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Cyclic Silylated Onium Ions of Group 15 Elements

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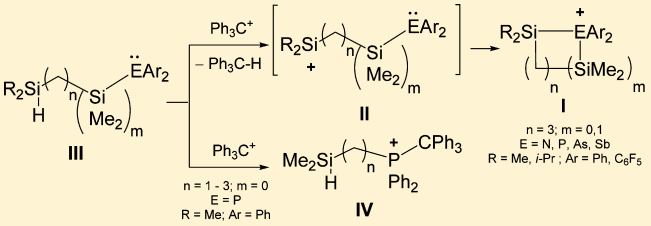
Supporting Information

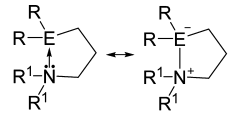
ABSTRACT: Five- and six-membered cyclic silylated onium ions of group 15 elements **I** were synthesized by intramolecular cyclization of transient silylium ions **II**. Silylium ions **II** were prepared by the hydride transfer reaction from silanes **III** using trityl cation as hydride acceptor. It was found that smaller ring systems could not be obtained by this approach. In these cases tritylphosphonium ions **IV** were isolated instead. Cations **I** and **IV** were isolated in the form of their tetrakispentafluorphenyl borates and characterized by multinuclear NMR spectroscopy and, in two cases, by X-ray diffraction analysis. Cyclic onium ions **I** showed no reactivity similar to that of isoelectronic intramolecular borane/phosphane frustrated Lewis pairs (FLPs). The results of DFT computations at the M05-2X level suggest that the strength of the newly formed Si−E linkage is the major reason for inertness of **I**$[B(C_6F_5)_4]$ versus molecular hydrogen.



INTRODUCTION

Silyl Lewis acids are potent silylating reagents.[1] Particularly powerful in this respect are silylium-like species such as perfluorinated tetraarylborates of silylated arenium ions ($[R_3Si(arene)]^+$), bissilylated hydronium ions ($[R_3Si{-}H{-}SiR_3]^+$), or their intramolecular variants.[2] This was recently demonstrated by the synthesis and structural characterization of persilylated haloniums,[3] pseudohaloniums,[4] chalconiums,[5,6] pseudochalconiums,[7] and pnictoniums[8] using these highly electrophilic species. The most recent landmark in this series of achievements is the report on the isolation of a tetrasilylammonium borate by the group of Schulz.[9] In the past, ammonium ion formation in an intramolecular fashion has been utilized to stabilize Lewis-acidic triorganoboron, -aluminum, -gallium, and -indium compounds, such as **1**.[10,11] In these experimental studies a qualitative relationship between the reactivity of the intramolecular stabilized species and the ring size and its flexibility had been drawn.[11] An extension of this work to silicon-based Lewis acids was demonstrated recently by Oestreich and co-workers.[12] They used remote sulfur (as in cation **2**) or nitrogen substituents (**3**) to stabilize silylium species by onium ion formation. Interestingly, these studies revealed a clear dependence of the reactivity of these cations on the donor atom. While the sulfur stabilized cation **2** showed significant catalytic activity in Diels−Alder reactions, iminium ion **3** was found to be inactive under similar conditions.[12]

A particularly interesting example of an intramolecular stabilized Lewis acid is the zwitterionic heterocyclic compound **4**.[13] In solution, it is in equilibrium with its acyclic isomer **5** and



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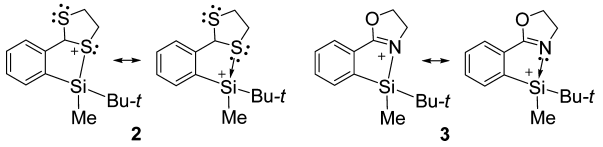
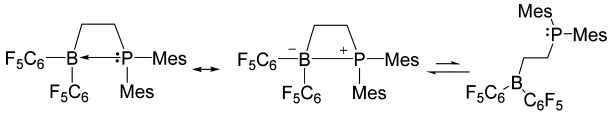


2 3

the isomer pair **4**/**5** represents the prime example for an intramolecular frustrated Lewis pair (FLP).[14,15] Compound **5** is able to split dihydrogen at mild conditions,[13] and it acts as a catalyst for hydrogenation of polar double bonds.[16]



4 5

On the basis of our recent results on dihydrogen activation by intermolecular silylium/phosphane Lewis pairs[17,18] we envisaged the use of silyl Lewis acids (**6**) which are stabilized

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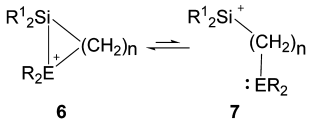
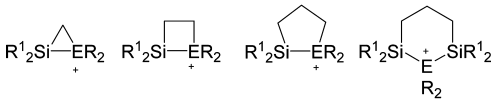
by onium ion formation as possible candidates for intramolecular FLPs. The tendency of onium ions **6** to form the noncyclic isomers **7**, which are thought to be the active species in FLP chemistry, is clearly a function of the strength of the element silicon bond. The strength of this linkage is controlled by the nature of the element E, by the ring size, and by the steric and electronic properties of the substituents R, R^1 at the two heteroatoms. Therefore, we studied the synthesis of representative examples of cyclic silylated onium ions of group 15 elements **8**–**11** and their possible use in bond activation reactions.



6 **7**

E = N, P, As, Sb; R^1 = alkyl; R = aryl



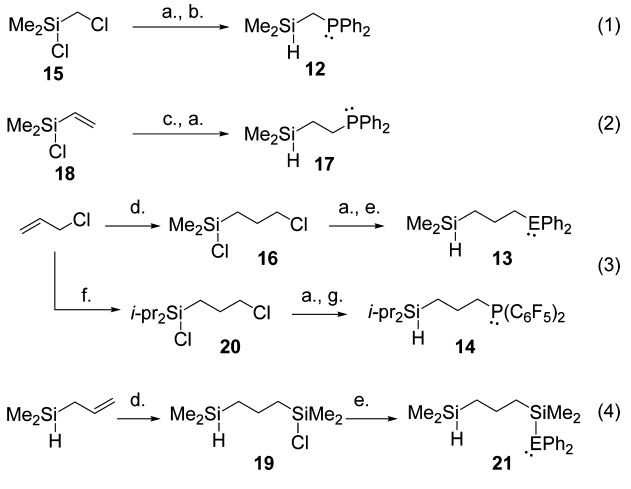
8 **9** **10** **11**

E = N, P, As, Sb; R^1 = alkyl; R = aryl

RESULTS AND DISCUSSION

The synthesis of the precursor compounds followed standard procedures and is summarized in Scheme 1.[19−21] The synthesis

Scheme 1. Syntheses of Precursor Compounds[19−21] [a]

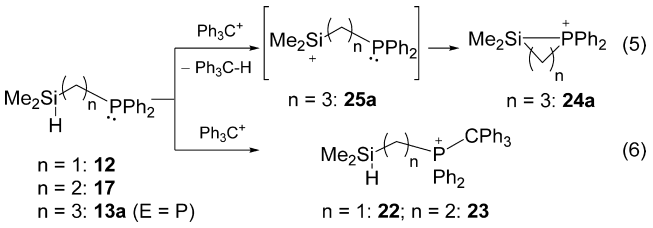


[a]Conditions: (a) $LiAlH_4$, Et_2O; (b) $LiPPh_2$, THF; (c) $HPPh_2$, $h\nu$, neat; Et_2O; (d) Me_2SiHCl, $[H_2PtCl_6]$, neat; (e) $MEPh_2$, THF, for E = P, As, Sb: M = Li; E = N: M = K; (f) $i\text{-}pr_2SiHCl$, $[H_2PtCl_6]$; (g) Mg, $BrP(C_6F_5)_2$, THF.

of silylalkyl phosphanes **12**, **13**, and **14** was achieved by conversion of the silyl chlorides **15** and **16** into the corresponding silanes followed by simple salt metathesis (overall yields 31% (**12**), 10% (**13a**, E = P), 13% (**13b**, E = As)).[19,20] For the buildup of the silylethyl derivative **17** a photohydrophosphanylation[20] of vinylchlorosilane **18** followed by a reduction step was applied (overall yield 32%). The propylsilyl compounds **16**, **19**, and **20** were synthesized according to a standard hydrosilylation protocol.[21] Salt metathesis between metalated diphenylpnictogenes and silyl chloride was also the final step for the synthesis of the silylpnictogen compounds **21** (overall yields 45% (**21a**, E = N), 47% (**21b**, E= P), 42% (**21c**, E = As), 33% (**21d**, E = Sb)).

The reaction of silanes **12**, **13**, **17**, and **21** with trityl tetrakispentafluorophenylborate $[Ph_3C][B(C_6F_5)_4]$ was expected to deliver the corresponding silylium ions as short-living intermediates according to the standard hydride transfer protocol.[2,22] The intermediate silylium ions would then undergo consecutive ring closure reactions to give cyclic silylated onium ions of different ring size (see eq 5, Scheme 2).

Scheme 2. Possible Reactions of Diphenyl(silylalkyl) Phosphanes, 12, 13, and 17 with Trityl Cation[a]



[a]The $[B(C_6F_5)_4]^-$ anion is omitted.

