

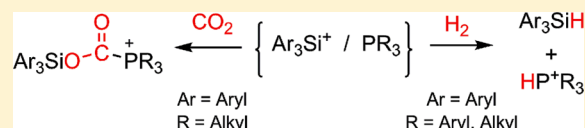
## Silylium Ion/Phosphane Lewis Pairs

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## Supporting Information

**ABSTRACT:** The reactivity of a series of silylium ion/phosphane Lewis pairs was studied. Triarylsilylium borates  $4[\text{B}(\text{C}_6\text{F}_5)_4]$  form frustrated Lewis pairs (FLPs) of moderate stability with sterically hindered phosphanes **2**. Some of these FLPs are able to cleave dihydrogen under ambient conditions. The combination of bulky trialkylphosphanes with triarylsilylium ions can be used to sequester  $\text{CO}_2$  in the form of silylacylphosphonium ions **12**. The ability to activate molecular hydrogen by reaction of silylium ion/phosphane Lewis pairs is dominated by thermodynamic and steric factors. For a given silylium ion increasing proton affinity and increasing steric hindrance of the phosphane proved to be beneficial. Nevertheless, excessive steric hindrance leads to a breakdown of the dihydrogen-splitting activity of a silylium/phosphane Lewis pair.



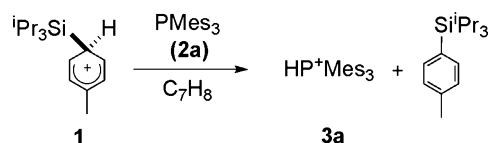
## INTRODUCTION

The concept of frustrated Lewis pairs (FLPs) has added new perspectives to bond activation chemistry.<sup>1</sup> The phenomenon of unquenched reactivity of sterically hindered Lewis pairs has been known since the 1940s.<sup>2–5</sup> However, it was the achievement of the Stephan group to show that the unquenched reactivity of sterically hindered borane/phosphane Lewis pairs can be used in bond activation chemistry: for example, in reversible heterolytic dihydrogen-splitting reactions<sup>6</sup> and  $\text{CO}_2$  fixation chemistry.<sup>7</sup> Shortly after Stephan et al.'s report, investigations on a series of intra- and intermolecular FLPs and on their chemical properties were published.<sup>1</sup> In addition, these experimental efforts prompted considerable theoretical work on the nature of the FLPs and on the mechanism of the bond activation reactions, in particular of the dihydrogen-splitting reaction.<sup>8–10</sup> The significance of this chemistry once again grew considerably, as it was shown that some of these FLPs can be used to catalyze hydrogenation reactions of polar double bonds.<sup>1,6,11</sup> The classical borane/phosphane frustrated Lewis pair experienced many variations, mostly and most effectively concerning the Lewis base.<sup>1,12</sup> Fewer results have been reported with respect to variations of the Lewis acid.<sup>13</sup> Here in particular the application of aluminum compounds as Lewis acids proved to be a successful strategy in small-molecule activation chemistry.<sup>14</sup> A recent contribution of our group disclosed that silylium ions,  $\text{R}_3\text{Si}^+$ , which are isolobal with boranes and alanes, form FLPs with sterically hindered phosphanes.<sup>15a</sup> These FLPs were successfully applied in dihydrogen activation. The increased Lewis acidity of the positively charged silylium ions in comparison to boranes is expected to enhance the reactivity of the silylium-based FLPs, and a shift of the reactivity spectrum to stronger Lewis acids and weaker Lewis bases can be assumed.<sup>16</sup> Against this background, we investigated the behavior of several silylium ion/phosphane Lewis pairs and their reactivity versus different

standard substrates, including dihydrogen, alkynes, alkyl fluorides, and  $\text{CO}_2$ .

## RESULTS AND DISCUSSION

Trialkylsilylium ions such as  $i\text{-Pr}_3\text{Si}^+$  form silylated arenium ions in aromatic hydrocarbons such as toluene, i.e. **1**, which act as very potent silylation agents versus many nucleophiles.<sup>17</sup> In some cases, however, the use of silylated arenium ions as Brønsted acids has been reported.<sup>18</sup> Similarly, the reaction of toluenium ion **1** with trimesitylphosphane (**2a**) results in formation of the phosphonium ion **3a** along with *p*-(tri-*iso*-propylsilyl)toluene (Scheme 1).<sup>19</sup>

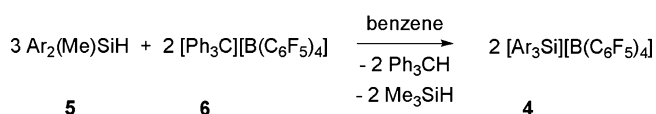
Scheme 1. Reaction of Toluenium Ion **1** with Phosphane **2a**

Consequently, for a comparative study on the chemistry of silyl cation/phosphane Lewis pairs the generation of silylated arenium ions has to be strictly excluded. This requirement restricts our investigations to the use of sterically hindered triarylsilylium ions **4** as Lewis acids. These triarylsilylium ions **4** were prepared in the form of their tetrakis(pentafluorophenyl)-borates according to a modified Bartlett–Condon–Schneider (BCS) hydride transfer from diarylmethylsilanes **5** and trityl borate ( $6[\text{B}(\text{C}_6\text{F}_5)_4]$ ), reported previously by our group (Scheme 2).<sup>15,20</sup>

**Special Issue:** Applications of Electrophilic Main Group Organometallic Molecules

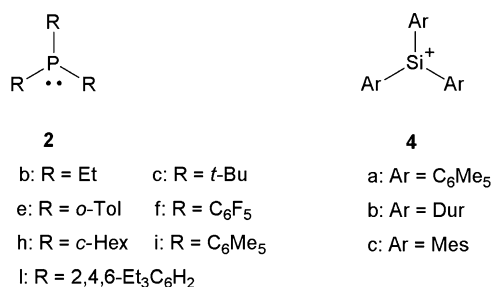
**Received:** June 15, 2013

**Published:** September 11, 2013

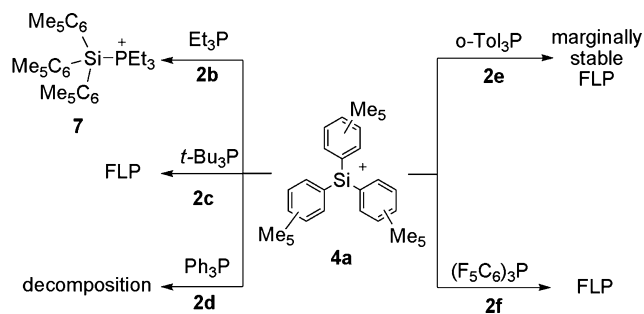
**Scheme 2. Synthesis of Triarylsilylium Ions 4 According to the Modified BCS Hydride Transfer Protocol<sup>a</sup>**


<sup>a</sup>a, Ar = pentamethylphenyl (Pemp); b, Ar = 2,3,5,6-tetramethylphenyl (duryl); c, Ar = 2,4,6-trimethylphenyl (Mes).

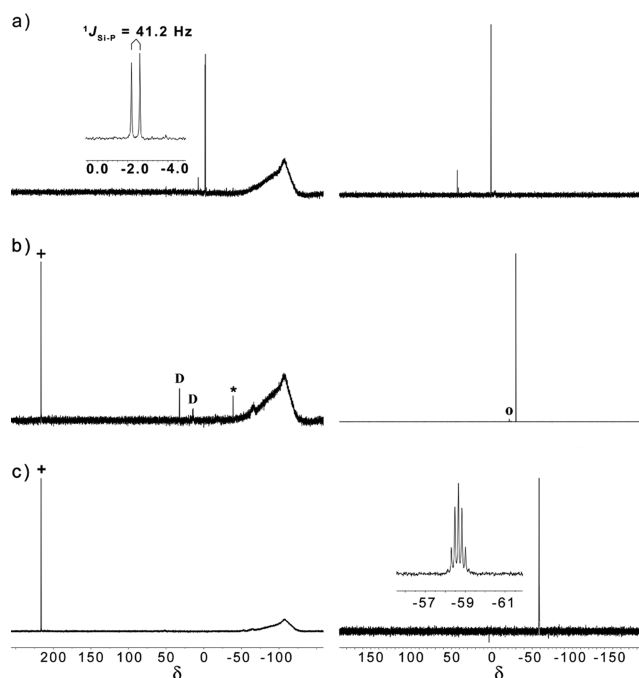
The next question that had to be addressed was the behavior of simple equimolar silylium ion 4/phosphane 2 mixtures.



