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Quantitative Assessment of the Lewis Acidity of Silylium Ions

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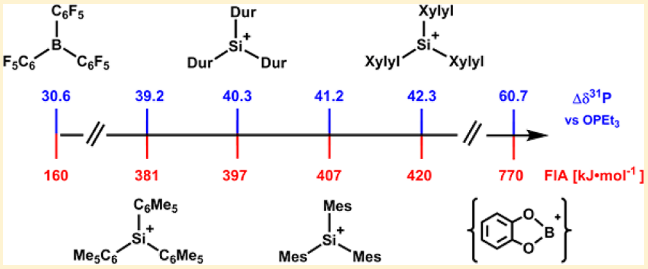
Supporting Information

ABSTRACT: The Lewis acidity of several aryl-substituted tetrylium ions was classified experimentally by applying the Gutmann–Beckett method and computationally by calculation of fluoride ion affinities (FIA) (tetrel elements = Si, Ge). According to these measures, tetrylium ions are significantly more Lewis acidic than boranes, and aryl-substituted silylium borates are among the strongest isolable Lewis acids. A fine-tuning of the Lewis acidity of silylium ions is possible by taking advantage of electronic and/or steric substituent effects.



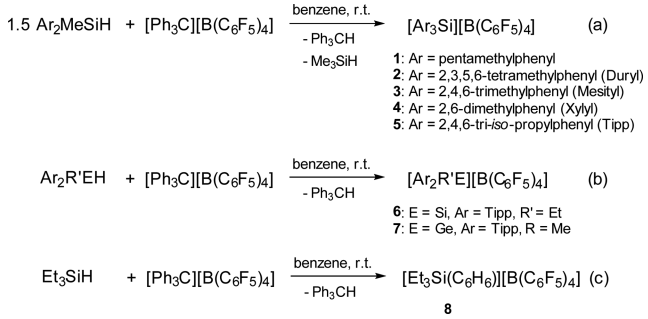
INTRODUCTION

Current interest in the synthesis and properties of strong Lewis acids is very high. The recent development and success of the concept of frustrated Lewis pairs (FLPs)[1,2] and the application of strong Lewis acids in bond activation reactions and catalysis are important driving forces for the further development of new main group based Lewis acids.[3−9] Recently, we have found a straightforward preparative access to a series of aryl-substituted silylium and germylium ions, the congeners of tricoordinated carbenium ions.[10] The high reactivity of this class of cationic species, previously the major obstacle for their isolation and characterization, is now successfully applied in bond activation chemistry, catalysis, and rearrangement reactions, to name only a few examples.[11,12] Clearly, the origin of this reactivity is the Lewis acidity of tetrylium ions (tetrel elements: silicon and germanium), and the notion of "strong Lewis acids" is omnipresent in reports describing the chemistry of silylium salts and related compounds, although a quantitative classification was in no case satisfactorily provided. For neutral silicon Lewis acids several methods are described to assess and quantify experimentally their Lewis acidity in comparison with other Lewis acids.[13] In this respect, methods based on the change in NMR chemical shifts of a probe Lewis base upon coordination to a series of Lewis acids found widespread application. For example, in the Gutmann–Beckett method the ^{31}P NMR chemical shift of the probe base $OPEt_3$ is monitored,[14,15] and in Child's method the base is crotonaldehyde and the ^{1}H NMR resonance of the γ-proton is probed.[16] Hilt and co-workers previously used the ^{2}H NMR chemical shift of the *para* deuterium in pyridine-d_5 adducts of silyl triflates to quantify their Lewis acidity.[17] Recently, Hilt, Oestreich, and co-workers probed the Lewis acidity of a family of ferrocene-stabilized silicon cations by Lewis pair formation with $OPEt_3$ and pyridine-d_5 by NMR spectroscopic methods and found that the Lewis acidity of silicon cations cannot be correlated with NMR resonances of the obtained adducts.[18] Subsequently, the Lewis acidity of these ferrocenyl-substituted silyl cations was studied computationally using fluoride anion affinities (FIA).[19] Here we report that for a well-defined subset of aryl-substituted silylium ions the Gutmann–Beckett method allows an assessment of their Lewis acidity and that correlation to Lewis acid scales based on theoretical derived negative ion affinities exists.[20−25]

RESULTS AND DISCUSSION

The cationic Lewis acids used in our study were prepared according to reported literature procedures.[10] Solutions of triarylsilylium borates **1**$[B(C_6F_5)_4]$–**5**$[B(C_6F_5)_4]$ in benzene were obtained by reaction of 1.5 equiv of the corresponding diarylmethylsilane with 1 equiv of trityl tetrakispentafluorophenyl borate, $[Ph_3C][B(C_6F_5)_4]$ (Scheme 1, eq a). Benzene solutions of diarylsilylium borate **6**$[B(C_6F_5)_4]$, diarylgermylium borate **7**$[B(C_6F_5)_4]$, and triethylsilylarenium borate **8**$[B(C_6F_5)_4]$ were synthesized by the standard hydride transfer reaction (Scheme 1, eqs b,c).[10,11] All attempts to adapt Childs method for quantifying the Lewis acidity of the prepared

Scheme 1. Synthesis of Cationic Silicon- and Germanium-Based Lewis Acids



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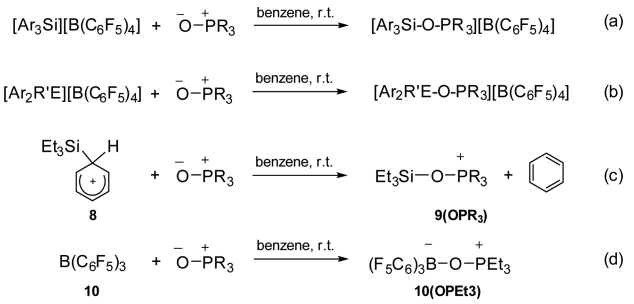
triarylsilylium ions failed due to extensive side reactions of the crotonaldehyde with the applied silylium ions or follow-up reactions of the silylium/aldehyde complex. In contrast, the reactions of silylium and germylium ions with phosphane oxides, R_3PO, are much cleaner, and therefore we concentrated our experimental investigation on the Gutmann–Beckett method. The siloxyphosphonium borates $[\mathbf{1}(OPR_3)]-[\mathbf{6}(OPR_3)][B(C_6F_5)_4]$ and germyloxyphosphonium borate $[\mathbf{7}(OPR_3)][B(C_6F_5)_4]$ (R = Et, Ph) were obtained as glassy amorphous solids by addition of a benzene solution of the phosphane oxide to the solution of the corresponding borate at room temperature (Scheme 2, eqs a,b). After washing with

Scheme 2. Synthesis of Siloxy- and Germyloxyphosphonium Borates from the Corresponding Silylium and Germylium Salts



benzene to remove byproducts and excess phosphane oxide, the residues were dissolved in benzene-d_6 and investigated by NMR spectroscopy to determine the ^{31}P NMR chemical shift difference ($\Delta\delta^{31}P$) between the free phosphane oxide and the formed complex with the cationic Lewis acid. Silylium ions **3** and **4** undergo slow decomposition at ambient conditions with the formation of protonated arenes. To obtain also for these cases meaningful results, addition of 1 equiv of the proton sponge 2,6-di-*tert*-butyl-4-methylpyridine prior to the phosphane oxide was necessary.[26] For comparison the triethylsiloxyphosphonium borates $[\mathbf{9}(OPR_3)][B(C_6F_5)_4]$ and betaine $\mathbf{10}(OPEt_3)$[27] were synthesized and investigated by NMR spectroscopy (Scheme 2, eqs c,d).

