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Differences Between Amine- and Phosphine-Boranes: Synthesis, Photoelectron Spectroscopy, and Quantum Chemical Study of the Cyclopropylic Derivatives

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Borane complexes of aziridine, phosphirane, cyclopropylamine, cyclopropylphosphine, cyclopropylmethylamine, and cyclopropylmethylphosphine have been prepared by the reaction at low temperatures of a borane complex or diborane on the free phosphine or amine. The products characterized by NMR spectroscopy and mass spectrometry have then been investigated by photoelectron spectroscopy and B3LYP/aug-cc-pVTZ quantum chemical study. The complexation led to rotamers with structures similar to the ones of the corresponding free systems. The main geometry change with the complexation is the P−C bond elongation and the N−C bond shortening, which can be rationalized by the charge transfer attached to the electron donation. The calculated relative stability order of the conformers changes with the complexation only in the case of cyclopropylamine. The calculated complexation energies are higher for the amines, in accord with the differences observed in the flash vacuum thermolysis of methylamine-, methylphosphine-, and aziridine-borane. The photoelectron spectra indicate essential differences between the amines and phosphines toward borane complexation. The dative bond is more stable in the studied amine-boranes than in phosphine-boranes, while the σ_{B-H} orbitals are more stable in the latter compounds. The enthalpy of the hydrogen release reaction of aziridine-borane is almost thermoneutral, indicating the potential of this complex as recyclable hydrogen storage material.

Introduction

The interest in phosphine-boranes and amine-boranes is currently growing since such compounds present potential as hydrogen storage materials.[1−9] It has been evidenced that the substitution on the nitrogen can reduce the exothermicity of the dehydrogenation.[10,11] Thus, to evaluate the hydrogen storage potentiality of such compounds, the first step is a better knowledge of the properties of simple amine- or phosphine-boranes. Gas electron diffraction (GED) studies of methylamine- and methylphosphine-borane have been recently reported.[12,13] In the latter compound, it was shown that the structural environment around the phosphorus atom changes significantly upon complexation with borane, with the P−C bond length shortening and the bond angles widening.[13]

The variation in the electronic effects during the complexation of the simplest unsaturated phosphine-boranes has been recently reported for methyl, vinyl, allyl, propargyl, ethynyl, and allenyl derivatives.[14] Surprisingly, the complexation has no remarkable influence for the

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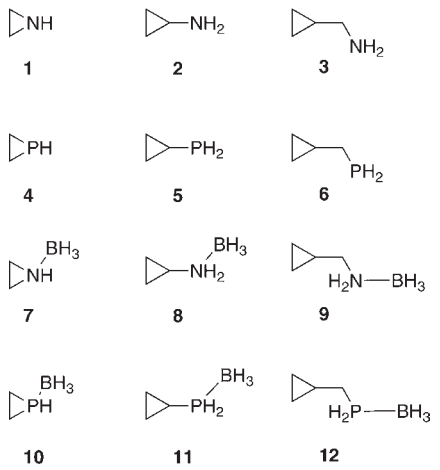
Chart 1

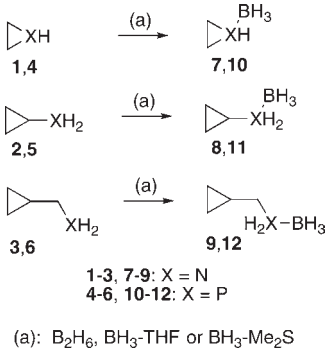


α,β-unsaturated compounds since similar structures have been found for the conformers of the complexes and the corresponding free systems. The only significant difference in the geometries, similarly to the methylphosphine-borane,[13] is the P−C bond shortening in the complexes, which is the obvious consequence of the charge transfer during the complexation. The photoelectron spectra were described in the case of α,β-unsaturated compounds since the direct conjugation between the lone electron pair and the π bond has to be exchanged to a hyperconjugation between the σ_{P-B} bond and the unsaturated moiety. As expected, no interaction of the π bond with the phosphorus atom or the dative bond could be observed in the β,γ-unsaturated derivatives.

The conjugative interaction between the cyclopropyl ring and the π system of the vinyl group has been investigated.[15−27] A similar effect can be presumed between the lone electron pair and cyclopropyl ring skeleton, as it was confirmed in the case of cyclopropylamine and suggested for cyclopropylphosphine.[28−35] In cyclopropanol, the same interaction was found, although theoretical and experimental studies of the cyclopropanethiol, cyclopropaneselenol, and cyclopropanetellurol did not indicate direct conjugation between the lone electron pair of X (X = S, Se, Te) and the three-membered ring.[33−38]

We report here the synthesis of borane complexes of aziridine, phosphirane, cyclopropylamine, cyclopropylphosphine, cyclopropylmethylamine, and cyclopropylmethylphosphine

Scheme 1



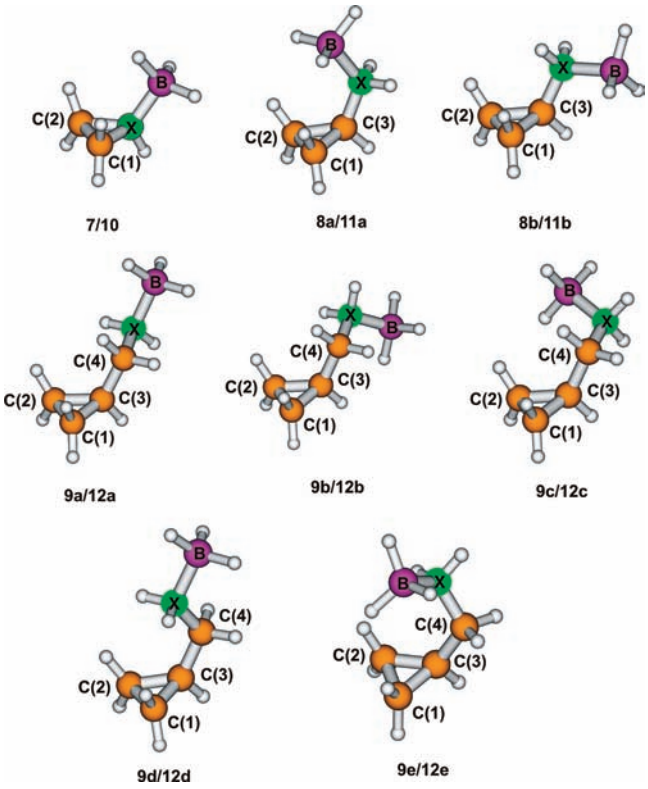


Figure 1. Stable conformers of **7**−**9** (X = N) and **10**−**12** (X = P) calculated at the B3LYP/aug-cc-pVTZ level.