Therefore, samples of silylium borates 4[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] were prepared in deuterated aromatic solvents such as benzene-*d*<sub>6</sub> and toluene-*d*<sub>8</sub> and were then treated with solutions of phosphanes 2 in the same solvent. When aromatic hydrocarbons were used, biphasic mixtures were obtained which are typical for [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup> salts. The mixtures were stirred for 30 min at room temperature; both phases were allowed to separate and were then independently subjected to multinuclear NMR spectroscopy. Control experiments in chlorobenzene-*d*<sub>5</sub> were conducted to test for the influence of the biphasic reaction medium, with virtually identical results. As expected, sterically less hindered phosphanes 2 form classical Lewis acid base pairs even with sterically highly congested silylium ions such as (Me<sub>5</sub>C<sub>6</sub>)<sub>3</sub>Si<sup>+</sup> (4a). For example, when a solution of 4a[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] in benzene was combined with triethylphosphane (2b), the formation of the silylated triethylphosphonium ion (Me<sub>5</sub>C<sub>6</sub>)<sub>3</sub>Si-P<sup>+</sup>Et<sub>3</sub> (7) was observed (Scheme 3). Phospho-

**Scheme 3. Reactivity of Silylium Ion 4a versus Different Phosphanes**


onium ion 7 was characterized by its <sup>31</sup>P NMR chemical shift δ(<sup>31</sup>P) -4.4 and the strongly high field shifted <sup>29</sup>Si NMR signal δ(<sup>29</sup>Si) -1.9 (Figure 1a). The detection of a substantial <sup>29</sup>Si/<sup>31</sup>P coupling constant (<sup>1</sup>J<sub>Si-P</sub> = 41.2 Hz) indicates the formation of a Si-P bond. *t*-Bu<sub>3</sub>P (2c), as an example of a sterically bulky trialkylphosphane, shows no Lewis acid-base adduct formation with silylium ion 4a. This is shown by the unchanged <sup>29</sup>Si and <sup>31</sup>P NMR data of the mixture. The situation is different in the



**Figure 1.** 99.32 MHz <sup>29</sup>Si{<sup>1</sup>H} NMR (left) and 202.25 MHz <sup>31</sup>P{<sup>1</sup>H} NMR spectra (right) in C<sub>6</sub>D<sub>6</sub> of the combinations of (Me<sub>5</sub>C<sub>6</sub>)<sub>3</sub>Si<sup>+</sup> (4a) and (a) Et<sub>3</sub>P (2b), (b) Mes<sub>3</sub>P (2a), and (c) (*p*-HF<sub>4</sub>C<sub>6</sub>)<sub>3</sub>P (2g) after 30 min at 305 K. Additional signals: (\*) (C<sub>6</sub>Me<sub>5</sub>)<sub>3</sub>SiH; (+) (C<sub>6</sub>Me<sub>5</sub>)<sub>3</sub>Si<sup>+</sup>; (0) Mes<sub>3</sub>PH<sup>+</sup>; (D) decomposition products.

case of aryl-substituted phosphanes. NMR investigations of a mixture of silylium borate 4a[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] with Ph<sub>3</sub>P (2d), show no sign of adduct formation. However, after 30 min of stirring the mixture at room temperature, complete decomposition in several unidentified products had occurred. An increase in the steric bulk of the aryl substituents at the phosphorus atom enhances the stability of the silylium/phosphane Lewis pair considerably. Therefore, the Lewis pair 4a and Mes<sub>3</sub>P (2a) shows no significant decomposition after 30 min at room temperature (Figure 1b). In addition, the use of less basic triarylsphosphanes has a marked influence on the stability of the silylium/phosphane Lewis pairs. For example, an equimolar mixture of 4a[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] with (*p*-HF<sub>4</sub>C<sub>6</sub>)<sub>3</sub>P (2g) shows no adduct formation and is stable at room temperature for at least several days (Scheme 3 and Figure 1c). A slight decrease of the steric hindrance at the silylium ion has no apparent influence. All three tested triarylsilylium ions, tris(pentamethylphenyl)- (4a), triduryl- (4b), and trimesitylsilylium (4c), form frustrated Lewis pairs of moderate stability with trimesitylphosphane (2a). The long-term instability of silylium/triarylsphosphane Lewis pairs seems to be related to the lack of stability of the silylium ion in solution. Triarylsilylium ions 4 tend to decompose over an extended period of time under ambient conditions, and protonated arenes have been isolated as products.<sup>15,21</sup> In the case of the Lewis pair 4a/2e the phosphonium ion *o*-Tol<sub>3</sub>P<sup>+</sup>H (3e) was detected. The instability of frustrated Lewis acid/base pairs has been noted previously also for other systems<sup>22</sup> and seems to be related to the high unquenched reactivity of the Lewis acid.

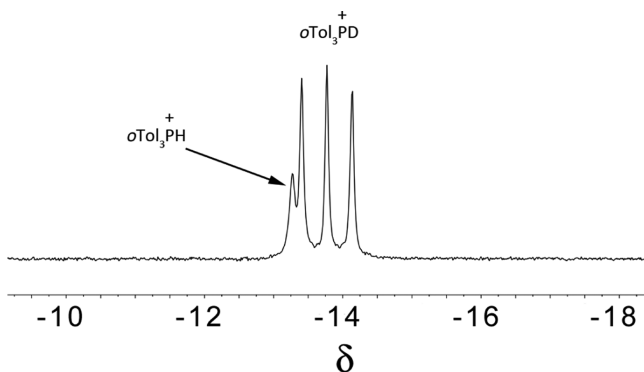
Several combinations of silylium ions 4a-c and phosphanes 2c,e-1 have been tested in dihydrogen activation experiments. For this purpose, a freshly prepared benzene-*d*<sub>6</sub> solution of the silylium borate 4[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] was mixed with a solution of an equimolar amount of the phosphane 2 in the same solvent and

**Table 1.** Behavior of Silylium Ion 4/Phosphane 2 Combinations versus Dihydrogen and Selected NMR Data of the Resulting Silane 8/Phosphonium Ion 3 Mixtures
$$\text{Ar}_3\text{Si}^+ + \text{R}_3\text{P} \xrightarrow[30 \text{ min}]{\text{H}_2, \text{r.t., } 0.1 \text{ MPa}} \text{Ar}_3\text{SiH} + \text{R}_3\text{P}^+\text{H} \quad (1)$$

Ar	R	H <sub>2</sub> cleavage	$\delta(^{29}\text{Si})$ for 8, ( $^1J_{\text{Si-H}}$ , Hz)	$\delta(^{31}\text{P})$ for 3, ( $^1J_{\text{P-H}}$ , Hz)
C <sub>6</sub> Me <sub>5</sub> , <b>4a</b>	Mes, <b>2a</b>	yes	<b>8a</b> : -38.9 (195.7)	<b>3a</b> : -27.2 (478)
	<i>t</i> -Bu, <b>2c</b>	yes	<b>8a</b> : -38.9 (195.7)	<b>3c</b> : 60.0 (430)
	<i>o</i> -Tol, <b>2e</b>	yes	<b>8a</b> : -38.9 (195.7)	<b>3e</b> : -13.4 (481)
	C <sub>6</sub> F <sub>5</sub> , <b>2f</b>	no		
	<i>p</i> -C <sub>6</sub> F <sub>4</sub> H, <b>2g</b>	no		
	<i>c</i> Hex, <b>2h</b>	yes	<b>8a</b> : -38.9 (195.7)	<b>3h</b> : 34.2 (442)
	C <sub>6</sub> Me <sub>5</sub> , <b>2i</b>	yes	<b>8a</b> : -38.9 (195.7)	<b>3i</b> : -17.3 (484)
	Tipp, <b>2k</b>	no		
	2,4,6-Et <sub>3</sub> C <sub>6</sub> H <sub>2</sub> , <b>2l</b>	yes	<b>8a</b> : -38.9 (195.7)	<b>3l</b> : -30.5 (477)
Dur, <b>4b</b>	Mes, <b>2a</b>	yes	<b>8b</b> : -40.1 (196.4)	<b>3a</b> : -27.2 (478)
Mes, <b>4c</b>	Mes, <b>2a</b>	yes	<b>8c</b> : -44.0 (194.6)	<b>3a</b> : -27.2 (478)

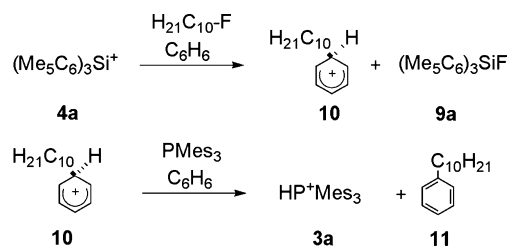
the mixture was immediately charged with dihydrogen gas under ambient conditions. The biphasic reaction mixture was stirred for 30 min; the two phases were allowed to separate and examined independently by NMR spectroscopy. Under these conditions the mixtures of silylium ion **4a–c** with trimesitylphosphane (**2a**) gave the products of dihydrogen cleavage, silanes **8a–c** and the phosphonium borate **3a**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]. Equimolar mixtures of silylium ion **4a** with phosphanes **2c,e,h,i,l** were active in dihydrogen activation as well; only the mixtures with the fluorinated phosphanes **2f,g** and the Tipp-substituted phosphane **2k** proved to be unreactive versus dihydrogen (see Table 1). In the case of phosphane **2k** also prolonged reaction times (24 h, room temperature) and elevated reaction temperatures (6 h, 80 °C) did not initiate dihydrogen activation.

The corresponding silanes **8** and the phosphonium borates **3**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] were obtained in almost quantitative yield and have been identified by NMR spectroscopy. Dihydrogen cleavage by the silylium/phosphane Lewis pairs is not reversible, as heating a mixture of silane **8a** with phosphonium borate **3a**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] in toluene shows no sign of dihydrogen evolution. When deuterium, D<sub>2</sub>, was reacted with the mixture **4a**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]/**2e** in toluene, the deuterated products **8a-d<sub>1</sub>** and **3e-d<sub>1</sub>** were obtained, as was shown by the detection of the corresponding triplets in the <sup>29</sup>Si NMR ( $^1J_{\text{SiD}} = 30$  Hz) and <sup>31</sup>P NMR spectra ( $^1J_{\text{PD}} = 74$  Hz). In these experiments a minor amount of protonated phosphane **3e** was detected (Figure 2), which results most probably from competing decomposition of

**Figure 2.** 202.25 MHz <sup>31</sup>P{<sup>1</sup>H} NMR spectrum (C<sub>6</sub>D<sub>6</sub>, 305 K) obtained from the reaction of silylium/phosphane pair **4a/2e** with D<sub>2</sub>.

the silylium ion/phosphane pair **4a/2e**. In control experiments using silylium borates **4a**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] in benzene, toluene, or chlorobenzene at dihydrogen pressures up to 0.4 MPa (4 atm) no reaction between silylium ions and dihydrogen was noted and only slow decomposition of the cations over days was observed.

