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Aluminum−Phosphorus Compounds with Low Coordination Numbers: Structures, Energies, and Vibrational Frequencies of the $AlPH_2$, $AlPH_3$, and $AlPH_4$ Isomers and the H_3Al-PH_3 Adduct

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Ab initio theoretical methods have been used to study small aluminum−phosphorus compounds. Geometries, relative energies, and harmonic vibrational frequencies of isomers of the formulas $AlPH_2$, $AlPH_3$, and $AlPH_4$ and the H_3Al-PH_3 adduct have been determined at the self-consistent-field level (SCF), by the single- and double-excitation configuration interaction (CISD), and by the single- and double-excitation coupled cluster (CCSD) method. The lowest energy isomers for $AlPH_2$, $AlPH_3$, and $AlPH_4$ are $Al-PH_2$, H_2Al-PH, and H_2Al-PH_2, respectively. The HAl−PH isomer is planar and has a short Al−P bond. An aluminum atom forms a weak complex with phosphine, and the barrier for insertion of Al into PH_3 is estimated to be 12.0 kcal mol^{-1}. Various conformations of the H_2Al-PH_2 molecule are investigated to give estimates of the energy of the π donor−acceptor bond. The energy of complexation for AlH_3 and PH_3 is obtained using triple-ζ-plus double-polarization function basis sets and the CCSD level. The theoretical energy of H_2 loss is also obtained for H_3Al-PH_3 and H_2Al-PH_2.

Introduction

Compounds of group III and group V elements in which the elements are four coordinate are well-known. Recently, advances have been made in the synthesis of Al−N and B−P compounds that contain three-coordinate or even two-coordinate atoms.[1−9] Recent theoretical studies have also reexamined the model compound HB−PH and its isomers.[10,11] The Lewis acid−base adducts of the general formula $R_3Al-PR'_3$ have of course been long known and were structurally characterized some time ago.[12] To our knowledge, however, the only molecules with bonding between three-coordinate Al and P are $(2,4,6\text{-(i-Pr)}_3C_6H_2)_2AlP(1\text{-adamantyl})SiPH_3$, which was reported by Wehmschulte, et al.,[13] and the six-membered ring $(Mes^*AlPPh)_3$ ($Mes^* = 2,4,6\text{-(t-Bu)}_3C_6H_2$) reported by Wehmschulte and Power.[3] These compounds allow for interesting studies of bonding because of the mixture of normal, dative (both σ dative and π dative) bonding and the possibility of multiple bonds. They are interesting from a practical standpoint, as pointed out by Cowley in his article "From Multiple Bonds to Materials Chemistry",[14] because one would like to carry out chemical vapor deposition of group III−V materials from precursors that have a 1:1 ratio of group III to group V atoms and for which the strongest bond is the one between the group III and group V atoms. Cowley et al. have already synthesized the $(RAl-PR')_4$ cube which decomposed at low temperature to form aluminum phosphide.[15]

Given the interest in this area, little theoretical work has been done on the bonding and energetics of the simplest model compounds that would include bonds between two- or three-coordinate Al and P. Three studies have examined the H_3Al-PH_3 adduct,[16−18] and the model ring compound $(HAl-PH)_3$ has been studied.[19,20] In order to provide information on the fundamental properties of Al−P bonds and the energetics of different bonding situations, we have determined theoretically the geometries, energies, and vibrational spectra of the compounds of formula $Al-PH_2$, $Al-PH_3$, and $Al-PH_4$. These compounds could occur as intermediates in the formation of rings and clusters from the simple adducts or as decomposition products as the clusters fell apart to form an aluminum phosphide layer. The $Al-PH_3$ isomers could also occur as products of the reaction of aluminum atoms with phosphine. The energy, geometry, and vibrational spectrum of the previously studied H_3Al-PH_3 adduct were also obtained to allow a consistent theoretical framework for the comparison of bonding and reaction energies. Also, theoretical vibrational frequencies, although evaluated,[17] have apparently not yet been published for this molecule. Our results will also be compared to published studies of analogous B−P and Al−N compounds.[9,21]

Theoretical Methods

Ab initio theoretical studies were carried out initially at the Hartree−Fock self-consistent-field (SCF) level. The restricted open-shell method was used for open-shell molecules, using a double-ζ-plus polarization (DZP) basis set. The Huzinaga−Dunning (4s/2s) basis set was used for hydrogen,[22,23] and the Huzinaga−Dunning (11s7p/6s4p) basis set was used for aluminum and phosphorus.[24,25] 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 the small basis set size. Triple-ζ-plus double-polarization function (TZ2P) basis sets consisting of the Huzinaga−Dunning[22,26] (5s/3s) basis set on hydrogen and the

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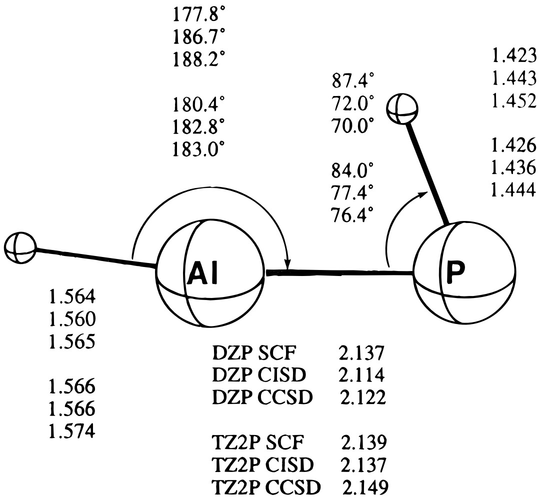


Figure 1. Theoretical geometries in angstroms and degrees at various levels of theory for HAl−PH.

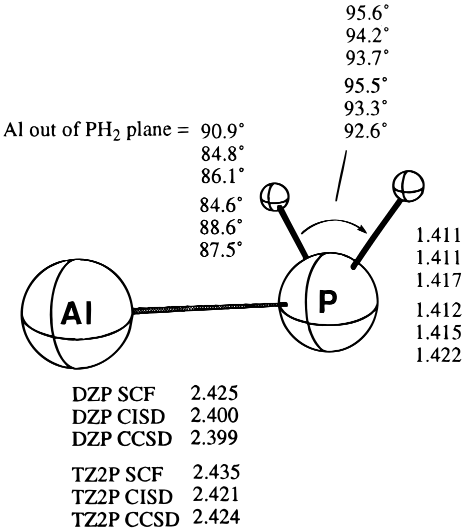


Figure 2. Theoretical geometries in angstroms and degrees at various levels of theory for Al−PH_2.