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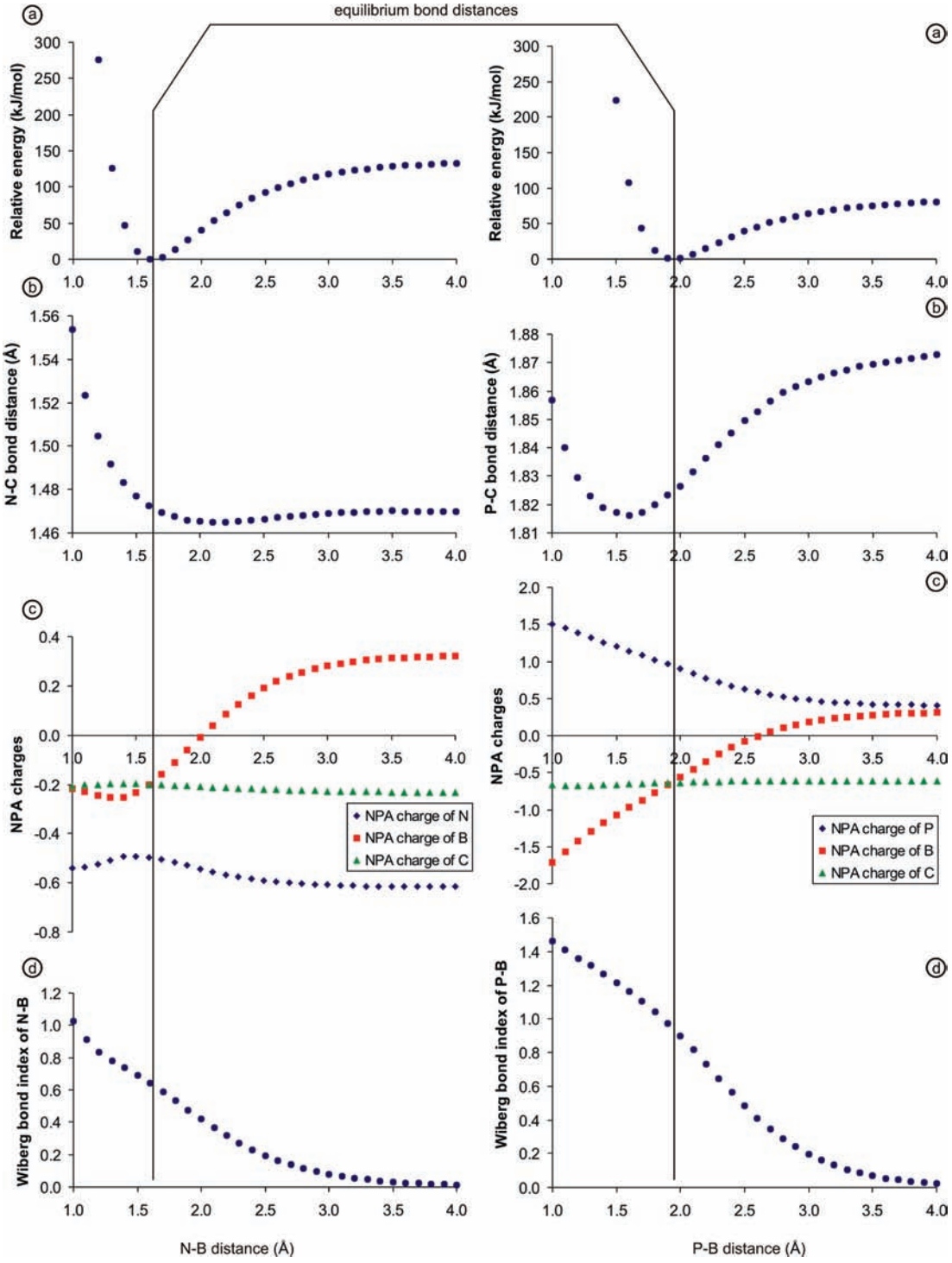

Figure 2. Complexation of aziridine **1** (left) and phosphirane **4** (right) with borane to form **7** and **10**. Variation of (a) relative energy, (b) X−C bond length (X = N, P in Å), (c) NPA (natural population analysis[46]) charges, and (d) Wiberg bond index[47] of the dative bond with the X−B distance.

(Chart 1) and their characterization by NMR spectroscopy and mass spectrometry. Photoelectron spectroscopy and a B3LYP/aug-cc-pVTZ quantum chemical study were investigated with the aim of defining the variation in the electronic effects between the free systems and the corresponding complexes and establishing comparisons between the nitrogen and phosphorus derivatives as a function of the distance of the heteroatom with the cyclopropyl group. The hydrogen storage possibility of the studied complexes was examined by theoretical methods.

Results and Discussion

Synthesis of Compounds. The free amines and phosphines used in this study are commercially available or have been synthesized following reported preparations.[31,39−41] Among the six complexes,[42−44] both

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Table 1. Calculated Structural Parameters of the Investigated Phosphines, Amines, and Their Borane Complexes[a]

no.[b]		X−B	X−C		C(3)−C(4)		C(1)−C(2)		C(1)−C(3)		C(2)−C(3)		Σ_{angle}[c]		Σ_{HBH}
base	complex	complex	base	complex	base	complex	base	complex	base	complex	base	complex	base	complex	complex
1	**7**	1.619	1.470	1.472			1.480	1.482					281.3	287.3	339.6
2a	**8a**	1.655	1.443	1.476			1.508	1.509	1.502	1.496			330.8	322.5	338.8
2b	**8b**	1.650	1.443	1.466			1.514	1.512	1.494	1.490	1.511	1.500	330.8	325.4	340.1
3a	**9a**	1.642	1.465	1.489	1.514	1.504	1.507	1.504	1.504	1.504	1.505	1.509	328.2	324.3	339.5
3b	**9b**	1.647	1.466	1.495	1.507	1.502	1.507	1.505	1.502	1.502	1.507	1.509	329.3	324.5	339.2
3c	**9c**	1.649	1.469	1.497	1.507	1.502	1.507	1.502	1.505	1.509	1.501	1.502	328.4	323.7	339.3
3d	**9d**	1.648	1.459	1.482	1.525	1.514	1.509	1.509	1.502	1.503			332.0	326.6	339.8
3e	**9e**	1.646	1.466	1.495	1.517	1.520	1.508	1.503	1.501	1.503	1.505	1.511	329.1	323.1	338.9
4	**10**	1.950	1.875	1.825			1.490	1.519					238.2	257.4	343.9
5a	**11a**	1.936	1.841	1.812			1.498	1.495	1.511	1.513			290.3	305.9	341.5
5b	**11b**	1.931	1.845	1.812			1.504	1.500	1.509	1.510	1.505	1.508	288.9	304.8	342.2
6a	**12a**	1.933	1.877	1.843	1.509	1.509	1.508	1.506	1.507	1.506	1.503	1.505	288.4	305.0	342.0
6b	**12b**	1.933	1.882	1.847	1.510	1.511	1.507	1.506	1.506	1.504	1.505	1.506	288.8	305.3	341.8
6c	**12c**	1.935	1.883	1.849	1.510	1.511	1.506	1.504	1.506	1.508	1.504	1.504	287.9	304.0	341.9
6d	**12d**	1.936	1.872	1.839	1.519	1.517	1.508	1.508	1.503	1.504			292.4	308.5	342.3
6e	**12e**	1.937	1.883	1.849	1.517	1.518	1.507	1.507	1.504	1.503	1.505	1.507	287.7	302.5	341.8

[a] B3LYP/aug-cc-pVTZ calculations, bond distances in Å, angles in degrees. [b] See Figure 1. [c] Sum of the bond angles around the heteroatom N or P.

cyclopropylmethyl derivatives **9** and **12** and phosphirane-borane **10** are new compounds. Complexes **7**−**12** were prepared by the addition of a freshly distilled BH_3-THF or BH_3-Me_2S complex or diborane on the corresponding free system (Scheme 1). The three amine-boranes were purified by removal of the low boiling compounds in vacuo and used without further purification. The phosphine complexes are much more volatile than the corresponding nitrogen derivatives and were purified by distillation in vacuo and selective trapping in a cold trap. The cyclopropylmethyl derivatives **9** and **12** are kinetically stable compounds easily characterized by their NMR and mass spectra. The phosphirane-borane **10** is kinetically very unstable, and the NMR spectra recorded at room temperature show the presence of about 20% free phosphine.

