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Contrasting Stabilities of Classical and Bridged Pyramidal Si_3H_3X Molecules (X = BH^-, CH, N, NH^+, NO, SiH, P, PH^+, and PO)

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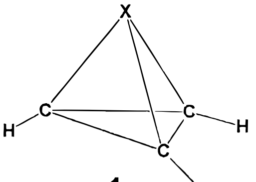
Abstract: Trigonal-pyramidal Si_3H_3X systems have been studied at HF/6-31G*, MP2(FC)/6-31G*, and Becke3LYP/6-31G* levels. The classical trigonal-pyramidal structure (**5**) is a higher order stationary point for X = BH^-, CH, NO, SiH, P, PH^+, and PO, whereas it is a minima for X = N and NH^+, at the MP2(FC)/6-31G* level. An alternative pyramidal structure (**6**, C_{3v}) with three SiHSi 3c−2e bonds is minima, lower in energy than **5** by 47.7 (X = BH^-), 39.1 (X = CH), 31.7 (X = N), 25.0 (X = NH^+), 20.6 (X = SiH), 20.7 (X = P), 16.1 (X = PH^+), and 18.2 (X = PO) kcal/mol. Isolobal analogy connects **6** with various triply hydrogen bridged pyramidal structures in organometallics.

Introduction

There is a well-developed chemistry based on the smallest carbocyclic π-ligand η^3-$C_3H_3^+$.[1−3] Derivatives of **1** with main group and transition metal fragments (e.g. C_4R_4 (T_d) and C_3R_3-$Co(CO)_3$) are available in the literature.[1,2] An all-boron analog of cyclopropenyl cation $B_3H_6^+$ is calculated to be a stable species.[4] Theoretical studies on pyramidal structures (**2**, C_{3v}) based on the $B_3H_6^+$ ligand have indicated them to be stable species on their potential energy surfaces.[5] There are no reports on trigonal-pyramidal structures based on $Si_3H_3^+$, the trisilacyclopropenyl cation, except for the studies on tetrasilatetrahedranes.[6] The cation $Si_3H_3^+$, found in the gas phase, is calculated to be more stable as trisilacyclopropenium ion (**3**, D_{3h}) with 2π electron delocalization.[7,8]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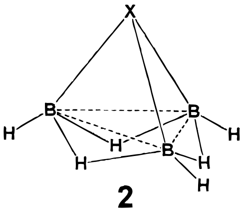
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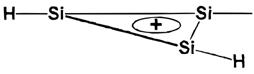
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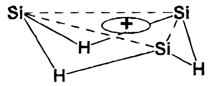
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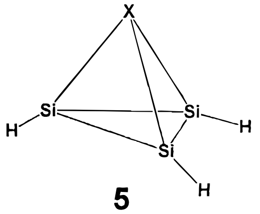
An alternative triply hydrogen bridged structure (**4**, C_{3v}) is also found to be a minimum for $Si_3H_3^+$, but it is 42.0 kcal/mol higher in energy than **3** at the MP2(FC)/6-31G* level.[8] There are reasons to believe that the Si_3H_3 ligand should be a more appropriate π-ligand than C_3H_3 on the basis of ring size. C_5H_5 is an ideal η^5 ligand in chemistry because of the ideal claw size of the π framework of the C_5H_5 ring for a range of caps from main group and transition metal fragments.[9] The cyclopropenyl cation provides a much smaller span of orbitals. This is compensated to an extent by the large out-of-plane bending of the ring substituents away from the capping group observed in $C_3R_3^+$ π-complexes.[2] The longer SiSi bond length in $Si_3H_3^+$ should reduce this orbital mismatch considerably. The bridged structure, **4**, has an even longer SiSi distance. This brings in the interesting question of the relative stabilities of the classical structure **5** and the bridging structure **6**. Structure **5** can be considered as a homolog of **1**, whereas structure **6** can be derived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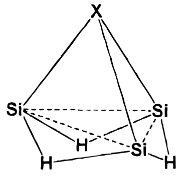
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	a	b	c	d	e	f	g	h	i
X	BH^-	CH	N	NH^+	NO	SiH	P	PH^+	PO

[⊗] Abstract published in *Advance ACS Abstracts*, April 1, 1996.