In contrast to the expectation in the case of the reaction of silylmethyl- and silylethylphosphanes **12** and **17** with trityl cation in benzene at room temperature we observed no formation of triphenylmethane. Instead, the phosphonium borates **22**$[B(C_6F_5)_4]$ and **23**$[B(C_6F_5)_4]$ were obtained by addition of trityl cation to the phosphanyl group (Scheme 2, eq 6). Notably, even after prolonged heating of the reaction mixture no formation of triphenyl methane was observed. The NMR spectroscopic results indicated the formation of phosphonium ions **22** and **23** (see Table 1). ^1H NMR resonances in the typical region for SiH hydrogen atoms with clearly visible SiH satellites and almost no change of the position of the ^{29}Si NMR signals upon ionization showed the presence of an intact $SiMe_2H$ functionality. Evidence for the quarternization of the phosphorus atom was provided by the significant low-field shift of the ^{31}P NMR resonance to a ^{31}P NMR chemical shift region that is characteristic for tetraalkylphosphonium ions.[23] The most prominent NMR feature for the newly formed C−P linkage is the duplet signal detected for the quarternary carbon atom of the trityl group in the ^{13}C NMR spectra of compounds **22**$[B(C_6F_5)_4]$ and **23**$[B(C_6F_5)_4]$ (see Table 1). Similar NMR spectroscopic data were reported previously for a series of tritylphosphonium borates.[24] In contrast, reaction of $[Ph_3C][B(C_6F_5)_4]$ with the silylpropyl phosphane **13a** (E = P) in benzene took the expected course (Scheme 2, eq 5). In this case, the formation of triphenyl methane accompanied by the disappearance of the Si−H resonance in the ^1H NMR spectrum demonstrated the successful hydride transfer reaction. In addition, the low-field shift of the ^{29}Si signal and the significant splitting due to coupling with the ^{31}P nuclei of this signal suggested the formation of the cyclic phosphonium ion **24a** via the acylic silyl cation **25a** (Scheme 2, Table 1).

An assessment of the energies of the two competing reactions shown in Scheme 2 (eqs 5 and 6) at the density functional M05-2X/6-31G(d) level of theory reveals some important insights.[25,26] The formation of the trityl cation/phosphane Lewis acid base complex according to eq 6 is for all

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Table 1. Pertinent NMR Parameters of Cations 22–24a ($[B(C_6F_5)_4]^-$ Salts in Benzene-d_6)

cation	n^a	δ^1H (SiH); ($^1J_{SiH}$ [Hz])	δ^{29}Si ($^mJ_{SiP}$ [Hz])	$\Delta\delta^{29}$Si^b (ΔJ_{SiP} [Hz])	δ^{31}P	$\Delta\delta^{31}$P^b	δ^{13}C(CPh$_3$) ($^1J_{CP}$ [Hz])
22	1	3.55 (205)	−12.6 (9, m = 2)	−2.8 (−8)	31.6	57.5	67.3 (39)
23	2	3.85 (191)	−14.8 (24, m = 3)	−3.2 (3)	38.3	48.3	67.2 (36)
24a	3		23.9 (37, m = 1)	37.9 (n.d.)^c	−6.2	10.6	

^{a}Number of methylene groups, see Scheme 2. ^{b}Calculated as the difference between the NMR parameter of the cation and the precursor compound. $^c J_{SiP}$ not detected in compound **13a** (E = P).

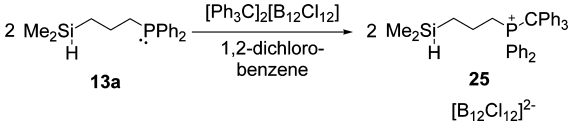
three tested phosphanes exothermic by a nearly constant value of 142–152 kJ mol^{-1} (Table 2), which corresponds roughly to the strength of the newly formed C–P bond. On the other hand, the reaction energy for the hydride transfer reaction with subsequent formation of cyclic onium ions (eq 5) strongly depends on their ring size. The increasing ring strain generated by the formation of four- and three-membered cyclic ions results in energies of reaction that are significantly smaller than those calculated for the formation of the corresponding acyclic phosphonium ions **22** and **23**. Only for the formation of the five-membered cyclic phosphonium ion **24a** is a significantly larger thermodynamic driving force predicted by the calculation (Table 2).

Table 2. Calculated DFT Reaction Energies ΔE for Possible Reactions of Phosphanes 12, 13a, and 17 with Trityl Cation (Reactions 5 and 6 (Scheme 2), in kJ mol^{-1}, at M05-2X/6-31G(d))

n	compound	eq 5	eq 6
1	**12**	−37	−149
2	**17**	−118	−152
3	**13a**	−187	−142

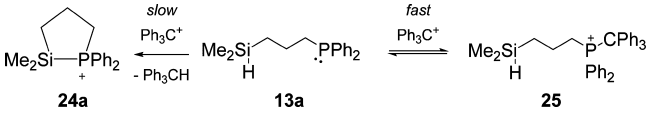
Despite this clear thermodynamic preference of formation of the cyclic onium ion **24a**, Lewis acid base complex formation is also an important competitive reaction channel for the reaction of silane **13a** with trityl cation. This became evident from the following crystallization experiment. When silane **13a** was reacted with 0.5 equiv of trityl *closo*-borate $[Ph_3C]_2[B_{12}Cl_{12}]$[27] in *o*-dichlorobenzene a colorless precipitate was formed immediately. X-ray diffraction (XRD) analysis of suitable crystals revealed that the precipitate consists of the dichlorobenzene solvate of the phosphonium *closo*-borate $\mathbf{25}_2[B_{12}Cl_{12}]$ (Scheme 3).

Scheme 3. Formation of Trityl Phosphonium Ion 25 from Silane 13a



On the basis of these experimental results the following mechanistic scenario appears to be plausible (Scheme 4). Alkylation of phosphane **13a** to give of trityl phosphonium ion **25** is fast when compared to the hydride transfer reaction that yields the cyclic silyl phosphonium ion **24a**. The trityl adduct formation is however reversible when $[Ph_3C][B(C_6F_5)_4]$ is applied. Therefore, the thermodynamically more favored cation **24a** is the final product. Due to the low solubility of *closo*-borate $\mathbf{25}_2[B_{12}Cl_{12}]$ the trityl phosphonium ion formation is practically irreversible and the hydride transfer reaction is efficiently prevented. This mechanistic proposal should be valid also for other cases where the hydrogen transfer reaction with trityl cations competes with onium ion formation and might explain the observed slow conversion of silanes to silyl cations in the presence of n-donor substituents.[12]

Scheme 4. Competitive Formation of Cyclic Silyl Phosphonium, 24a, and Trityl Phosphonium, 25, Ions by Reaction of Silaalkylphosphane 13a with Trityl Cation



Compound $\mathbf{25}_2[B_{12}Cl_{12}]$ crystallizes as *o*-dichlorobenzene solvate in the centrosymmetric space group $P2_1/n$ (see Figure 1a). The closest contact between cation and *closo*-borate dianion was detected between one methyl group of the dimethylsilyl unit and a chlorine atom (d(Cl···C) = 362 pm).

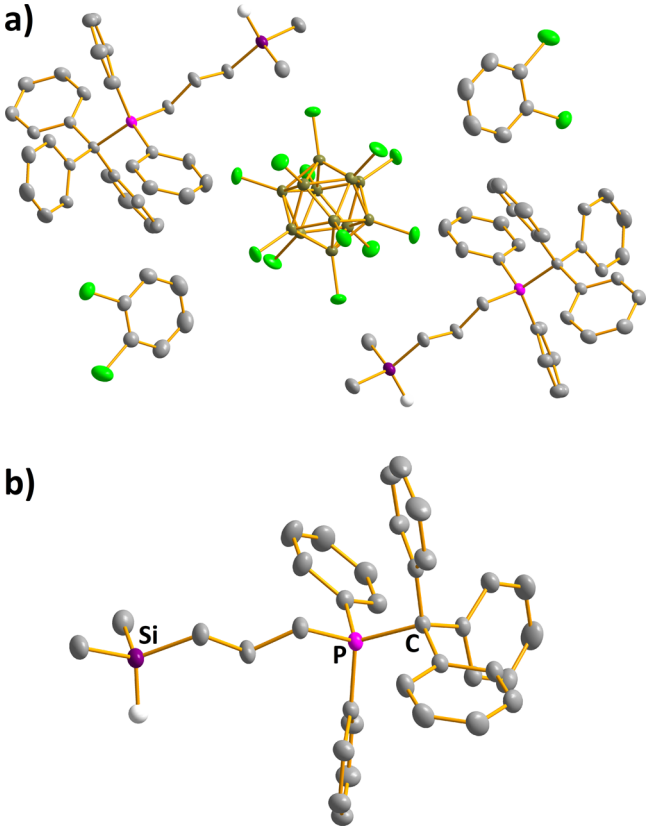


Figure 1. (a) Structure of $[\mathbf{25}]_2[B_{12}Cl_{12}]$ (1,2-$Cl_2C_6H_4$) in the crystal. (b) Molecular structure of phosphonium ion **25** as obtained by single-crystal XRD analysis. Selected bond length P–C 192.76(9) pm (ellipsoids drawn at 75% probability level; H atoms, except (Si)–H, omitted for clarity. Color code: gray = C, white = H, bronze = B, green = Cl, purple = P, pink = Si).