McLean−Chandler (12s9p/6s5p) basis set on aluminum and phosphorous were used.[24,27] The exponents of the polarization functions were H = (1.50, 0.375), P = (1.20, 0.30), and Al = (0.80, 0.20). Geometry optimizations were performed via analytic first-derivative methods. Open-shell molecules were not optimized at the CCSD level. Harmonic vibrational frequencies were obtained via analytic second derivatives for the SCF method and by finite differences of analytic first derivatives for the CISD and CCSD methods. The PSI suite of programs was used throughout.[28]

Results and Discussion

The optimized geometries of the $AlPH_2$ isomers are given in Figures 1−3, and harmonic vibrational frequencies are given in Tables 1−3. The optimized geometries of the Al−PH_3 structure are given in Figures 4−6, and the structure of the transition state for Al insertion into the P−H bond is given in Figure 7. Tables 4−6 give the harmonic vibrational frequencies of the $AlPH_3$ isomers. The structures for the $AlPH_4$ isomers are given in Figures 8 and 9, and their harmonic vibrational frequencies are given in Tables 7 and 8. The geometry of the H_3Al−PH_3 adduct is given in Figure 10, and its vibrational frequencies are given in Table 9. Tables 10−12 give the relative energies of the isomers of $AlPH_2$, $AlPH_3$, and $AlPH_4$, respectively, at various levels of theory, Table 13 gives the energy of the H_3Al−PH_3 adduct vs separated AlH_3 and PH_3 fragments, and Table 14 gives the total energies of all isomers studied. We will analyze the structure, spectra, and potential energy surface for the Al−PH_2, Al−PH_3, and Al−PH_4 isomers separately and then analyze the energies of hydrogenation for Al−PH_2 and Al−PH_4.

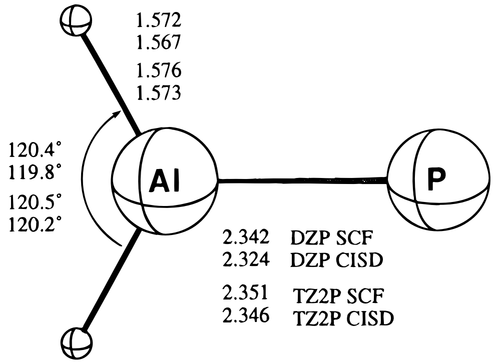


Figure 3. Theoretical geometries in angstroms and degrees at various levels of theory for H_2Al−P.

TABLE 1: Theoretical Harmonic Vibrational Frequencies (in cm^{-1}) and Intensities[a] (in km mol^{-1}) for the HAlPH Isomer at Various Levels of Theory

	SCF		CISD	
assignment (intensity)	DZP	TZ2P	DZP	TZ2P
a′ P−H str (76)	2436	2378	2304	2282
a′ Al−H str (199)	2065	2054	2056	2020
a′ Al−P str (21)	647	653	666	677
a′ H−Al−P bend (31)	554	544	523	642
a″ H−Al−P−H tors (17)	368	412	341	525
a′ Al−P−H bend (71)	294	321	259	280

[a] Obtained at the DZP SCF level.

TABLE 2: Theoretical Harmonic Vibrational Frequencies (in cm^{-1}) and Intensities[a] (in km mol^{-1}) for the $AlPH_2$ Isomer at Various Levels of Theory

	SCF		CISD	
assignment (intensity)	DZP	TZ2P	DZP	TZ2P
a″ P−H asym str (65)	2512	2464	2497	2402
a′ P−H sym str (47)	2509	2463	2487	2395
a′ H−P−H bend (15)	1198	1180	1145	1121
a″ PH_2 rock (77)	491	466	437	434
a′ Al−P str (41)	437	434	384	417
a′ PH_2 wag (64)	373	355	337	330

[a] Obtained at the DZP SCF level.

TABLE 3: Theoretical Harmonic Vibrational Frequencies (in cm^{-1}) and Intensities[a] (in km mol^{-1}) for the H_2AlP Isomer at Various Levels of Theory

	SCF		CISD	
assignment (intensity)	DZP	TZ2P	DZP	TZ2P
b_2 Al−H asym str (243)	2032	2005	2038	1989
a_1 Al−H sym str (152)	2030	2004	2030	1984
a_1 H−Al−H bend (440)	857	838	846	814
b_1 AlH_2 wag (324)	593	588	570	566
a_1 Al−P (80)	457	447	446	426
b_2 AlH_2 rock (8)	441	430	442	423

[a] Obtained at the DZP SCF level.

Al−PH_2. At all levels of theory, the Al−PH_2 isomer is the lowest in energy, with the HAl−PH isomer lying 13 kcal/mol above Al−PH_2 at the TZ2P CCSD level including zero-point vibrational energy (ZPVE) corrections. The next highest state is the $^3A_2$ H_2Al−P isomer, which is +22 kcal/mol from the lowest lying Al−PH_2 (TZ2P CISD + ZPVE). These results

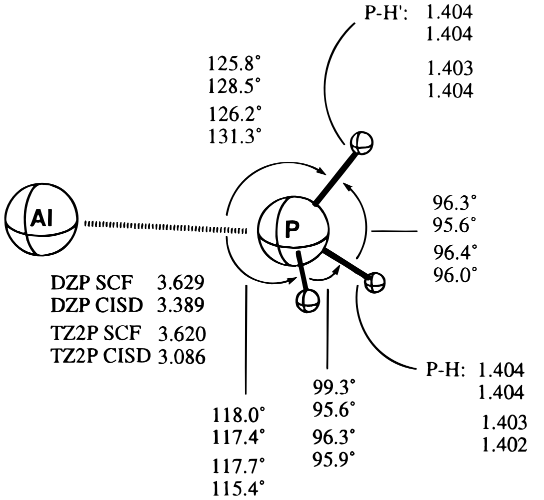


Figure 4. Theoretical geometries in angstroms and degrees at various levels of theory for Al−PH$_3$.

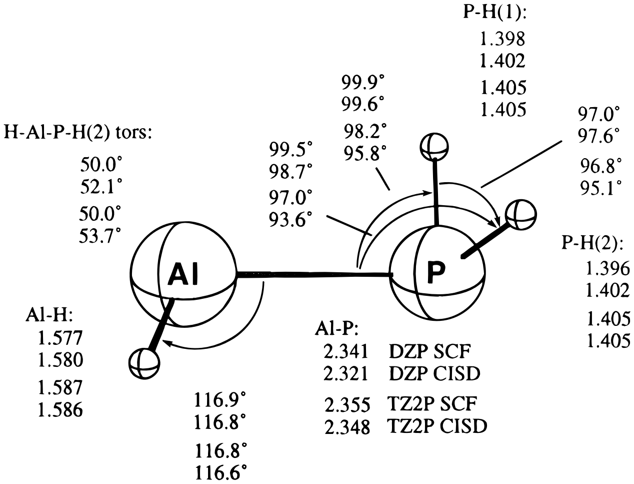


Figure 5. Theoretical geometries in angstroms and degrees at various levels of theory for HAl−PH$_2$.