In the ^{1}H NMR spectra of compounds **7**−**12**, the complexation led to chemical shifts downfield, especially for the signal of the hydrogen on the heteroatom ($\Delta\delta$ 2−3 ppm). While a very strong downfield effect was observed in the ^{31}P NMR spectra of phosphine-boranes **10**−**12** compared to those of phosphines **4**−**6** (up to 115 ppm between **4** and **10**), the complexation of amines **1**−**3** only led to a weak downfield effect (5−8 ppm) of the ^{15}N NMR chemical shifts of **7**−**9** (Table S1, Supporting Information). In contrast, a weaker effect was observed for the ^{13}C NMR chemical shifts of the α-carbon of phosphine-boranes **10**−**12** ($\Delta\delta$ −3 to +2.5 ppm) than those of amine-boranes **7**−**9** ($\Delta\delta$ 7−10 ppm).

We then performed the flash vacuum thermolysis (FVT) of methylamine-borane and aziridine-borane **7**. In a previous study,[14] we reported the complete decomplexation of methylphosphine-borane under FVT conditions above 300 °C. At this temperature, the thermolysis of methylamine-borane resulted in about 30% of the free amine according to the ^{1}H NMR spectra of the thermolysis products. This ratio increased to 75% for FVT at 500 °C, and traces of the complex were still observed after FVT at 700 and 900 °C. Similar results were obtained in the FVT of aziridine-borane **7**. These two examples exemplify higher thermodynamic stability of amine-boranes compared to the phosphorus derivatives. In all of the ^{1}H and ^{11}B NMR spectra of the thermolysis products, attempts to detect a monomeric or dimeric compounds corresponding to the loss of dihydrogen were unsuccessful.[45]

Structure. Two and five stable rotamers were calculated for **2**, **5**, **8**, and **11** and **3**, **6**, **9**, and **12**, respectively, and there is no remarkable difference between the nitrogen and the phosphorus derivatives (Figure 1). The complex formation does not modify the number and orientation of the conformers. Obviously, only one stable aziridine **7** or phosphirane derivative **10** could be found.

In Figure 2, the structural changes during the complex formation of **1** and **4** with one borane molecule are shown. In each case, the geometrical parameters except the X−B (X = N, P) bond distance were optimized. The most striking observation is that the N−C bond elongates while the P−C bond shortens around the equilibrium bond distance during the complex formation. This tendency is even much stronger for compounds **2**, **3**, **5**, and **6** (Table 1 and Figures S1b and S2b in the Supporting Information). This can be explained by the variations of the atomic charges. The difference between the atomic charges of P and C are higher after the complexation than in the free phosphines (Figure 2c and Table S2 in the Supporting Information). On the other hand, the N and C atomic charge difference is smaller in the complexes than in the free amines.

The electron donation during the complexation leads the nitrogen and the phosphorus atoms to become more positive while the boron atom becomes definitely negative. It was shown before that the atomic charges of P and B change almost linearly within the P−B distance around

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Table 2. Relative Energies, Complexation Energies, Free Energy, and Reaction Enthalpies of the H_2 Release Reactions[a]

no.		$\Delta E^{mes}_{amine/phos\ phine}$ [b]	$\Delta E^{calc}_{amine/phos\ phine}$	$\Delta E^{calc}_{complex}$	$E^{calc}_{complexati\ on}$	$\Delta H^{calc}_{H_2release}$ [c]	$\Delta G^{calc}_{H_2release}$ [c]
1 (7)					117.0	1.1	−35.8
2 (8)	**a**	o.	0.0	0.0	98.8	−31.3	−65.6
	b	n. o.	7.4	−1.7	108.0		
3 (9)	**a**	0.00	0.0	0.0	116.3	−24.6	−59.6
	b	0.1 ± 0.2	0.4	4.6	112.0		
	c	n. o.	3.9	10.8	109.3		
	d	n. o.	6.2	11.4	111.1		
	e	n. o.	6.4	22.8	99.8		
4 (10)					72.1	75.7	40.3
5 (11)	**a**	o.	0.0	0.0	96.9	84.0	47.1
	b	n. o.	5.0	3.8	98.3		
6 (12)	**a**	0.0	0.0	0.0	98.8	83.5	48.4
	b	1.7	1.6	1.6	98.8		
	c	2.4	2.2	4.0	96.9		
	d	n. o.	9.5	11.8	96.5		
	e	n. o.	10.4	15.0	94.1		

[a] Energy values are in kJ/mol, calculations performed at B3LYP/aug-cc-pVTZ + ZPE level, counter Poise correction[48,49] was used for calculating complexation energies. [b] Microwave measurements seen in refs 28, 31, 50, and 51. o. = observed, n. o. = not observed. [c] Considering the most stable conformers.

the equilibrium bond distance (1.9 Å).[14] In the case of amines, however, at small N−B distances, the nitrogen withdraws electrons from the boron and becomes more negative. Around the equilibrium bond distance (1.65 Å), the nitrogen atomic charge is close to the maximum. As can be seen, the charge on the carbon atom adjacent to nitrogen is almost unchanged during the complex formation. From this, it may follow that the complexation affects only the close surrounding of the N−B (or P−B) bond, and there is only a small effect on the farther parts of the molecules.

Comparing the P−B and N−B bonds, the Wiberg indices in phosphine-boranes indicate a single bond (about 0.96), while in the amine-boranes they are significantly lower (cc. 0.63, see Figure 2 and Table S3 in the Supporting Information). This can be rationalized by the larger σ electron withdrawing effect of N versus that of P against B. Although the complexation of phosphines causes bond angle widening around the heteroatom, the opposite effect is observed in the studied primary amines. The BH_3 is more planar in the studied phosphine-boranes than in amine-boranes.

From the microwave measurements, two and three possible conformers were found for **3** and **6**, respectively (Table 2).[50,51] These results are in line with the calculated relative energies and the rotational barriers of PH_2 and NH_2 groups. The calculated rotational barriers for all the studied molecules vary in a wide range between 4 and 53 kJ/mol (Table S4, Supporting Information). The good agreement for the free systems may suggest that the calculated relative energies between the conformers are also reliable for the investigated complexes. In the case of cyclopropylamine, the complexation causes larger N−C bond elongation in the symmetric (**a**) conformer than in the asymmetric (**b**) conformer, and this is the only case where the relative stability order of the conformers changes with the complexation.