In the case of the silyl cationic Lewis acids, the formation of the donor–acceptor complex is indicated in each case by a significant high-field shift of the ^{29}Si NMR resonance and by a doublet splitting of the ^{29}Si NMR signal due to the $^2J(SiP)$ coupling (see Figure 1 for an example). This coupling was also

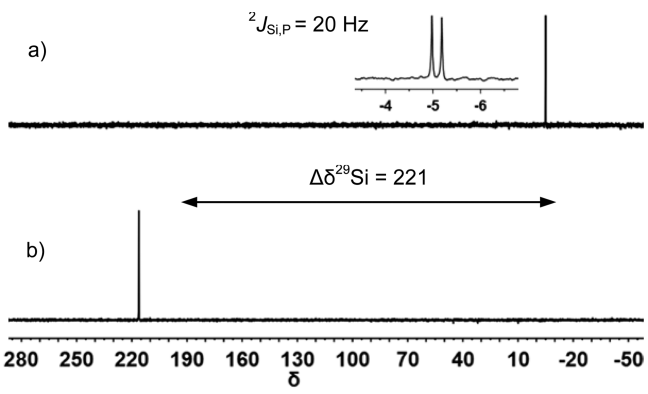


Figure 1. 99.32 MHz $^{29}Si\{H\}$ NMR spectra (C_6D_6, 305 K): (a) $[\mathbf{1}(OPEt_3)][B(C_6F_5)_4]$, (b) $\mathbf{1}[B(C_6F_5)_4]$.

identified in the ^{31}P NMR spectra of the formed complexes by detection of the corresponding satellites (see Figure 2). Additional ^1H and ^{13}C NMR spectra further confirm the quantitative formation of the phosphonium ions $[\mathbf{1}(OPR_3)]^+-[\mathbf{7}(OPR_3)]^+$ and $[\mathbf{9}(OPR_3)]^+$.

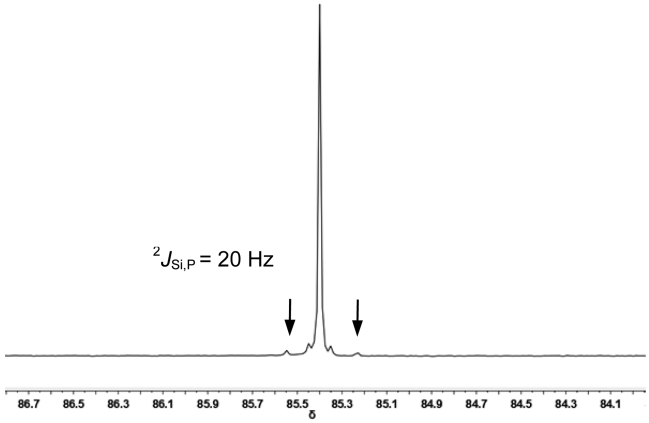


Figure 2. 202.35 MHz $^{31}P\{H\}$ NMR spectrum (C_6D_6, 305 K) of $[\mathbf{1}(OPEt_3)][B(C_6F_5)_4]$.

Structural evidence for the Lewis acid/base adduct formation was obtained in the case of $[\mathbf{1}(OPPh_3)]^+$. Crystals suitable for X-ray diffraction analysis (XRD) were grown from a 1,2-difluorobenzene solution of the aluminate $[\mathbf{1}(OPPh_3)][Al(OC(CF_3)_3)_4]$.[28,29] The compound crystallizes in the trigonal space group *R*3. The quality of the structure solution suffered from significant structural disorder of the aluminate anion; it allows however a short discussion of the main structural features of the siloxyphosphonium cation. Noteworthy is the linear arrangement of the Si–O–P linkage with a relatively long Si–O bond (d(SiO) = 172.7 pm in $[\mathbf{1}(OPPh_3)]^+$ vs 161.6 pm in $Ph_3Si-O-SiPh_3$) (Figure 3). In addition, the P–O bond is clearly elongated compared to that in triphenylphosphane (d(PO) = 153.1 pm in $[\mathbf{1}(OPPh_3)]^+$ vs 146 pm in Ph_3PO), but it is still markedly shorter than a standard P–O single bond

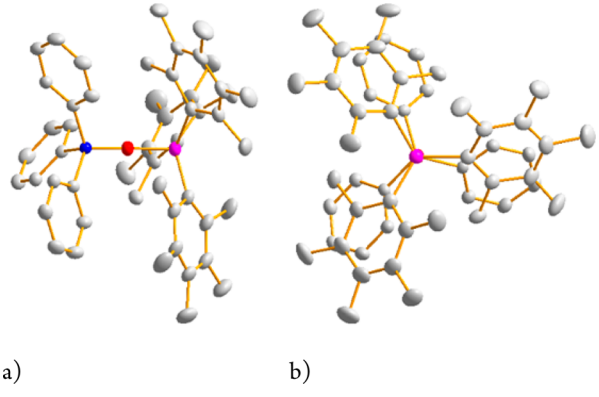


Figure 3. Ellipsoid presentation of the molecular structure of $[\mathbf{1}(OPPh_3)]^+$ in the crystal (the aluminate anion is not shown for clarity reasons): (a) view perpendicular to the SiOP vector; (b) view along the SiOP vector (H atoms omitted for clarity; thermal ellipsoids at 50% probability). Color code: gray, carbon; purple, silicon; red, oxygen; blue, phosphorus. Pertinent bond lengths [pm] and bond and dihedral angles [deg]: Si–C^{ipso}: 188.89(28), Si–O: 172.73(33); P–O: 153.14(33); P–C^{ipso}: 178.33(33); P–O–Si: 180.00; C^{ipso}–Si–P–C^{ipso} 13.596(136).

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Table 1. Selected NMR Parameters of Silylium and Germylium/Phosphane Oxide Complexes and $\Delta\delta$ ^{31}P Values Derived Therefrom and Their Calculated FIA Values[a]