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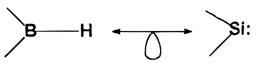
Table 1. The Total Energies (au) and Zero-Point Energies (ZPE, kcal/mol) of Structures **5** and **6** for Various Caps at HF/6-31G*, MP2(FC)/6-31G*, and Becke3LYP/6-31G* Levels

	HF/6-31G*				MP2(FC)/6-31G*				Becke3LYP/6-31G*			
	5		**6**		**5**		**6**		**5**		**6**	
cap	total energy	ZPE	total energy	ZPE	total energy	ZPE	total energy	ZPE	total energy	ZPE	total energy	ZPE
BH^-	−893.58893	22.8	−893.65458	24.1	−893.93912	21.2	−894.01933	24.0	−895.62773	20.7	−895.70808	22.8
CH	−906.75329	26.3	−906.82467	27.4	−907.14051	24.3	−907.20677	26.9	−908.83666	23.3	−908.91038	25.8
N	−922.78286	19.9	−922.84882	19.2	−923.21175	18.1	−923.26361	19.0	−924.91116	17.5	−924.977621	18.0
NH^+	−923.17848	28.0	−923.22223	28.6	−923.58258	25.7	−923.62580	27.9	−925.29129	25.1	−925.34796	26.9
NO	−997.51493	20.4	−997.58465	21.0			−998.17220	20.5	−1000.04626	19.1	−1000.07783	18.6
SiH	−1157.82123	23.0	−1157.84049	22.7	−1158.14842	20.5	−1158.18403	22.3	−1160.23571	20.3	−1160.28032	21.2
P	−1209.10052	18.8	−1209.12337	18.5	−1209.45535	16.8	−1209.49043	18.2	−1211.54589	16.5	−1211.59051	17.2
PH^+	−1209.41746	23.5	−1209.43578	23.5	−1209.75711	21.5	−1209.78535	23.2	−1211.85828	20.8	−1211.90181	22.0
PO	−1283.89647	20.7	−1283.92219	20.4	−1284.43948	18.1	−1284.47116	19.9	−1286.71660	18.0	−1286.76027	18.9

from **2** by replacing the BH group by Si using the isolobal analogy between BH and Si (**7**).[10]

The triply hydrogen bridged trigonal-pyramidal structures with metallacycles are known in the literature. For example, **6b** (C_{3v}) can be related to (μ-H)$_3$Fe$_3$(CO)$_9$(μ_3-CMe) (**8**) through isolobal analogy.[11] We present here the results of a theoretical study on a series of pyramidal $Si_3H_3(X)$ compounds with BH^- (**5a**, **6a**), CH (**5b**, **6b**), N (**5c**, **6c**), NH^+ (**5d**, **6d**), NO (**5e**, **6e**), SiH (**5f**, **6f**), P (**5g**, **6g**), PH^+ (**5h**, **6h**), and PO (**5i**, **6i**) as capping groups (X) which support our contention that there is more flexibility for **4** in ring-cap bonding. H-bridged structures **6** are calculated to be more favorable than the classical, **5**, in all cases.



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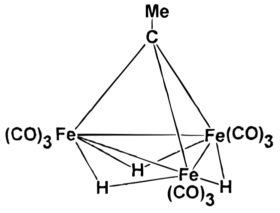

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Method of Calculation

Geometries **5a**−**5i** and **6a**−**6i** were optimized under C_{3v} symmetry (except **5f**, which has T_d symmetry) at the HF/6-31G* level.[12,13] The effect of electron correlation is obtained by further optimizing the structures at the MP2(FC)/6-31G* level.[14] The density functional calculations at the Becke3LYP/6-31G* level were also done for comparison of relative energies.[15] The nature of the stationary points was determined by analytical evaluation of the harmonic force constants and vibrational frequencies.[16] All the calculations were carried out using the GAUSSIAN92 program package.[17] The total and relative energies obtained from these calculations are given in Tables 1 and 2. Important geometrical parameters are listed in Tables 3 and 4. The MP2(FC)/6-31G* results are used in the discussion unless otherwise specified. These are qualitatively similar to those obtained at other levels.