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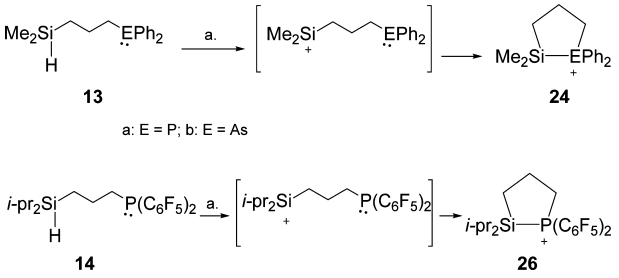
The most remarkable feature of the molecular structure of phosphonium ion **25** (Figure 1b) is a very long C−P bond (d(C−P) = 192.7 pm). It is slightly longer than the P−C bond in tetra-*tert*-butyl phosphonium tetrafluoroborate (d(C−P) = 192.5 pm)[29] and significantly longer than the C−P bond determined for the trityl phosphonium borate $[Ph_3C{-}PMe_3][B(C_6F_5)_4]$ (d(C−P) = 188.7 pm).[24]

The formation of cyclic onium ions is also observed in the case of the reaction of the arsapropyl-substituted silane **13b** and the di-*iso*-isopropylsilane **14** with $[Ph_3C][B(C_6F_5)_4]$ (Scheme 5). This is shown by the disappearance of the Si−H resonance

Scheme 5. Formation of Onium Ions 24 and 26[a]



[a](a) Ph_3C^+, $-Ph_3CH$; $[B(C_6F_5)_4]^-$ anion is omitted.

in the ^{1}H NMR spectra and by a significant low-field shift of the ^{29}Si NMR signal upon ionization ($\Delta\delta^{29}$Si 45.0 (**24b**), 44.2 (**26**); see Table 3). Compared to cation **24a** the $^1J_{SiP}$ coupling

Table 3. Significant NMR Parameters of Onium Ions 24, 26, and 27

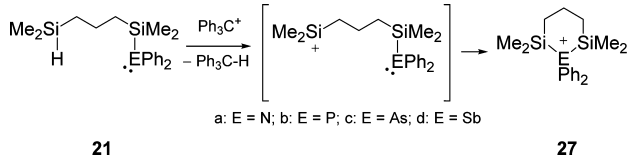
ion	E	δ^{29}Si[a] ($^1J_{SiP}$ [Hz])	$\Delta\delta^{29}$Si[b]	δE[a]	$\Delta\delta E$[b]
24a	P	23.9 (37)	37.9	−6.2	−9.4
24b	As	30.9	45.0		
26	P	50.1 (18)	44.2	−26.9	20.1
27a	N	44.0	38.4	79	−6.5
27b	P	8.6 (11)	6.0	−51.3	5.4
27c	As	17.7	12.0		
27d	Sb	17.5	15.3		

[a]At room temperature in C_6D_6. [b]Calculated as the difference between the NMR parameter of the cation and the precursor compound.

constant of cation **26** is decreased, which suggests a weaker donor−acceptor interaction for cation **26** (see Table 3). This assumption is further supported by the stronger deshielding that is detected for both nuclei involved in the donor−acceptor interaction in cation **26**.

On the basis of these results it is not surprising that the reaction of disilanes **21** with trityl borate $[Ph_3C][B(C_6F_5)_4]$ in benzene provides access to the complete series of cyclic disilylpnictonium ions **27** as colorless to pale yellow microcrystalline solids in high yields. The ammonium, phosphonium, and arsonium borates [**27a**−**c**]$[B(C_6F_5)_4]$ are stable in arene solution at room temperature for a period of several days. In contrast, the stibonium ion **27d** quickly decomposes into several nonidentified products during the NMR measurements at ambient temperatures. In each case, the equivalence of both $SiMe_2$ groups in ^{1}H, ^{13}C, and ^{29}Si NMR spectra and only two ^{13}C NMR signals for the propadiyl backbone indicates the symmetrical structure of the formed cation in solution. In addition, the low-field shift of the ^{29}Si NMR resonance of the Si−E group suggests the formation of the bissilylated pnictonium (see Figure 2 for the ^{29}Si and ^{31}P NMR spectra of compound **27b**$[B(C_6F_5)_4]$). Remarkably, silylation of the nitrogen atom to give cation **27a** has a shielding effect on the ^{15}N NMR chemical shift compared to the precursor silylamine ($\Delta\delta^{15}$N = −6.5).[30] Alkylation of trialkylamines results in a low-field shift for the ^{15}N NMR resonance, for example, $\Delta\delta^{15}$N = 28.6 for the Me_4N^+/Me_3N couple.[31] In the case of the phosphonium ion **27b** the deshielding of the phosphorus nuclei is only modest ($\Delta\delta^{31}$P = 5.4)[32] compared to that found for the $[(Me_3Si)_4P]^+/P(SiMe_3)_3$ pair ($\Delta\delta^{31}$P = 49.9). The $^1J_{SiP}$ coupling constant of disilylphosphonium ion **27b** is surprisingly small ($^1J_{SiP}$ = 11 Hz). It is only one-half of that detected for the precursor silylphosphane **21b** ($^1J_{SiP}$ = 22 Hz), which indicates a weakening of the Si−P linkage upon quarternization. For tetrakis(trimethylsilyl)phosphonium an even smaller $^1J_{SiP}$ coupling constant was reported ($^1J_{SiP}$ = 1.4 Hz).[8]

Scheme 6. Formation of Disilylpnictoniums 27[a]



[a]The $[B(C_6F_5)_4]^-$ anion is omitted.

Crystals suitable for XRD analysis of the borate **27b**$[B(C_6F_5)_4]$ were obtained from a hexafluorobenzene solution at 6 °C. The crystal structure of **27b**$[B(C_6F_5)_4]$ revealed well-separated anions and cations with the shortest Si···F distance well above the sum of the corresponding van der Waals radii (d(SiF) = 377.5 pm, Σ(vdWr(Si,F)) = 357 pm, see Figure

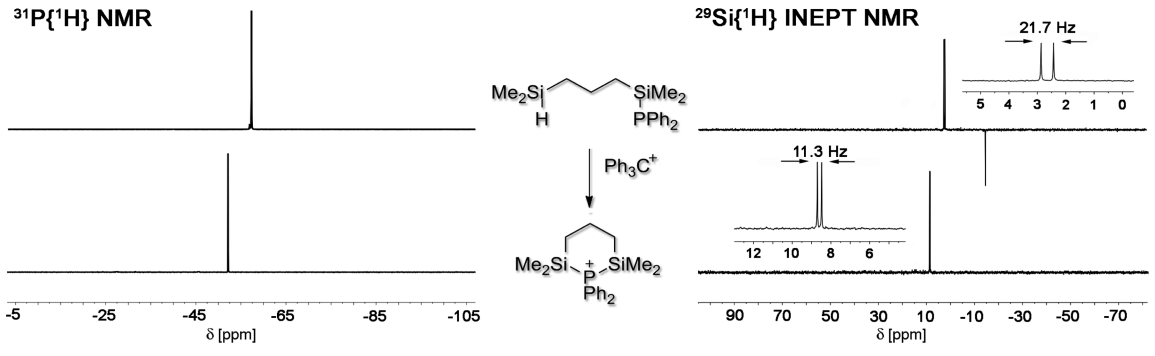


Figure 2. ^{31}P{^{1}H} NMR (left) and ^{29}Si{^{1}H} INEPT NMR (right) spectra of compounds **21b** (top) and **27b**$[B(C_6F_5)_4]$ (bottom).

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3a).[33] The molecular structure of phosphonium ion **27b** in the crystal shows a regular chair conformation for the six-membered ring (Figure 3b). The most prominent feature of the molecular structure is an almost symmetric Si−P−Si unit in which both Si−P bonds are elongated compared to neutral silylphosphanes ($r(Si^1P)$ = 230.8 pm, $r(Si^2P)$ = 231.2 (**27b**) pm vs r(SiP) = 226.5 pm reported for tricoordinated silylphosphanes).[34] Similar elongated Si−P bonds in silylated phosphonium ions were reported recently (r(SiP) = 231.0 pm).[35] The innercyclic Si^1−P−Si^2 bond angle is close to the ideal tetrahedral angle (Si^1−P−Si^2 = 105.0°). Both silicon atoms adopt a tetrahedral coordination as indicated by the sum of the three C−Si−C bond angles (Σ(C−Si^1−C) = 337° and Σ(C−Si^2−C) = 339.4°.[36]

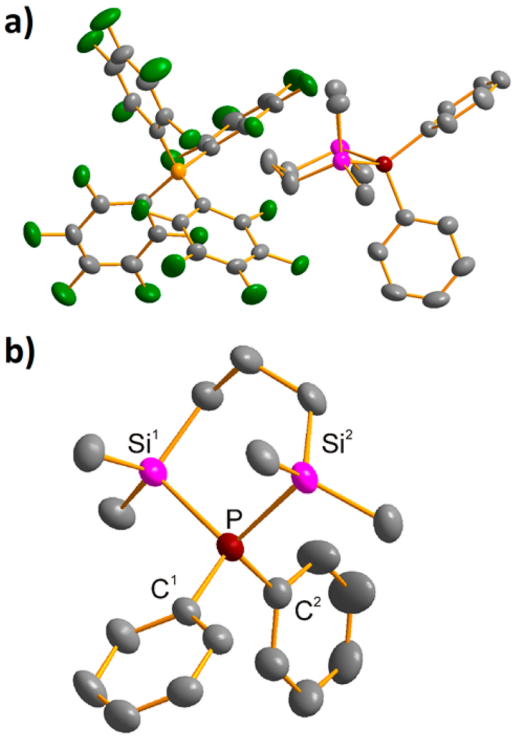

Figure 3. (a) Structure of **27b**[$B(C_6F_5)_4$] in the crystal. (b) Molecular structure of **27b** as obtained by single-crystal X-ray diffraction. Selected bond lengths [pm] and angles [degrees]: Si^1−P 230.76(11); Si^2−P 231.24(11); C^1−P 180.92(28); C^2−P 182.81(29); Si^1−P−Si^2 105.025(41); C^1−P−C^2 106.934(125); (ellipsoids drawn at 50% probability level; H atoms omitted for clarity. Color code: gray = C, yellow = B, medium green = F, magenta = P, pink = Si).