Table 3. Complexation Energy (in kJ/mol) of NH_3BH_3 System Calculated by Different Methods

method	$E^{calc}_{complexation\_on}$
estimated[52]	130.1
CCSD(T)/CBS[3]	108.4
G3	87.6
CBS-QB3	84.6
MP2/aug-cc-pVTZ//MP2/aug-cc-pVTZ	104.4
B3LYP/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ	95.5

The complexation energy between amines and borane is larger than that between phosphines and borane, which agrees with earlier results.[3,5,6,14,52] The reliability of the employed computational methods for phosphine-boranes was studied in our former work.[14] The best available computational value for the complexation energy of the NH_3BH_3 system is 108.4 kJ/mol at the CCSD(T)/CBS level.[3] The experimental value (130.1 kJ/mol) was extrapolated from the measured bond strengths of a set of methylamine−BH_3 and methylamine−BMe_3 complexes.[52] This value is significantly higher than all the calculated results (Table 3). The B3LYP functional gives a value 34.6 kJ/mol lower than the experimental value and 12.9 kJ/mol lower than that reported by Dixon and Gutowski.[3]

The calculated proton affinities (PA) on the N or P site are in line with the complexation energies; the relatively low stability of the phosphirane-borane complex (**10**) can be assumed from both properties (Table S5, Supporting Information).

An appropriate material for hydrogen storage should be stable both with and without hydrogen and should release a relatively high amount of H_2 reversibly in a facile process. It was published in earlier studies that the hydrogen release in the case of phosphine-borane is a strongly endothermic process (72.8 kJ/mol),[6] similarly to our studied cases; thus, these compounds are not expected to be appropriate materials in this aspect. Dixon et al. have already suggested that NH_3BH_3 and $CH_3NH_2BH_3$

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Table 4. Reaction Enthalpy and Free Energy of the H_2 Release Reaction of Aziridine-Borane[a]

method	$\Delta H_{H_2release}^{calc}$	$\Delta G_{H_2release}^{calc}$
CBS-QB3	12.3	−23.0
G3	16.2	−18.7
CCSD/aug-cc-pVDZ	26.2	−11.5
CCSD/6-311+G(2df,p)(scaled)	13.8	−23.5
MP2/aug-cc-pVTZ(scaled)	22.5	−14.7
B3LYP/aug-cc-pVDZ(anharm)	11.9	−23.1

[a] Values are in kJ/mol. scaled = published scaling factors were used to determine the thermal corrections at MP2/6-311+G(2df,p) level;[56] anharm = anharmonic correction was used to determine the enthalpy and free energy.

are potentially good chemical hydrogen storage compounds on the basis of the calculated −21.3 kJ/mol[3] and −14.6 kJ/mol[10] reaction enthalpies, respectively. Manners et al. recently studied the reversibility of the hydrogen uptake. They found that electron donating substituents on the N site and an electron withdrawing substituent on B site raise the endothermicity of ammonia-boranes.[53] As can be seen in Table 2, the hydrogen elimination reaction for cyclopropylamine- (**8**) and cyclopropylmethylamine-borane (**9**) is more exothermic; hence the regeneration process is difficult.[3−5,10,11] On the other hand, the hydrogen elimination reaction of aziridine-borane (**7**) is almost thermoneutral according to the DFT (density functional theory) level. Although the removable hydrogen content is only 4 wt %, the compound is kinetically stable, it can be easily handled, and, as a consequence, the utility for practical purposes seems to be possible. To confirm this unexpected result, some more reliable theoretical methods were employed (Table 4). The most accurate methods are CBS-QB3 and G3, which predict the enthalpy changes (for gas phase deprotonation) with chemical accuracy. (According to previous tests, the predicted mean absolute deviation was less than 5.27 kJ/mol.[54] It was shown, however, that for boron−nitrogen compounds [$B_xN_xH_y$, $x = 2, 3$; $y \geq 2x$] the G3 method provided a 25 kJ/mol difference from the CCSD(T)/CBS data.[55])

The results in the enthalpy of the H_2 elimination of aziridine-borane suggest somewhat higher but acceptable endothermicity. The free energy change of this reaction is about 35 kJ/mol exergonic. (The calculated enthalpy and free energy differences for all the studied borane complexes are similar, see Tables 3 and 4.) It is understandable since the number of products is larger than the number of reagents. Since the FVT experiment of aziridine-borane does not result in the estimated dehydrogenated product, the reaction pathway was studied using B3LYP/aug-cc-pVTZ level (Figure 3). As can be seen on the free energy profile of the H_2 release of aziridine-borane, the energy of the calculated transition state is high (163.2 kJ/mol); therefore the favorable process is the dissociation. This observation is in line with the earlier results of Minh et al.

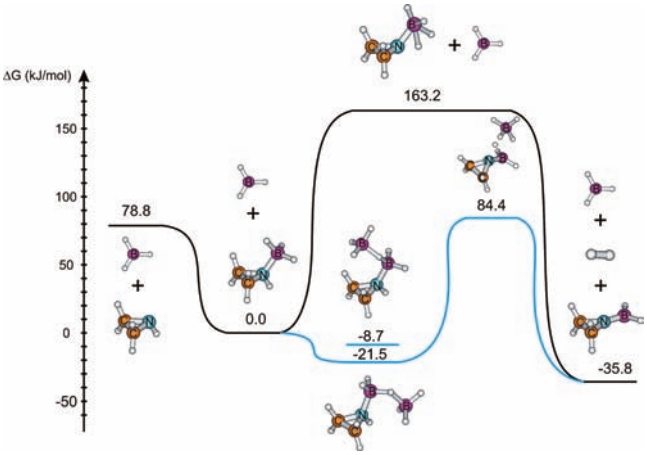

Figure 3. Free energy profile showing the H_2 release and the dissociation of aziridine-borane (**7**) at the B3LYP/aug-cc-pVTZ level.

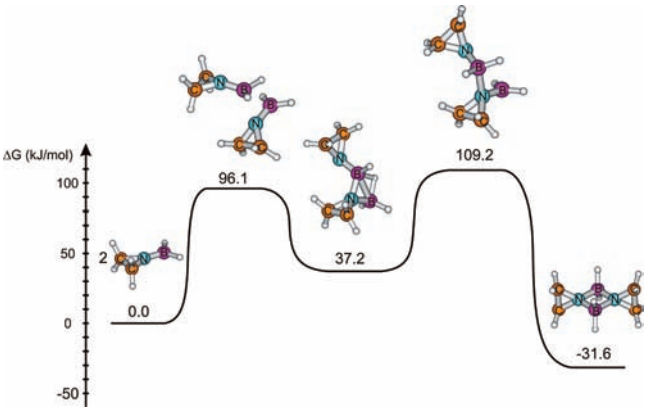

Figure 4. Free energy profile of the dimerization of aziridine-boron at the B3LYP/aug-cc-pVTZ level.

showing that the H_2 release from the NH_3BH_3 has a higher barrier than the dissociation energy of the complex.[4] They suggest that, after the B−N bond cleavage, BH_3 behaves as a catalyst, which explains the experimental observations of the thermal decomposition of ammonia-borane.[57] Since our thermolysis experiments were carried out in vacuo, this catalytic mechanism could not be observed. It is known that the closely related compound $(CH_3)_2N{=}BH_2$ dimerizes.[58−64] Therefore, we also investigated the dimerization of the dehydrogenated aziridine-borane. A stepwise mechanism was found in which the first B−N bond formation is followed by the B−N−B−N four-membered ring closure (Figure 4). The dimer is more stable by 31.6 kJ/mol (ΔG at B3LYP/aug-cc-pVTZ level) than two monomers. Since the activation