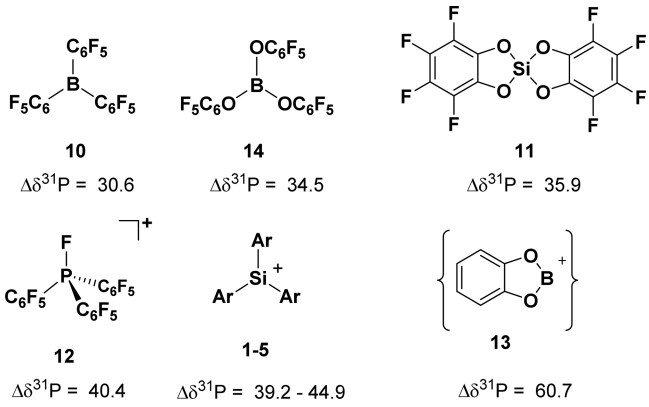
Lewis acid/phosphanoxide complex	δ^{31}P (R = Et)	$\Delta\delta^{31}$P (R = Et)	δ^{29}Si (^2J(SiP)) (R = Et) [Hz]	δ^{31}P (R = Ph)	$\Delta\delta^{31}$P (R = Ph)	δ^{29}Si (^2J(SiP)) (R = Ph) [Hz]	FIA[f] [kJ mol^{-1}]
OPR_3[b]	46.2			25.1			
$[(Me_5C_6)_3SiOPR_3]^+$ [**1**(OPR_3)]$^+$	85.4	39.2	−5.1 (20.3)	54.7	29.6	−2.6 (21.7)	381
$[Dur_3SiOPR_3]^+$ [**2**(OPR_3)]$^+$	86.5	40.3	−5.1 (20.2)	55.4	30.3	−2.8 (21.7)	397
$[Mes_3SiOPR_3]^+$ [**3**(OPR_3)]$^+$	87.4	41.2	−5.3 (20.1)	56.5	31.4	−3.9 (21.5)	407
$[Xylyl_3SiOPR_3]^+$ [**4**(OPR_3)]$^+$	88.5	42.3	−6.3 (20.3)	57.2	32.1	−5.1 (21.3)	420
$[Tipp_3SiOPR_3]^+$ [**5**(OPR_3)]$^+$	91.1	44.9	6.8 (14.5)	56.3	31.2	10.2 (16.0)	358
$[Tipp_2EtSiOPR_3]^+$ [**6**(OPR_3)]$^+$	91.3	45.1	11.1 (14.7)				401
$[Tipp_2MeGeOPR_3]^+$ [**7**(OPR_3)]$^+$	86.6	40.4	11.1 (14.7)				352
$[Et_3SiOPR_3]^+$ [**9**(OPR_3)]	88.6	42.4	35.4 (17.7)	52.7	27.6	38.5 (16.7)	
$(C_6F_5)_3BOPR_3$ [**10**(OPR_3)]	76.8[c]	30.6[c]		45.8[d]	20.3[d]		160
$(C_6F_5O)_3BOPR_3$[d] [**14**(OPR_3)]	80.9	34.5		46.6	21.1		153
$[CatBOPR_3]^+$[e] [**13**(OPR_3)]	106.9	60.7					770
[**11**(OPR_3)][g]		35.9					
[**12**(OPR_3)][h]	91.1	40.4					331

[a]For comparison literature data from boron- and phosphorus-based Lewis acids are provided. [b]Slightly different ^{31}P NMR chemical shifts for the phosphane oxides in C_6D_6 are reported in ref 4: δ^{31}P($OPEt_3$) = 46.4; δ^{31}P($OPPh_3$) = 25.5. [c]Ref 4 reports δ^{31}P = 76.6 and $\Delta\delta^{31}$P = 30.2. [d]Data from ref 4. [e]Data from ref 5a. [f]Calculated at PCM/M05-2X/6-31G(d) (see the SI for details). [g]Data from ref 33. [h]Data from ref 8.

(d(PO) = 174 pm) (Figure 3).[30,31] Not too surprising, from a structural point of view the cation [**1**$(OPPh_3)$]$^+$ takes an intermediate position between the covalently bound tetracoordinated silanes and tricoordinated silylium ions. For example, the Si−C^{ipso} bond lengths in [**1**$(OPPh_3)$]$^+$ are intermediate between that found for silylium ion **1** and for silane **1**(H) (d(SiC^{ipso}) = 188.9 pm ([**1**$(OPPh_3)$]$^+$); 184.7 pm (**1**); 194.6 pm (**1**(H)).[10] Similarly, the sum of the bond angles around the silicon atom in [**1**$(OPPh_3)$]$^+$ is $\sum\alpha$(Si) = 348.3°, which deviates significantly from $\sum\alpha$(Si) = 360.0° found for silylium ion **1** and from $\sum\alpha$(Si) = 333.2° detected for **1**(H).[10]

The obtained ^{31}P NMR chemical shift differences, $\Delta\delta^{31}$P, are the key quantities to determine the Gutmann−Beckett acceptor numbers (AN) for Lewis acids. The transformation to a specific AN is done applying a constant scaling factor (2.348), which is used in the original paper to span a scale from hexane (AN = 0) to $SbCl_5$ (AN = 100).[14] As the ^{31}P NMR chemical shift of the used phosphane oxides and their complexes with Lewis acids are solvent dependent and our measurements were done in benzene-d_6 in contrast to most literature data, which refer to values obtained in dichloromethane-d_2, we refrain from giving acceptor numbers but use in our analysis the NMR chemical shift difference $\Delta\delta^{31}$P in benzene.[32] The Lewis acidity of the investigated silylium ions is characterized by $\Delta\delta^{31}$P values between 39 and 45 when Et_3PO is used as the reference base (Table 1). Therefore, triarylsilylium and diarylalkylsilylium ions are significant stronger Lewis acids than neutral boron compounds such as $B(C_6F_5)_3$ ($\Delta\delta^{31}$P = 30.6) and $B(OC_6F_5)_3$ ($\Delta\delta^{31}$P = 34.5)[4] or than the neutral silicon Lewis acid $Si(CatF)_2$, **11** ($\Delta\delta^{31}$P = 35.9), recently reported by Liberman-Martin et al. (Scheme 3).[33] Their Lewis acidity is in the same range as that determined for electrophilic phosphorus(V) cations such as $[(F_5C_6)_3PF]^+$, **12** ($\Delta\delta^{31}$P = 40.4).[8] Silylium ions are outperformed with respect to Lewis acidity only by cationic borenium compounds such as **13**. Ingleson and co-workers reported that cation **13** is formed as a transient species and is isolated in the form of its complex [**13**$(OPEt_3)$], which is characterized by a ^{31}P NMR chemical shift of δ^{31}P = 106.9 and the corresponding $\Delta\delta^{31}$P value of 61.[5] The Lewis acidity of triarylsilylium ions varies only little with the substitution at the aryl group. The data summarized in Table 1 indicate however a clear and significant trend, despite the small absolute NMR chemical shift differences. The Lewis acidity of triarylsilylium ions is a function of the π/3p(Si) conjugation between the aryl substituents and the central silicon atom. In a simple FMO picture this interaction raises the LUMO energy and weakens the Lewis acidity of the cation. This is verified in the series of methyl-substituted triarylsilylium ions, in which the Lewis acidity increases slightly with decreasing number of methyl groups at the aryl substituent. To understand the increased Lewis acidity of the tri-*iso*-propylphenyl (Tipp)-substituted silylium ion **5**, two opposing effects have to be considered. (i) Larger alkyl groups in the *ortho*-position of the arylsubstituents disfavor π/3p(Si) conjugation; consequently the Tipp substituent increases the Lewis acidity of cation **5** compared to that of the mesityl-substituted cation **3**. (ii) The large substituents in

Scheme 3. Selected Main Group Lewis Acids and Their $\Delta\delta^{31}$P Values Obtained with $OPEt_3$ as a Reference Lewis Base[4,5,8,33]



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the *ortho*-position disfavor the formation of the tetracoordinated Lewis acid/base complex for steric reasons. Therefore, a decreased Lewis acidity for cation **5** might be expected.[34] The experimental data (Table 1) clearly show that in contrast to the situation for isoelectronic boron compounds the steric argument (ii) is of only minor importance and that the Lewis acidity of triarylsilylium ions is mainly determined by electronic conjugation effects. In line with these arguments also the replacement of one aryl substituent by an alkyl group (cation **5** versus cation **6**) slightly increases the Lewis acidity of silylium ions. Only one germylium ion, cation **7**, was tested, and the comparison with the related silylium ion **6** suggests that germylium ions are weaker Lewis acids compared to silylium ions (Table 1). The experimental data obtained for the $OPPh_3$ complexes provide a general picture that is completely in accordance with the conclusions drawn from the results when $OPEt_3$ is used as a reference Lewis base (Table 1).