The reactivity of silylium phosphane Lewis pairs versus several other exemplary substrates was also tested. Phenylacetylene gave only polymeric material in a strongly exothermic reaction. In the reaction of the silylium/phosphane pair **4a/2a** with decyl fluoride the silyl fluoride **9a** ( $\delta(^{29}\text{Si}) -4.7$ ;  $\delta(^{19}\text{F}) -146.2$ ;  $^1J(\text{CF}) = 274$  Hz) was formed along with a mixture of alkylated benzenes (Scheme 4). The tertiary phosphonium ion

**Scheme 4.** Reactivity of Silylium Ion/Phosphane Pair **4a/2a** versus Decyl Fluoride

**3a** was obtained as an ionic product. Interestingly, no trimesitylalkylphosphonium ion was detected. This suggests a two-step reaction in which the silylium ion initiates the reaction by fluoride abstraction and the formation of silyl fluoride **9a** along with alkylated benzenium ion **10**. The phosphane acts as a Brønsted base in this reaction, as it accepts the proton from the arenium ion and delivers the alkylated benzene **11**. Therefore, this reaction clearly shows some parallels to the reaction of silyl arenium or disilylated hydronium ions with alkyl fluorides.<sup>23</sup> As already noted for these catalytic CF activation reactions by silyl cations,<sup>23f</sup> the reaction described herein is very unspecific. The product **11** was formed as a mixture of isomeric compounds with side chains of different constitutions.

No reaction with CO<sub>2</sub> was detected when silylium/triaryl phosphanes Lewis pairs were applied. A fast reaction occurred, however, when trialkylphosphanes such as **2c,h** were applied. These reactions yielded acylphosphonium borates **12**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (Scheme 5), which were identified by their

Scheme 5. CO<sub>2</sub> Fixation by Silylium Ion/Phosphane Lewis Pairs **4a**/**2c** (R = *t*Bu) and **4a**/**2h** (R = *c*Hex)

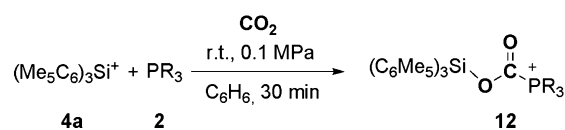
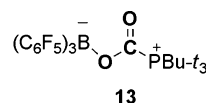


Table 2. Selected Spectroscopic Parameters of Acylphosphonium Ions **12**

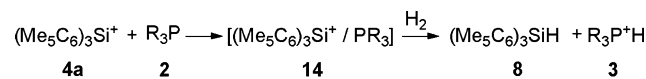
R	$\delta(^{13}\text{C}),$ ( $^1J_{\text{C-P}}$ [Hz])	$\delta(^{29}\text{Si})$	$\delta(^{31}\text{P}),$ ( $^1J_{\text{P-C}}$ , Hz)	$\nu(\text{C}=\text{O}),$ $\text{cm}^{-1}$
<i>t</i> -Bu, <b>12c</b>	159.6 (88)	-0.3	56.4 (88)	1712
<i>c</i> -Hex, <b>12h</b>	157.7 (109)	-1.9	46.6 (109)	1714
<b>13</b>	162 (93)		46.1	1695

characteristic spectroscopic parameters (see Table 2 and the Supporting Information). These parameters are very close to those reported for the related betaine **13**.<sup>7a</sup> Phosphonium borates **12**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] are only marginally stable compounds at ambient conditions. Upon heating in toluene, the phosphonium ions **12** decomposed before CO<sub>2</sub> was released. Therefore, the CO<sub>2</sub> fixation by silylium ion/phosphane Lewis pairs—as depicted in Scheme 5—is irreversible.



Quantum mechanical calculations<sup>24,25</sup> at the M05-2X/6-31G(d) level were performed to obtain a more detailed picture of the dihydrogen activation by silylium ion/phosphane Lewis pairs. In particular, the noticeable dependence of the reactivity of the Lewis pairs versus dihydrogen on the nature of the phosphane was addressed. For this purpose the reaction of silylium ion **4a** with phosphanes **2** to form the encounter complexes **14** and their reaction with dihydrogen was studied computationally (Scheme 6). The formation of complexes **14**

Scheme 6. Dihydrogen Splitting by Silylium Ion **4a**/Phosphane **2** Pairs via The Encounter Complex **14**



from the silylium Lewis acid **4a** and the phosphane Lewis bases **2** is predicted to be exothermic (association energy  $E_A = -38$  to  $-63 \text{ kJ mol}^{-1}$ ; see Table 3). Inclusion of entropy and thermal effects already results in slightly positive values for the Gibbs free energy ( $G^{298}_A = +3$  to  $+22 \text{ kJ mol}^{-1}$ ). These findings suggest that under ambient conditions only small amounts of complexes **14** are present in equilibrium with its components. As previously shown for other frustrated Lewis pairs, the determining factors for the formation of these complexes are attractive dispersion forces.<sup>8,9,22</sup> In the present case this is supported by single-point calculations for the optimized structure of complex **14a** using the B3LYP hybrid density functional. This functional is known to neglect dispersion energy contributions,<sup>26</sup> and the calculations with this functional predict a destabilization of the complex **14a** in comparison to its constituents by  $10 \text{ kJ mol}^{-1}$  ( $E_A(\text{B3LYP}) = +10 \text{ kJ mol}^{-1}$ ). The calculated structures of the encounter complexes **14** show that the Lewis acidic silicon atom and the basic phosphorus

Table 3. Calculated Thermodynamic Quantities for the Dihydrogen Activation by Lewis Pairs of Silylium Ion **4a** with Different Phosphanes **2** and SiP Distances,  $d(\text{SiP})$ , in the Corresponding Encounter Complexes **14** (M05-2X/6-31G(d))

PR <sub>3</sub>	R	$E_A$ for <b>14</b> , $\text{kJ mol}^{-1}$	$d(\text{SiP})$ for <b>14</b> , pm	$\Delta E_R$ , $\text{kJ mol}^{-1}$	PA for PR <sub>3</sub> , $\text{kJ mol}^{-1}$
<b>2a</b>	Mes	-46	555	-146	1058
<b>2b</b>	Et	-159	244	-71	994
<b>2c</b>	<i>t</i> -Bu	-38	556	-132	1044
<b>2d</b>	Ph	-53	464	-86	999
<b>2e</b>	<i>o</i> -Tol	-45	540	-102	1014
<b>2f</b>	C <sub>6</sub> F <sub>5</sub>	-38	566	+45	868
<b>2g</b>	C <sub>6</sub> F <sub>4</sub> H	-45	512	+22	890
<b>2h</b>	<i>c</i> -Hex	-47	445	-120	1033
<b>2i</b>	C <sub>6</sub> Me <sub>5</sub>	-63	524	-181	1093
<b>2l</b>	C <sub>6</sub> H <sub>2</sub> Et <sub>3</sub>	-53	573	-163	1075
<b>2k</b>	Tipp	-61	766	-177	1089

atom are separated by distances which are significantly longer than the sum of the van der Waals radii ( $\sum r(\text{vdW})$ ) of both elements ( $\sum r(\text{vdW})_{\text{SiP}} = 390 \text{ pm}$ ).<sup>27</sup> The smallest distance is predicted for **14h** ( $d(\text{SiP}) = 445 \text{ pm}$ ) and the majority of the calculated encounter complex structures show SiP separations between 512 and 573 pm (Table 3).<sup>28</sup> These structural features of the encounter complexes **14** suggest an unquenched reactivity of the Lewis partners as is typical for FLPs.

The overall heterolytic splitting reaction of dihydrogen is predicted to be exothermic for most of the combinations of silylium ion **4a** with phosphanes **2**. This is shown by significant negative calculated reaction energies  $\Delta E_R$  (Table 3 and Figure 3). The only exceptions are the Lewis pairs built from the two

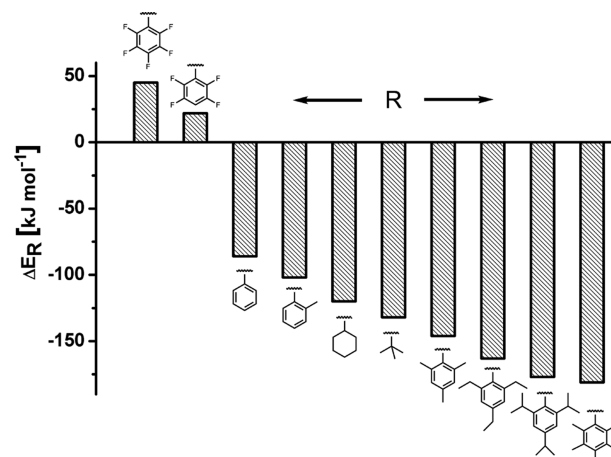
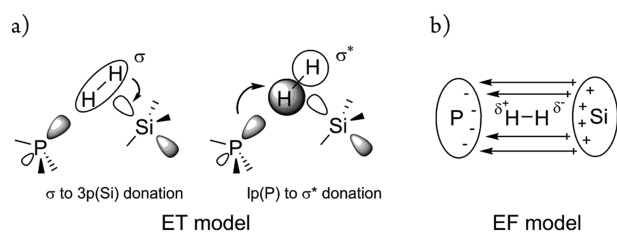