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Table 5. Experimental and Calculated Ionization Energies (in eV)[a]

	base						complex				
	calculated			measured	assign.		calculated			measured	assign.
	a	**b**	**c**				**a**	**b**	**c**		
1	9.84			9.83	8a′ n_N-σ_s	**7**	10.35			10.20	5a″ σ_{B-H}
	12.16			11.79	7a′ n_N+σ_s		10.60			10.6	11a′ σ_{B-H}
	12.33			12.16	4a″ σ_a		12.21			12.2	10a′ σ_{N-B}-σ_s
	13.59			13.45	3a″ σ_{C-H}		13.64			13.45	9a′ σ_{N-B}+σ_s
	16.18			15.69	6a′ σ_{ring}		14.18			14.2	4a″ σ_a
	17.69			17.19	5a′ σ_{ring}		14.77			14.5	3a″ σ_{C-H}
							15.97			15.9	8a′ π_{ring}
							18.39			17.9	5a′ σ_{ring}
2	9.49	8.98		9.40	11a′ n_N-σ_s	**8**	10.61	10.54		10.14	σ_{B-H}
	10.45	10.73		10.55	5a″ σ_a		10.66	10.60		10.8−11.2	σ_{B-H}
	11.10	11.92		11.45	10a′ n_N+σ_s		11.30	11.15			σ_{N-B}-σ_a
	13.06	13.21		12.80	4a″ σ_{C-H}		11.41	11.64		11.6	σ_s
	13.89	13.54		13.76	9a′ π_{ring}-σ_{C-N}		12.45	13.18		13.1−13.6	σ_{N-B}+σ_a
	15.73	15.87		15.47	8a′ σ_{ring}		13.64	13.98			σ_{C-H}
	16.61	16.31		16.30	3a″ σ_{N-H}		14.94	14.68		14.53	π_{ring}-σ_{C-N}
	17.19	17.31		16.86	7a′ π_{ring}+σ_{C-N}		16.41	16.66		16.15	σ_{ring}
							17.21	17.51		16.9	π_{ring}+σ_{C-N}
							18.36	17.86			
							18.38	18.84			
3[b]	9.28	9.45	9.44	9.36	n_N	**9**[b]	10.49	10.49	10.35	10.1	σ_{B-H}
	10.44	10.36	10.40	10.31	σ_s		10.55	10.53	10.45	10.8	σ_{B-H},
	10.87	10.59	10.49	10.99	σ_a		11.16	11.01	10.88		σ_a
	12.95	12.41	12.26	12.8−13.0	σ_{C-H}		11.32	11.21	11.18	11.3	σ_s
	13.15	13.11	13.03		σ_{C-H}		12.32	12.12	12.29	12.4	σ_{N-B}
	13.39	13.85	13.83	13.5	σ_{C-C}		13.72	13.25	13.08	13.3	σ_{C-H}
	14.52	14.89	15.07	14.7	σ_{C-N}		13.77	13.64	13.40		σ_{C-H}
	15.79	15.45	15.41	15.5	σ_{ring}		14.47	14.79	14.63	14.0−14.1	σ_{C-H}
	16.50	16.57	16.71	16.2	σ_{N-H}		15.69	15.87	15.69	15.5	σ_{N-H},σ_{C-N}
	17.27	17.17	16.77	16.9	σ_{N-H}		16.41	16.10	16.34	16.1	σ_{ring},σ_{C-N}
							17.46	17.28	17.15	16.9	π_{ring},σ_{N-H}
							17.81	17.99	18.05		
							18.80	18.53	18.25		
4	9.86			9.82	11a′ n_P	**10**				9.82	
	9.93			10.2	5a″ σ_a					10.2	
	11.85			11.78	10a′ σ_s		10.32			10.69	6a″ σ_a
	13.35			13.1	4a″ σ_{C-H}		10.84				14a′ σ_{P-B}
	14.84			14.74	9a’ σ_{C-C}		11.16			12.0	13 a′ σ_{B-H}
	16.42			15.9	8a′ π_{C-C}		11.94				5a″ σ_{B-H}
										13.1	
							12.77			13.25	12a′ σ_s
	18.55						14.11			14.74	4a″ σ_{C-H}
							15.57			15.9	11a′ σ_{ring}
							16.83				
							17.50				
5	9.59	9.30		9.50	14a′ n_P	**11**	10.78	10.42		10.4−10.5	17a′ σ_{P-B}
	10.67	10.68		10.51	6a″ σ_a		10.95	10.91			16a′ σ_{BH}
	10.71	11.57		11.06	13a′ σ_s-σ_{C-P}		10.97	10.95		10.9−11.3	7a″ σ_{BH}
	12.71	12.21			12a′ σ_s+σ_{C-P}		11.33	11.48			6a″ σ_a
	13.27	13.28		12.7−13.1	5a″ σ_{C-H}-σ_{P-H}		11.44	12.22		11.6	15a′ σ_s (σ_{C-P})
	13.64	13.52			4a″ σ_{C-H}+σ_{P-H}		13.58	13.27		13.3	14a′ σ_{C-P} (σ_{ring})
	15.45	15.59		15.22	11a′ σ_{ring}		13.68	13.90		13.6	5a″ σ_{C-H}
	16.90	16.76		16.5	10a′ π_{ring}		14.96	14.82		14.2−14.5	4a″ σ_{P-H}
	18.84	19.02					16.06	16.37		15.7	13a′ σ_{ring} (σ_s)
							16.81	16.78		16.3	12a′ σ_{BH}
							17.48	17.59			
6[b]	9.23	9.45	9.38	9.33	n_P	**12**[b]	10.25	10.40	10.25	10.36	σ_{P-B}
	10.47	10.17	10.32	10.31	σ_a		10.91	10.84	10.71	10.76	σ_{BH}
	10.77	10.63	10.60	10.87	σ_s		10.92	10.91	10.88		σ_{BH}
	12.57	12.46	12.42		σ_{P-H}-σ_{C-P}		11.12	10.99	11.13	11.3−11.4	σ_s
	12.74	12.74	12.52	12.3−13.1	σ_{P-H}+σ_{C-P}		11.50	11.14	11.20		σ_a
	12.86	13.18	13.18		σ_{C-C}		13.35	13.04	13.00	12.59	σ_{C-C}
	13.22	13.41	13.52		σ_{C-H}		13.56	13.51	13.34	13.06	σ_{C-H}
	14.71	14.58	14.61	14.43	σ_{CH2}		13.83	13.99	13.68	13.5−14.3sh	σ_{P-H}-σ_{C-P}
	15.74	15.73	15.74	15.5	σ_{ring}		14.03	14.39	14.68		σ_{P-H}+σ_{C-P}
	16.84	16.86	16.78	16.47	π_{ring}		15.57	15.27	15.18	15.4	σ_{CH2}
	19.08	18.94	19.00				16.21	16.19	16.21		σ_{ring}
							16.97	16.90	16.71		σ_{BH}
							17.40	17.30	17.30		π_{ring}

[a] Calculations are performed using the OVGF/cc-pVTZ method. [b] Calculated ionization energies for conformers **d** and **e** are in Table S6 in the Supporting Information.