Lewis acid scales based on calculated anion affinities, such as fluoride ion affinities (FIA) and hydride anion affinities (HIA), have the advantage of being applicable to a wide range of possible Lewis acids and are therefore very popular. Recently several computational approaches toward a systematic evaluation of the Lewis acidity of chemically very diverse Lewis acids have been published.[19−25] In the context of our study the recent computational study by Muether et al. on FIAs of internally stabilized silyl cations is of interest.[19] This study revealed a significantly higher Lewis acidity for substituted silyl cations than for equally substituted carbocations. We used in our work the quasi-isodesmic reactions shown in Scheme 4 to

Scheme 4. Reactions Used to Determine Fluoride and Hydride Affinity of Main Group Lewis Acids (LA)

$$[Et_3BF]^- + LA \longrightarrow Et_3B + [LAF]^- \quad (a)$$

$$[Et_3BH]^- + LA \longrightarrow Et_3B + [LAH]^- \quad (b)$$

assess the Lewis acidity also computationally.[35−37] In principle, these two equations provide the fluoride ion (4a) and the hydride ion affinity (4b) of the investigated Lewis acids and use triethyl borane as an anchor point for both scales. Both affinity scales are used frequently for the thermodynamic quantification of Lewis acidity, and their simultaneous use allows evaluating the influence of the hardness/softness of the applied Lewis base on the relative Lewis acidity of the investigated species.[24,25] As both calculated anion affinities gave for silylium ions nearly identical results, we will limit our discussion on the fluoride ion affinities. All relevant data for both anion affinities and additional plots are given in the SI. An independent measure of Lewis acidity that is accessible by quantum mechanical calculations is the energy level of the LUMO.[24a] Both theoretically assessed criteria, the calculated FIA and the LUMO energy level, show for the series of investigated boron-, germanium-, and silicon-based Lewis acids a rough correlation with the determined $\Delta\delta^{31}P$ values using Et_3PO as a reference base. That is, the FIA increases with increasing $\Delta\delta^{31}P$ value and the LUMO energy decreases with increasing $\Delta\delta^{31}P$ value (see Figure 4). Particularly good is the correlation between $\Delta\delta^{31}P$ values and FIA/LUMO energies in the series of methyl-substituted triarylsilylium ions. In both cases almost linear correlations exist between the FIA/LUMO energies computed for the silylium ions **1**−**4** and the corresponding $\Delta\delta^{31}P$ values.[38] More interesting is the clear deviation from these correlations for the Tipp-substituted silylium ions **5** and **6**. The

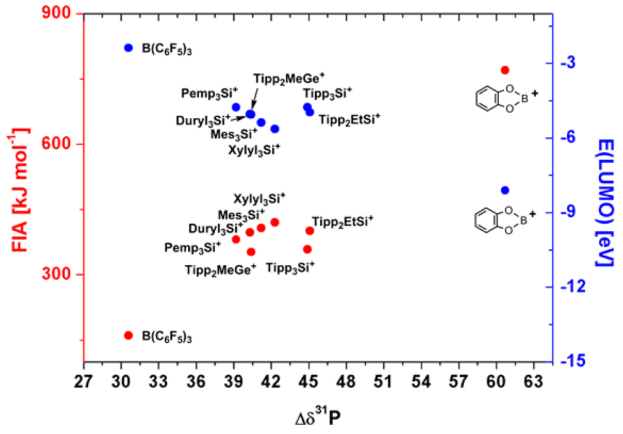

Figure 4. Plot of the fluoride ion affinities of Lewis acids calculated according to eq 4a vs $\Delta\delta^{31}P$ determined using $OPEt_3$ as a reference Lewis base (red circles). Plot of the LUMO energies of Lewis acids vs $\Delta\delta^{31}P$ (blue circles).

determined ^{31}P NMR chemical shift differences for both cations indicate a higher Lewis acidity than the theoretical methods suggest. In the case of these Tipp-substituted silylium ions NMR spectroscopic evidence that was supported by the results of quantum mechanical calculations indicated an interaction between the *ortho-iso*-propyl methine groups and the central silicon atom (Figure 5).[10b] This C−H···Si^+ interaction lowers

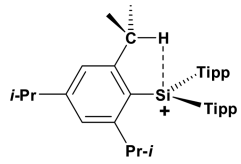

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Figure 5. Sketch of the C−H···Si^+ interaction that is operative in triisopropylphenyl-substituted cations such as silylium ion **5**.[10b]

the Lewis acidity of the Tipp-substituted silylium ions **5** and **6** compared to that of methyl-substituted triarylsilylium ions such as trimesitylsilylium **3**. The calculated FIA clearly accounts for this decreased Lewis acidity in cations **5** and **6** since the calculated structure and energy of the cations directly influence the result of reaction 4a. On the other hand, the basis for the Gutmann−Beckett method is the interaction of the phosphine oxide with the silylium ion in the investigated complex, and this strong interaction cancels the more subtle C−H···Si^+ interaction in the free cation. Consequently, the Gutmann−-Beckett method is not well suited for determining the Lewis acidity for either intra- or intermolecular stabilized Lewis acids such as the Tipp-substituted silylium ions **5** and **6**.[39] Similar problems of the Gutmann−Beckett method were recently encountered for intramolecular ferrocenyl-stabilized silyl cations[18] and have to be expected for every Lewis acid stabilized by donors.

CONCLUSION

The Gutmann−Beckett method was applied for the determination of the Lewis acidity of aryl-substituted silylium and germylium ions. The $\Delta\delta^{31}P$ values determined for these tricoordinated cationic Lewis acids indicate a significantly higher Lewis acidity than for neutral boranes. In the case of

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triarylsilylium ions, which show no indication of intra- or intermolecular interaction, the $\Delta\delta^{31}$P values correlate with theoretically obtained measures of Lewis acidity such as anion affinities and LUMO energy level. This correlation is mainly dominated by the electronic factors that determine the energetic position of the LUMO. In contrast with this finding, deviations from this correlation indicate inter- or intramolecular interactions that influence the Lewis acidity of silylium ions. This was shown previously of ferrocenyl-substituted silyl cations[18] and is extended here to even very subtle interactions, for example, C−H···Si$^+$ agostic interaction. Finally, from a practical point of view, it is worth mentioning that the investigated arylsilylium salts are among the strongest isolable Lewis acids and that a fine-tuning of the Lewis acidity is possible by taking advantage of electronic and/or steric substituent effects.