Figure 3. Dependence of the calculated reaction energies  $\Delta E_R$  for the heterolytic splitting of dihydrogen on the substituent R of the phosphane PR<sub>3</sub> (M05-2X/6-31G(d)).

fluorinated triarylphosphanes **2f,g** and silylium ion **4a**. For these combinations the process of hydrogen splitting is calculated to be endothermic (Table 3 and Figure 3). This is in agreement with the experimental result that the Lewis pairs **4a**/**2f** and **4a**/**2g** do not react with dihydrogen under ambient conditions. The reason for the reduced reactivity of these Lewis pairs is the significantly smaller proton affinity (PA), of the fluorinated triaryl phosphanes **2f,g** in comparison to other triaryl- and trialkylphosphanes (Table 3). The PA of the phosphane is the

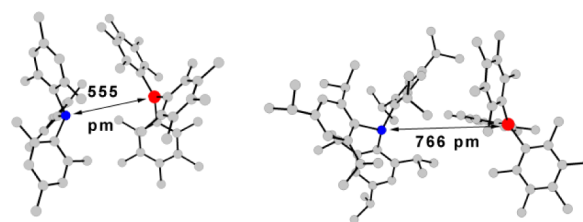
second factor in addition to the hydride affinity of the silylium ion which determines the reaction energy  $\Delta E_R$ . Therefore, the formation of the fluorinated phosphonium ions **3f,g** does not provide enough additional driving force to allow the dihydrogen splitting by these Lewis pairs. In view of the data summarized in Table 3, the inertness of dihydrogen versus the Lewis pair  $(\text{Me}_5\text{C}_6)_3\text{Si}^+$  (**4a**)/ $\text{Tipp}_3\text{P}$  (**2k**) is of particular interest. In agreement with the high calculated PA of phosphane **2k**,  $\Delta E_R$  for the heterolytic dihydrogen splitting by the Lewis pair **5a/2k** is predicted to be markedly exothermic.

There is only a small amount of experimental information about the mechanism of dihydrogen cleavage by frustrated Lewis pairs.<sup>29</sup> The two major mechanistic scenarios which are in discussion for dihydrogen activation by FLPs are based in essence on theoretical work and computational modeling (Figure 4). Pápai and colleagues suggested an electron transfer



**Figure 4.** Models for dihydrogen activation by silylium ion/phosphane Lewis pairs: (a) electron transfer (ET) model; (b) electric field (EF) model.<sup>8,9</sup>

model (ET model) in which electron density is transferred from the lone pair of the Lewis base to the  $\sigma^*$  orbital of dihydrogen and from the  $\sigma$  orbital of dihydrogen to the empty orbital of the Lewis acid (Figure 4a).<sup>8</sup> These synergistic ETs lead to weakening and finally to heterolytic cleavage of the H–H bond. Later, Grimme and co-workers called the FLP community's attention to the significant electric field (EF) present in the interior of the encounter complex (Figure 4b).<sup>9</sup> It was shown computationally that dihydrogen exposed to sufficiently strong EFs can be cleaved heterolytically in a barrierless process (Figure 4b). Both models have the need for formation of an encounter complex between the Lewis acid and base in common. These encounter complexes bring donor and acceptor atoms to a close spatial proximity, which is needed either for the simultaneous electron transfer or for the generation of an electric field of sufficient strength. Considering this background, the calculated structure of the encounter complex **14k** from silylium ion **4a** and the Tipp-substituted phosphane **2k** is of particular interest. Against all other optimized structures of complexes **14** this encounter complex is characterized by an extremely large separation of donor and acceptor atoms ( $d(\text{SiP}) = 766$  pm; see Table 3 and Figure 5). This long separation excludes a synchronous electron transfer among the phosphorus donor atom, the dihydrogen molecule, and the silicon acceptor. Similarly it does not allow the buildup of an electric field, which is sufficiently strong for dihydrogen cleavage. The silylium ion/phosphane Lewis pair **4a/2k** is an example for an overfrustrated Lewis pair for which the antagonistic reactivity of the Lewis partners is not quenched. The structure of the formed encounter complex **14k**, however, does not provide the correct spatial requirements which are needed for dihydrogen splitting.



**Figure 5.** Computed molecular structures of encounter complexes **14a** (a) and **14k** (b). Distances between Si and P atoms are accentuated (M05-2X/6-31G(d), hydrogen atoms omitted). Color code: gray, carbon; red, silicon; blue, phosphorus.

## CONCLUSION

The high electrophilicity of silylium ions was successfully exploited for small-molecule activation by using the concept of frustrated Lewis pairs. Combining triarylsilylium ions **4** with sterically bulky substituted phosphanes such as trialkylphosphanes **2c,h** or triarylphosphanes **2a,e,i,l** gave highly reactive FLPs. These are able to split dihydrogen irreversibly under ambient condition, resulting in the formation of the corresponding silanes **8** and phosphonium ions **3**. During these investigations it became clear that the phosphanes **2** must meet several criteria to form FLPs with silylium ions **4** which are active in dihydrogen activation. Apart from the necessary steric hindrance, a proton affinity of the phosphane at least as high as that of  $\text{PPh}_3$  (**2d**) is needed to provide a thermodynamic driving force for the heterolytic dihydrogen cleavage by the silylium ion/phosphane Lewis pair. In addition, the use of sterically overloaded phosphanes such as  $\text{Tipp}_3\text{P}$  (**2k**) also proved to be counterproductive for dihydrogen activation. Although we cannot securely rule out kinetic reasons for the failure of the dihydrogen activation in this particular case, the results of model calculations suggest that the encounter complex **14k**, formed from  $\text{Tipp}_3\text{P}$  (**2k**) and  $(\text{Me}_5\text{C}_6)_3\text{Si}^+$  (**4a**), provides a reaction compartment which is too large to allow for an effective dihydrogen splitting. Furthermore, silylium ion/phosphane Lewis pairs composed of trialkylphosphanes **2c,h** are able to bind  $\text{CO}_2$  in the form of silylacylphosphonium ions **12**. Further work to combine dihydrogen activation with  $\text{CO}_2$  fixation by silylium ion/phosphane Lewis pairs is currently under way in our laboratory.

## EXPERIMENTAL SECTION

**General Considerations.** Diethyl ether and tetrahydrofuran were distilled from sodium/benzophenone. Benzene,  $[\text{D}_6]$ benzene,  $[\text{D}_8]$ -toluene, and *n*-hexane were distilled from sodium.  $[\text{D}_1]$ chloroform was dried over molecular sieves 4 Å. Bromopentafluorobenzene, tri-*tert*-butylphosphane, 1-bromo-2,4,6-tri-*iso*-propylbenzene, bromopentamethylbenzene, and 1-bromo-2,3,5,6-tetrafluorobenzene were purchased from ABCR and used as received. 1-Bromo-2-methylbenzene, 1-decyl fluoride, phenylacetylene, and 2.0 M *iso*-propylmagnesium chloride solution in THF were purchased from Sigma Aldrich and used as received. Phosphorus trichloride, phosphorus tribromide, triphenylphosphane, and triethylphosphane were purchased from Merck Chemicals and used as received. Bromomesitylene was purchased from Alfa Aesar and was used as received. Dihydrogen gas (99.999%) was purchased from Air Liquide and was further dried by bubbling through concentrated sulfuric acid; carbon dioxide gas (99.998%) was bought from Linde and was dried by conducting it through a Sicapent column. Deuterium gas and  $(^{13}\text{C})$ carbon dioxide gas were purchased from Sigma Aldrich Isotec and were used as received without further purification. The  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  salt was synthesized as described previously.<sup>30</sup>

All reactions were carried out under inert conditions using standard Schlenk and glovebox techniques, unless stated otherwise. Argon (99.999%) was used as an inert gas and was dried over Sicapent prior to use. NMR spectra were recorded on Bruker Avance 500 and Avance III 500 spectrometers at 305 K, if not stated otherwise.  $^1\text{H}$  NMR spectra were calibrated using residual protio signals of the solvent ( $\delta(^1\text{H})$   $\text{CHCl}_3$  7.24,  $\delta(^1\text{H})$   $\text{C}_6\text{D}_6$  7.20,  $\delta(^1\text{H})$   $\text{C}_6\text{D}_5(\text{CD}_2\text{H})$  2.08).  $^{13}\text{C}$  NMR spectra were calibrated using the solvent signals ( $\delta(^{13}\text{C})$   $\text{CDCl}_3$  77.0,  $\delta(^{13}\text{C})$   $\text{C}_6\text{D}_6$  128.0,  $\delta(^{13}\text{C})$   $\text{C}_7\text{D}_8$  20.4 ( $\text{CD}_3$ )).  $^{29}\text{Si}$  NMR spectra were calibrated using external  $\text{Me}_3\text{HSiCl}$  ( $\delta(^{29}\text{Si})$  11.1 vs TMS),  $^{31}\text{P}$  NMR spectra against external  $(\text{MeO})_3\text{P}$  ( $\delta(^{31}\text{P})$  141 vs 85%  $\text{H}_3\text{PO}_4(\text{aq})$ ),  $^{19}\text{F}$  NMR spectra against external  $\text{CFCl}_3$  ( $\delta(^{19}\text{F})$   $\text{CFCl}_3$  0.0), and  $^{11}\text{B}$  NMR spectra against  $\text{BF}_3\cdot\text{OEt}_2$  ( $\delta(^{11}\text{B})$   $\text{BF}_3\cdot\text{OEt}_2$  0.0). High-resolution mass spectra were recorded on a Finnigan MAT 95 instrument. IR spectra were recorded on a Bruker Tensor 27 spectrometer.