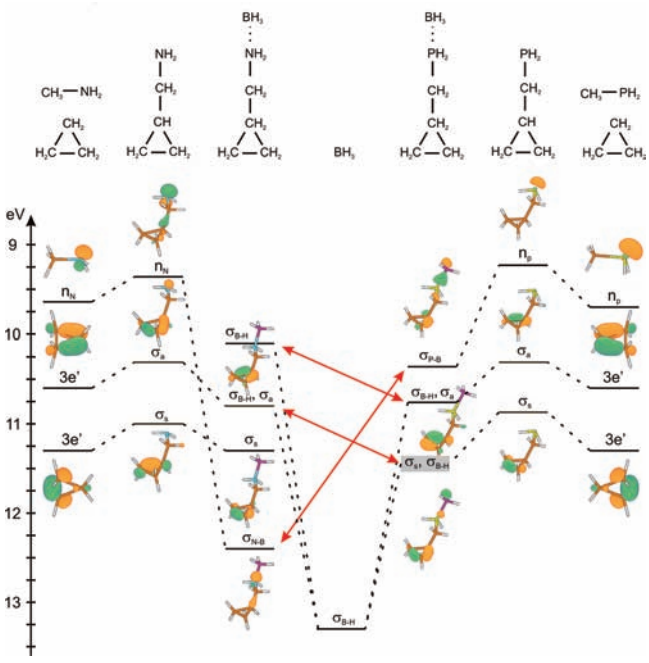

Figure 5. Correlation diagram of cyclopropylmethyl derivatives **3**, **6**, **9**, and **12**.

barrier is $G^{\#} = 109.2$ kJ/mol, it suggests that the dimer is thermodynamically stable, but the dimerization is kinetically hindered and not preferred under mild conditions. Nevertheless, the dimerization seems to be a more facile process than the H_2 addition; therefore we tried the effect of a catalyst. An analogous reaction pathway as Minh et al. suggested with a second BH_3 molecule[4] was investigated, and we found a good catalytic effect (Figure 3). On the new reaction channel, the activation barrier reduced by 78.8 kJ/mol, suggesting that seeking an appropriate catalyst is a promising way toward an applicable reaction. For a similar compound, dimethylamine-borane, several catalysts are known to be effective in the H_2 release reaction.[59−64]

Photoelectron Spectroscopy. The UV photoelectron spectra of aziridine **1**, cyclopropylamine **2**, and phosphirane **4** have been previously published.[29,30,65,66] The spectra of cyclopropylmethylamine **3**, cyclopropylphosphine **5**, and cyclopropylmethylphosphine **6** and the investigated borane complexes **7**−**12** are collected in the Supporting Information (Figures S3−S11). The observed and calculated ionization energies and the assignment based on OVGF (outer valence Green's function[67]) calculations and MO correlations can be seen in Table 5. To study the important electronic effects in the molecules, we compare the first few PE bands of the studied molecules to those of cyclopropane, methylamine (or methylphosphine), and BH_3.[29,68] The correlations of the

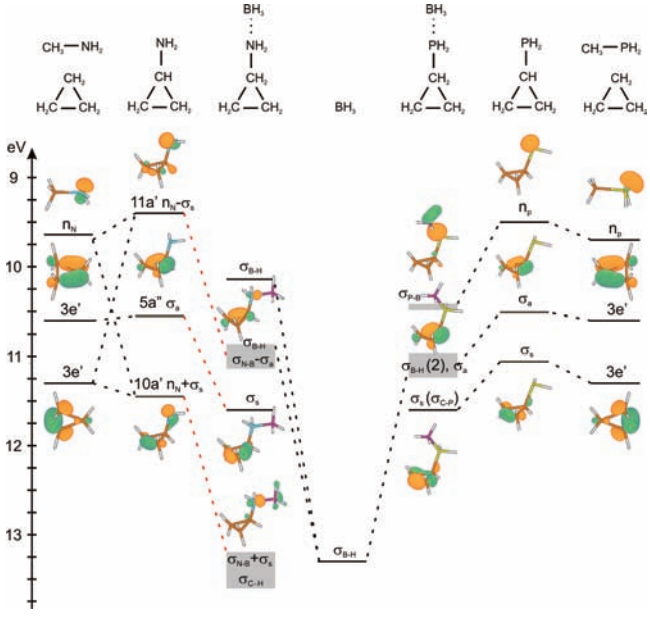

Figure 6. Correlation diagram of cyclopropyl derivatives **2**, **5**, **8**, and **11**.

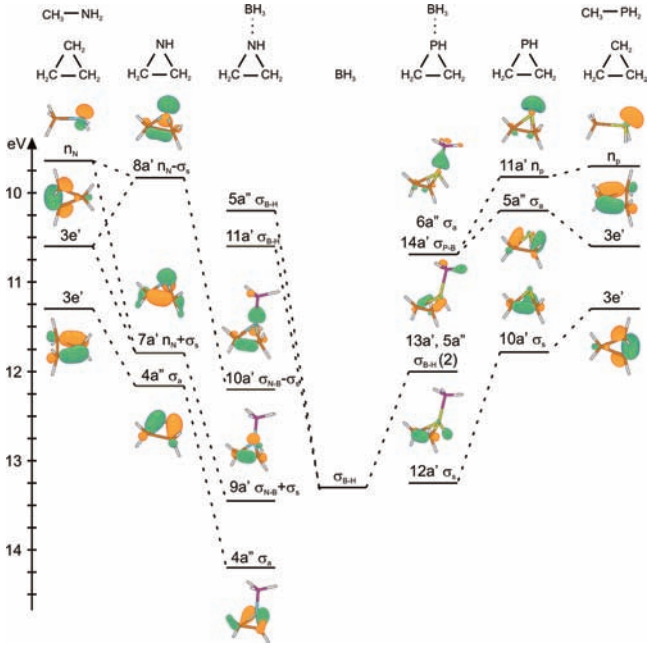

Figure 7. Correlation diagram of **1**, **4**, **7**, and **10**.

respective bands with the shapes of the important MOs can be seen in Figures 5−7.

The two lowest energy bands in the PE spectrum of cyclopropane originate from the 3e′ orbitals (split by the Jahn−Teller effect). The first two bands can be assigned to the orbital antisymmetrical and symmetrical to a σ_v symmetry plane (σ_a and σ_s, Figure 5). The third band of cyclopropane originates from the a_1 orbital of the ring, and it will be symbolized by σ_{ring}. In the cyclopropylmethyl derivatives **3** and **6**, both σ_s and σ_a and the lone pair bands of N or P can be clearly recognized. The bands are destabilized within a few tenths of an electrovolt relative to their parent compounds (Figure 5).

Conjugation between the lone electron pair and the cyclopropyl ring could not be expected for **9** and **12**

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because of the distance between the respective orbitals. Nevertheless, a slight conjugation can be seen on the shape of the MOs of the most stable conformer **12a**. In the complexes, the newly formed B−N (B−P) bond substitutes the lone electron pair of N or P. Therefore the photoelectron spectra of **9** and **12** differ significantly from those of the free systems (**3** and **6** respectively). σ_{P-B} is less stable than σ_{N-B}, in line with the higher complexation energy of the amine derivatives. The Wiberg bond indices suggest a lower electron density between the N−B atoms than P−B atoms, which is in accord with the IP difference of the two dative bonds (Table S3, Supporting Information). In the BH_3 group, the hydrogen atoms are positive in **12** while they are negative in **9** (Table S2, Supporting Information). This is why the positions of the respective σ_{B-H} bands in **9** and **12** are different.