EXPERIMENTAL SECTION

General Procedures. Benzene, [D$_6$]benzene, [D$_8$]toluene, and *n*-hexane were distilled from sodium. The [Ph$_3$C][B(C$_6$F$_5$)$_4$] and [Ph$_3$C][Al(OC(CF$_3$)$_3$)$_4$] salts were synthesized as described previously.[40,41]

All reactions were carried out under inert conditions using standard Schlenk and glovebox techniques, unless stated otherwise. Argon 99.999% was used as inert gas and was dried over Si-capent prior to use. NMR spectra were recorded on Bruker Avance 500 and Avance III 500 spectrometers at 305 K, 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$_6$D$_5$H) = 7.20, δ^1H(C$_6$D$_5$(CD$_2$H)) = 2.08). ^{13}C NMR spectra were calibrated using the solvent signals (δ^{13}C(CDCl$_3$) = 77.0, δ^{13}C(C$_6$D$_6$) = 128.0, δ^{13}C(C$_7$D$_8$) = 20.4 (CD$_3$)). ^{29}Si NMR spectra were calibrated using external Me$_2$HSiCl (δ^{29}Si = 11.1 vs TMS), ^{31}P NMR spectra against external (MeO)$_3$P (δ^{31}P = 141 vs 85% H$_3$PO$_4$(aq)), ^{19}F NMR spectra against external CFCl$_3$ (δ^{19}F(CFCl$_3$) = 0.0), and ^{11}B NMR spectra against BF$_3$ OEt$_2$ (δ^{11}B(BF$_3$ OEt$_2$) = 0.0). X-ray diffraction analyses were performed on a Bruker Apex II. Structure solution and refinement was done using the SHELXS97 and SHELXL97 software.[42]

General Procedure for the Preparation of Tetrylium Borates [1−7][B(C$_6$F$_5$)$_4$]. A Schlenk tube was oven-dried and then charged with 400 mg of [Ph$_3$C][B(C$_6$F$_5$)$_4$] (0.43 mmol) and the corresponding diarylmethylsilane or -germane (0.69 mmol). The mixture was evacuated for at least 1 h. After that period the flask was flushed with dry argon and the mixture was dissolved in 4 mL of dry benzene. The resulting biphasic mixture (an upper, unpolar phase and a lower, polar phase; typical for salts of [B(C$_6$F$_5$)$_4$]$^-$ in aromatic hydrocarbons) was stirred for 1 h. Then, the phases were allowed to separate. The polar phase was washed twice with 4 mL of dry benzene. The solutions of the obtained silylium, **1**−**6**, or germylium, **7**, borates were used in further experiments as obtained.

General Procedure for the Preparation of Tetryloxyphosphonium Borates [1−7, 9(OPEt$_3$)][B(C$_6$F$_5$)$_4$]. A 0.53 mL portion of a Et$_3$PO solution (0.81 M in C$_6$D$_6$) was transferred to the solution of the corresponding tetrylium borate in C$_6$H$_6$ via a PTFE cannula. The dark-colored polar phase lightened up appreciably upon stirring the mixture for 1 h. The polar phase was then washed two times with portions of 4 mL of dry benzene. The solvent was removed under vacuum and replaced by 1 mL of dry C$_6$D$_6$.

General Procedure for the Preparation of Tetryloxyphosphonium Borates [1−5, 9(OPPh$_3$)][B(C$_6$F$_5$)$_4$]. A Schlenk tube was oven-dried and then charged with 123 mg (0.44 mmol) of Ph$_3$PO and evacuated for 1 h. A 2 mL amount of C$_6$H$_6$ was transferred via a PTFE cannula to Ph$_3$PO. The colorless solution of Ph$_3$PO in C$_6$H$_6$ was transferred to the corresponding tetrylium borate in C$_6$H$_6$ via a PTFE cannula. The dark-colored polar phase lightened up appreciably upon stirring the mixture for 1 h. The polar phase was then washed two times with portions of 4 mL of dry benzene. The solvent was removed under vacuum and replaced by 1 mL of dry C$_6$D$_6$.

Preparation of Silyloxyphosphonium Aluminate [(Me$_5$C$_6$)$_3$SiOPPh$_3$][Al(OC(CF$_3$)$_3$)$_4$]. A Schlenk tube was oven-dried, charged with 252 mg (0.74 mmol) of (Me$_5$C$_6$)$_2$SiMeH, and evacuated for at least 1 h. The flask was flushed with dry argon, and 500 mg of [Ph$_3$C][Al(OC(CF$_3$)$_3$)$_4$] (0.41 mmol) was added. The mixture was dissolved in 3 mL of dry benzene. The resulting biphasic mixture was stirred for 30 min. Then, the phases were allowed to separate. The polar phase was washed twice with portions of 2 mL of dry benzene. The solution of the obtained silylium aluminate [(Me$_5$C$_6$)$_3$Si][Al(OC(CF$_3$)$_3$)$_4$] was treated with a solution of 114 mg (0.41 mmol) of Ph$_3$PO in 2 mL of dry C$_6$H$_6$ and stirred for 10 min. The dark-colored polar phase lightened up quickly. The polar phase was then washed twice with portions of 2 mL of dry benzene and washed once with 2 mL of CH$_2$Cl$_2$. The solvent was removed under vacuum, replaced by 1 mL of dry 1,2-difluorobenzene, and stored overnight at −20 °C to obtain colorless crystals suitable for XRD analysis.

Characterization of Tetryloxyphosphonium Borates [1−7, 9(OPEt$_3$)][B(C$_6$F$_5$)$_4$]. (Signals of anion omitted for clarity.) [**1**(**OPEt$_3$**)]$^+$: ^{1}H NMR (499.87 MHz, 305.0 K, C$_6$D$_6$): δ 0.44 (dt, 9H, $^3J_{P,H}$ = 19.8 Hz, $^3J_{H,H}$ = 7.7 Hz, PCH$_2$C$\underline{H}_3$), 1.38 (dq, 6H, $^2J_{P,H}$ = 12.1 Hz, $^3J_{H,H}$ = 7.7 Hz, PC$\underline{H}_2$CH$_3$), 2.05−2.13 (m, 45H, C$\underline{H}_3$). ^{13}C{^{1}H} NMR (125.71 MHz, 305.0 K, C$_6$D$_6$): δ 4.7 (d, $^2J_{C,P}$ = 5.0 Hz, PCH$_2$C$\underline{H}_3$), 16.1 (s, *m*-C$\underline{H}_3$), 16.8 (s, *p*-C$\underline{H}_3$), 18.4 (d, $^1J_{C,P}$ = 64.3 Hz, PC$\underline{H}$2CH$_3$), 23.1 (s, *o*-C$\underline{H}_3$), 134.3 (b, 2 × Cq), 135.2 (Cq), 138.9 (Cq). ^{31}P{^{1}H} NMR (202.35 MHz, 305.2 K, C$_6$D$_6$): δ 85.4 (s). ^{29}Si{^{1}H} NMR (99.32 MHz, 305.0 K, C$_6$D$_6$): δ −5.1 (d, $^2J_{Si,P}$ = 20.3 Hz).