Optimization of the molecular structure of cation **27b** at the density functional M05-2X/6-311+G(d,p) level of theory reveals structural parameters which are very close to the experiment (see Table 4).[25,26] This suggests that this computational level provides reliable structural data for the investigated species. According to the results of the calculations the six-membered cyclic onium ions **27a−c** adopt regular chair conformations, only for stibonium ion **27d** a twisted half-chair conformation is predicted. The five-membered onium ions **24** take up an envelope conformation with the central methylene group twisted out of the plane of the four remaining ring atoms (Figure 4a). Finally, for cation **26** the calculations predict a half-chair conformation (Figure 4b).

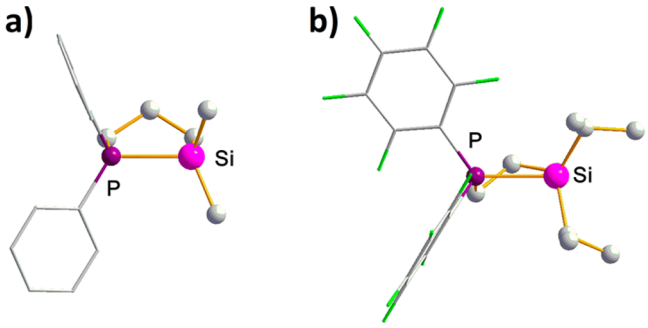

Figure 4. Calculated molecular structures (M05-2X/6-311+G(d,p)) of (a) phosphonium ion **24a** and (b) phosphonium ion **26**. Selected bond lengths [pm] **24a**, P−Si 231.9; **26**, P−Si 242.8 (H atoms omitted for clarity; aryl substituents presented in wireframe mode. Color code: light gray = C, green = F, purple = P, pink = Si).

The bonding parameters of the Si−E linkage are of particular interest in view of an application of these cyclic onium ions in bond activation reactions. Therefore, the following discussion is concentrated on the properties of the Si−E linkage. In all investigated cases, the bonds between the silicon acceptor atom and the tetracoordinated pnictogen donor atom are slightly elongated compared to standard values (see Table 4).[37] Not surprisingly, the relative elongation Δ(Si−E) is calculated to be larger for the five-membered onium ions **24** and **26** than for the six-membered cations **27**. Comparison of the bond elongation data for the disilylpnictoniums **27** reveals no clear trend for the different group 15 elements.

More informative are Si−E bond energies, E(Si−E), which are calculated to a first approximation as the energy differences

Table 4. Calculated Structural Parameters of Onium Ions 24, 26, and 27 and Their Calculated Intramolecular Stabilization Energies ΔE_{intra}[a]

cation	E	Si−E [pm]	Δ(Si−E)[b] [%]	Si−E−Si(C) [deg]	E(Si−E)[c] [kJ·mol^{-1}]
24a	P	232.9	3	95.3	−231
24b	As	241.9	2	92.9	−196
26	P	237.9	5	89.4	−156
27a	N	194.5; 195.4	4	107.6	−169
27b	P	231.1; 231.3 (230.8; 231.2)	2 (2)	105.3 (105.0)	−253
27c	As	239.8; 240.5	1	104.6	−232
27d	Sb[d]	259.9; 260.6	2	100.6	−163

[a]M05-2X/6-311+G(d,p), experimental values in parentheses. [b]Elongation of the Si−E bond compared to standard single bond lengths (SiN 187 pm, SiP 227 pm, SiAs 237 pm, SiSb 256 pm). [c]Difference of energies of the cyclic onium ions and the acyclic silylium ions at M05-2X/6-311+G(d,p). [d]The stibonium ion adopts a twisted half-chair conformation.

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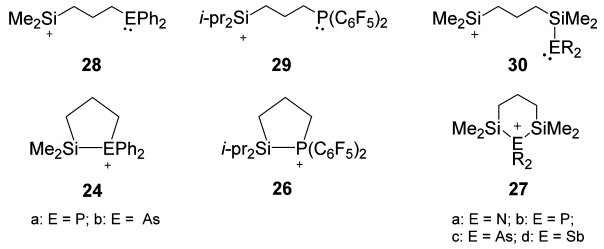
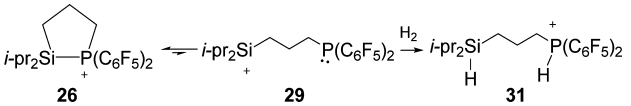
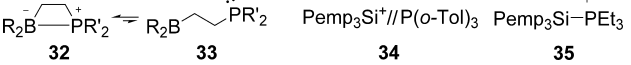


between the acyclic silylium ions **28**, **29**, and **30** and the corresponding cyclic onium ion **24**, **26**, and **27**. The calculated Si−E bond energies are substantial, ranging from −156 (for the pair **26**/**29**) to −253 kJ mol^{-1} (**27b**/**30b**) (Table 4). The smaller bond energies predicted for the five-membered silylonium ions **24a**,**b** compared to those of the six-membered disilylpnictoniums **27b**,**c** indicate the destabilization of the Si−E linkage due to increased ring strain. In the series of six-membered disilylpnictoniums **27** the largest bond energy E(Si−E) is computed for the phosphonium ion **27b**. As expected, E(Si−E) decreases substantially for the arsonium ion **27c** and for the stibonium ion **27d** (Table 4). Surprisingly weak is also the Si−N bond in ammonium ions **27a**. This is a consequence of the small size of the nitrogen atom and the resulting steric interaction between the substituents of the ammonium ion.[9] Steric and electronic factors greatly influence E(Si−E). For example, the increased steric hindrance produced by the isopropyl groups at silicon and the decreased donating ability induced by the fluorine substituents weaken the Si−P linkage in phosphonium ion **26** by 75 kJ mol^{-1} compared to the closely related cation **24a**. In fact, the Si−P bond in onium ion **26** is the weakest of all Si−E bonds in the series of cyclic onium ions which were investigated. Therefore, we choose phosphonium ion **26** as a test case for its possible use in bond activation reactions. According to the results of the calculation the hydrogenation reaction of cation **26** to give phosphonium ion **31** is thermodynamically slightly disfavored by 21 kJ mol^{-1}. Also, experimentally, no dihydrogen activation was observed. Exposition of a benzene solution of **26**[B(C$_6$F$_5$)$_4$] to a dihydrogen atmosphere (0.4 MPa, room temperature, 2 h) led to no reaction, as no NMR signal due to the phosphonium ion **31** was detected (Scheme 7 and Figure S60, Supporting Information).

Scheme 7. Attempted Dihydrogen Activation by Silylated Onium Ion 26 To Give Silaalkyl Phosphonium Ion 31



Scheme 8. Borane/Phosphane and Silylium Phosphane Lewis Pairs That Are Pertinent to the Discussion[a]

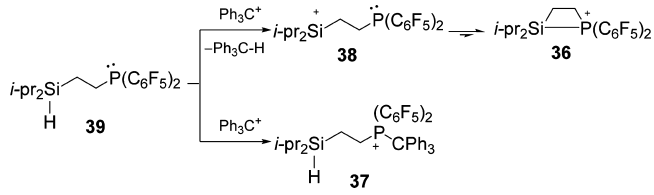


[a]Pemp: pentamethylphenyl.

Against the background of recent literature reports, this failure is not unexpected. Isoelectronic zwitterionic borylphosphonium systems, **32**, show energy differences compared to the active boraalkylphosphanes isomers **33** of around −50 kJ mol^{-1}.[38] In addition, for intermolecular silylium phosphane Lewis pairs that are active in dihydrogen activation, interaction energies between the phosphane and the silylium ion of −63 kJ mol^{-1} (for Lewis pair **34**) or less have been predicted by density functional computations.[18] For comparison the strength of the Si−P bond in the related silylphosphonium ion **35**, which is not active in dihydrogen cleavage, is calculated to be 159 kJ mol^{-1}, as strong as the Si−P linkage in cation **26**. Consequently, the Si−P linkage in cation **26** is by far too stable to deliver isomer **29**, which is believed to be the active species in bond activation reactions. Therefore, phosphonium ion **26** and all other investigated onium ions **24** and **27** are not active in dihydrogen activation. Test reactions for **27b** supported this conclusion.

Si−E bond energies as low as −50 kJ mol^{-1} and thereby FLP-like reactivity could be approached simply by further decreasing the ring size and by simultaneously increasing the steric bulk around the Si−E linkage. The results of DFT computations, however, illustrate the limitations of this approach. In the case of the four-membered cyclic cation **36** a Si−P bond energy is predicted which is reduced to ca. 2/3 of the bond energy in cation **26** (E(Si−P) (**36**) = −111 kJ mol^{-1}) (Scheme 9). This Si−P bond energy is still significantly higher

Scheme 9. Possible Reactions of Silane 39 with Trityl Cation (anion is omitted)



than the benchmark of −50 kJ mol^{-1} aimed at. On the other hand, the results of the computations also indicate that the formation of the trityl addition product **37** would compete efficiently with the hydride transfer reaction to give the phosphonium ion **36** via the silylium ion **38** (Scheme 9). The computed reaction energies for both reaction channels are nearly identical (formation of **37** (E_R = −48 kJ mol^{-1}); formation of **36** (E_R = −54 kJ mol^{-1})), which makes this approach rather unattractive for further experimental investigations.