**General Procedure for the Preparation of Silylium Borate Salts  $4[\text{B}(\text{C}_6\text{F}_5)_4]$ .** A Schlenk tube was oven-dried and then charged with 400 mg of  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  (0.43 mmol) and the corresponding amount of diarylmethylsilane **5** (0.78 mmol). The mixture was evacuated for at least 1 h. After that period it was flushed with dry argon and dissolved in 4 mL of dry benzene. The resulting biphasic mixture (an upper nonpolar phase and a lower polar phase; typical for salts of  $[\text{B}(\text{C}_6\text{F}_5)_4]^-$  in aromatic hydrocarbons) was stirred for 1 h. Then the phases were allowed to separate. The polar phase was then washed two times with 4 mL portions of dry benzene. Then, the benzene was removed and replaced by 1 mL of dry  $\text{C}_6\text{D}_6$ . The obtained NMR spectroscopic data of the silylium borates  $4[\text{B}(\text{C}_6\text{F}_5)_4]$  and the preparation of the starting silanes **5** can be referred to in earlier reports.<sup>15</sup> The solutions of the so obtained silylium ion salts  $4[\text{B}(\text{C}_6\text{F}_5)_4]$  could now be used in further experiments.

**Trimesitylphosphane (2a).** This phosphane was prepared similarly to literature procedures.<sup>31</sup> A three-necked, oven-dried flask was equipped with a dropping funnel and a reflux condenser. In this flask were placed 2.44 g of magnesium turnings (100.5 mmol). A solution of 20.0 g of 1-bromo-2,4,6-trimethylbenzene (100.5 mmol) in 150 mL of dry THF was added dropwise. The reaction started after gently heating with a water bath. After the addition was completed, the mixture was heated to reflux for 1 h. After it was cooled to room temperature, the solution of the Grignard reagent was transferred into the dropping funnel of an identical apparatus using a PTFE cannula. The solution was then added dropwise to a solution of 4.60 g of phosphorus trichloride (33.5 mmol) in 50 mL of dry THF at  $-78^\circ\text{C}$ . Afterward, the resulting suspension was stirred for 1 h at this temperature. Then, 250 mL of a saturated NaCl solution was added. The organic layer was separated. The aqueous layer was extracted two times with 50 mL portions of THF. The combined organic phases were dried using sodium sulfate. The solvent was evaporated under reduced pressure to yield a slightly orange solid. The raw product was recrystallized from hot chloroform to give the desired product as a colorless, crystalline solid. Yield: 11.07 g, 85%.  $^1\text{H}$  NMR (500.130 MHz,  $\text{C}_6\text{D}_6$ , 305 K):  $\delta$  2.14 (s,  $\text{CH}_3$ , 9 H), 2.29 (s,  $\text{CH}_3$ , 18 H), 6.77 (s, CH, 6 H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.758 MHz,  $\text{C}_6\text{D}_6$ , 305 K):  $\delta$  20.9 (*p*- $\text{CH}_3$ ), 23.0 (d,  $^3J_{\text{P-C}} = 17.2$  Hz, *o*- $\text{CH}_3$ ), 130.3 (CH), 132.1 (d,  $^2J_{\text{C-P}} = 18.0$  Hz, C), 137.8 (C), 142.8 (d,  $^1J_{\text{C-P}} = 17.3$  Hz, C).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202.454 MHz,  $\text{C}_6\text{D}_6$ , 305 K):  $\delta$  -23.1.

**Tri-*o*-tolylphosphane (2e).** This phosphane was prepared by a slightly modified literature procedure.<sup>32</sup> A three-necked, oven-dried flask was equipped with a dropping funnel and a reflux condenser, and 1.71 g of magnesium turnings (70.2 mmol) was placed in it. A solution of 10.0 g of 1-bromo-2-methylbenzene (58.5 mmol) in 30 mL of dry THF was added dropwise. The reaction started spontaneously after 2–3 min. After the addition was completed, the mixture was heated to reflux for 2 h. After it was cooled to room temperature, the solution of the Grignard reagent was transferred into the dropping funnel of an identical apparatus using a PTFE cannula. The reagent was then added dropwise to a solution of 2.68 g of phosphorus trichloride (19.5 mmol) in 10 mL of dry THF at ambient temperature. Afterward, the resulting suspension was stirred for 30 min and was then treated with 100 mL of deionized water. The organic layer was separated. The

aqueous layer was extracted two times with 50 mL portions of THF. The combined organic phases were dried using sodium sulfate. The solvent was evaporated under reduced pressure to yield a slightly yellow solid. The raw product was recrystallized from hot ethanol to give the desired product as a colorless, crystalline solid. Yield: 12.37 g, 70%.  $^1\text{H}$  NMR (500.130 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  2.46 (s,  $\text{CH}_3$ , 9 H), 6.91–6.96 (m, CH, 3 H), 7.03–7.13 (m, CH, 9 H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.760 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  21.3 (d,  $^3J_{\text{P-C}} = 22.3$  Hz,  $\text{CH}_3$ ), 126.6 (CH), 129.1 (CH), 130.5 (d,  $^3J_{\text{C-P}} = 4.8$  Hz, CH), 133.4 (CH), 135.0 (d,  $^2J_{\text{C-P}} = 11.0$  Hz, C), 143.0 (d,  $^1J_{\text{C-P}} = 26.5$  Hz, C).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202.351 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  -16.3.

**Tris(pentafluorophenyl)phosphane (2f).** This phosphane was synthesized according to a procedure slightly modified from that in the literature.<sup>33</sup> A three-necked, oven-dried flask was equipped with a dropping funnel and a reflux condenser. In this flask were placed 6.00 g of magnesium turnings (245 mmol). A solution of 61.74 g of bromopentafluorobenzene (250 mmol) in 100 mL of dry diethyl ether was added dropwise. The reaction started spontaneously after 2–3 min. The mixture was refluxed for 1 h. After that mixture was cooled to  $-6^\circ\text{C}$ , a solution of 32.48 g of phosphorus tribromide (120 mmol) in 40 mL of dry diethyl ether was added dropwise. After the mixture was stirred for 1 h, a mixture of 300 g of crushed ice and 2 mL of concentrated HCl was added carefully. The layers were separated, and the aqueous phase was extracted with three 50 mL portions of diethyl ether. The combined organic phases were dried using sodium sulfate. The solvent was removed under reduced pressure. The dark brown crude product was recrystallized from hot methanol two times to yield the desired product as a slightly brown powder. Yield: 19.79 g, 31%.  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.692 MHz,  $\text{CDCl}_3$ , 305 K):  $\delta$  104.4–104.9 (m, *ipso*-C), 137.7 (dm,  $^1J_{\text{F-C}} = 251.1$  Hz, *p*-CF), 134.2 (dm,  $^1J_{\text{F-C}} = 259.6$  Hz, *m*-CF), 147.7 (dm,  $^1J_{\text{C-F}} = 247.6$  Hz, *o*-CF).  $^{19}\text{F}\{^1\text{H}\}$  NMR (470.348 MHz,  $\text{CDCl}_3$ , 305 K):  $\delta$  -159.4 to -159.2 (m, 6 F, *m*-CF), -147.5 to -147.3 (m, 3 F, *p*-CF), -130.0 to -129.7 (m, 6 F, *o*-CF).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202.351 MHz,  $\text{CDCl}_3$ , 305 K):  $\delta$  -73.7 (sept,  $^3J_{\text{P-F}} = 34.0$  Hz).

**Tris(2,3,5,6-tetrafluorophenyl)phosphane (2g).** This phosphane was prepared analogously to a procedure known in the literature for the generation of the respective triarylborane.<sup>34</sup> A three-necked, oven-dried flask was equipped with a dropping funnel and a reflux condenser. In this flask were placed 4.90 g of 1-bromo-2,3,5,6-tetrafluorobenzene (21.4 mmol) dissolved in 100 mL of dry diethyl ether. Then, 10.2 mL of a 2 M solution of *iso*-propylmagnesium chloride (20.3 mmol) in diethyl ether was added dropwise at ambient temperature. A colorless suspension was formed after a few minutes of stirring. The mixture was stirred for an additional 1 h at room temperature. Subsequently, a solution of 1.74 g of phosphorus tribromide (6.42 mmol) in 10 mL of dry diethyl ether was added swiftly. The resulting mixture was stirred overnight and was then refluxed for 8 h. The solvent was removed under reduced pressure and was replaced by 100 mL of dry *n*-hexane. The suspension was filtered using a glass frit (P4). The residue was washed two times with 50 mL portions of dry diethyl ether. The filtrate was concentrated under reduced pressure to yield a colorless solid. The raw product was recrystallized from hot *n*-hexane to yield the desired product as a crystalline, colorless solid. Yield: 2.20 g, 72%.  $^1\text{H}$  NMR (499.870 MHz,  $\text{C}_6\text{D}_6$ , 305 K):  $\delta$  6.13–6.24 (m, 3 H, *p*-CH).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.693 MHz,  $\text{C}_6\text{D}_6$ , 305 K):  $\delta$  109.0 (t,  $^2J_{\text{C-F}} = 22.7$  Hz, *p*-CH), 110.8–111.7 (m, *ipso*-C), 146.0 (dm,  $^1J_{\text{C-F}} = 251.1$  Hz, *o*-CF), 147.5 (dm,  $^1J_{\text{C-F}} = 248.6$  Hz, *m*-C).  $^{19}\text{F}\{^1\text{H}\}$  NMR (470.348 MHz,  $\text{C}_6\text{D}_6$ , 305 K):  $\delta$  -137.3 to -137.2 (m, 6 F, *m*-CF), -131.5 to -131.2 (m, 6 F, *o*-CF).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202.348 MHz,  $\text{CDCl}_3$ , 305 K):  $\delta$  -58.7 (sept,  $^3J_{\text{P-F}} = 37.5$  Hz). HR-MS (EI, 70 eV): calcd 477.9775, found 477.9773. Anal. Found/calcd: C, 45.25/45.21; H, 0.518/0.63.