In cyclopropylamine **2** and its complex **8**, a conjugation between the lone electron pair of the nitrogen atom and the cyclopropyl ring can be assumed (Table 5, Figure 6). The conjugation is, however, different in the two cyclopropylamine conformations. In the symmetric conformer (**2a**), the σ_s ring orbital combines with the lone electron pair similarly to that observed in allylamine (Figure 6).[69] On the other hand, in the asymmetric conformer (**2b**), σ_a mixes with the n_N orbital, similarly to in vinylamine. The ionization energies calculated by the OVGF method are closer to the experimental values for **2a** than for **2b**, which is in line with the relative energy calculations and the microwawe measurement.[28] Therefore, we assume that mainly this conformer was observed in the spectrum (Tables 2 and 5, Figure 6). In complex **8**, the lone electron pair of nitrogen disappears, and the N−B dative bond appears, which substitutes the lone pair conjugation with a hyperconjugation. In **8a**, however, the mutual orientation makes any interaction between the N−B bond and the ring impossible. Hyperconjugation can take place only in the **b** conformer, as shown in Figure 6; therefore the stability order changes in favor of **8b**. However, the energy difference between **8a** and **8b** is less than 2 kJ/mol, the rotational barrier is 4.4 kJ/mol, and the calculated IPs of both conformers fit with the broad peaks obtained in the spectrum. Hence, we assume that both conformers exist together in the gas phase.

Investigating the band positions of the respective phosphines **5** and **11**, it can be concluded that these interactions are formally negligible, although in allyphosphine a conjugation between the lone electron pair and the unsaturation was observed.[70]

Earlier assignments[65,66] of the aziridine spectrum did not indicate any conjugation. According to our calculations, however, the lone electron pair mixes with the σ_s orbital (Figure 7). In the complex, all the molecular orbitals are stabilized, and according to the reduced split between the σ_s and the dative bond, only a weak interaction can be assumed.

Unfortunately, we could not separate **4** and **10** because of the decomposition of the complex at the experimental conditions of the measurement. Therefore, the photoelectron spectrum provides only a mixture of the compounds. This fact makes the assignment uncertain. Nevertheless, the same differences can be seen between the positions of σ_{B-H} in **7** and **10**. Also, σ_{P-B} is destabilized compared to the σ_{N-B} band of aziridine.

Conclusions

A series of amine- and phosphine-boranes which contain a cyclopropyl ring was synthesized. ^1H, ^{13}C, ^{15}N, or ^{31}P NMR; photoelectron; and mass spectra were recorded to study the differences between the complexation of amine and phosphine group with borane. Quantum chemical calculations were performed to gain extensive insight into the borane complexation of the lone electron pair of these amines and phosphines and to have greater knowledge of the properties of these new complexes. The observed ionization potentials, the flash vacuum thermolysis, as well as the results of the complexation energy calculations denote that the dative σ_{N-B} bond is more stable than the σ_{P-B} bond. In the case of amine-boranes, more electrons are donated to the B−H bonds than in the phosphine analogues, which can be seen by the comparison of the photoelectron spectra. It is in accord with the calculated atomic charges and Wiberg bond indices. Similar conformers and in all but one case similar relative energy orders of the conformers were obtained after the complexation of nitrogen and phosphorus compounds. The most conspicuous geometry difference is that the P−C bond shortens while the N−C bond elongates during the complexation, which is in line with the changes of the atomic charges; the atomic charge difference increases between P and C while decreases between N and C.

The photoelectron spectra of cyclopropylamine **2** and its complex **8** prove a conjugation between the σ_s ring orbital and the lone electron pair or the σ_a and the dative bond (σ_{N-B}), respectively. The observed σ_s-n_N direct conjugation in aziridine changes to a $\sigma_s-\sigma_{N-B}$ interaction with the complexation. The energy of the investigated hydrogen elimination reactions exhibits a wide range from strongly exothermic to endothermic. The hydrogen elimination of aziridine-borane **7** is however close to thermoneutral. It was shown by high level quantum chemical calculations that the reaction is slightly endothermic. Moreover, it is a stable and easily handled compound; thus it has a huge potentiality of being convenient hydrogen storage material.

Experimental Section

Caution! *Phosphines and phosphine-boranes are malodorous and potentially toxic compounds. All reactions and handling should be carried out in a well-ventilated hood.*

Materials. Cyclopropylamine **2** and cyclopropylmethylamine **3** were purchased from the Aldrich Company and used without further purification. 2-Chloroethylphosphine,[71] cyclopropyldiethylphosphonate,[72] cyclopropylmethylphosphine,[41] cyclopropylphosphine-borane,[44] aziridine,[39] aziridine-borane,[42] and methylamine-borane[31] were prepared as previously reported. Phosphirane **4**, cyclopropylphosphine **5**, and cyclopropylamine-borane **8** have been prepared as described in the Supporting Information.

General. ^1H (400.13 MHz), ^{13}C (100.62 MHz), ^{31}P (161.97 MHz), ^{11}B (128.4 MHz), and ^{15}N (40.55 MHz) NMR spectra were

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recorded on a Bruker Avance III 400 MHz spectrometer. For the ^{15}N NMR experiments, an INEPT pulse sequence with decoupling was employed. Chemical shifts are given in ppm (δ) relative to tetramethylsilane (^{1}H), solvent (^{13}C, $CDCl_3$, δ 77.0 ppm), external H_3PO_4 (85% in water; ^{31}P NMR), external BF_3-Et_2O (^{11}B NMR), and external nitromethane (^{15}N NMR). All the experiments were performed under nitrogen. In all the studied compounds, only the phosphirane (**4**) and the corresponding borane complex (**10**) are kinetically unstable compounds and were kept at a low temperature (−78 °C).

He I photoelectron spectra were recorded on an instrument described earlier.[73] The resolution at the Ar $^{2}P_{1/2}$ line was 40 meV during the measurements. For internal calibration, N_2, MeI, and He^+ peaks were used.

Calculations. DFT calculations for some phosphine-boranes have already proved that using the hybrid functional B3LYP (Becke's three-parameter functional employing the Lee, Yang, and Parr correlational functional)[74,75] and aug-cc-pVTZ basis set gives reliable molecular geometries to make a comparison between the free and the complexed systems;[14] therefore in this study, the same method was employed. The stationary points were characterized by second derivative calculations. Zero-point vibrational energy (ZPE) correction for relative energies and counterpoise correction[48,49] for complexation energies were calculated using the same level of theory. All calculated reaction pathways were justified by intrinsic reaction coordinate (IRC) calculations at the B3LYP/6-31G* level. To determine atomic charges in the studied molecules, NPA calculations[46] were carried out at the B3LYP/aug-cc-pVTZ level. Wiberg bond indices[47] are obtained at the same level of the theory. The OVGF[67] method was employed for the prediction of ionization energies with the cc-pVTZ basis set. In our earlier study, the mean absolute deviation (MAD) of this method for free phosphines and their borane complexes was found to be 0.30 eV, which is similar to the present investigation (0.26 eV).[14] For different system, in a recent paper, the MAD was found to be between 0.09 and 0.21 eV.[76] The influence of the diffuse function was studied for some phosphine-boranes (Table S7−S8 in the Supporting Information), and only a weak and almost constant effect was obtained; therefore it was concluded that, for the assignment, the cc-pVTZ basis set is sufficient. HF/aug-cc-pVTZ molecular orbitals were calculated to support the assignment of the ionization bands. All calculations were carried out using the Gaussian 03 program package.[77]