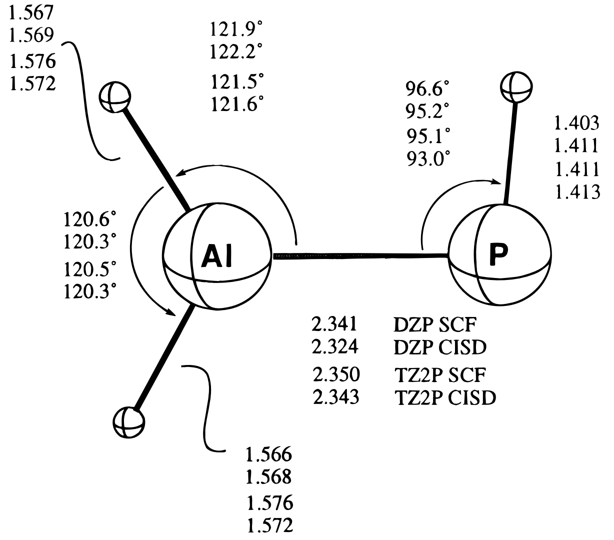


Figure 6. Theoretical geometries in angstroms and degrees at various levels of theory for H$_2$Al−PH.

are in contrast to the BPH$_2$ system, in which HB−PH is the most stable isomer and B−PH$_2$ the least stable.[9] Our AlPH$_2$ results are analogous to those for the AlNH$_2$ isomers, which have the same order of energy, i.e., Al−NH$_2$ < HAl−NH < H$_2$Al−N.[21] The nitrogen system, however, has a much larger spacing of energies for the isomers, with the HAl−NH isomer lying 41 kcal/mol above Al−NH$_2$. HAl−PH and H$_2$Al−P are low-lying because the electronegativities of Al and P differ by less than those of Al and N, and the P−H and Al−H bond energies are more nearly equal than the Al−H and N−H bond energies.

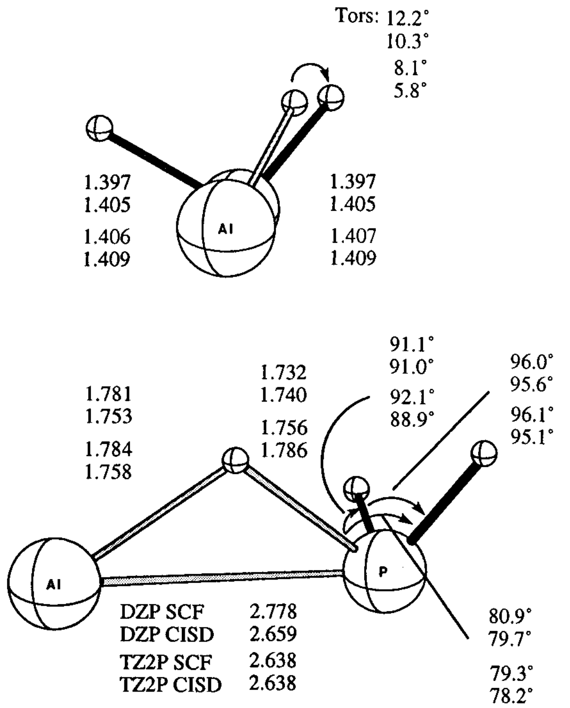


Figure 7. Theoretical geometries in angstroms and degrees at various levels of theory for the transition state for insertion of Al into the P−H bond of PH$_3$.

TABLE 4: Theoretical Harmonic Vibrational Frequencies (in cm^{-1}) and Intensities[a] (in km mol^{-1}) for the AlPH$_3$ Isomer at Various Levels of Theory

	SCF		CISD	
assignment (intensity)	DZP	TZ2P	DZP	TZ2P
a′ P−H str (47)	2565	2534	2556	2485
a′ P−H str (62)	2564	2532	2553	2480
a″ P−H str (60)	2564	2532	2545	2466
a″ H−P−H bend (15)	1248	1234	1190	1200
a′ H−P−H bend (17)	1247	1233	1181	1170
a′ H−P−H bend (107)	1109	1096	1073	1033
a′ PH$_3$ wag (107)	119	119	135	173
a′ Al−P str (4)	57	43	67	69
a″ PH$_3$ wag (3)	23	35i	80i	108

[a] Obtained at the DZP SCF level.

TABLE 5: Theoretical Harmonic Vibrational Frequencies (in cm^{-1}) and Intensities[a] (in km mol^{-1}) for the HAlPH$_2$ Isomer at Various Levels of Theory

	SCF		CISD	
assignment (intensity)	DZP	TZ2P	DZP	TZ2P
P−H asym str (65)	2643	2513	2581	2460
P−H sym str (21)	2626	2500	2558	2438
H−Al str (265)	2028	1950	1990	1921
H−P−H bend (26)	1245	1192	1174	1133
PH$_2$ rock (60)	770	731	741	705
PH$_2$ wag (6)	549	509	517	476
H-Al−P bend (97)	487	473	464	542
Al−P str (13)	423	473	464	405
H-Al−P−H tors (14)	270	245	277	236

[a] Obtained at the DZP SCF level.

Although the H$_2$Al−P isomer is higher in energy than Al−PH$_2$, it is still low-lying, especially compared to the Al−N

TABLE 6: Theoretical Harmonic Vibrational Frequencies (in cm^{-1}) and Intensities^a (in km mol^{-1}) for the H$_2$AlPH Isomer at Various Levels of Theory

	SCF		CISD	
assignment (intensity)	DZP	TZ2P	DZP	TZ2P
a′ P−H str (96)	2598	2483	2520	2420
a′ Al−H asym str (234)	2090	2008	2062	1995
a′ Al−H sym str (230)	2082	2004	2049	1988
a′ H−Al−H bend (443)	862	842	840	821
a′ H−P−Al bend (24)	765	725	741	698
a″ AlH$_2$ wag (320)	602	592	578	573
a′ Al−P str (17)	445	433	447	431
a′ AlH$_2$ rock (59)	440	427	430	412
a″ H−P-Al−H tors (16)	104	103	85	60

^{a} Obtained at the DZP SCF level.

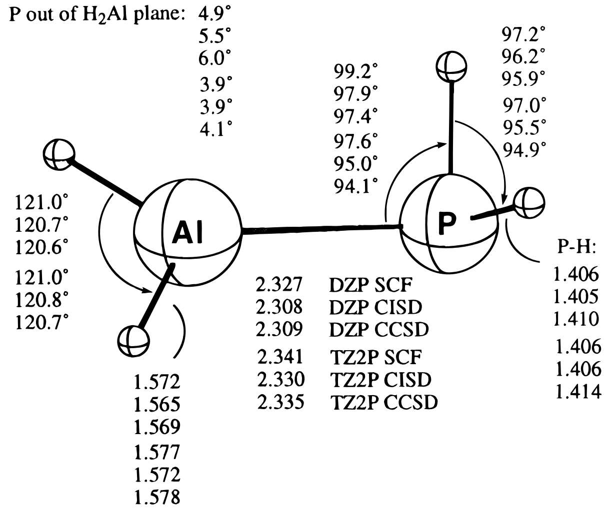


Figure 8. Theoretical geometries in angstroms and degrees at various levels of theory for H$_2$Al−PH$_2$.

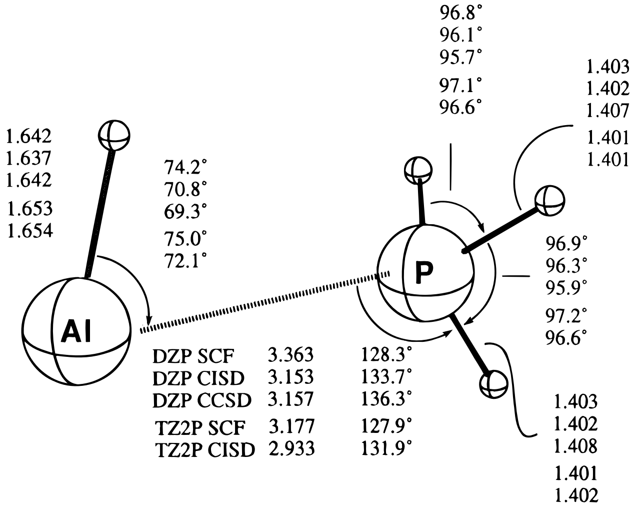


Figure 9. Theoretical geometries in angstroms and degrees at various levels of theory for HAl−PH$_3$.