**Tricyclohexylphosphane (2h).** The phosphane **2h** was prepared according to literature procedures.<sup>35</sup>  $^1\text{H}$  NMR (500.13 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  1.14–1.42 (m, CH/CH<sub>2</sub>, 15 H), 1.63–1.73 (m, CH<sub>2</sub>, 6 H), 1.73–1.81 (m, CH<sub>2</sub>, 6 H), 1.85–1.94 (m, CH<sub>2</sub>, 6 H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.76 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  27.0 (s, CH<sub>2</sub>), 28.0 (d,  $^3J_{\text{P-C}} = 9.6$  Hz, CH<sub>2</sub>), 31.6 (d,  $^2J_{\text{P-C}} = 12.8$  Hz, CH<sub>2</sub>), 32.2 (d,  $^1J_{\text{C-P}} = 18.7$  Hz, CH).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202.46 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  10.2.

**Tris(pentamethylphenyl)phosphane (2i).** A three-necked, oven-dried flask was equipped with a dropping funnel and a reflux condenser. In this flask were placed 1.35 g of magnesium turnings (55.6 mmol). A solution of 11.48 g of bromopentamethylmethylbenzene (50.6 mmol) in 150 mL of dry THF was added dropwise. The reaction started after gentle heating with a water bath. After the addition was completed, the mixture was heated to reflux for 2 h. After it was cooled to room temperature, the solution of the Grignard reagent was transferred into the flask of an identical apparatus using a PTFE cannula. The mixture was then cooled to  $-40\text{ }^{\circ}\text{C}$ . Then, 5.51 g of dry copper(I) chloride (55.6 mmol) was added using a solid dropping funnel. The mixture was warmed to room temperature overnight. The resulting gray solution was then cooled to  $0\text{ }^{\circ}\text{C}$ , and 4.52 g of phosphorus tribromide (16.68 mmol) in 20 mL of dry THF was added dropwise. The mixture was warmed to room temperature and was then stirred for 72 h and refluxed for an additional 6 h. The solvent was removed under reduced pressure and was replaced by 200 mL of dry *n*-hexane. The suspension was filtered using a glass frit (P4). The solvent of the filtrate was removed under reduced pressure to yield a slightly yellow solid. The crude product was recrystallized from hot *n*-hexane to give a colorless, crystalline solid. Yield: 1.64 g, 21%.  $^1\text{H}$  NMR (500.130 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  2.09 (s,  $\text{CH}_3$ , 18 H), 2.13 (s,  $\text{CH}_3$ , 9 H), 2.49 (s,  $\text{CH}_3$ , 18 H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.758 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  17.2 (superposition of *m*- and *p*- $\text{CH}_3$ ), 20.5 (d,  $^3J_{\text{P-C}} = 19.0$  Hz, *o*- $\text{CH}_3$ ), 133.0 (d,  $^3J_{\text{C-P}} = 4.2$  Hz, C), 134.9 (C), 136.5 (d,  $^2J_{\text{C-P}} = 18.5$  Hz, C), 137.7 (d,  $^1J_{\text{C-P}} = 17.9$  Hz, C).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202.456 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$   $-25.4$ . HR-MS (EI, 70 eV): calcd 472.3259, found 472.3255. Anal. Found/calcd: C, 83.368/83.85; H, 10.187/9.60.

**Tris(2,4,6-triisopropylphenyl)phosphane (2k).** This phosphane was prepared according to a slightly modified literature procedure.<sup>36</sup> A three-necked, oven-dried flask was equipped with a dropping funnel and a reflux condenser. In this flask were placed 1.91 g of magnesium turnings (78.6 mmol). A solution of 22.26 g of 1-bromo-2,4,6-triisopropylbenzene (78.6 mmol) in 150 mL of dry THF was added dropwise. The reaction started spontaneously after 2–3 min while it was heated gently. After the addition was completed, the mixture was heated to reflux for 2 h. The solution of the Grignard reagent was then cooled to  $-78\text{ }^{\circ}\text{C}$ . Subsequently, 8.32 g of dry copper(I) chloride (84.1 mmol) was added using a solid dropping funnel. The mixture was first stirred at this temperature for an additional 20 min and was then warmed to room temperature overnight. The resulting greenish solution was then again cooled to  $-78\text{ }^{\circ}\text{C}$ , and 3.60 g of phosphorus trichloride (26.2 mmol) was added dropwise. The mixture was stirred for 15 min at this temperature and was then warmed to room temperature. Then, the mixture was refluxed for 24 h. After the mixture was cooled to ambient temperature, 300 mL of dry *n*-hexane was added. The suspension was filtered through Celite using a glass frit (P4). The solvent of the filtrate was removed under reduced pressure to yield a slightly yellow oil. The crude product was recrystallized from hot *n*-hexane to give a colorless, crystalline solid. Yield: 4.58 g, 11%.  $^1\text{H}$  NMR (500.130 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  0.93 (d,  $^3J_{\text{H-H}} = 6.7$  Hz, *p*- $(\text{CH}(\text{CH}_3)_2)$ , 18 H), 1.22 (d,  $^3J_{\text{H-H}} = 7.2$  Hz, *o*- $(\text{CH}(\text{CH}_3)_2)$ , 18 H), 1.43 (d,  $^3J_{\text{H-H}} = 6.7$  Hz, *o*- $(\text{CH}(\text{CH}_3)_2)$ , 18 H), 2.78 (sept,  $^3J_{\text{H-H}} = 6.7$  Hz, *CH*, 3 H), 3.80–3.91 (m, *CH*, 6 H), 7.13 (d,  $^4J_{\text{H-H}} = 3.6$  Hz, *CH*, 6 H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.758 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  23.4 (*p*- $(\text{CH}(\text{CH}_3)_2)$ , 24.0 (d,  $^4J_{\text{P-C}} = 11.6$  Hz, *o*- $(\text{CH}(\text{CH}_3)_2)$ , 25.0 (s, *o*- $(\text{CH}(\text{CH}_3)_2)$ , 32.4 (d,  $^3J_{\text{H-H}} = 18.1$  Hz, *o*- $(\text{CH}(\text{CH}_3)_2)$ , 34.4 (s, *p*- $(\text{CH}(\text{CH}_3)_2)$ , 122.5 (d,  $^3J_{\text{C-P}} = 4.4$  Hz, *m*-C), 132.8 (d,  $^1J_{\text{P-C}} = 24.4$  Hz, *ipso*-C), 149.8 (s, *p*-C), 153.6 (d,  $^2J_{\text{C-P}} = 18.2$  Hz, *o*-C).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202.456 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$   $-52.1$ .

**Tris(2,3,5-triethylphenyl)phosphane (2l).** This phosphane was prepared as described in the literature.<sup>36</sup> The raw product was recrystallized from hot *n*-hexane to give the desired product as a colorless solid. Yield: 1.26 g, 10%.  $^1\text{H}$  NMR (499.870 MHz,  $\text{CDCl}_3$ , 305 K):  $\delta$  0.79–0.98 (br m, *o*- $(\text{CH}_2\text{CH}_3)$ , 18 H), 1.19 (t,  $^3J_{\text{H-H}} = 7.6$  Hz, *p*- $(\text{CH}_2\text{CH}_3)$ , 9 H), 2.48–2.64 (m,  $\text{CH}_2$ , 18 H, superposition of *o*- and *p*- $\text{CH}_2$ ), 6.80 (d,  $J_{\text{H-H}} = 3.2$  Hz, ArH, 6 H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.710 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  14.9 (*o*- $(\text{CH}_2\text{CH}_3)$ , 15.3 (*p*- $(\text{CH}_2\text{CH}_3)$ , 28.5 ( $\text{CH}_2$ ), 28.6 ( $\text{CH}_2$ ), 126.5 (s, ArH), 132.4 (d,  $^1J_{\text{P-C}} =$

27.2 Hz, *ipso*-C), 144.1 (C), 148.8 (C).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202.350 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$   $-41.6$ .

#### General Procedure for the Preparation of FLPs 14 (Studies Concerning Stability of Silylium Ion 4/Phosphane 2 Mixtures).

The relevant phosphane 2 was charged into a Schlenk tube and was degassed for at least 30 min. Then, it was flushed with dry argon and was dissolved in 0.5 mL of dry  $\text{C}_6\text{D}_6$ . The resulting solution was then transferred to the solution of the silylium borate  $4[\text{B}(\text{C}_6\text{F}_5)_4]$  in  $\text{C}_6\text{D}_6$  via a PTFE cannula. The dark polar phase lightened appreciably upon stirring the mixture for 30 min. The two phases were then allowed to separate and were examined by multinuclear NMR spectroscopy. After 30 min of stirring at room temperature Lewis pairs 4a–c/2a and 4a/2c,f–k showed no decomposition, while the NMR spectra obtained from the pairs 4a/2e,l already indicated significant amounts of decomposition products.