[**2**(**OPEt$_3$**)]$^+$: ^{1}H NMR (499.87 MHz, 305.1 K, C$_6$D$_6$): δ 0.44 (dt, 9H, $^3J_{P,H}$ = 19.7 Hz, $^3J_{H,H}$ = 7.7 Hz, PCH$_2$C$\underline{H}_3$), 1.38 (dq, 6H, $^2J_{P,H}$ = 12.0 Hz, $^3J_{H,H}$ = 7.7 Hz, PC$\underline{H}_2$CH$_3$), 1.95 (s, 18H, *m*-C$\underline{H}_3$), 2.04 (s, 18H, *o*-C$\underline{H}_3$), 6.96 (s, 3H, *p*-C$\underline{H}_3$). ^{13}C{^{1}H} NMR (125.71 MHz, 305.0 K, C$_6$D$_6$): δ 4.7 (d, $^2J_{C,P}$ = 4.9 Hz, PCH$_2$C$\underline{H}_3$), 18.4 (d, $^1J_{C,P}$ = 64.0 Hz, PC$\underline{H}_2$CH$_3$), 19.8 (s, *o*-C$\underline{H}_3$), 21.6 (s, *m*-C$\underline{H}_3$), 135.2 (C$\underline{H}$), 135.7 (2 × Cq), 136.8 (Cq). ^{31}P{^{1}H} NMR (202.35 MHz, 305.3 K, C$_6$D$_6$): δ 86.5 (s). ^{29}Si{^{1}H} NMR (99.32 MHz, 305.0 K, C$_6$D$_6$): δ −5.1 (d, $^2J_{Si,P}$ = 20.2 Hz).

[**3**(**OPEt$_3$**)]$^+$: ^{1}H NMR (499.87 MHz, 305.0 K, C$_6$D$_6$): δ 0.45 (dt, 9H, $^3J_{P,H}$ = 19.8 Hz, $^3J_{H,H}$ = 7.7 Hz PCH$_2$C$\underline{H}_3$), 1.42 (dq, 6H, $^2J_{P,H}$ = 11.9 Hz, $^3J_{H,H}$ = 7.7 Hz, PC$\underline{H}_2$CH$_3$), 1.98 (s, 18H, *o*-C$\underline{H}_3$), 2.16 (s, 9 H, *p*-C$\underline{H}_3$), 6.74 (s, 6H, *m*-C$\underline{H}$). ^{13}C{^{1}H} NMR (125.71 MHz, 305.0 K, C$_6$D$_6$): δ 5.1 (d, $^2J_{C,P}$ = 5.3 Hz, PCH$_2$C$\underline{H}_3$), 18.4 (d, $^1J_{C,P}$ = 63.2 Hz, PC$\underline{H}_2$CH$_3$), 20.8 (s, *p*-CH$_3$), 24.2 (s, *o*-C$\underline{H}_3$), 130.6 (CH), 130.9 (Cq), 142.2 (Cq), 144.1 (Cq). ^{31}P{^{1}H} NMR (202.35 MHz, 305.2 K, C$_6$D$_6$): δ 87.4 (s). ^{29}Si{^{1}H} NMR (99.32 MHz, 305.0 K, C$_6$D$_6$): δ −5.3 (d, $^2J_{Si,P}$ = 20.1 Hz).

[**4**(**OPEt$_3$**)]$^+$: ^{1}H NMR (499.87 MHz, 305.0 K, C$_6$D$_6$): δ 0.42 (dt, 9H, $^3J_{P,H}$ = 19.8 Hz, $^3J_{H,H}$ = 7.7 Hz, PCH$_2$C$\underline{H}_3$), 1.38 (dq, 6H, $^2J_{P,H}$ = 11.8 Hz, $^3J_{H,H}$ = 7.7 Hz, PC$\underline{H}_2$CH$_3$), 1.94 (s, 18H, *o*-C$\underline{H}_3$), 6.71−6.75 (m, 6H), 6.80−6.86 (m, 6H), 7.24−7.26 (m, 3H). ^{13}C{^{1}H} NMR (125.71 MHz, 305.0 K, C$_6$D$_6$): δ 5.0 (d, $^2J_{C,P}$ = 4.7 Hz, PCH$_2$C$\underline{H}_3$), 18.4 (d, $^1J_{C,P}$ = 63.5 Hz, PC$\underline{H}_2$CH$_3$), 24.3 (s, *o*-C$\underline{H}_3$), 129.6 (CH), 134.0 (Cq), 142.1 (CH), 144.0 (Cq). ^{31}P{^{1}H} NMR (202.35 MHz, 305.2 K, C$_6$D$_6$): δ 88.5 (s). ^{29}Si{^{1}H} NMR (99.32 MHz, 305.0 K, C$_6$D$_6$): δ −6.3 (d, $^2J_{Si,P}$ = 20.3 Hz).

[**5**(**OPEt$_3$**)]$^+$: ^{1}H NMR (499.87 MHz, 297 K, C$_6$D$_6$): δ 0.57 (dt, 9H, $^3J_{P,H}$ = 19.7 Hz, $^3J_{H,H}$ = 7.7 Hz, PCH$_2$C$\underline{H}_3$), 1.19 (d, 14H, $^3J_{H,H}$ = 6.9 Hz, *o*-CH(C$\underline{H}_3$)$_2$), 1.27 (d, 7H, $^3J_{H,H}$ = 7.0 Hz, *p*-CH(C$\underline{H}_3$)$_2$), 1.43 (dq, 6H, $^2J_{P,H}$ = 11.9 Hz, $^3J_{H,H}$ = 7.0 Hz, PC$\underline{H}_2$CH$_3$), 2.74 (sep, 6H, $^3J_{H,H}$ = 6.9 Hz, *o*-C$\underline{H}$(CH$_3$)$_2$), 2.84 (sep, 3H, $^3J_{H,H}$ = 6.9 Hz, *p*-C$\underline{H}$(CH$_3$)$_2$), 7.00 (s, 2H, *m*-C$\underline{H}$). ^{13}C{^{1}H} NMR (125.71 MHz, 297.0 K, C$_6$D$_6$): δ 4.38 (d, $^2J_{C,P}$ = 5.4 Hz, PCH$_2$C$\underline{H}_3$), 17.53 (d, $^1J_{C,P}$ = 62.2 Hz, PC$\underline{H}_2$CH$_3$), 23.6 (*p*-CH(C$\underline{H}_3$)$_2$), 24.4 (*o*-CH(C$\underline{H}_3$)$_2$), 34.5 (*p*-C$\underline{H}$(CH$_3$)$_2$), 34.8 (*o*-C$\underline{H}$(CH$_3$)$_2$), 122.4 (CH), 149.1 (Cq), 153.6 (broad, 2 × Cq). ^{31}P{^{1}H} NMR (202.35 MHz, 297.1 K, C$_6$D$_6$): δ 91.1 (s). ^{29}Si{^{1}H} NMR (99.32 MHz, 296.9 K, C$_6$D$_6$): δ 6.8 (d, $^2J_{Si,P}$ = 14.5 Hz).