Phosphirane-Borane (10).[78] In a Schlenk flask under nitrogen and cooled at −60 °C were introduced under stirring the phosphirane (60 mg, 1 mmol), diborane (56 mg, 2 mmol), and dichloromethane (5 mL). The mixture was allowed to warm to room temperature, stirred for 20 min, and then distilled in a vacuum line equipped with a trap immersed in a bath at −70 °C. The phosphirane-borane complex was selectively condensed in vacuo in this trap. The complex is kinetically unstable (half-life $\tau_{1/2}$ (3% of **10** in CD_2Cl_2): 1 h). ^{1}H NMR (CD_2Cl_2): δ 0.88 (q, 3H, $^{1}J_{BH}$ = 103 Hz, BH_3); 1.19 (m, 2H, 1 H of each CH_2); 1.53 (m, 2H, 1 H of each CH_2); 2.50 (d, 2H, $^{1}J_{PH}$ = 384.6 Hz, PH_2). ^{13}C NMR ($CDCl_3$): δ 0.20 (t, $^{1}J_{CH}$ = 165.7 Hz, $^{1}J_{CP}$ = 7.3 Hz (d), $(CH_2)_2$). ^{31}P NMR (CD_2Cl_2): δ − 194.3 ($^{1}J_{PB}$ = 22 Hz (q)). ^{11}B NMR (CD_2Cl_2): δ −39.4 ($^{1}J_{BP}$ = 22 Hz (d)). Attempts to record the mass spectrum of **10** were unsuccessful and only led to that of the free phosphine.

Cyclopropylmethylphosphine-Borane (12). In a Schlenk flask under nitrogen, a borane-tetrahydrofurane or borane-dimethylsulfide complex solution (5 mL of 1 M sol., 5 mmol) was slowly added to the previously frozen (−196 °C) solution of cyclopropylmethylphosphine (0.40 g, 4.5 mmol) in dry dichloromethane (5 mL). The reaction mixture was allowed to warm to room temperature and was stirred for 5 min at this temperature. The mixture was then distilled off in a vacuum line, and the cyclopropylmethylphosphine-borane **12** was selectively condensed in a trap cooled at −40 °C (0.1 mmHg). The compound is stable at room temperature under nitrogen.

Yield: 96% (based on the free phosphine). ^{1}H NMR ($CDCl_3$): δ 0.14 (m, 2H, CH_2 cycle); 0.50 (qt, 3H, $^{1}J_{BH}$ = 96.6 Hz, $^{3}J_{HH}$ = 6.1 Hz, BH_3); 0.56 (m, 2H, CH_2 cycle); 0.87 (m, 1H, CH); 1.70 (m, 2H, CH_2P); 4.45 (dq, 2H, $^{2}J_{HP}$ = 360.9 Hz, $^{3}J_{HH}$ = 7.7 Hz, PH_2). ^{13}C NMR ($CDCl_3$): δ 5.6 (td, $^{1}J_{CH}$ = 157.4 Hz, $^{3}J_{CP}$ = 7.3 Hz, CH_2 cycle); 8.0 (dd, $^{1}J_{CH}$ = 156.9 Hz, $^{2}J_{CP}$ = 5.8 Hz, CH); 22.0 (t, $^{1}J_{CH}$ = 133.5 Hz, $^{1}J_{CP}$ = 35.6 Hz, CH_2P). ^{31}P NMR ($CDCl_3$): δ −52.5 (q, $^{1}J_{PB}$ = 63 Hz). ^{11}B NMR ($CDCl_3$): δ −42.3 (d, $^{1}J_{PB}$ = 63 Hz). IR (ν, cm^{-1}, film, 293 K): 1029 (m), 1455 (m), 2350 (m, ν_{BH}), 2401 (s, ν_{PH}), 2936 (w), 2960 (m). HRMS calcd for $C_4H_{11}BP^+$. $[M - H]^+$: 101.069. Found: 101.069.

Cyclopropylmethylamine-borane (9). In a flask under nitrogen, a borane-tetrahydrofurane or borane-dimethylsulfide complex solution (5 mL of 1 M sol., 5 mmol) was slowly added to a cooled (−78 °C) solution of cyclopropylmethylamine (5 mmol) in dry dichloromethane (5 mL). The reaction mixture was allowed to warm to room temperature and was stirred for 15 min at this temperature. The solvent and low boiling compounds were removed in vacuo at room temperature, and the crude cyclopropylmethylamine-borane was used without further purification. Yield: 97%. Compound **9** is stable for months at room temperature under nitrogen. ^{1}H NMR ($CDCl_3$): δ 0.24 (m, 2H, $^{3}J_{HH}$ = 4.8 Hz, 1 H of each CH_2 cycle); 0.58 (m, $^{3}J_{HH}$ = 5.7 Hz, 1 H of each CH_2 cycle); 1.08 (m, 1H, $^{3}J_{HH}$ = 7.5 Hz, $^{3}J_{HH}$ = 5.7 Hz, $^{3}J_{HH}$ = 4.8 Hz, CH); 1.46 (m, 3H, $^{1}J_{BH}$ = 92.7 Hz, BH_3); 2.61 (m, 2H, AB system, $^{3}J_{HH}$ = 7.5 Hz, CH_2); 3.94 (s brd, 2H, NH_2). ^{13}C NMR ($CDCl_3$): δ 3.8 (t, $^{1}J_{CH}$ = 160.6 Hz, CH_2 cycle); 10.5 (d, $^{1}J_{CH}$ = 160.6 Hz, CH); 53.8 (t, $^{1}J_{CH}$ = 140.9 Hz, CH_2). ^{11}B NMR ($CDCl_3$): δ −19.5. ^{15}N NMR ($CDCl_3$): δ −345.2 ppm. HRMS calcd for $C_4H_{11}BN^+$. $[M - H]^+$: 84.0988. Found: 84.0984. IR (ν, cm^{-1}, film, 298 K): 3262 (m), 3161 (m), 3085 (m), 2954 (s), 2379 (s, ν_{BH}), 1457 (s), 1377 (s), 1270 (m), 1027 (s), 722 (m).

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Supporting Information Available: Preparation of phosphirane, cyclopropylphosphine, and cyclopropylamine-borane; flash vacuum pyrolysis of methylamine-borane and aziridine-borane (**7**); ^{15}N and ^{31}P NMR chemical shifts (Table S1); NPA charges of heavy atoms in the investigated structures (Table S2); calculated Wiberg indices (Table S3); calculated P−C rotational barriers (Table S4); calculated PAs (Table S5); calculated IEs for cyclopropylmethyl derivatives (Table S6); OVGF calculations for some phosphine-boranes with different basis sets (Tables S7 and S8). Variation of (a) relative energy, (b) X−C bond length (X = N, P in Å), (c) NPA charges, and (d) Wiberg bond index of the dative bond with the X−B distance for the cyclopropyl derivatives (Figures S1 and S2). Photoelectron spectra (S3−S11); *x*,*y*,*z* coordinates of all the studied molecules and their total energies (in a.u.). This material is available free of charge via the Internet at http://pubs.acs.org.