#### General Procedure for Dihydrogen Activation Experiments.

The relevant phosphane 2 was charged into a Schlenk tube and was degassed for at least 30 min. Then, it was flushed with dry argon and was dissolved in 0.5 mL of dry  $\text{C}_6\text{D}_6$ . The resulting solution was then transferred to the solution of the silylium borate  $5[\text{B}(\text{C}_6\text{F}_5)_4]$  in  $\text{C}_6\text{D}_6$  via a PTFE cannula. Immediately after addition the mixture was flushed with 0.1 MPa (1 atm) of dihydrogen gas. Residual argon was removed by rinsing the Schlenk tube with dihydrogen (using a septum and a syringe as wastegate). The tube was then sealed, and the mixture was stirred for at least 30 min under an  $\text{H}_2$  atmosphere. Then, the phases were allowed to separate and were examined via multinuclear NMR spectroscopy. The formed phosphonium ions and silanes were identified by comparison with literature data or authentic samples.

**Characterization of Silanes 8.** Data for  $(\text{Me}_3\text{C}_6)_3\text{SiH}$  (8a)<sup>15</sup> are as follows.  $^1\text{H}$  NMR (499.87 MHz,  $\text{C}_6\text{D}_6$ , 305 K):  $\delta$  2.08 (s, 18 H,  $\text{CH}_3$ ), 2.14 (s, 9 H,  $\text{CH}_3$ ), 2.51 (s, 18 H,  $\text{CH}_3$ ), 6.23 (s,  $^1J_{\text{Si-H}} = 195$  Hz, 1 H, SiH).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.69 MHz,  $\text{C}_6\text{D}_6$ , 305 K):  $\delta$  15.3 ( $\text{CH}_3$ ), 15.7 ( $\text{CH}_3$ ), 20.5 ( $\text{CH}_3$ ), 128.5 ( $\text{C}_q$ ), 131.5 ( $\text{C}_q$ ), 134.9 ( $\text{C}_q$ ), 138.5 ( $\text{C}_q$ ).  $^{29}\text{Si}\{^1\text{H}\}$  NMR (99.31 MHz,  $\text{C}_6\text{D}_6$ , 305 K):  $\delta$   $-38.9$  (s).

Data for  $\text{Dur}_3\text{SiH}$  (8b)<sup>37</sup> are as follows.  $^1\text{H}$  NMR (499.87 MHz,  $\text{C}_6\text{D}_6$ , 305 K):  $\delta$  2.11 (s, 18 H, *m*- $\text{CH}_3$ ), 2.38 (s, 18 H, *o*- $\text{CH}_3$ ), 6.23 (s, 1 H, SiH), 7.02 (s, 3 H, *p*-CH).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.71 MHz,  $\text{C}_6\text{D}_6$ , 305 K):  $\delta$  19.8 (br s,  $\text{CH}_3$ ), 20.0 (s,  $\text{CH}_3$ ), 133.2 (s, CH), 133.6 (s, C), 140.0 (s, C), 137.3 (s, C), 140.0 (s, C).  $^{29}\text{Si}\{^1\text{H}\}$  NMR (99.32 MHz,  $\text{C}_6\text{D}_6$ , 305 K):  $\delta$   $-40.1$  (s).

Data for  $\text{Mes}_3\text{SiH}$  (8c)<sup>38</sup> are as follows.  $^1\text{H}$  NMR (500.13 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  2.16 (s, 9 H, *p*- $\text{CH}_3$ ), 2.35 (s, 18 H, *o*- $\text{CH}_3$ ), 6.15 (s, 1 H, SiH), 6.79 (s, 6 H, *m*-CH).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.77 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  20.6 (s,  $\text{CH}_3$ ), 23.2 (s,  $\text{CH}_3$ ), 129.1 (s, *m*-CH), 131.1 (s, C), 138.7 (s, C), 144.4 (s, C).  $^{29}\text{Si}\{^1\text{H}\}$  NMR (99.37 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$   $-44.0$  (s).

#### Characterization of Phosphonium Borate Salts 3 $[\text{B}(\text{C}_6\text{F}_5)_4]$ .

Signals of the anion are omitted for clarity. Data for 3a<sup>15</sup> are as follows.  $^1\text{H}$  NMR (305 K; 499.870 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  2.00 (s, 9 H,  $\text{CH}_3$ ), 2.27 (s, 9 H,  $\text{CH}_3$ ), 2.37 (s, 9 H,  $\text{CH}_3$ ), 6.83 (d,  $^4J_{\text{P-H}} = 18$  Hz, 6 H, *m*-H), 7.91 (d,  $^1J_{\text{P-H}} = 478$  Hz, 1 H, PH);  $^{13}\text{C}\{^1\text{H}\}$  NMR (305 K; 125.692 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  20.9 (*o*- $\text{CH}_3$ ), 21.2 (*p*- $\text{CH}_3$ ), 21.8 (*o*- $\text{CH}_3$ ), 111.2 (d,  $^1J_{\text{C-P}} = 83$  Hz, *ipso*-C), 111.3 (d,  $^1J_{\text{C-P}} = 83$  Hz, *ipso*-C'), 131.8 (d,  $^3J_{\text{C-P}} = 12$  Hz, *m*-CH), 133.2 (d,  $^3J_{\text{C-P}} = 12$  Hz, *m*-CH), 142.5 (d,  $^2J_{\text{C-P}} = 10$  Hz, *o*-C), 144.0 (d,  $^2J_{\text{C-P}} = 10$  Hz, *o*-C), 147.3 (d,  $^4J_{\text{C-P}} = 3$  Hz, *p*-C);  $^{31}\text{P}\{^1\text{H}\}$  NMR (202.454 MHz,  $\text{C}_6\text{D}_6$ , 298 K)  $\delta$   $-27.2$  (s).

Data for 3c are as follows.  $^1\text{H}$  NMR (500.13 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  0.81 (d,  $^3J_{\text{P-H}} = 15.7$  Hz,  $\text{CH}_3$ ), 3.69 (d,  $^1J_{\text{P-H}} = 430.2$  Hz, PH).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.77 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  29.0 (s,  $\text{CH}_3$ ), 36.6 (d,  $^1J_{\text{P-C}} = 26.7$  Hz, C).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202.47 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  60.0 (s).

For 3e, the polar phase of the reaction mixture was evacuated to dryness and was washed with *n*-pentane. It was again dried under vacuum and then dissolved in  $\text{CDCl}_3$ . Data for 3e are as follows.  $^1\text{H}$  NMR (499.87 MHz,  $\text{CDCl}_3$ , 305 K):  $\delta$  2.38 (s, 9 H, *o*- $\text{CH}_3$ ), 7.07–7.16 (m, 3 H, CH), 7.39–7.48 (m, 3 H, CH), 7.52–7.59 (m, 3 H, CH), 7.73–7.80 (m, 3 H, CH), 8.36 (d,  $^1J_{\text{P-H}} = 481$  Hz, 1 H, PH).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.69 MHz,  $\text{CDCl}_3$ , 305 K):  $\delta$  20.5 (d,  $^3J_{\text{C-P}} = 8.6$  Hz, *o*- $\text{CH}_3$ ), 111.4 (d,  $^1J_{\text{C-P}} = 90.1$  Hz, *ipso*-C), 128.5 (d,  $^2J_{\text{C-P}} = 13.9$

H<sub>2</sub>, CH), 133.2 (d,  $^3J_{C-P}$  = 10.8 Hz, CH), 134.4 (d,  $^3J_{C-P}$  = 12.9 Hz, CH), 136.8 (s, *p*-CH), 143.3 (d,  $^2J_{C-P}$  = 9.0 Hz, C).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202.35 MHz, CDCl<sub>3</sub>, 305 K):  $\delta$  -13.4 (s)

Data for **3h** are as follows.  $^1\text{H}$  NMR (499.87 MHz, CDCl<sub>3</sub>, 305 K):  $\delta$  1.2–1.4 (m, 8 H), 1.41–1.55 (m, 5 H), 1.77–1.84 (m, 3 H), 1.86–1.94 (m, 9 H), 2.10–2.16 (m, 4 H), 2.20–2.27 (m, 2 H), 2.30–2.41 (m, 2 H), 4.89 (dm,  $^1J_{P-H}$  = 441.6 Hz, 1 H, PH).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.71 MHz, C<sub>6</sub>D<sub>6</sub>, 305 K):  $\delta$  24.7 (s, CH<sub>2</sub>), 25.9 (d, 12.9 Hz, CH<sub>2</sub>), 28.1 (d, 3.3 Hz, CH<sub>2</sub>), 28.4 (s, CH).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202.35 MHz, C<sub>6</sub>D<sub>6</sub>, 305 K):  $\delta$  34.2 (s).

Data for **3i** are as follows.  $^1\text{H}$  NMR (499.87 MHz, C<sub>6</sub>D<sub>6</sub>, 305 K):  $\delta$  1.80–2.10 (m, 45 H, CH<sub>3</sub>; not distinguishable), 7.88 (d,  $^1J_{P-H}$  = 483.7 Hz, PH).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.71 MHz, C<sub>6</sub>D<sub>6</sub>, 305 K):  $\delta$  16.3 (superposition of *m*- and *p*-CH<sub>3</sub>), 17.4 (s, CH<sub>3</sub>), 117.4 (d,  $^1J_{C-P}$  = 81.8 Hz, C), 128.5 (C), 136.8 (d,  $^2J_{C-P}$  = 11.4 Hz, C), 144.0 (d,  $^3J_{C-P}$  = 3.2 Hz, C).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202.35 MHz, C<sub>6</sub>D<sub>6</sub>, 305 K):  $\delta$  -17.3 (s).