CONCLUSION

The synthesis of borates of five- and six-membered cyclic silylated onium ions of group 15 elements by intramolecular addition of transient silylium ions to pnictogenyl groups is reported. Silylium ions are prepared by the classical hydride transfer reaction between trityl cation and silanes. Attempts to synthesize four- and three-membered cyclic silylated phosphonium ions using this synthetic approach failed however. In these cases, Lewis acid−base formation between trityl cation and the phosphanyl group is energetically more favored than hydride transfer between silane and trityl cation. Interestingly, we found that under kinetic control, the formation of the five-membered cyclic onium ion **24a** is prevented and the Lewis acid−base complex between trityl cation and the phosphanyl substituent, **25**, is formed instead. This suggests that the competition between trityl coordination to the Lewis-basic center and hydride transfer is a general phenomenon and that it influences the course of the hydride transfer reaction when donor atoms are present.[12]

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We found that the strength of the newly formed bond between the group 15 element and the silicon atom E(Si−E) in cyclic onium ions **24**, **26**, and **27** is substantial (E(Si−E) = −156 to −253 kJ mol^{-1}). It is predicted to be larger for six-membered rings, and it depends on the nature of the element. In general, the Si−P linkages of phosphonium ions are more stable than the Si−As bond of arsonium ions. In the case of the bissilylated onium ions **27** it was found that the Si−Sb and Si−N bonds are of similar strength but weaker than the Si−As bond in **27c**. Steric and electronic substituent effects can be used to modify the strength of the Si−E linkage to a certain extent. Increased steric congestion at the silyl group and decreased Lewis basicity of the phosphanyl substituent result in a relatively small bond energy for the Si−P linkage (E(Si−P) = −156 kJ mol^{-1}) in cation **26**. Even in cation **26** the Si−P bond is, however, too strong to allow the formation of the acyclic, silylium/phosphane isomer **29** in significant concentrations. Therefore, the perspectives for establishing a FLP-like reactivity for these compounds are rather low.

EXPERIMENTAL SECTION

General. All reactions were carried out under inert conditions using standard Schlenk techniques and 5.0 atm argon unless stated otherwise. Diethyl ether and tetrahydrofuran were distilled from sodium/benzophenone. Benzene, toluene, [D$_6$]benzene, [D$_8$]toluene, pentane, and hexane were distilled from sodium. Chlorosilane was dried over P_4O_{10} and stored over 4 Å molecular sieves. Starting materials were purchased from standard commercial suppliers and used as received. $[Ph_3C][B(C_6F_5)_4]$[39] and $[Ph_3C]_2[B_{12}Cl_{12}]$[27] were synthesized according to modified literature procedures. NMR spectra were recorded on Bruker Avance 250 and Avance III 500 spectrometers, if not stated otherwise. ^{1}H NMR spectra were calibrated using residual protio signals of the solvent (δ^1H($CHCl_3$) = 7.24, δ^1H(C_6D_5H) = 7.20). ^{13}C NMR spectra were calibrated using the solvent signals (δ^{13}C($CDCl_3$) = 77.0, δ^{13}C(C_6D_6) = 128.0). ^{29}Si NMR spectra were calibrated using external Me_2HSiCl (δ^{29}Si = 11.1 vs TMS), ^{31}P NMR spectra against external $(MeO)_3P$ (δ^{31}P = 141 vs 85% H_3PO_4(aq)), ^{19}F NMR spectra against external $CFCl_3$ (δ^{19}F-($CFCl_3$) = 0.0), ^{15}N NMR spectra against external formamide (δ^{15}N = 112.67 vs NH_3), and ^{11}B NMR spectra against $BF_3{\cdot}OEt_2$ (δ^{11}B(BF_3 OEt_2) = 0.0). ^{15}N NMR chemical shifts were obtained using inverse detection (^{1}H,^{15}N HMBC). High-resolution mass spectra were recorded on a Finnigan MAT 95. IR spectra were recorded on a Bruker Tensor 27. X-ray diffraction analyses were performed on a Bruker Apex II. Structure solution and refinement was done using the SHELXS97 and SHELXL97 software.[40]

2-((Dimethylsilyl)ethyl)diphenylphosphane ***17.***[20] In a photoreactor 2.28 g of dimethylvinylchlorosilane **18** (18.8 mmol) and 3.50 g of diphenylphosphane (18.8 mmol) were combined and irradiated (Mercury-Medium-Pressure Lamp, TQ-150, 150 W, 200−280 nm, distance ca. 5 cm) for 5 h at room temperature while stirring vigorously. The resulting highly viscous, colorless oil was suspended in 5 mL of benzene. The clear solution was separated from the precipitate by decanting. The solvent was then removed under reduced pressure to yield 2-((dimethylchlorosilyl)ethyl)diphenylphosphane in high purity (almost quantitative yield). The chlorosilane (5.77 g, 18.8 mmol) was dissolved in 20 mL of dry diethyl ether. This solution was then dropped slowly to a suspension of 471 mg of lithium aluminumhydride (12.42 mmol) in 50 mL of dry diethyl ether. The mixture was stirred at room temperature for 3 h. The solvent was removed under reduced pressure. The residue was suspended in 80 mL of dry *n*-pentane. The suspension was filtered using a P4 glass frit. The filtrate was evaporated to give an oily, colorless residue. The raw product was fractionally distilled (100 °C, 1 × 10^{-3} mbar) to yield the desired product as a colorless oil (yield 1.65 g, 32%). ^{1}H NMR (500.130 MHz, C_6D_6, 298 K): δ 0.17 (d, 6 H, $^3J_{HH}$ = 6 Hz, Si(CH_3)$_2$), 0.85−0.92 (m, 2 H, CH_2), 2.14−2.19 (m, 2 H, CH_2), 4.12 (sept, 1 H, $^3J_{HH}$ = 6 Hz, $^1J_{SiH}$ = 186 Hz, Si*H*), 7.09−7.16 (m, 6 H, Ar*H*), 7.46−7.52 (m, 4 H, Ar*H*). ^{13}C{^{1}H} NMR (125.758 MHz, C_6D_6, 298 K): δ 1.20 (CH_3), 14.8 (d, $^2J_{CP}$ = 12.0 Hz, CH_2), 21.2 (d, $^1J_{CP}$ = 15.0 Hz, CH_2), 128.5 (*C*H), 128.8 (d, $^3J_{CP}$ = 6.5 Hz, *C*H), 133.1 (d, $^2J_{CP}$ = 18.3 Hz, *C*H), 139.0 (d, $^1J_{CP}$ = 15.0 Hz, *C*). ^{29}Si{^{1}H} NMR (99.362 MHz, C_6D_6, 298 K): δ −11.6 (d, $^3J_{SiP}$ = 21 Hz). ^{31}P{^{1}H} NMR (202.456 MHz, C_6D_6, 298 K): δ 3.2. HRMS (CI, isobutane): m/z calcd for $C_{16}H_{21}PSi$ [M + H]$^+$ 273.1223; found 273.1119. IR (ATR, neat), ν(SiH): 2108 cm^{-1}

((Dimethylsilyl)methyl)diphenylphosphane ***12.***[20] A solution of 3.43 g of diphenylphosphane (18.41 mmol) in 60 mL of dry THF was cooled to −80 °C and then treated dropwise with 11.5 mL of a 1.6 M *n*-hexane solution of *n*-BuLi (18.41 mmol). The mixture was stirred at this temperature for 3 h. Then it was allowed to warm to room temperature and stirred for 30 min. Subsequently, a solution of 2.00 g of chlorosilane **15** (18.41 mmol) in 10 mL of dry THF was added dropwise at −40 °C. The mixture was then stirred overnight at ambient temperature. The solvent was replaced by 100 mL of dry *n*-pentane, and the resulting suspension was filtered using a glass frit (P4). The residue was washed two times with portions of 10 mL of *n*-pentane. The solvent of the combined filtrates was removed under reduced pressure to yield the desired product in the form of a colorless oil (yield 3.95 g, 83%). ^{1}H NMR (499.870 MHz, C_6D_6, 305 K): δ 0.02 (d, $^3J_{HH}$ = 3.8 Hz, 6 H, (CH_3)$_2$), 1.26−1.27 (m, 2 H, CH_2), 4.17 (nonett, $^3J_{HH}$ = 3.7 Hz, Si*H*), 7.06−7.15 (m, 6 H, Ar*H*), 7.46−7.51 (m, 4 H, Ar*H*). ^{13}C{^{1}H} NMR (125.693 MHz, C_6D_6, 305 K): δ −4.5 (d, $^3J_{CP}$ = 5.3 Hz, CH_3), 11.3 (d, $^1J_{CP}$ = 29.7 Hz, CH_2), 131.5 (d, $^2J_{CP}$ = 20 Hz, *o*-*C*H), 132.9 (d, $^3J_{CP}$ = 16.9 Hz, *m*-*C*H), 140.2 (d, $^4J_{CP}$ = 15.4 Hz, *p*-*C*H). ^{29}Si{^{1}H} NMR (99.310 MHz, C_6D_6, 305 K): δ −15.4, $^2J_{SiP}$ = 17 Hz. ^{31}P{^{1}H} NMR (202.348 MHz, C_6D_6, 305 K): δ −21.0. MS (EI, 70 eV): m/z (relative intensity in %): 258 (20), 200 (38), 183 (37), 135 (67), 78 (100). HRMS (CI, isobutane): m/z calcd for $C_{15}H_{20}PSi$ [M + H]$^+$ 259.1077; found 259.1072. IR (ATR, neat), ν(SiH): 2128 cm^{-1}.