[**6**(**OPEt$_3$**)]$^+$: ^{1}H NMR (499.87 MHz, 305.1 K, C$_6$D$_6$): δ 0.58 (dt, 9H, $^3J_{P,H}$ = 19.9 Hz, $^3J_{H,H}$ = 7.7 Hz, PCH$_2$C$\underline{H}_3$), 0.8 (t, 3H, $^3J_{H,H}$ = 7.7 Hz, SiCH$_2$C$\underline{H}_3$), 0.91−0.97 (m, 2H), 1.00 (d, 3H, $^3J_{H,H}$ = 6.5 Hz), 1.03 (d, 3H, $^3J_{H,H}$ = 6.3 Hz), 1.16−1.22 (m, 18H), 1.24 (d, 6H, $^3J_{H,H}$ =

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6.8 Hz), 1.29 (d, 4H, $^{3}J_{H,H}$ = 6.8 Hz), 1.33−1.40 (m, 2H), 1.47 (dq, 6H, $^{2}J_{P,H}$ = 12.3 Hz, $^{3}J_{H,H}$ = 7.7 Hz, PC$\underline{H}_2$CH$_3$), 2.54−2.59 (m, 1H), 2.71−2.79 (m, 3H), 3.02−3.08 (m, 1H), 3.24−3.30 (m, 1H), 6.88 (s, 1H), 6.94 (s, 1H), 7.02−7.06 (m, 1H), 7.34−7.37 (m, 1H). ^{13}C{^{1}H} NMR (125.71 MHz, 305.0 K, C_6D_6): δ 4.5 (d, $^{2}J_{C,P}$ = 4.3 Hz, PCH$_2$CH$_3$), 8.6 (SiCH$_2$CH$_3$), 15.9 (SiCH$_2$CH$_3$), 17.7 (d, $^{1}J_{C,P}$ = 62.5 Hz, PCH$_2$CH$_3$), 22.0, 22.9, 23.7, 23.9, 24.7, 25.7, 31.1, 33.2, 35.1, 122.5 (CH), 123.4 (CH), 152.5 (Cq), 153.4 (Cq), 153.7 (Cq), 153.8 (Cq), 154.1 (Cq), 155.5 (Cq). ^{31}P NMR (202.35 MHz, 305.2 K, C_6D_6): δ 91.3 (s). ^{29}Si NMR (99.32 MHz, 305.0 K, C_6D_6): δ 11.1 (d, $^{2}J_{Si,P}$ = 14.7 Hz).

[**7**(**OPEt$_3$**)]$^+$: ^{1}H NMR (499.87 MHz, 305.1 K, C_6D_6): δ 0.58 (dt, 9H, $^{3}J_{P,H}$ = 19.2 Hz, $^{3}J_{H,H}$ = 7.6 Hz, PCH$_2$C$\underline{H}_3$), 1.05 (s, 3H, GeC$\underline{H}_3$), 1.17−1.20 (m, 22H), 1.25−1.27 (m, 10H), 1.34 (dq, 6H, $^{2}J_{P,H}$ = 11.9 Hz, $^{3}J_{H,H}$ = 7.6 Hz, PC$\underline{H}_2$CH$_3$), 2.72−2.87 (m, 6H, *o*-C$\underline{H}$(CH$_3$)$_2$, *p*-CH(CH$_3$)$_2$), 7.00 (s, 1H), 7.05 (s, 5H). ^{13}C{^{1}H} NMR (125.71 MHz, 305.0 K, C_6D_6): δ 4.5 (d, $^{2}J_{C,P}$ = 5.4 Hz, PCH$_2$C$\underline{H}_3$), 12.6 (s, CH$_3$), 18.2 (d, $^{1}J_{C,P}$ = 63.4 Hz, P$\underline{C}$H$_2$CH$_3$), 23.6 (CH$_3$), 24.3 (CH$_3$), 34.5 (CH$_3$), 34.9 (CH$_3$), 38.1 (CH$_3$), 122.4 (CH$_3$), 123.3 (CH$_3$), 132.1 (Cq), 147.63 (Cq), 149.1 (Cq), 152.9 (Cq), 153.3 (Cq). ^{31}P{^{1}H} NMR (202.35 MHz, 305.2 K, C_6D_6): δ 86.6 (s).

[**9**(**OPEt$_3$**)]$^+$: ^{1}H NMR (499.87 MHz, 305.1 K, C_6D_6): δ 0.32 (q, 6H, $^{3}J_{H,H}$ = 7.9 Hz, SiC$\underline{H}_2$CH$_3$), 0.54 (dt, 9H, $^{3}J_{P,H}$ = 19.6 Hz, $^{3}J_{H,H}$ = 7.8 Hz, PCH$_2$C$\underline{H}_3$), 0.65−0.72 (m, 27H, 2 × *PCH$_2$C$\underline{H}_3$, SiCH$_2$C$\underline{H}_3$), 1.05−1.16 (m, 18H, 2 × *PC$\underline{H}_2$CH$_3$, PCH$_2$CH$_3$); *signals from the starting material Et$_3$PO. ^{13}C{^{1}H} NMR (125.71 MHz, 305.0 K, C_6D_6): δ 4.1 (d, $^{2}J_{C,P}$ = 5.05 Hz, PCH$_2$C$\underline{H}_3$), 5.3 (SiC$\underline{H}_2$CH$_3$), 5.7 (SiCH$_2$C$\underline{H}_3$), 17.0 (d, $^{1}J_{C,P}$ = 63.5 Hz, PC$\underline{H}_2$CH$_3$). ^{31}P{^{1}H} NMR (202.35 MHz, 305.2 K, C_6D_6): δ 88.6 (s). ^{29}Si{^{1}H} NMR (99.32 MHz, 305.0 K, C_6D_6): δ 35.4 (d, $^{2}J_{Si,P}$ = 17.7 Hz).

Characterization of Tetryloxyphosphonium Borates [1−5, 9(OPPh$_3$)][B(C$_6$F$_5$)$_4$]. (Signals of anion omitted for clarity.) [**1**-(**OPPh$_3$**)]$^+$: ^{1}H NMR (499.87 MHz, 305.0 K, C_6D_6): δ 1.68 (s, 18H), 2.04 (s, 9H), 2.20 (s, 9H), 2.30 (s, 9H), 6.88−6.93 (m, 6H), 6.95−6.99 (m, 6H), 7.28−7.31 (m, 3H). ^{13}C{^{1}H} NMR (125.71 MHz, 305.0 K, C_6D_6): δ 16.0 (CH$_3$), 16.3 (CH$_3$), 16.8 (CH$_3$), 23.0 (CH$_3$), 23.5 (CH$_3$), 123.0 (d, $^{1}J_{C,P}$ = 113.1 Hz, *i*-C$\underline{P}$), 129.6 (d, $^{2}J_{C,P}$ = 14.0 Hz, *o*-C$\underline{H}$), 133.0 (d, $^{3}J_{C,P}$ = 12.2 Hz, *m*-C$\underline{H}$), 134.5 (Cq), 135.1 (Cq), 135.5 (d, $^{4}J_{C,P}$ = 2.6 Hz, *p*-C$\underline{H}$), 138.6 (Cq), 138.7 (Cq), 140.5 (Cq). ^{31}P{^{1}H} NMR (202.35 MHz, 305.2 K, C_6D_6): δ 54.7 (s). ^{29}Si{^{1}H} NMR (99.32 MHz, 305.0 K, C_6D_6): δ −2.6 (d, $^{2}J_{Si,P}$ = 21.7 Hz).

[**2**(**OPPh$_3$**)]$^+$: ^{1}H NMR (499.87 MHz, 305.1 K, C_6D_6): δ 1.61 (s, 9H), 1.72 (s, 9H), 2.07 (s, 9H), 2.14 (s, 9H), 6.87−6.92 (m, 6H), 6.95−6.98 (m, 6H), 7.26−7.29 (m, 3H). ^{13}C{^{1}H} NMR (125.71 MHz, 305.0 K, C_6D_6): δ 19.6 (CH$_3$), 20.1 (CH$_3$), 21.7 (CH$_3$), 21.8 (CH$_3$), 122.8 (d, $^{1}J_{C,P}$ = 112.7 Hz, *i*-C$\underline{P}$), 129.7 (d, $^{2}J_{C,P}$ = 14.1 Hz, *o*-C$\underline{H}$), 132.3 (d, $^{3}J_{C,P}$ = 12.0 Hz, *m*-C$\underline{H}$), 133.2 (d, $^{3}J_{C,P}$ = 12.0 Hz, *m*-C$\underline{H}$), 135.0 (CH), 135.3 (Cq), 135.6 (d, $^{4}J_{C,P}$ = 2.6 Hz, *p*-C$\underline{H}$), 136.7 (Cq), 139.5 (Cq), 141.1 (Cq). ^{31}P{^{1}H} NMR (202.35 MHz, 305.3 K, C_6D_6): δ 55.4 (s). ^{29}Si{^{1}H} NMR (99.32 MHz, 305.0 K, C_6D_6): δ −2.8 (d, $^{2}J_{Si,P}$ = 21.7 Hz).