Table 2. Relative Energies[a] (kcal/mol) of Structures **5** and **6** at HF/6-31G*, MP2(FC)/6-31G*, and Becke3LYP/6-31G* Levels (Values in Parentheses Are the Number of Imaginary Frequencies)

	HF/6-31G*		MP2(FC)/6-31G*		Becke3LYP/6-31G*	
cap	**5**	**6**	**5**	**6**	**5**	**6**
BH^-	40.0(2)	0.0(0)	47.7(2)	0.0(0)	48.6(2)	0.0(0)
CH	43.8(0)	0.0(0)	39.1(2)	0.0(0)	44.0(2)	0.0(0)
N	42.0(0)	0.0(0)	31.7(0)	0.0(0)	41.3(0)	0.0(0)
NH^+	26.9(0)	0.0(0)	25.0(0)	0.0(0)	34.0(0)	0.0(0)
NO	43.2(2)	0.0(0)	67.3(0)[b]	0.0(0)	20.3(2)	0.0(0)
SiH	12.4(0)	0.0(0)	20.6(2)	0.0(0)	27.2(0)	0.0(0)
P	14.6(0)	0.0(0)	20.7(2)	0.0(0)	27.4(0)	0.0(0)
PH^+	11.5(0)	0.0(0)	16.1(2)	0.0(0)	26.3(2)	0.0(0)
PO	16.4(0)	0.0(0)	18.2(2)	0.0(0)	26.6(0)	0.0(0)

[a] The relative energies are calculated after scaling the zero-point energy by 0.89 for HF/6-31G* and Becke3LYP/6-31G* levels and by 0.95 for the MP2(FC)/6-31G* level (ref 12). [b] The structure corresponds to 9 (ref 37).

Results and Discussion

The H-bridged structure **6** is calculated to be lower in energy than the classical structure **5** at all three levels for all ring-cap combinations (Table 1). The stability of **6** over **5** ranges from 47.7 kcal/mol for X = BH^- to 16.1 kcal/mol for X = PH^+. Similar trends are seen at the HF and Becke3LYP levels (Table 2). Structure **6** is found to be a minimum with all the caps. However, this is not true for the classical structure **5**, which is a higher order saddle point for BH^-, CH, SiH, P, PH^+, and PO caps. Structure **5** is calculated to be a minimum for NH^+ and N. The caps BH^-, CH, and PH^+ followed the same trend at the Becke3LYP level, whereas structures with SiH, P, and PO caps are shown to be minimum at this level. The classical structure with NO cap (**5e**) collapses to **9** (C_{3v}) on optimization at the MP2(FC) level. On the other hand the triply hydrogen bridged structure **6e** is a minimum. The classical structure **5f**, with SiH cap (one of the nine caps considered in the present study), is tetrasilatetrahedrane. Previous calculations on Si_4H_4 have shown that the tetrasilatetrahedrane is a local minimum at the HF/6-31G* level on the potential energy surface of Si_4H_4.[6] However, Nagase et al. predicted that two SiSi bonds in **5f** can be broken without a barrier to form a four-membered ring isomer at higher levels.[18] In the present study the tetrasilatetrahedrane is found to be a

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Table 3. Important Geometrical Parameters for Si_3H_3X (**5**) at HF/6-31G*, MP2(FC)/6-31G*, and Becke3LYP/6-31G* Levels[a]

	HF/6-31G*				MP2(FC)/6-31G*				Becke3LYP/6-31G*			
cap	X−Si	Si−Si	Si−H	θ_1[b]	X−Si	Si−Si	Si−H	θ_1[b]	X−Si	Si−Si	Si−H	θ_1[b]
BH^-	2.072	2.285	1.479	20.4	2.051	2.289	1.491	21.1	2.078	2.298	1.494	22.7
CH	1.900	2.257	1.465	−7.8	1.904	2.337	1.489	−31.7	1.908	2.430	1.504	−41.2
N	1.808	2.238	1.467	−18.0	1.861	2.286	1.486	−29.5	1.843	2.308	1.492	−30.9
NH^+	1.869	2.249	1.458	−15.5	1.886	2.298	1.477	−23.7	1.887	2.308	1.482	−25.0
NO	1.824	2.267	1.462	−18.0					1.975	2.484	1.500	−49.9
SiH	2.314	2.314	1.464	19.5	2.315	2.315	1.478	19.5	2.327	2.327	1.479	19.5
P	2.292	2.247	1.463	4.4	2.304	2.256	1.479	−2.6	2.325	2.266	1.481	−0.6
PH^+	2.266	2.301	1.457	2.9	2.265	2.318	1.475	−2.3	2.284	2.332	1.477	−2.8
PO	2.247	2.319	1.462	15.8	2.272	2.333	1.478	18.6	2.287	2.343	1.499	18.4

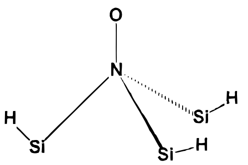
[a] Distances are in angstroms and angles are in degrees. [b] θ_1 is the angle of deviation of terminal hydrogens from the Si_3 plane; positive θ_1 indicates that the hydrogens are bent away from the cap (X).