3-((Dimethylsilyl)propyl)diphenylphosphane ***13a.***[20] To a suspension of 583 mg of freshly prepared lithium turnings (84 mmol) a solution of 7.34 g of triphenylphosphane (28 mmol) in 100 mL of THF was added dropwise. The mixture was stirred overnight, resulting in a dark red suspension. The solution was separated from excess lithium turnings via a cannula and then treated at 10 °C with 2.59 g of *tert*-butyl chloride (28 mmol) and stirred 2 h at room temperature. Then 3.85 g of silane **16**[41] (28 mmol) was added dropwise, and the mixture was stirred for 1 h at room temperature. All volatiles were removed in vacuo, and the residue was suspended in *n*-hexane and filtered using a glass frit (P4). The filtrate was concentrated in vacuo. The crude product was fractionally distilled at 135−137 °C and 0.1 mbar to afford a colorless oil (yield 4.01 g, 50%). ^{1}H NMR (499.870 MHz, C_6D_6, 305 K): δ −0.02 (d, $^3J_{HH}$ = 4.0 Hz, 6 H, Si(CH_3)$_2$), 0.70−0.74 (m, 2 H, Si$CH_2$$CH_2$$CH_2$P), 1.56−1.65 (m, 2 H, SiCH$_2$$CH_2$$CH_2$P), 2.07−2.10 (m, 2 H, SiCH$_2$$CH_2$$CH_2$P), 4.11 (nonett, $^3J_{HH}$ = 4.0 Hz, $^1J_{SiH}$ = 182.0 Hz, Si*H*), 7.09−7.16 (m, 6 H), 7.48−7.51 (m, 4 H). ^{13}C{^{1}H} NMR (125.692 MHz, C_6D_6, 305 K): δ −4.5 (Si(CH_3)$_2$), 16.3 (d, $^3J_{PC}$ = 12.0 Hz, SiCH$_2$CH$_2$CH$_2$P), 21.5 (d, $^2J_{PC}$ = 18.0 Hz, SiCH$_2$CH$_2$CH$_2$P), 32.3 (d, $^1J_{PC}$ = 13.0 Hz, SiCH$_2$CH$_2$CH$_2$P), 128.6, 128.7 (d, J_{PC} = 6.0 Hz), 133.1 (d, J_{PC} = 18.0 Hz), 139.9 (d, J_{PC} = 15 Hz). ^{29}Si{^{1}H} NMR (99.310 MHz, C_6D_6, 305 K): δ −14.0. ^{31}P{^{1}H} NMR (202.351 MHz, C_6D_6, 305 K): δ −16.8. IR (ATR, neat), ν(SiH): 2106 cm^{-1}.

3-((Dimethylsilyl)propyl)diphenylarsane ***13b.*** The arsane **13b** was prepared in a similar fashion described above for the phosphane **13b** using 8.57 g of triphenylarsane (28 mmol) instead of triphenylphosphane. Fractioning distillation of the crude product at 145−150 °C and 0.1 mbar afforded a colorless oil (yield 5.83 g, 63%). ^{1}H NMR (499.870 MHz, C_6D_6, 305 K): δ −0.03−0.01 (m, 6 H, Si(CH_3)$_2$), 0.67−0.73 (m, 2 H, Si$CH_2$$CH_2$$CH_2$P), 1.60−1.67 (m, 2 H, SiCH$_2$$CH_2$$CH_2$P), 2.05−2.08 (m, 2 H, SiCH$_2$$CH_2$$CH_2$P), 4.01−4.10 (m, $^1J_{SiH}$ = 176.0 Hz, Si*H*), 7.10−7.16 (m, 6 H), 7.43−7.50 (m, 4 H). ^{13}C{^{1}H} NMR (125.710 MHz, C_6D_6, 305 K): δ −4.4 (Si(CH_3)$_2$), 16.9 (SiCH$_2$CH$_2$CH$_2$P), 22.0 (SiCH$_2$CH$_2$CH$_2$P), 32.2 (SiCH$_2$CH$_2$CH$_2$P),

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128.4, 128.8, 133.4, 141.4. ^{29}Si{^{1}H} NMR (99.310 MHz, C_6D_6, 305 K): δ −14.1. IR (ATR, neat), ν(SiH): 2106 cm^{-1}.

3-Di-isopropylsilyl)propyl-bispentafluorophenylphosphane ***14***. A solution of 615 mg of chloropropylsilane **20** (4.5 mmol) in 50 mL of THF was added dropwise to 120 mg of magnesium turnings (4.96 mmol). The resulting suspension was heated to reflux for 3 h. Excess magnesium was filtered off. Then a solution of 2.00 g of BrP(C_6F_5)$_2$ (4.5 mmol) in 20 mL of THF was slowly added at 0 °C. After complete addition, the reaction mixture was warmed to room temperature and stirred for an additional hour. The solvent THF was removed under reduced pressure, and 50 mL of *n*-hexane was added. The resulting suspension was filtered, and from the filtrate the solvent was removed under reduced pressure. The remaining oily residue was distilled to give a highly viscous oil (bp 190 °C, 30 mbar; yield 1.17g, 59%). ^{1}H NMR (499.870 MHz, $CDCl_3$, 305 K): δ 0.75−0.81 (m, 2 H, CH_2), 0.95−1.02 (m, 14 H, (CH(CH_3)$_2$)$_2$), 1.46−1.57 (m, 2 H, CH_2), 2.50−2.58 (m, 2 H, CH_2), 3.36−3.40 (m, 1 H, SiH). ^{13}C{^{1}H} NMR (125.692 MHz, $CDCl_3$, 305 K): δ 10.1 (d, $^{3}J_{CP}$ = 14 Hz, CH_2), 10.5 (CH), 18.6 (CH_3), 18.9 (CH_3), 22.5 (d, $^{2}J_{CP}$ = 20 Hz, CH_2), 27.2−27.5 (m, CH_2), 109.1 (br s, C), 137.6 (d, $^{1}J_{CF}$ = 257 Hz, C), 142.3 (d, $^{1}J_{CF}$ = 257 Hz, C), 147.8 (d, $^{1}J_{CF}$ = 257 Hz, C). ^{19}F{^{1}H} NMR (470.348 MHz, $CDCl_3$, 305 K): δ −160.41 to −160.26 (m, 4F), −150.16 to −150.04 (t, $^{3}J_{FF}$ = 20 Hz, 2 F), −130.19 to −130.03 (m, 4 F). ^{29}Si{^{1}H} NMR (99.310 MHz, $CDCl_3$, 305 K): δ 5.89. ^{31}P{^{1}H} NMR (202.351 MHz, $CDCl_3$, 305 K): δ −47.03 (p, $^{3}J_{PF}$ = 25 Hz). MS (CI, isobutane): m/z (relative intensity, %) 522 (1), 479 (100), 365 (12), 296 (8), 217 (5), 129 (8), 69 (17), 43 (41). HRMS (CI, isobutane): m/z $C_{17}H_{14}F_{10}SiP$ [M + H]$^{+}$: 523.1069; found:523.1055. IR (neat): 2109 cm^{-1}.

Diphenylaminosilane ***21a***. A 1.56 g amount of diphenylamine (9.2 mmol) was dissolved in 75 mL of dry THF. At −50 °C 5.8 mL of 1.6 M methyllithium solution in diethyl ether (9.3 mmol) was added dropwise over a period of 30 min. The mixture was warmed to −10 °C and stirred for 30 min before it was cooled to −40 °C. At this temperature 1.80 g of chlorosilane **19**[42] (9.2 mmol) was added dropwise. The mixture was stirred at room temperature overnight. The ether was removed under reduced pressure, and 20 mL of *n*-pentane was added. The lithium salts were filtered off using a glass frit (P4). The solvent of the filtrate was removed under reduced pressure. The raw product was fractionally distilled at 145 °C and 0.2 mbar to yield the desired product as a viscous, colorless oil (yield 1.81 g, 58%). ^{1}H NMR (500.133 MHz, $CDCl_3$, 300 K): δ 0.00 (d, $^{3}J_{HH}$ = 3.3 Hz, Si(CH_3)$_2$, 6 H), 0.18 (s, Si(CH_3)$_2$, 6 H), 0.55−0.59 (m, CH_2, 2 H), 0.88−0.91 (m, CH_2, 2 H), 1.41−1.46 (m, CH_2, 2 H), 3.79 (sept, $^{3}J_{HH}$ = 3.3 Hz, $^{1}J_{SiH}$ = 179.8 Hz, SiH, 1 H), 6.86−6.89 (m, ArH, 2 H), 6.91−6.93 (m, ArH, 4 H), 7.08−7.12 (m, ArH, 4 H). ^{13}C{^{1}H} NMR (62.902 MHz, $CDCl_3$, 300 K): δ −4.3 (Si(CH_3)$_2$), −0.3 (Si(CH_3)$_2$), 18.6 (CH_2), 18.8 (CH_2), 21.3 (CH_2), 122.1, 124.5, 129.2, 148.6 (C_q). ^{15}N NMR (50.680 MHz, C_6D_6, 300 K): δ 85.5. ^{29}Si{^{1}H} NMR (49.695 MHz, C_6D_6, 300 K): δ −14.4 (Me_2SiH), 5.6 (SiMe_2).