[**3**(**OPPh$_3$**)]$^+$: ^{1}H NMR (499.87 MHz, 305.1 K, C_6D_6): δ 1.83−2.03 (m, 18H, *o*-C$\underline{H}_3$), 2.19 (s, 9H, *p*-CH$_3$), 6.57−6.75 (m, 6H, *m*-C$\underline{H}$), 6.98−7.02 (m, 6H), 7.24−7.27 (m, 3H). ^{13}C{^{1}H} NMR (125.71 MHz, 305.0 K, C_6D_6): δ 20.8 (s, *p*-C$\underline{H}_3$), 24.2−24.6 (broad, *o*-C$\underline{H}_3$), 122.7 (d, $^{1}J_{C,P}$ = 112.0 Hz, *i*-C$\underline{P}$), 129.8 (d, $^{2}J_{C,P}$ = 14.2 Hz, *o*-C$\underline{H}$), 131.1 (Cq), 132.3 (d, $^{3}J_{C,P}$ = 12.3 Hz, *m*-C$\underline{H}$), 133.3 (d, $^{3}J_{C,P}$ = 12.0 Hz, *m*-C$\underline{H}$), 135.8 (d, $^{4}J_{C,P}$ = 2.7 Hz, *p*-C$\underline{H}$), 135.8 (*m*-C$\underline{H}$), 142.1 (Cq), 144.2 (Cq). ^{31}P{^{1}H} NMR (202.35 MHz, 305.2 K, C_6D_6): δ 56.5 (s). ^{29}Si{^{1}H} NMR (99.32 MHz, 305.0 K, C_6D_6): δ −3.9 (d, $^{2}J_{Si,P}$ = 21.5 Hz).

[**4**(**OPPh$_3$**)]$^+$: ^{1}H NMR (499.87 MHz, 305.0 K, C_6D_6): δ 1.86 (s, 9H), 2.06 (s, 9H), 6.71−6.86 (m, 9H). ^{13}C{^{1}H} NMR (125.71 MHz, 305.0 K, C_6D_6): δ 24.2 (C$\underline{H}_3$), 24.7 (C$\underline{H}_3$), 122.4 (d, $^{1}J_{C,P}$ = 112.1 Hz, *i*-C$\underline{P}$), 129.2 (C$\underline{H}$), 129.8 (d, $^{2}J_{C,P}$ = 14.3 Hz, *o*-C$\underline{H}$), 131.8 (C$\underline{H}$), 132.3 (d, $^{3}J_{C,P}$ = 11.8 Hz, *m*-C$\underline{H}$), 133.2 (d, $^{3}J_{C,P}$ = 12.2 Hz, *m*-C$\underline{H}$), 134.1 (Cq), 135.9 (d, $^{4}J_{C,P}$ = 2.0 Hz, *p*-C$\underline{H}$). ^{31}P{^{1}H} NMR (202.35 MHz, 305.2 K, C_6D_6): δ 57.2 (s). ^{29}Si{^{1}H} NMR (99.32 MHz, 305.0 K, C_6D_6): δ −5.1 (d, $^{2}J_{Si,P}$ = 21.3 Hz).

[**5**(**OPPh$_3$**)]$^+$: ^{1}H NMR (499.87 MHz, 295.1 K, C_6D_6): δ 0.86−0.91 (m, 36H), 1.22 (d, 9H, $^{3}J_{H,H}$ = 7 Hz, *p*-CH(C$\underline{H}_3$)$_2$), 1.23 (d, 9H, $^{3}J_{H,H}$ = 7 Hz, *p*-CH(C$\underline{H}_3$)$_2$), 2.77 (sep, 3H, 6H, $^{3}J_{H,H}$ = 6.9 Hz, *o*-C$\underline{H}$(CH$_3$)$_2$), 3.10−3.24 (m, 6H, *o*-C$\underline{H}$(CH$_3$)$_2$, 7.06−7.10 (m, 12H), 7.22−7.28 (m). ^{13}C{^{1}H} NMR (125.71 MHz, 297.8 K, C_6D_6): δ 23.8 (*p*-CH(C$\underline{H}_3$)$_2$), 24.2 (*o*-CH(C$\underline{H}_3$)$_2$), 33.1 (*p*-C$\underline{H}$(CH$_3$)$_2$), 34.5 (*o*-C$\underline{H}$(CH$_3$)$_2$), 121.3 (d, $^{1}J_{C,P}$ = 111.2 Hz, *i*-CP), 122.9 (CH), 130.1 (d, $^{2}J_{C,P}$ = 13.8 Hz, *o*-CH), 133.3 (d, $^{3}J_{C,P}$ = 12.2 Hz, *m*-CH), 136.1 (d, $^{2}J_{C,P}$ = 2.3 Hz, *p*-CH), 153.0 (Cq), 154.0 (Cq). ^{31}P NMR (202.35 MHz, 305.3 K, C_6D_6): δ 56.3 (s). ^{29}Si NMR (99.32 MHz, 305.0 K, C6D6): δ 10.2 (d, $^{2}J_{Si,P}$ = 16.0 Hz).

[**9**(**OPPh$_3$**)]$^+$: ^{1}H NMR (499.87 MHz, 298.1 K, C_6D_6): δ 0.36 (d, 6H, $^{3}J_{H,H}$ = 8.1 Hz, SiC$\underline{H}_2$CH$_3$), 0.65 (t, 9H, $^{3}J_{H,H}$ = 8.1 Hz SiCH$_2$C$\underline{H}_3$), 7.11−7.18 (m, 12H), 7.30−7.33 (m, 3H). ^{13}C{^{1}H} NMR (125.71 MHz, 298.1 K, C_6D_6): δ 5.4 (SiC$\underline{H}_2$CH$_3$), 5.7 (SiCH$_2$C$\underline{H}_3$), 122.0 (d, $^{1}J_{C,P}$ = 111.1 Hz, *i*-C$\underline{P}$), 130.2 (d, $^{2}J_{C,P}$ = 13.9 Hz, *o*-C$\underline{H}$), 132.3 (d, $^{3}J_{C,P}$ = 12.5 Hz, *m*-C$\underline{H}$). ^{31}P{^{1}H} NMR (202.35 MHz, 297.9 K, C_6D_6): δ 52.7 (s). ^{29}Si{^{1}H} NMR (99.32 MHz, 305.0 K, C_6D_6): δ 38.5 (d, $^{2}J_{Si,P}$ = 16.7 Hz).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00556.

Experimental, computational, and analytical details and data (PDF)

Crystallographic data (CIF)

Chemical structure (XYZ)

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Notes

The authors declare no competing financial interest.

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