TABLE 7: Theoretical Harmonic Vibrational Frequencies (in cm^{-1}) and Intensities^a (in km mol^{-1}) for the H$_2$AlPH2 Isomer at Various Levels of Theory

	SCF		CISD	
assignment (intensity)	DZP	TZ2P	DZP	TZ2P
a′ asym P−H str (60)	2552	2511	2544	2461
a′ sym P−H str (41)	2548	2509	2533	2452
a″ asym Al−H str (234)	2034	2006	2048	1997
a′ sym Al−H str (152)	2032	2005	2039	1991
a′ H−P−H bend (37)	1210	1192	1158	1135
a′ H−Al−H bend (436)	851	835	841	815
a″ PH$_2$ rock (9)	745	718	721	692
a′ AlH$_2$ wag (203)	676	668	661	649
a′ PH$_2$ wag (73)	493	471	469	447
a′ Al−P str (24)	440	432	438	432
a″ AlH$_2$ rock (60)	407	397	394	384
a″ H−Al−P−H tors (4)	220	205	223	198

^{a} Obtained at the DZP SCF level.

TABLE 8: Theoretical Harmonic Vibrational Frequencies (in cm^{-1}) and Intensities^a (in km mol^{-1}) for the HAlPH$_3$ Isomer at Various Levels of Theory

	SCF		CISD
assignment (intensity)	DZP	TZ2P	DZP
a″ P−H str (49)	2574	2547	2570
a′ P−H str (54)	2574	2545	2566
a′ P−H str (42)	2573	2544	2557
a′ Al−H str (558)	1765	1700	1766
a″ H−P−H bend (13)	1248	1233	1190
a′ H−P−H bend (13)	1244	1229	1184
a′ H−P−H bend (107)	1103	1093	1071
a′ H−Al−P bend (40)	484	540	545
a″ PH$_3$ wag (1)	157	179	195
a′ PH$_3$ wag (6)	135	156	155
a″ H−Al−P−H tors (0)	85	90	109
a' Al−P (6)	71	67	80

^{a} Obtained at the DZP SCF level.

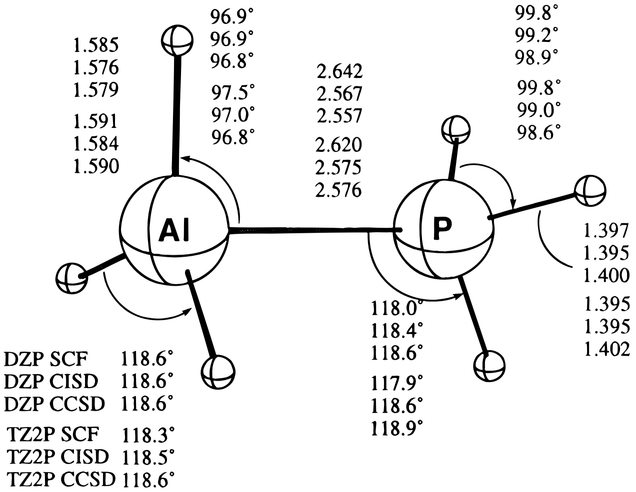


Figure 10. Theoretical geometries in angstroms and degrees at various levels of theory for H$_3$Al−PH$_3$.

system, for which the H$_2$Al−N isomer is 75 kcal/mol higher than the Al−NH$_2$ isomer at the DZP CISD level. Clearly an isomer that results in a monovalent nitrogen is much higher in energy than one with a monovalent phosphorus.

The Al−P bond length in the Al−PH$_2$ isomer is 2.424 Å (TZ2P CCSD), which is shorter by about 0.1 Å than a typical alane−phosphine derivative donor−acceptor bond but longer than the normal (i.e., not dative) bond which is predicted by a modified Schomaker−Stevenson rule to be 2.31 Å.[29] Even though the Al−P bond is not dative, the strength of the bond is decreased by the absence of hydrogens on aluminum, which tend to withdraw electrons, increasing the attraction of the more electron-rich phosphorus. The Al−PH$_2$ isomer has a pyramidal phosphorus, as one would expect in analogy with H$_2$B−PH$_2$.

The HAl−PH isomer has the shortest Al−P bond of any molecule examined in this work, only 2.149 Å (TZ2P CCSD). A nondative π interaction apparently does occur and has an effect on the bond length. This is supported by the density plot of the HOMO for the HAl−PH molecule given in Figure 11. It shows substantial overlap of the out-of-plane p orbitals for Al and P. The Mulliken bond populations, although qualitative,

TABLE 9: Theoretical Harmonic Vibrational Frequencies (in cm^{-1}) and Intensities^a (in km mol^{-1}) for the H_3AlPH_3 Molecule at Various Levels of Theory

	SCF		CISD
assignment (intensity)	DZP	TZ2P	DZP
e P−H str (46)	2619	2591	2600
a_1 P−H str (13)	2613	2584	2600
a_1 Al−H str (31)	1995	1955	2005
e Al−H str (538)	1972	1928	1995
e H−P−H bend (34)	1234	1226	1185
a_1 H−P−H bend (29)	1097	1103	1077
e H−Al−H bend (481)	848	826	834
a_1 H−Al−H bend (893)	784	775	770
e PH_3, AlH_3 comb (10)	541	549	543
e PH_3, AlH_3 comb (5)	251	255	242
a_1 Al−P str (18)	184	216	218
a_2 H−Al−P−H tors (0)	115	122	131

[a] Obtained at the DZP SCF level.

TABLE 10: Relative Energy (in kcal mol^{-1}) at Various Levels of Theory for $AlPH_2$ Isomers

	SCF	CISD	CCSD
$Al-PH_2$			
DZP	0.0	0.0	0.0
TZ2P	0.0	0.0	0.0
$HAl-PH$			
DZP	17.9	14.5	14.5
TZ2P	15.5	13.7	14.3
H_2Al-P			
DZP	9.2	21.2	26.3^a
TZ2P	8.7	21.7	26.7^a

[a] These are obtained from CCSD energies at the CISD-optimized geometries for the respective basis sets.

TABLE 11: Relative Energy (in kcal mol^{-1}) at Various Levels of Theory for $AlPH_3$ Isomers

	SCF	CISD	CCSD
H_2Al-PH			
DZP	0.0	0.0	0.0
TZ2P	0.0	0.0	0.0
$HAl-PH_2$			
DZP	2.4	1.0	0.5^a
TZ2P	1.7	0.7	
$Al-PH_3$			
DZP	14.2	0.9	−3.0^a
TZ2P	20.6	19.1	17.6^a
Al, PH_3 fragments			
DZP	15.8	3.2	−0.6^a
TZ2P	21.8	21.8	19.7^a
insertion transition state			
DZP	46.8	37.9	
TZ2P	43.8	33.6	

[a] These are obtained from CCSD energies at the CISD-optimized geometries for the respective basis sets.