Table 4. Important Geometrical Parameters for Si_3H_3X (6) at HF/6-31G*, MP2(FC)/6-31G*, and Becke3LYP/6-31G* Levels[a]

	HF/6-31G*				MP2(FC)/6-31G*				Becke3LYP/6-31G*			
cap	X−Si	Si−Si	Si−H	θ_2[b]	X−Si	Si−Si	Si−H	θ_2[b]	X−Si	Si−Si	Si−H	θ_2[b]
BH^-	2.008	2.618	1.714	35.2	1.988	2.558	1.715	35.1	2.006	2.614	1.731	35.5
CH	1.885	2.629	1.700	33.9	1.884	2.595	1.698	33.3	1.897	2.635	1.714	33.5
N	1.793	2.563	1.714	35.0	1.829	2.534	1.706	34.7	1.825	2.565	1.725	34.7
NH^+	1.871	2.695	1.683	31.8	1.879	2.678	1.684	30.9	1.889	2.712	1.699	30.9
NO	1.807	2.644	1.715	33.3	1.838	2.626	1.706	32.4	1.878	2.654	1.713	32.9
SiH	2.317	2.833	1.695	29.6	2.283	2.715	1.695	30.0	2.316	2.822	1.711	30.0
P	2.265	2.694	1.684	32.2	2.257	2.619	1.686	32.1	2.286	2.696	1.702	32.1
PH^+	2.276	2.926	1.697	27.5	2.245	2.842	1.695	27.2	2.283	2.923	1.712	27.3
PO	2.245	2.827	1.694	29.6	2.230	2.721	1.692	29.5	2.271	2.821	1.709	29.7

[a] Distances are in angstroms and angles are in degrees. [b] θ_2 represents the angle between the Si_3 plane and SiHSi plane.

second-order saddle point at the MP2(FC) level. The two imaginary frequencies are found to follow the path suggested by Nagase et al. to break the two SiSi bonds. However, **5f** is calculated to be a minimum at the Becke3LYP level supporting the HF level of calculations. It was also indicated that silyl substitution can stabilize **5f**.[19] The tetrasilatetrahedrane (Si_4R_4) has been synthesized with a "super silyl" group ($R = t$-Bu_3Si).[20] The C_{3v} isomer of Si_4H_4, **6f**, is calculated to be 20.6 kcal/mol (12.4 and 27.2 kcal/mol at the HF and Becke3LYP levels, respectively) more stable than the T_d arrangement, **5f**. But **6f** is 28.7 kcal/mol higher in energy than the lowest energy isomer (**10**, C_s), reported in the literature for Si_4H_4.[6e,21] The tetrahedral structure observed for Si_4R_4 experimentally points to the effect of substituents in controlling the structures; the propensity for bridging does not seem to go beyond hydrogens.



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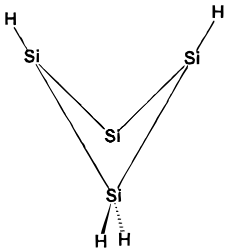

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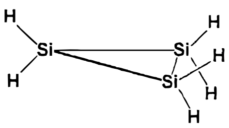
The SiSi distances (Table 3) in the classical structure **5** are in the range of single bonds (2.332 Å in trisilacyclopropane (**11**, D_{3h}) and 2.334 Å in disilane).[22−24] The bridged structure **6** has considerably shortened SiSi distances (Table 4) compared to the triply hydrogen bridged trisilacyclopropane (**12**, C_{3v}), Si_3H_6 (3.080 Å).[23]



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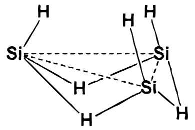

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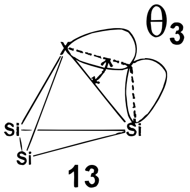

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NBO analysis shows the bonding in **5** to be classical.[25] The triply hydrogen bridged structure **6** has three each of 2c−2e XSi bonds, the SiHSi 3c−2e bond, and lone pairs on the silicon atom of the Si_3H_3 ring. The geometrical constraints in **5** force bent bonds between the cap (X) and Si_3H_3 ring (**13**). The deviation of the XSi bonds from the internuclear axis (θ_3) at X in **5** and **6** obtained from the NBO analysis is listed in Table 5. θ_3 is smaller in **6** compare to **5**. That is the XSi bond becomes more directed in **6** leading to better bonding. The NBO analysis also reveals that the lone pair on divalent Si in **6** is predominantly of s character (∼73%). This leaves maximum p-character for XSi bonds (∼86%). Since the lone pair on Si has greater s character, it looses the directionality and is in the plane of the Si_3 ring rather than in the anticipated direction, away from the cap. Thus the coplanarity of lone pairs on the Si_3 ring pushes the p_π orbital toward X, resulting in better overlap between X and the Si_3H_3 ring.[26] This type of arrangement is absent in **5**, leading to poor overlap between X and the Si_3H_3 ring. The Mulliken overlap population between X and Si increases in going from **5** to **6** for all X (0.210, 0.388 for BH^-;