Diphenylphosphanylsilane ***21b***. A 375 mg amount of lithium turnings (54 mmol) was suspended in 40 mL of dry THF. A solution of 2.02 g of triphenylphosphane (7.7 mmol) in 20 mL of THF was added. The mixture was stirred at room temperature for 4 h. The dark red solution was then decanted from the excessive lithium turnings. At 10 °C 713 mg of *tert*-butyl chloride (7.7 mmol) was added slowly. The mixture was stirred for 1 h while slowly warming to room temperature. At 10 °C 1.50 g of chlorosilane **19**[42] (7.7 mmol) was added dropwise. The solution became colorless and was stirred for 1 h at room temperature. The solvent was then replaced by 50 mL of dry *n*-pentane. The lithium salts were removed using a glass frit (P 4). The solvent was subsequently removed under reduced pressure. The crude product was fractionally distilled at 170 °C and 0.1 mbar to obtain desired product as a colorless oil (yield 2.17 g, 82%). ^{1}H NMR (250.131 MHz, $CDCl_3$, 305 K): δ 0.00 (d, $^{3}J_{HH}$ = 3.6 Hz, Si(CH_3)$_2$H, 6 H), 0.15 (d, $^{3}J_{HP}$ = 4.8 Hz, Si(CH_3)$_2$P, 6 H), 0.55−0.62 (m, CH_2, 2 H), 0.71−0.79 (m, CH_2, 2 H), 1.35−1.43 (m, CH_2, 2 H), 3.79 (sept, $^{3}J_{HH}$ = 3.6 Hz, $^{1}J_{SiH}$ = 180.5 Hz, SiH, 1 H), 7.23−7.31 (m, ArH), 7.38−7.45 (m, ArH). ^{13}C{^{1}H} NMR (62.902 MHz, $CDCl_3$, 305 K): δ −4.5 (Si(CH_3)$_2$H), −2.9 (d, $^{2}J_{CP}$ = 12.6 Hz, Si(CH_3)$_2$P), 18.6 (CH_2), 19.0 (d, $^{3}J_{CP}$ = 4.4 Hz, CH_2), 19.5 (d, $^{2}J_{CP}$ = 11.1 Hz, CH_2), 127.4, 128.3 (d, $^{3}J_{CP}$ = 6.7 Hz), 133.8 (d, $^{2}J_{CP}$ = 17.1 Hz), 135.7 (d, $^{1}J_{CP}$ = 14.8 Hz, C_q). ^{29}Si{^{1}H} NMR (49.695 MHz, $CDCl_3$, 305 K): δ −14.4 (SiH), 2.5 (d, $^{1}J_{SiP}$ = 21.7 Hz, SiP). ^{31}P{^{1}H} NMR (161.951 MHz, $CDCl_3$, 305 K): δ −56.7.

Diphenylarsanylsilane ***21c***. To 0.14 g of freshly grated lithium turnings (20 mmol) in 20 mL of dry THF 3.06 g of triphenylarsane (10 mmol) was added under stirring. The mixture was stirred for 2 h at room temperature; excessive lithium turnings were separated. The red brown solution was treated with 0.9 g of *tert*-butyl chloride (10 mmol) at 10 °C and stirred for 30 min while slowly warming to room temperature. At 10 °C 1.94 g of chlorosilane **2** (10 mmol) was added dropwise. The solution lost its color, and a colorless precipitate was formed. After 20 min of stirring at room temperature the solvent was replaced by 30 mL of *n*-pentane and the lithium salts were filtered off using a glass frit (P 4). The *n*-pentane was removed under reduced pressure. The crude product was purified by fractioning distillation at 195−200 °C and 0.2 mbar to yield a colorless oil (yield 2.2 g, 57%). ^{1}H NMR (250.131 MHz, $CDCl_3$, 300 K): δ −0.03 (d, $^{3}J_{HH}$ = 3.3 Hz, $SiMe_2$H, 6 H), 0.15 ($SiMe_2$), 0.52−0.60 (m, CH_2, 2 H), 0.72−0.79 (m, CH_2, 2 H), 1.16−1.42 (m, CH_2, 2 H), 3.77 (sept, $^{3}J_{HH}$ =3.3 Hz, $^{1}J_{SiH}$ = 180 Hz, $SiMe_2$H, 1 H), 7.19−7.25 (m, ArH, 6 H), 7.38−7.47 (m, ArH, 4 H). ^{13}C{^{1}H} NMR (62.902 MHz, $CDCl_3$, 300 K): δ −4.3 ($SiMe_2$H), −2.6 ($SiMe_2$), 18.5 (CH_2), 19.2 (CH_2), 20.0 (CH_2), 127.2, 128.5, 134.3, 137.2 (C_q). ^{29}Si{^{1}H} NMR (49.695 MHz, $CDCl_3$, 300 K): δ −14.4 (Si−H), 5.7 (Si−As).

Diphenylstibanylsilane ***21d***. To a suspension of 0.14 g of freshly grated lithium turnings (20 mmol) in 20 mL of dry THF 3.53 g of triphenylstibane (10 mmol) was added. The mixture was stirred for 2 h at room temperature. A deep red solution is decanted from the excessive lithium turnings. At 0 °C 0.90 g of *tert*-butyl chloride (10 mmol) was added. After the mixture was stirred for 30 min, 1.94 g of chlorosilane **2** (10 mmol) was added. A black suspension was formed. After 20 min the solvent was replaced by 50 mL of *n*-pentane. The salts were removed using a glass frit (P 4). The solvent of the filtrate was removed under reduced pressure. The crude product was fractionally distilled at 160 °C and 0.2 mbar to yield the desired product in the form of a yellow liquid (yield 1.90 g, 44%). ^{1}H NMR (250.131 MHz, $CDCl_3$, 300 K): δ 0.00 (d, $^{3}J_{HH}$ = 3.7 Hz, $SiMe_2$H, 6 H), 0.23 ($SiMe_2$), 0.55−0.62 (m, CH_2, 2 H), 0.80−0.87 (m, CH_2, 2H), 1.31−1.45 (m, CH_2, 2 H), 3.78 (sept, $^{3}J_{HH}$ = 3.7 Hz, $SiMe_2$H, 1 H), 7.22−7.25 (m, ArH, 6 H), 7.47−7.51 (m, ArH, 4 H). ^{13}C{^{1}H} NMR (62.902 MHz, $CDCl_3$, 300 K): δ −4.4 ($SiMe_2$H), −1.6 ($SiMe_2$), 18.6 (CH_2), 19.8 (CH_2), 21.1 (CH_2), 127.6, 128.7, 132.1 (C_q), 137.4. ^{29}Si{^{1}H} NMR (49.695 MHz, $CDCl_3$, 300 K): δ −14.4 (SiH), 2.3 (SiSb).

General Procedure for Hydride Transfer Reactions. In a typical reaction 500 mg of [Ph_3C][B(C_6F_5)$_4$] (0.54 mmol) was evacuated over 1 h in a Schlenk tube. Then, 2 mL of dry benzene, toluene, or chlorobenzene was condensed onto the solid, resulting in a typical two-phase solution. The corresponding silane **13** or **21** (0.54 mmol) was added via a syringe. The mixture was stirred for 30−60 min until the color of the upper, nonionic layer changed from orange to light brown or even colorless. After that, stirring was stopped and the phases were allowed to separate. The upper layer, which mostly contained triphenylmethane, was discarded. The lower, ionic layer was washed three times with portions of 5 mL of dry *n*-pentane. The volatiles were evaporated, resulting in a colorless to light brown foam. The residue was dissolved in the respective deuterated solvent for NMR spectroscopy.

NMR Data for the [B(C_6F_5)$_4$]$^{-}$ Anion. [B(C_6F_5)$_4$]$^{-}$. ^{11}B{^{1}H} NMR (160.378 MHz, C_6D_6, 305 K): δ −16.6. ^{13}C{^{1}H} NMR (125.692 MHz, C_6D_6, 305 K): δ 124.6 (br s, *i*-C), 136.7 (dm, $^{1}J_{CF}$ = 246 Hz), 138.6 (dm, $^{1}J_{CF}$ = 246 Hz), 148.7 (d, $^{1}J_{CF}$ = 241 Hz). ^{19}F{^{1}H} NMR (470.348 MHz, C_6D_6, 305 K): δ −166.9 (t, $^{3}J_{FF}$ = 18 Hz), −163.3 (tm, $^{3}J_{FF}$ = 20 Hz), −132.4 (dm, $^{3}J_{FF}$ = 7 Hz).

24a*[B(C_6F_5)$_4$]*. ^{1}H NMR (499.870 MHz, C_6D_6, 305 K) δ −0.05 (d, $^{3}J_{PH}$ = 7.8 Hz, 6 H, PSi(CH_3)$_2$), 0.61−0.68 (m, 2 H, SiCH_2CH$_2$CH$_2$P), 1.44−1.56 (m, 2 H, SiCH$_2$CH_2CH$_2$P), 1.77−1.86

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(m, 2 H, $SiCH_2CH_2CH_2P$), 6.81−6.88 (m, 4 H, Ar*H*), 7.14−7.19 (m, 4 H, Ar*H*), 7.23−7.27 (m, 2 H, Ar*H*). $^{13}C\{^1H\}$ NMR (125.692 MHz, C_6D_6, 305 K): δ −4.4 (d, $^2J_{PC}$ = 9.3 Hz, $Si(CH_3)_2$), 15.4 (CH_2), 21.5 (CH_2), 26.4 (CH_2), 118.3 (d, *J*CP = 62 Hz, Cq), 130.5 (d, *J*CP = 12 Hz, CH), 132.1 (d, *J*CP = 11 Hz, CH), 134.1 (d, *J*CP = 3 Hz, CH). $^{29}Si\{^1H\}$ NMR (99.310 MHz, C_6D_6, 305 K): δ 23.9 (d, $^1J_{SiP}$ = 37 Hz). $^{31}P\{^1H\}$ NMR (202.348 MHz, C_6D_6, 305 K): δ −6.2.

***24b*[$B(C_6F_5)_4$]**. ^1H (499.87 MHz; C_6D_6, 305 K): δ = 0.05 (s, 6H, $Si(CH_3)_2$), 0.65 (t, 2H, $^3J_{HH}$ = 7 Hz, 2H, $SiCH_2CH_2CH_2As$), 1.51 (p, 2H, $^3J_{HH}$ = 7 Hz, 2H, $SiCH_2CH_2CH_2As$), 1.90 (t, 2H, $^3J_{HH}$ = 7 Hz, 2H, $SiCH_2CH_2CH_2As$), 6.83 (d, $^3J_{HH}$ = 8 Hz 4H, *o*-H), 7.17 (t, $^3J_{HH}$ = 8 Hz 4H, *m*-H), 7.25 (t, $^3J_{HH}$ = 7 Hz 2H, *p*-H). $^{13}C\{^1H\}$ (125.69 MHz; C_6D_6, 305 K): δ = −4.42 ($Si(CH_3)_2$), 17.0 ($SiCH_2CH_2CH_2As$), 22.0 ($SiCH_2CH_2CH_2As$), 28.5 ($SiCH_2CH_2-CH_2As$), 122.2 (C^q), 130.8 (CH), 131.8 (CH), 133.2 (CH). $^{29}Si\{^1H\}$ (99.31 MHz; C_6D_6, 305 K): δ = 30.9.