TABLE 12: Energy in (kcal mol^{-1}) of the $HAl-PH_3$ Isomer Relative to H_2Al-PH_2 at Various Levels of Theory

	SCF	CISD	CCSD
DZP	29.6	30.0	27.5
TZ2P	31.0	31.3	29.2

TABLE 13: Energy (in kcal mol^{-1}) of the H_3Al-PH_3 Relative to Separated Fragments at Various Levels of Theory

	SCF	CISD	CCSD
DZP	−10.2	−12.4	−12.5
TZ2P	−11.3	−13.7	−13.6

TABLE 14: Total Energies (in hartrees)

	SCF	CISD	CCSD
$AlPH_2$			
DZP	−583.767 064	−584.094 931	−584.128 152
TZ2P	−583.811 708	−584.156 180	−584.196 053
$HAl-PH$			
DZP	−583.738 581	−584.071 779	−584.105 045
TZ2P	−583.787 080	−584.134 387	−584.173 132
H_2Al-P			
DZP	−583.752 477	−584.061 066	−584.086 195^a
TZ2P	−583.797 783	−584.121 607	−584.153 548^a
H_2Al-PH			
DZP	−584.335 320	−584.648 897	−584.676 029^a
TZ2P	−584.387 115	−584.735 553	−584.772 961^a
$HAl-PH_2$			
DZP	−584.331 428	−584.647 290	−584.675 279^a
TZ2P	−584.384 328	−584.734 477	
$Al-PH_3$			
DZP	−584.312 594	−584.647 399	−584.680 797^a
TZ2P	−584.354 347	−584.705 063	−584.744 853^a
Al, PH_3			
DZP	−584.310 070	−584.643 648^b	−584.676 982
TZ2P	−584.352 373	−584.700 756^b	−584.741 538
Al-to-PH_3 insertion transition state			
DZP	−584.226 785	−584.588 553	
TZ2P	−584.317 285	−584.682 046	
H_2Al-PH_2			
DZP	−584.946 772	−585.302 294	−585.337 476
TZ2P	−584.992 144	−585.364 133	−585.406 781
$HAl-PH_3$			
DZP	−584.899 533	−585.254 416	−585.293 651
TZ2P	−584.942 710	−585.314 180	−585.360 285^a
H_3Al-PH_3			
DZP	−586.094 192	−586.479 110	−586.520 976
TZ2P	−586.140 758	−586.540 850	−586.590 783
H_3Al, PH_3			
DZP	−586.077 978	−586.459 403^b	−586.501 073
TZ2P	−586.122 780	−586.519 056^b	−586.569 037

[a] These are CCSD energies at the CISD-optimized geometries for the respective basis sets. [b] These are energies of supermolecules that consist of optimized fragment geometries fixed at 100 Å from each other.

show a distinct difference for the three isomers; the bond orders for H_2Al-P and $Al-PH_2$ are 1.05 and 1.07, respectively, while that for $HAl-PH$ is 1.95. $HAl-PH$ forms a double bond at a much smaller energy cost than $HAl-NH$. Although the Mulliken bond orders are nearly the same, the Al−P bond in the H_2Al-P isomer is also significantly shorter than that of $Al-PH_2$. This can be rationalized based on the degree of charge separation. The atomic charges on Al and P for H_2Al-P are +0.8 and −0.3, respectively, whereas they are only +0.4 and −0.2 for Al and P in $Al-PH_2$. The order of the Al−P bond strength is also reflected in the Al−P stretching frequencies for these molecules. At the TZ2P CISD level, $HAl-PH$ has an Al−P stretching frequency of 677 cm^{-1} vs 426 cm^{-1} for H_2Al-P and 417 cm^{-1} for $Al-PH_2$.

In all isomers, the aluminum center maintains planarity and the H−Al−P angles are either approximately 180° or 120°. In $Al-PH_2$, the H−P−H and H−P−Al bond angles are about 90°. In $HAl-PH$, the hydrogen on phosphorus bends significantly toward the Al, but even the shortest Al−H distance at 2.290 Å (TZ2P CCSD) remains too long for a P−H bond.

$Al-PH_3$. The two isomers $^2A''$ H_2Al-PH and ^2A $HAl-PH_2$ have almost the same energy. Our best estimate puts H_2Al-PH lower by 2.8 kcal mol^{-1}, with roughly half of that difference due to ZPVE corrections. The relative energy of the $^2A'$ $Al-PH_3$ adduct is sensitive to basis set. However, the TZ2P SCF and CISD results are consistent; for each, the $Al-PH_3$ adduct is 17 kcal mol^{-1} (17.2 kcal mol^{-1} TZ2P CISD + ZPVE) higher in energy than the $HAl-PH_2$ insertion product. The energy surface for the $AlPH_3$ isomers is quite different from that of the Al−N isomers. As was the case for the $AlPH_2$

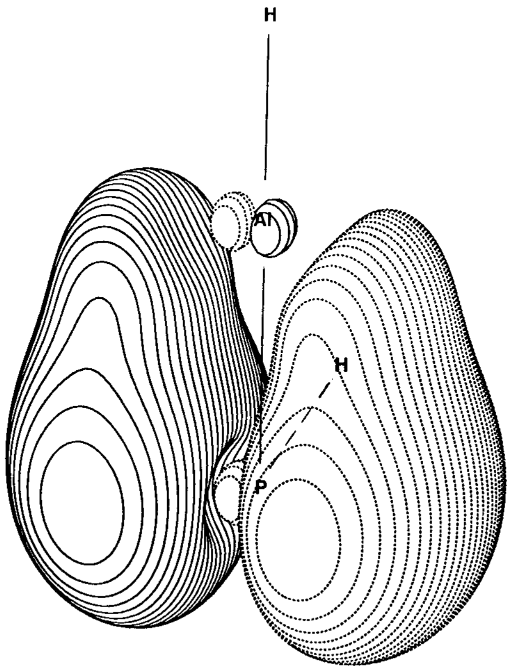


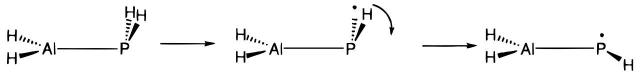
Figure 11. Highest occupied molecular orbital for HAl−PH.

compounds, the differences in energy are smaller among the Al−P compounds than they are for the analogous Al−N compounds. Also, in contrast to the Al−N system, the lowest energy isomer is H_2Al-PH, whereas H_2Al-NH is the highest energy $AlNH_3$ isomer investigated.