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Table 5. The Bond Bending Angle (θ_3, the Deviation of Hybrid Orbital from the XSi Axis) (in deg) at X at the HF/6-31G*//MP2(FC)/6-31G* Level from NBO Analysis

cap	θ_3(**5**)	θ_3(**6**)
BH^-	29.7	22.8
CH	25.7	18.3
N	19.6	14.5
NH^+	25.5	15.3
NO		14.5
SiH	32.6	25.4
P	25.1	18.8
PH^+	32.6	23.0
PO	32.0	23.9

Table 6. Energy of the Reaction (ΔE_1) for Eq 1 and ΔE_2 for Eq 2 at the MP2(FC)/6-31G* Level

cap	ΔE_1 (kcal/mol)	ΔE_2 (kcal/mol)
BH^-	−89.7	−129.5
CH	−81.1	−120.9
N	−73.7	−113.5
NH^+	−67.1	−106.8
SiH	−62.7	−102.5
P	−62.7	−102.5
PH^+	−58.1	−97.9
PO	−60.2	−100.0

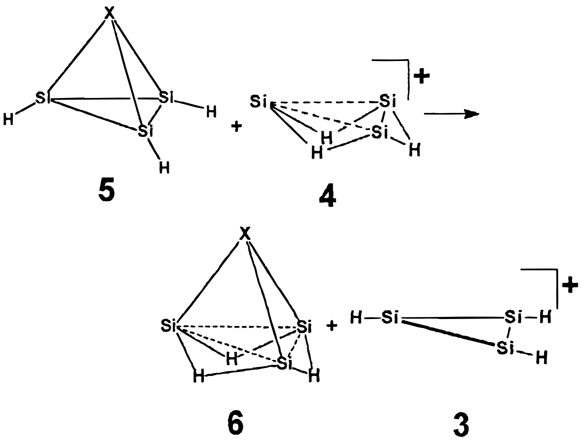
0.206, 0.309 for CH; 0.180, 0.253 for N; 0.053, 0.144 for NH^+; −0.001, 0.271 for SiH; 0.132, 0.248 for P; −0.019, 0.178 for PH^+; and 0.011, 0.240 for PO). These changes in overlap population also indicate the better bonding between X and Si_3H_3 ring in **6** compared to **5**.

The bonding in **5** and **6** can also be explained by the six interstitial electron rule for three-dimensional delocalization in pyramidal systems.[3] According to this rule, the Si_3H_3 ring provides 3π electrons and the cap, X, provides three electrons leading to a total of six electrons to fill the three bonding combinations obtained from the ring and cap orbitals. All X groups considered here are selected on the basis of this interstitial electron rule. The caps BH^-, CH, N, and NH^+ are selected from the previous theoretical calculations on carbocyclic pyramidal structures.[3] P, PH^+, and SiH are selected to see the effect of heavier analogs. The report on interaction between CO and cyclobutadiene[27] suggested the possibility of nitrosyl (NO) and phosphoryl (PO) groups as caps in the present study. The bonding with these caps (NO and PO) is due to the degenerate π-orbitals of Si_3H_3 and the degenerate π*-orbitals of NO and PO. Therefore, the N−O (**6e**: 1.396 Å) and P−O (**5i**: 1.512 Å, **6i**: 1.517 Å) distances in **5** and **6** are close to their respective single bond distances.[28] The changes in B−H, C−H, N−H, Si−H(cap), and P−O bond lengths are found to be minimal between structures **5** and **6**.[29] The negative θ_1 (bending of terminal Si−H bonds toward the cap) in **5b**, **5c**, **5d**, **5g**, and **5h** (Table 3) can be explained by the concept of the compatibility of orbitals in overlap.[3] The relatively less diffuse p_π-orbital on the cap (X) pushes the H_t toward the cap for better interaction.