***27a*[$B(C_6F_5)_4$]**. ^1H NMR (499.870 MHz, C_6D_6, 305 K): δ 0.02 (s, 12 H, $Si(CH_3)_2$), 0.70−0.77 (m, 4 H, CH_2), 1.58−1.67 (m, 2 H, CH_2), 6.71−6.75 (m, 4 H, ArH), 6.99−7.07 (m, 6 H, ArH). $^{13}C\{^1H\}$ NMR (125.692 MHz, C_6D_6, 305 K): δ 0.4 (CH_3), 15.8 (CH_2), 18.5 (CH_2), 125.5 (CH), 128.5 (CH), 130.1 (CH), 143.1 (C). $^{15}N\{^1H\}$ NMR (50.651 MHz, C_6D_6, 305 K): δ 79.0. $^{29}Si\{^1H\}$ INEPT NMR (99.310 MHz, C_6D_6, 305 K): δ 44.0.

***27b*[$B(C_6F_5)_4$]**. ^1H NMR (250.131 MHz, C_7D_8, 300 K): δ −0.05 (d, $^3J_{PH}$ = 7.0 Hz, 12 H, $SiMe_2$), 0.57−0.66 (m, 4 H, CH_2), 1.47−1.55 (m, 2 H, CH_2), 6.86−7.16 (m, ArH). $^{13}C\{^1H\}$ NMR (62.902 MHz, C_7D_8, 300 K): δ −4.4 (d, $^2J_{PC}$ = 8.1 Hz, $SiMe_2$), 16.3 (d, $^2J_{PC}$ = 11.3 Hz, CH_2), 16.9 (CH_2), 118.9 (d, 1J_{PC} = 47.7 Hz, C), 130.9 (d, $^3J_{PC}$ = 11.1 Hz, CH), 133.5 (d, $^2J_{CP}$ = 8.0 Hz, CH), 133.5 (CH). $^{29}Si\{^1H\}$ NMR (49.695 MHz, C_7D_8, 300 K): δ 8.6 (d, $^1J_{SiP}$ = 11.3 Hz, SiP). $^{31}P\{^1H\}$ NMR (161.951 MHz, C_7D_8, 300 K): δ −51.3.

***27c*[$B(C_6F_5)_4$]**. ^1H NMR (250.131 MHz, C_7D_8, 300 K): δ 0.01 (s, 12 H, $Si(CH_3)_2$), 0.59−0.63 (m, 4 H, CH_2), 1.47−1.53 (m, 2 H, CH_2), 6.89−6.92 (m, ArH), 7.08−7.19 (m, ArH). $^{13}C\{^1H\}$ NMR (62.902 MHz, C_7D_8, 300 K): δ −4.0 ($Si(CH_3)_2$), 16.5 (CH_2), 17.0 (CH_2), 122.1 (C), 131.1 (CH), 132.3 (CH), 133.0 (CH). $^{29}Si\{^1H\}$ NMR (99.367 MHz, C_6D_6, 300 K): 17.7.

***27d*[$B(C_6F_5)_4$]**. ^1H NMR (250.131 MHz, C_7D_8, 283 K): δ 0.10 (s, 12 H, $Si(CH_3)_2$), 0.57−0.61 (m, 4 H, CH_2), 1.43−1.52, (m, 2 H, CH_2), 6.89−7.14 (m, 10 H, ArH). $^{13}C\{^1H\}$ NMR (62.902 MHz, C_7D_8, 263 K): δ −2.8 ($Si(CH_3)_2$), 16.9 (CH_2), 18.5 (CH_2), 118.7 (C), 131.2 (CH), 136.2 (CH) (the missing CH signal could not be identified due to overlapping signals). $^{29}Si\{^1H\}$ NMR (49.695 MHz, C_7D_8, 263 K): δ 17.5.

***22*[$B(C_6F_5)_4$]**. ^1H NMR (499.87 MHz, 305 K, C_6D_6): δ −0.27 (d, $^3J_{HH}$ = 3.6 Hz, 6 H, $Si(CH_3)_2$), 2.12−2.22 (m, 2 H, CH_2), 3.50−3.59 (m, 1 H, $^1J_{SiH}$ = 205.1 Hz, Si*H*), 6.75−6.82 (m, 4 H, Ar*H*), 7.00−7.09 (m, 7 H, Ar*H*), 7.09−7.17 (m, 7 H, Ar*H*), 7.21−7.31 (m, 7 H, Ar*H*). $^{13}C\{^1H\}$ NMR (125.69 MHz, 305 K, C_6D_6): δ −3.6 (d, $^3J_{CP}$ = 3.4 Hz, $Si(CH_3)_2$), 8.8 (d, $^1J_{PC}$ = 37.3 Hz, CH_2), 67.3 (d, $^1J_{CP}$ = 39.3 Hz, $PCPh_3$), 119.7 (d, $^1J_{CP}$ = 76.8 Hz, *ipso*-ArC), 129.2 (s, ArC), 129.7 (d, 12.6 Hz, ArC), 129.9 (s, ArC), 131.6 (d, 6.2 Hz, ArC), 134.0 (d, 7.3 Hz, ArC), 135.1 (d, 2.1 Hz, ArC). $^{29}Si\{^1H\}$ NMR (99.31 MHz, 305 K, C_6D_6): δ −12.6 (d, $^2J_{SiP}$ = 9.0 Hz). $^{31}P\{^1H\}$ NMR (202.35 MHz, 305 K, C_6D_6): δ 31.6 (s).

***23*[$B(C_6F_5)_4$]**. ^1H NMR (500.13 MHz, 298 K, C_7D_8): δ −0.06 (6 H, $^3J_{HH}$ = 3.7 Hz, $Si(CH_3)_2$), 0.40−0.49 (m, 2 H, CH_2), 2.91−3.00 (m, 2 H, CH_2), 3.82−3.88 (m, 1 H, $^1J_{SiH}$ = 190.7 Hz, Si*H*), 6.77−6.83 (4 H, Ar*H*), 6.97−7.13 (br m, 18 H, Ar*H*), 7.22−7.28 (m, 3 H, Ar*H*). $^{13}C\{^1H\}$ NMR (125.76 MHz, 298 K, C_7D_8): δ −5.7 (s, CH_3), 8.5 (d, $^2J_{CP}$ = 9.5 Hz, CH_2), 20.6 (d, $^1J_{PC}$ = 37.0 Hz, CH_2), 67.2 ($^1J_{PC}$ = 35.7 Hz, $PCPh_3$), 118.3 ($^1J_{CP}$ = 73.3 Hz, *ipso-C*), 129.3 (s, ArCH), 129.9 (d, 11.7 Hz, CH), 130.1 (s, ArCH), 131.6 (d, 5.3 Hz, ArCH), 134.7 (d, 7.2 Hz, ArCH), 135.2 (d, 3.1 Hz, ArCH). $^{29}Si\{^1H\}$ NMR (99.31 MHz, 298 K, C_7D_8): δ −14.8 (d, $^3J_{SiP}$ = 23.6 Hz). $^{31}P\{^1H\}$ NMR (202.46 MHz, 298 K, C_7D_8): δ 38.3 (s).

***26*[$B(C_6F_5)_4$]**. ^1H NMR (499.87 MHz, C_6D_6, 305 K): δ 0.66−0.84 (m, 14 H, $(CH(CH_3)_2)_2$), 1.14−1.24 (m, 2 H, CH_2), 1.75−1.90 (m, 2 H, CH_2), 2.46−2.55 (m, 2 H, CH_2). $^{13}C\{^1H\}$ NMR (125.692 MHz, C_6D_6, 305 K): δ 7.5 (d, $^2J_{CP}$ = 26.7 Hz, CH_2), 12.5 (d, $^2J_{CP}$ = 8.7 Hz, CH), 16.3 (d, $^3J_{CP}$ = 3.5 Hz, CH_3), 17.0 (d, $^3J_{CP}$ = 2.1 Hz, CH_3), 21.0 (d, $^3J_{CP}$ = 11.0 Hz, CH_2), 27.5 (d, $^1J_{CP}$ = 32.7 Hz, CH_2), 128.2 (C), 130.0 (C), 141.9 (C), 142.9 (C). $^{19}F\{^1H\}$ NMR (470.35 MHz, C_6D_6, 305 K): δ −167.85 to −167.64 (m, 8 F), −163.65 to −163.40 (m, 4 F), −154.75 to −154.53 (m, 4 F), −136.75 to −136.50 (m, 2 F), −133.10 to −132.60 (m, 8 F), −127.15 to −126.90 (m, 4 F). $^{29}Si\{^1H\}$ NMR (99.31 MHz, C_6D_6, 305 K): δ 50.09 (d, $^1J_{SiP}$ = 17 Hz). $^{31}P\{^1H\}$ NMR (202.35 MHz, C_6D_6, 305 K): δ −26.88.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Relevant NMR spectra, cif files, additional X-ray crystallographic information for compounds **25**$_2$[$B_{12}Cl_{12}$] and **27b**[$B(C_6F_5)_4$], and all computational details including a table of absolute energies and Cartesian coordinates of relevant molecular structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Author Contributions

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Notes

The authors declare no competing financial interest.

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