The optimized geometries of the various $Al-PH_3$ isomers are a particularly good source of information about Al−P bonding. The Al−P distance in the $Al-PH_3$ adduct is highly variable; including the correlation at the CISD level causes the distance to decrease by 0.54 Å with the TZ2P basis set. Thus, our best estimate of the Al−P bond length is 3.086 Å, significantly shorter than that reported by Sakai.[30] Even this Al−P distance remains 0.54 Å beyond typical Al−P donor−acceptor bonds, which generally are around 2.55 Å. This observation raises the question of whether this interaction can truly be called a bond. The energy difference between the $Al-PH_3$ complex and the separated fragments is 2.7 kcal mol^{-1} at the TZ2P CISD level. This is quite consistent across the methods; the value is 2.3 kcal mol^{-1} at the DZP CISD level and 2.4 kcal mol^{-1} for DZP CCSD energies at the DZP CISD optimized geometry. The PH_3 fragment geometry does change, but the change is small. The P−H distance shortens by 0.002 Å compared to free phosphine. The change from free phosphine to the H_3Al-PH_3 adduct is about −0.010 Å. The H−P−H bond angles in $Al-PH_3$ open (vs free phosphine) by 0.5° compared to a change of 5° for H_3Al-PH_3. The charge on the Al atom is +0.04 according to the generalized atomic polar tensor (GAPT) method of Cioslowski.[31] The aluminum has not received electrons from phosphorus but rather donated them to the phosphine hydrogens via the phosphorus. Because the phosphorus is more electronegative than the aluminum, there is little drive for donation of electrons from P to Al, especially when there are no substituents on the aluminum to take electrons and build up its positive charge. The Al−P vibrational frequency is 69 cm^{-1} at the TZ2P CISD level of theory.

The $HAl-PH_2$ isomer is closely related to the H_2Al-PH_2 molecule. If one of the hydrogen atoms in H_2Al-PH_2 is simply removed from aluminum, the resulting geometry is quite close to the optimized geometry for $HAl-PH_2$. The Al−P bond of $HAl-PH_2$ is slightly longer than that of H_2Al-PH_2, but its stretching frequency is higher; the minimum of the potential well moves farther out, but the walls are steeper. The remaining Al−H bond lengthens slightly and bends toward the phosphorus, and the H−Al−P−H torsion angle increases by about 8.0°; i.e., the remaining hydrogen twists away from the phosphorus hydrogens.

The H_2Al-PH isomer is also closely related to the H_2Al-PH_2 molecule. The relationship is not readily apparent for H_2Al-PH, because it is planar, whereas H_2Al-PH_2 is not. It is also initially mysterious that loss of a hydrogen atom would induce planarity. This mystery is resolved when it is remembered that the H_2Al-PH molecule has a $^2A''$ ground state. The change in geometry from H_2Al-PH_2 is not a flattening of the phosphorus but rather rotation:



The planar H_2Al-PH isomer has nearly the same Al−P bond length as the nonplanar $HAl-PH_2$ isomer. It is slightly shorter (0.015 Å TZ2P CISD), and the approximately 45° rotation of the P−H bond into the AlH_2 plane could be due to the π interaction between the unpaired electron on P and the empty Al p orbital, but it is difficult to determine whether the π interaction is cause or effect.

All of the $Al-PH_3$ isomers could conceivably be produced by the reaction of energetic Al atoms with phosphine. The reaction of Al with PH_3 has also been studied theoretically by Sakai.[30] He found a structure for $Al-PH_3$ at the SCF/6-31G** level that is very similar to our DZP SCF geometry, but he did not reoptimize the geometry at correlated levels. The reaction of Al with PH_3 apparently covers a more complicated potential energy surface than the other Al atom insertion reactions studied by Sakai. He characterized the reaction to form $HAl-PH_2$ as hydrogen abstraction rather than aluminum insertion, and his plot of the H−Al, H−P, and Al−P bond lengths along the reaction path shows the shortest Al−P distance of about 2.8 Å, corresponding to the transition state. However, Sakai's plot of the reaction path shows the Al−P distance *lengthening* after the transition state to a geometry that does not correspond to the $HAl-PH_2$ molecule. Analysis of the imaginary frequency mode obtained for our transition state shows that the reaction coordinate involves Al−P shortening as the H atom swings away from P to Al.

Our results for the energy of the transition state for insertion are in agreement with the lower level results of Sakai but only when the TZ2P basis set is used at the CISD level. Including ZPVE at the TZ2P CISD level, we find the transition state lies 12.7 kcal mol^{-1} above the $Al-PH_3$ adduct in energy, and the adduct lies 19.8 kcal mol^{-1} above the $HAl-PH_2$ insertion product. Sakai obtains energy differences of 12.1 and 17.4 kcal mol^{-1}, respectively. It is worth noting that neither geometries nor energetics are trustworthy for the weakly bound complex using basis sets below TZ2P quality.

In a matrix IR study of Al reactions with SiH_4, Lefcourt and Ozin found that photoactivated Al atoms did insert into bonds, and their results are consistent with a concerted mechanism.[32] They assigned an absorption at 1784 cm^{-1} to the Al−H stretching fundamental. Our highest level results for $HAl-PH_2$ give an Al−H stretch of 1921 cm^{-1} at the TZ2P CISD level; reduction[33] of this theoretical harmonic vibrational frequency by 7% yields 1787 cm^{-1} .

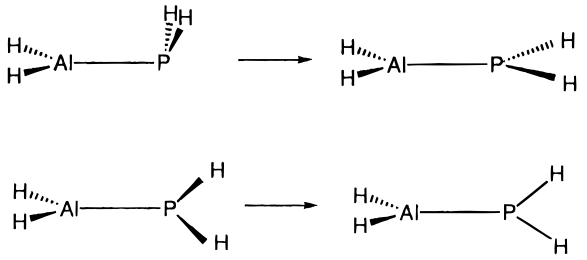
$AlPH_4$. The H_2Al-PH_2 isomer is the lowest in energy at all levels of theory. The difference in energy between it and the $HAl-PH_3$ isomer is quite consistent across different levels of theory at about 30 kcal mol^{-1}. This is quite similar to the results found for the analogous Al−N compounds,[21] for which H_2Al-NH_2 lies 32 kcal mol^{-1} lower in energy than $HAl-NH_3$.

The geometry of the H_2Al-PH_2 molecule fits simple predictions of the geometry of compounds with normal Al−P bonds. The Al−P bond length is 2.335 Å at the TZ2P CCSD level and is quite consistent across theoretical methods, and this matches quite well with the prediction, mentioned above, that a nondative Al−P bond between three-coordinate Al and P should have a bond length of 2.31 Å. There is a slight shortening of Al−H bonds and a slight lengthening of P−H bonds going from H_3Al-PH_3 to H_2Al-PH_2, as the H−P−H angle closes down from about 99° to 96° and the H−Al−H angle opens from about 118° to 121°.

The $HAl-PH_3$ molecule has a long, weak donor−acceptor bond. As in the case of $Al-PH_3$, the Al−P bond shortens substantially at correlated levels. At all levels of theory, $HAl-PH_3$ has an Al−P bond distance roughly 0.25 Å shorter than that of $Al-PH_3$. This emphasizes the strong dependence of the donor−acceptor bond strength on the presence of substituents on Al that can withdraw electrons. The $HAl-PH_3$ geometry is remarkable for being the only molecule studied in which an H−Al−P angle is not within 5° of 120° or 180°. The H−Al bond is also at least 0.05 Å longer than that of any other compound reported here, and the harmonic stretching frequencies are correspondingly low.