Structure **6** is related to the triply hydrogen bridged isomer of Si_3H_6 (**12**).[23] Bridged structure **12** is calculated to be 84.0 kcal/mol higher in energy than the classical structure **11**. Since the three terminal hydrogens are directed toward a converging point along SiH_t axes in **12**, these hydrogens can be replaced by a 3-electron donor cap (X) (similar to the replacement of nonbonded hydrogen repulsions in [10]-annulene by a CH_2 bridge[30]) leading to structure **6**. In contrast, the classical structure of Si_3H_6 (**11**) has divergent hydrogens. The advantage in the formation of the pyramidal molecules with capping X provided by the SiH bond directions in **12** in comparison to those in **11** is reflected in the uniformly lower energy of **6**.

Similarly the "isosynaptic analogy" connects the structural patterns in silicon chemistry with organometallic chemistry.[31] Thus using this analogy, we can equate (μ-H)$_3$Fe$_3$(CO)$_9$(μ_3-CMe),[11] (μ-H)$_3$Os$_3$(CO)$_9$(μ_3-CX) (X = H, C_6H_5, Cl),[32] (μ-H)$_3$Co$_3$Cp*(μ_3-CMe),[33] and (μ-H)$_3$Os$_3$(CO)$_9$(μ_3-CBCl$_2$)[34] with **6b** and (μ-H)$_3$Os$_3$(CO)$_9$(μ_3-BCO)[35] with **6a**.

The low relative energies of **5** and **6** hide the enormous advantage of the triply bridging **4** in interacting with X^-. Even though **4** is less stable than **3**, **6** obtained by complexing **4** and X^- is more favorable than **5** (eq 1, Table 6). The strain energies involved in going from **12** to **6** and from **11** to **5** are not the same. An estimate of their difference is obtained from eq 2. The high exothermicity of this equation is also a reflection of the increased strain in **5** in relation to **6**. Thus the classical trigonal-pyramidal structure (**5**) is found to be relatively more strained compared to the triply hydrogen bridged structure **6**. The X−Si_3H_3 binding is more favorable in **6**. In fact structure **6** is more favorable than **5**, not only for Si_4H_4 but also for Ge_4H_4. The triply H-bridged Ge_4H_4 is calculated to be 57.6 kcal/mol more stable than the classical structure at the Becke3LYP/LANL1DZ level.[36] The classical tetrahedrane structure is a higher order saddle point for Ge_4H_4.



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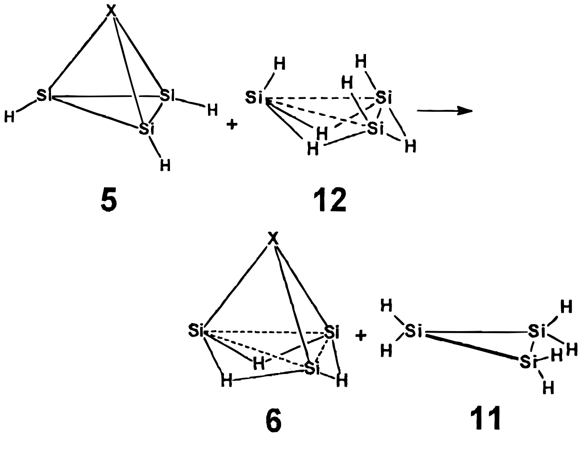

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[29] The bond lengths (Å) calculated at the MP2(FC)/6-31G* level—**5**: B−H = 1.194, C−H = 1.084, N−H = 1.021, P−H = 1.402 P−O = 1.512. **6**: B−H = 1.189, C−H = 1.081, N−H = 1.021, Si−H = 1.469, P−H = 1.394 P−O = 1.517.

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Other heavier analogs are expected to follow this trend. Therefore the pyramidal compounds (**6**) should be attractive synthetic targets.

Conclusions

Calculations at the HF/6-31G*, MP2(FC)/6-31G* and Becke3LYP/6-31G* levels show the following: The classical pyramidal structure is a second-order stationary point for all **5** except for X = N and NH^+ at the MP2(FC) level. The C_{3v} alternatives (**6**) are minima and lower in energy than **5**. Structure **6** is related to B_3H_6X through isolobal analogy and to triply hydrogen bridged pyramidal structures in organometallics through isosynaptic analogy. The isodesmic equation between X^- and $Si_3H_3^+$ has shown that ring-cap interaction in **6** is better than that in **5**. Similarly, eq 2 shows that **6** is relatively less strained than **5**.

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(37) The MP2(FC)/6-31G* energy for structure **9** is −998.16338 au and the zero-point energy is 85.5 kcal/mol.