{-1}. They are lower than the ring modes of $(HAl-PH)_2$, the highest of which is 478 cm^{-1}, and higher than those found in $(H_2Al-PH_2)_2$, for which the highest Al−P stretch is 352 cm^{-1}.

Reaction Energies. A model reaction sequence for synthesis of the Al−P cubic cluster may be constructed as

$$H_3Al{-}PH_3 \rightarrow H_2Al{-}PH_2 + H_2 \qquad \text{(dehydrogenation)} \tag{1a}$$

$$2(H_2Al{-}PH_2) \rightarrow (H_2Al{-}PH_2)_2 \qquad \text{(ring formation)} \tag{1b}$$

$$(H_2Al{-}PH_2)_2 \rightarrow (HAl{-}PH)_2 + 2H_2 \qquad \text{(dehydrogenation)} \tag{2a}$$

$$2(HAl{-}PH)_2 \rightarrow (HAl{-}PH)_4 \qquad \text{(cube formation)} \tag{2b}$$

We can assess the energy required to carry out these reactions in this completely stepwise (nonconcerted) fashion. Early work by Beachley, Coates, and Koonstan[24] indicated that the analogous reactions for Al−N compounds do not take place by this simple mechanism. Our results provide thermodynamic parameters for the concerted mechanism and thus upper limits for other mechanisms. They also provide estimates of bond energies for σ and π Al−P bonds. We have determined in a separate study of Al−P compounds that the energy of step 1a is 8.3 kcal mol^{-1}, 3.3 kcal mol^{-1} if zero point vibrational energy (ZPVE) is included.[12] For all energy difference calculations, ZPVE is determined using unscaled DZP SCF vibrational frequencies. Dimerization of the resulting $H_2Al{-}PH_2$ monomer (reaction 1b) has a ΔE value of −34.1 kcal mol^{-1} at the DZP SCF level and −34.3 at the TZ2P SCF level. The small variation with basis set size is consistent with a lack of significant basis set superposition (BSSE) error. Including electron correlation gives a value of −38.9 kcal mol^{-1} at the DZP CCSD, −36.0 kcal mol^{-1} including ZPVE correction. The overall energy change for step 1 at the DZP CCSD level is −30.6 kcal mol^{-1} (−32.7 with ZPVE corrections). This large negative value is consistent with initial ring formation in the synthesis of the cube occuring at low temperature.[1]

As the $(H_2Al{-}PH_2)_2$ ring is formed in step 1b, the Al and P atoms become four coordinate by forming two σ dative bonds. If we divide the total energy change for dimerization in half, we obtain a value of 15.3 kcal mol^{-1} per bond formed in the ring. Estimates for ΔE values for the σ dative bond between AlH_3 and PH_3 range from 13.2 to 15.2 kcal mol^{-1} (without ZPVE or BSSE corrections). The best value from the earlier $AlH_3{-}PH_3$ study[12] was 13.6 kcal mol^{-1} at the TZ2P CCSD level, but if we compare at identical levels of theory, namely, DZP CCSD, the value was 12.5 kcal mol^{-1}. Thus dative bond formation in the ring is more favorable energetically by 2.8 kcal mol^{-1} at the DZP CCSD level than the simple $AlH_3{-}PH_3$ dative bond.

In the synthesis[1] of the Al−P cube, initial alkane loss to form a four-membered ring proceeded at 25 °C, but loss of alkane from that ring accompanied melting at 80 °C. We would therefore expect that H_2 loss from the $(H_2Al{-}PH_2)_2$ ring (step 2a) would require more energy than the H_2 loss in step 1a. At the DZP CCSD level, the energy required for step 2a is 39.2 kcal mol^{-1} (31.3 including ZPVE). The DZP SCF and TZ2P SCF values are 41.7 and 36.4 kcal mol^{-1}, respectively. For this reaction the extension of the basis set results in a 5.3 kcal mol^{-1} change in ΔE. We estimate the reaction energy to be 39.2 kcal mol^{-1} (DZP CCSD) − 5.3 kcal mol^{-1} (TZ2P correction) = 33.9, or approximately 34 kcal mol^{-1}. Including ZPVE corrections drops this value to 26 kcal mol^{-1}, which is substantially lower than that found for the same reaction in the analogous Al−N rings, 43 kcal mol^{-1}.[20]

Dimerization of $(HAl{-}PH)_2$ to form the cube (step 2b) has a ΔE value of −68.1 kcal mol^{-1} (−65.3 kcal mol^{-1} including ZPVE). This value is also substantially smaller (in absolute value) than that obtained for the analogous Al−N system, −112 kcal mol^{-1}.[20] The overall energy for step 2 is estimated to be −34 kcal mol^{-1} (−39 kcal mol^{-1} including ZPVE), which is somewhat larger than the overall energy of −27 kcal mol^{-1} for the same reaction in the Al−N system. The major difference between the Al−N and the Al−P reactions is thus the relatively greater stability of the Al−P intermediate $(HAl{-}PH)_2$ ring.

Conclusions

The overall shape of the rings and the bond lengths and angles are consistent with the simple understanding of bonds as being dative, nondative, or a mixture, as elaborated by Haaland.[4] The unknown $(HAl{-}PH)_2$ ring is predicted here to be puckered in the lowest energy configuration, but a planar geometry is nearly isoenergetic. The small bond angles at phosphorus and large angles at aluminum in this ring are due to the 120° angles between sp^2 orbitals on Al and the 90° angles between p orbital bonds on P. The bonds in this ring are also shorter than those of the cube or the saturated ring, because they are completely nondative. The Al−P bond length is longest in the $(H_2Al{-}PH_2)_2$ ring, for which the bonds are half dative and half nondative. Compared to the Al−N analogs, the unsaturated four-membered $(HAl{-}PH)_2$ ring is lower in energy relative to the saturated $(H_2Al{-}PH_2)_2$ ring. Four-membered rings with three coordinate Al and N have been synthesized,[3,23] and one would expect that, on the basis of thermodynamic considerations, an $(RAl{-}PR')_2$ ring should also be achievable in the laboratory. The overall energetics of cube formation are similar for the Al−N and Al−P synthesis, with the results for Al−P being consistent with formation of the cube under milder conditions than those required for the Al−N cube.

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