Schade and Schleyer have compared the relative energies of the optimized H_2Al-PH_2 structure, which has a pyramidal phosphorus center, with a planar structure and a structure for which the H_2Al group has been rotated so that it bisects the H_2P plane.[34] They reported energies but not optimized geometries. The geometries are of interest because they will reflect the Al−P interaction when the molecule is forced to be planar. The analogous H_2AlNH_2 molecule is planar and has a shorter bond than expected by the Schomaker−Stevenson rule.[29] If H_2Al-PH_2 is constrained to be planar and the geometry reoptimized, the Al−P bond shortens by about 0.1 Å (from 2.308 to 2.205 Å DZP CISD). The shortening can be attributed to two factors. The first is rehybridization of the σ-bonding orbitals on phosphorus from mostly p atomic orbital character (evidenced by the approximately 94° bond angles) to orbitals that contain more s character, accompanied by an increase in the H−P−H bond angle to about 108°. The second factor in the Al−P bond distance reduction is P-to-Al π donation. If the phosphorus center is maintained planar but the H_2Al group is rotated by 90° about the Al−P bond, the Al−P bond lengthens by 0.06 Å to 2.265 Å; thus, 60% of the original shortening of the bond is lost upon rotation. This lengthening might be due to factors besides the loss of the π donation. If the H_2Al group is kept rotated 90° but the PH_2 group is allowed to relax back to a pyramidal geometry, the Al−P bond lengthens even further to 2.340 Å (DZP CISD), which is 0.022 Å longer than the Al−P distance in the fully optimized geometry. There are multiple factors affecting the Al−P distance as the out-of-plane and torsional angles are changed, but the above analysis suggests that the Al−P π interaction, although not strong enough to overcome the barrier to planarity for the phosphorus center, does affect the Al−P distance if a planar geometry is enforced.

We find the energy required to force H_2Al-PH_2 planar to be about 10 kcal mol^{-1}, in good agreement with the results of Schade and Schleyer.[34] This compares to a value of 37 kcal mol^{-1} for the barrier to inversion for PH_3[35] and a barrier of about 6 kcal mol^{-1} for H_2BPH_2.[36] The energy for rotation by 90° about the Al−P bond of the planar geometry is 15.5 kcal mol^{-1} (DZP CISD), somewhat larger than Schade and Schleyer's value of 11.4 kcal mol^{-1} . When the planar PH_2 group in the twisted geometry is allowed to pyramidalize, the resulting twisted pyramidal molecule is only 3.4 kcal mol^{-1} (DZP CISD) above the totally optimized geometry. Thus, for the simplest estimate of the Al−P π-bond energy, which is obtained from the energy required for rotation about the Al−P bond of the molecule that has been forced planar, we find theoretically 15.5 kcal mol^{-1}. Another estimate can be obtained from the difference between the barrier to pyramidalization at phosphorus in the twisted and nontwisted structures as shown below:



We obtain a value of 12.2 kcal mol^{-1} for this difference, again somewhat larger value than the value of 8.5 kcal mol^{-1} obtained by Schade and Schleyer.

H_3Al-PH_3. Authors of earlier studies of the H_3Al-PH_3 adduct have reported theoretical geometries and dissociation energies. Chaillet et al.,[16] who used the MP2 method with core pseudopotentials and DZP valence basis sets, obtained an Al−P distance of 2.566 Å. Jungwirth and Zahradnik[17] optimized geometries using 631G* basis sets at the MP2 level and found an Al−P distance of 2.544 Å. If one compares these results with the present work, one sees that the Al−P distance is stable over a range of theoretical methods, with our best estimate being 2.576 based on the TZ2P CCSD results. All other geometrical parameters are similar, with our highest level results giving shorter Al−H and P−H bond lengths, due most likely to the lack of polarization functions on H in the other studies. Our theoretical Al−P bond stretching mode is also lower than that reported by Jungwirth and Zahradnik. Although the larger TZ2P basis set gives a shorter Al−P bond than the DZP basis set, it flattens the potential well so that the Al−P stretching frequency decreases. Electron correlation has little effect on either the Al−P bond length or stretching frequency. The electron diffraction study of Almenningen et al.[18] found an Al−P distance of 2.53 Å for $Me_3Al-PMe_3$.

The dissociation energy of H_3Al-PH_3 (without ZPVE or basis set superposition corrections) found by Bennet et al. was 13.2 kcal mol^{-1}. Jungwirth and Zahradnik obtained 15.2 kcal mol^{-1}, while Chaillet et al. found 14.6 kcal mol^{-1}. The dissociation energy was evaluated at different theoretical levels to assess convergence. At the CISD level, the energy of a fragment supermolecule is subtracted from the adduct to assure size consistency. As the basis set is increased and correlation is included at higher levels, the value converges quite well. Our best estimate is from the TZ2P CCSD level and is 13.6 kcal mol^{-1}. If ZPVE energy is included, the value for D_0 is 11.0 kcal mol^{-1}.

The changes in fragment geometry upon complexation are consistent across theoretical levels. Upon complexation, the P−H bond shortens by about 0.012 Å, and the Al−H bond lengthens by about 0.012 Å. The H−Al−H angles close by about 1.5°, as the hydrogens bend back away from the phosphorus, and the H−P−H angle opens by 5°, as the hydrogens on phosphorus bend toward the aluminum. Experimentally, for $Me_3Al-PMe_3$, the Al−C bonds lengthen by 0.016 Å, and the P−C bonds shorten by 0.024 Å. The C−Al−C angle closes by 2.9°, and the C−P−C angle opens by 4.8°. The similar values for the change in angles suggests that the changes are due to rehybridization due to electron donation rather than simple valence shell electron pair repulsion (VSEPR) considerations, which should affect the much larger methyl groups differently than the hydrogens.

Energies of Dehydrogenation. Formation of rings or clusters from Lewis acid–base adducts generally proceeds through alkane elimination. For our model compounds, it would be loss of hydrogen. We can evaluate the energy of dehydrogenation for both H_3Al-PH_3 and H_2Al-PH_2. The energy required for dehydrogenation of H_3Al-PH_3

$$H_3Al-PH_3 \rightarrow H_2Al-PH_2 + H_2$$

is quite consistent across various levels of theory at about 10 kcal mol^{-1}, with our best estimate being 8.3 kcal mol^{-1} at the TZ2P CCSD level. This result is reduced to only 3.3 including ZPVE corrections. Hydrogen loss from the analogous H_3Al-NH_3 was found theoretically to require about 4 kcal mol^{-1}; [21] for the related H_3B-NH_3, hydrogen loss results in a decrease in energy, the value of which is estimated to be about −6 to −8 kcal mol^{-1}.[37,38] These reactions show a consistent trend: as Al and P are replaced by lighter atoms, H_2 loss is more favorable.

Dehydrogenation of H_2Al-PH_2 and its analogues H_2Al-NH_2 and H_2B-NH_2 is harder to compare because the lowest energy isomers upon hydrogen loss are $Al-PH_2$, $Al-NH_2$, and HB–NH. We are interested in comparing the energy required to lose hydrogen and form the HX–YH isomer, because this isomer in each case has a nondative π bond. The energy required for the reaction

$$H_2Al-PH_2 \rightarrow HAl-PH + H_2$$

is about 39.4 kcal mol^{-1} at the TZ2P CCSD level. This can be compared to 62 kcal mol^{-1} for H_2Al-NH_2[21] and 30 kcal mol^{-1} for H_2B-NH_2.[37] The energy required to form these monomeric compounds with two-coordinate Al and P is not much higher than that required for the formation of B–N analogues, which are known. However, in the B–N case, this isomer has the lowest energy, whereas for Al–P the $Al-PH_2$ isomer is lowest, which adds the possibility of rearrangement to the already thermodynamically unstable situation. It is seen, based on a comparison of the Al–P results with Al–N, that the π bond between Al–P lowers the energy of HAl–PH substantially. The loss of H_2 from the Al atom in H_2Al-PH_2 requires about 25 kcal mol^{-1} at the TZ2P CCSD level, which is close to the value obtained for the analogous reaction for H_2Al-NH_2, 21 kcal mol^{-1}.[21]

Concluding Remarks. The aluminum–phosphorus compounds considered here have a greater wealth of low-lying isomers than the analogous Al–N compounds. All three isomers of the formula $AlPH_2$ are within about 20 kcal mol^{-1} of one another, and particularly noteworthy is that the planar H_2Al-PH isomer is the lowest in energy of all $AlPH_3$ compounds. The reaction of aluminum atoms with phosphine, provided the aluminum atoms are activated, should produce a wealth of interesting products. The Al–P bond distance is very consistently in the range of 2.33–2.35 Å for those compounds that contain two- or one-coordinate phosphorus and aluminum. These bonds all have stretching frequencies of 430–450 cm^{-1}. The Al–P π donor–acceptor bond is estimated to be worth about 12 kcal mol^{-1} based on barriers to inversion for H_2Al-PH_2. The nondative π bond in HAl–PH does shorten the Al–P bond to 2.149 Å, substantially shorter than a typical nondative bond between Al–P.

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References and Notes

(1) Paine, R. T.; Noth, H. *Chem. Rev.* **1995**, *95*, 343.

(2) Schulz, S.; Hämig, L.; Herbst-Immer, R.; Roesky, H. W.; Sheldrick, G. M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 969.

(3) Wehmshulte, R. J.; Power, P. P. *J. Am. Chem. Soc.* **1996**, *118*, 791.

(4) Arif, A. M.; Boggs, J. E.; Cowley, A. H.; Lee, J.-G.; Pakulski, M.; Power, J. M. *J. Am. Chem. Soc.* **1986**, *108*, 6093.

(5) Cowley, A. H. *Phosphorus, Sulfur* **1987**, *30*, 129.

(6) Waggoner, K. M.; Hope, H.; Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1699.

(7) Dias, H. V. R.; Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1270.

(8) Pestana, D. C.; Power, P. P. *J. Am. Chem. Soc.* **1991**, *113*, 8426.

(9) Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 449.

(10) Watts, J. D.; Van Zant, L. C. *Chem. Phys. Lett.* **1996**, *251*, 119.

(11) Kerins, M. C.; Fitzpatrick, N. J.; Nguyen, M. T. *Polyhedron* **1989**, *8*, 969.

(12) Almenningen, A.; Fernhalt, L.; Haaland, A.; Weidlen, J. *J. Organomet. Chem.* **1978**, *145*, 109.

(13) Wehmschulte, R. J.; Ruhlandt-Senge, K.; Power, P. P. *Inorg. Chem.* **1994**, *33*, 3205.

(14) Cowley, A. H. *J. Organomet. Chem.* **1990**, *400*, 71.

(15) Cowley, A. H.; Jones, R. A.; Mardones, M. A.; Atwood, J. L.; Bott, S. G. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1409.

(16) Chaellet, M.; Dargelos, A.; Marsden, C. J. *New. J. Chem.* **1994**, *18*, 693.

(17) Jungwirth, P.; Zahradnik, R. *THEOCHEM* **1993**, *283*, 317.

(18) Bennett, F. R.; Elms, F. M.; Gardiner, M. G.; Koutsantonis, G. A.; Raston, L.; Roberts, N. K. *Organometallics* **1992**, *11*, 1457.

(19) Matsunaga, N.; Cundari, T. R.; Schmidt, M. W.; Gordon, M. S. *Theor. Chim. Acta* **1992**, *83*, 57.

(20) Matsunaga, N.; Gordon, M. S. *J. Am. Chem. Soc.* **1994**, *116*, 11408.

(21) Davy, R. D.; Jaffrey, K. L. *J. Phys. Chem.* **1994**, *98*, 8930.

(22) Huzinaga, S. *J. Chem. Phys.* **1965**, *45*, 1293.

(23) Dunning, T. H., Jr. *J. Chem. Phys.* **1970**, *53*, 2823.

(24) Huzinaga, S. Approximate Atomic Functions II. Deparment of Chemistry Report, University of Alberta, Edmonton, Alberta, Canada, 1971.

(25) Dunning, T. H., Jr.; Hay, P. J. In *Methods of Electronic Structure Theory*; Schaefer, H. F., Ed.; Plenum: New York, 1977.

(26) Dunning, T. H., Jr. *J. Chem. Phys.* **1971**, *55*, 716.

(27) McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639.

(28) Janssen, C. L.; Seidl, E. T.; Scuseria, G. E.; Hamilton, T. P.; Yamaguchi, Y.; Remington, R. B.; Xie, Y.; Vacek, G.; Sherrill, C. D.; Crawford, T. D.; Fermann, J. T.; Allen, W. D.; Brooks, B. R.; Fitzgerald, G. B.; Fox, D. J.; Gaw, J. F.; Handy, N. C.; Laidig, W. D.; Lee, T. J.; Pitzer, R. M.; Rice, J. E.; Saxe, P.; Scheiner, A. C.; Schaefer, H. F. PSI 2.0.8; PSITECH, Inc.: Watkinsville, GA, 30677, 1994.

(29) Haaland, A. In *Coordination Chemistry of Aluminum*; Robinson, G. H., Ed.; VCH: New York, 1994; pp 1–56.

(30) Sakai, S. *J. Phys. Chem.* **1992**, *96*, 8369.

(31) Cioslowski, J. *J. Am. Chem. Soc.* **1989**, *111*, 8333.

(32) Lefcourt, M. A.; Ozin, G. A. *J. Phys. Chem.* **1991**, *95*, 2623.

(33) Schaefer, H. F.; Thomas, J. R.; Yamaguchi, Y.; DeLeeuw, B. J.; Vacek, G. In *Modern Electronic Structure Theory, Part I*; Yarkony, D. R., Ed.; World Scientific: Englewood Cliffs, NJ, 1995; pp 3–54.

(34) Schade, C.; Schleyer, P. v. R. *J. Chem. Soc., Chem Commun.* **1987**, 1399.

(35) Lehn, J. M.; Munsch, B. *Mol. Phys.* **1972**, *23*, 91.

(36) Allen, T. L.; Scheiner, A. C.; Schaefer, H. F. *Inorg. Chem.* **1990**, *29*, 1930.

(37) McKee, M. L. *J. Phys. Chem.* **1992**, *96*, 5380.

(38) Sana, M.; Leroy, G. Wilamte, C. *Organomettalics* **1992**, *11*, 787.