The phosphonium borate **3**[B(C<sub>6</sub>F<sub>4</sub>)<sub>4</sub>] was characterized only by its characteristic  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR signals in a mixture with unknown decomposition products due to the instability of the Lewis pair **4a**/2L. Data for **3** are as follows.  $^1\text{H}$  NMR (499.87 MHz, C<sub>6</sub>D<sub>6</sub>, 305 K):  $\delta$  8.05 (d,  $^1J_{P-H}$  = 477.4 Hz, 1H, PH).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202.35 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta$  -30.54 (s).

**Procedure for Generation of Lewis Acid–Base Adduct 7.** The tris(pentamethylphenyl)silylium borate salt **4a**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (0.43 mmol) was prepared in benzene as described above. The salt was washed two times with benzene, was dried in vacuo, and was then dissolved in 1 mL of C<sub>7</sub>D<sub>8</sub>. At -28 °C 51 mg of triethylphosphane **2b** (0.43 mmol) was added via a syringe with vigorous stirring. The mixture was slowly warmed to ambient temperature over a period of 1 h. Upon 1 h of subsequent stirring at room temperature the formerly dark brown mixture lightened to a intensive orange. Then the phases were allowed to separate. The lower ionic phase was subjected to multinuclear NMR spectroscopy.

**Characterization of Acid–Base Adduct 7.** Signals of the anion are omitted for clarity.  $^1\text{H}$  NMR (499.87 MHz, CDCl<sub>3</sub>, 305 K):  $\delta$  1.02–1.10 (m, 9 H, CH<sub>2</sub>CH<sub>3</sub>), 1.58–1.76 (m, 6 H, CH<sub>2</sub>CH<sub>3</sub>), 1.89 (s, 9 H, CH<sub>3</sub>), 2.07 (s, 18 H, CH<sub>3</sub>), 2.11 (s, 9 H, CH<sub>3</sub>), 2.19 (s, 9 H, CH<sub>3</sub>).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.71 MHz, CDCl<sub>3</sub>, 305 K):  $\delta$  8.9 (d,  $^2J_{P-C}$  = 8.4 Hz, CH<sub>3</sub>, CH<sub>2</sub>CH<sub>3</sub>), 14.9 (d,  $^1J_{P-C}$  = 28.7 Hz, CH<sub>2</sub>CH<sub>3</sub>), 16.0 (s, CH<sub>3</sub>), 16.7 (d, 38.5 Hz, CH<sub>3</sub>), 24.1 (d, 79.6 Hz, CH<sub>3</sub>), 130.3 (d, 9.5 Hz, C), 133.4 (s, C), 136.0 (s, C), 137.7 (s, C), 139.6 (s, C), 141.7 (d, 4.2 Hz, C).  $^{29}\text{Si}\{^1\text{H}\}$  NMR (99.32 MHz, CDCl<sub>3</sub>, 305 K):  $\delta$  -1.90 (d,  $^1J_{P-Si}$  = 42.3 Hz).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202.35 MHz, C<sub>7</sub>D<sub>8</sub>, 305 K):  $\delta$  -4.35.

**Procedure for C–F Activation Experiments.** The tris(pentamethylphenyl)silylium borate salt **4a**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (0.43 mmol) was prepared in benzene as described above. The salt was washed two times with benzene and was then dissolved in 1 mL of C<sub>6</sub>D<sub>6</sub>. Then, a solution of 168 mg of trimesitylphosphane (**2a**; 0.43 mmol) in 0.5 mL of C<sub>6</sub>D<sub>6</sub> was added via a PTFE cannula. Immediately, 70 mg of 1-decyl fluoride (0.43 mmol) was added via a syringe at room temperature. The previously dark brown mixture lightened considerably upon stirring for 30 min. The phases were allowed to separate and were subjected to multinuclear NMR spectroscopy. The upper nonionic phase was additionally investigated via GC/MS analysis.

**Characterization of C–F Activation Products.** Data for (Me<sub>5</sub>C<sub>6</sub>)<sub>3</sub>SiF (**9**) are as follows.  $^1\text{H}$  NMR (499.87 MHz, C<sub>6</sub>D<sub>6</sub>, 305 K):  $\delta$  2.06 (s, 18 H, *m*-CH<sub>3</sub>), 2.13 (s, 9 H, *p*-CH<sub>3</sub>), 2.51 (m, 18 H, *o*-CH<sub>3</sub>).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.71 MHz, C<sub>6</sub>D<sub>6</sub>, 305 K):  $\delta$  16.0 (s, CH<sub>3</sub>), 16.5 (s, CH<sub>3</sub>), 20.4 (s, CH<sub>3</sub>), 129.8 (s), 136.4 (s), 137.0 (d, 13.8 Hz), 137.3 (s), 142.4 (d, 18.2 Hz).  $^{19}\text{F}\{^1\text{H}\}$  NMR (470.30 MHz, C<sub>6</sub>D<sub>6</sub>, 305 K):  $\delta$  -146.2 (s,  $^{29}\text{Si}$  satellites at 274.0 Hz).  $^{29}\text{Si}\{^1\text{H}\}$  NMR (99.31 MHz, C<sub>6</sub>D<sub>6</sub>, 305 K):  $\delta$  -4.71 (d,  $^1J_{Si-F}$  = 274.2 Hz). Characterization of alkylated benzenes **11a–e** by GC/MS (EI) analysis [retention time; relative GC/MS rate]:  $^{39}$  decan-5-ylbenzene **11a** [15.36 min; 9%] *m/z* (%) 55 (3), 65 (2), 77 (4), 91 (100), 105 (12), 115 (3), 147 (11), 161 (7), 218 (4); decan-4-ylbenzene **11b** [15.50 min; 12%] *m/z* (%) 55 (4), 65 (2), 77 (4), 91 (100), 105 (8), 119 (4), 133 (17), 175 (4), 218 (4); decan-3-ylbenzene **11c** [15.76 min; 23%] *m/z* (%) 55 (5), 65 (3), 77 (5), 91 (100), 105 (10), 119 (26), 133 (3), 147 (1), 189 (6), 218 (5); decan-2-ylbenzene **11d** [16.23 min; 40%] *m/z* (%) 55 (4), 65 (1),

77 (9), 91 (14), 105 (100), 115 (1), 218 (5); *n*-decylbenzene **11e** [17.13 min; 16%] *m/z* (%) 55 (14), 65 (8), 77 (7), 84 (4), 92 (100), 105 (9), 119 (3), 132 (2), 147 (1), 218 (9).

**General Procedure for CO<sub>2</sub> Fixation Experiments.** The tris(pentamethylphenyl)silylium borate salt **4a**[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (0.43 mmol) was prepared in benzene as described above. The salt was washed two times with benzene and was then dissolved in 1 mL of C<sub>6</sub>D<sub>6</sub>. Then, a solution of the corresponding phosphane **2c** or **2h** (0.43 mmol) in 0.5 mL of C<sub>6</sub>D<sub>6</sub> was added via a PTFE cannula. The resulting dark brown mixture was immediately purged with carbon dioxide gas and was stirred under a CO<sub>2</sub> atmosphere for at least 30 min. Upon this treatment the formerly dark brown mixture lightened considerably. The phases were then allowed to separate and were then subjected to multinuclear NMR spectroscopy.

**Characterization of CO<sub>2</sub> Fixation Products.** Signals of the anion are omitted for clarity. Data for silylated phosphanyl ester **2c** are as follows.  $^1\text{H}$  NMR (499.87 MHz, C<sub>6</sub>D<sub>6</sub>, 305 K):  $\delta$  1.02 (d,  $^3J_{P-H}$  = 15.0 Hz, 27 H, C(CH<sub>3</sub>)<sub>3</sub>), 2.06 (s, 18 H, *m*-CH<sub>3</sub>), 2.12 (s, 9 H, *p*-CH<sub>3</sub>), 2.25 (s, 18 H, *o*-CH<sub>3</sub>).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.71 MHz, C<sub>6</sub>D<sub>6</sub>, 305 K):  $\delta$  15.7 (s, CH<sub>3</sub>), 16.3 (s, CH<sub>3</sub>), 23.2 (s, CH<sub>3</sub>), 28.5 (s, CH<sub>3</sub>), 29.1 (s, CH<sub>3</sub>), 40.9 (d,  $^2J_{P-C}$  = 17.2 Hz, CH<sub>3</sub>), 133.3 (s), 134.1 (s), 138.1 (s), 139.0 (s), 159.0 (d,  $^1J_{P-C}$  = 88.2 Hz, PC=O).  $^{29}\text{Si}\{^1\text{H}\}$  NMR (99.31 MHz, C<sub>6</sub>D<sub>6</sub>, 305 K):  $\delta$  -0.28 (s).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202.35 MHz, C<sub>6</sub>D<sub>6</sub>, 305 K):  $\delta$  56.43 (s). IR (ATR, neat):  $\nu$  (cm<sup>-1</sup>) 1712 (C=O).

Data for silylated phosphanyl ester **2h** are as follows.  $^1\text{H}$  NMR (499.87 MHz, C<sub>6</sub>D<sub>6</sub>, 305 K):  $\delta$  0.87–0.90 (m, CH/CH<sub>2</sub>, 6 H), 0.93–0.99 (m, CH/CH<sub>2</sub>, 6 H), 1.17–1.22 (m, CH/CH<sub>2</sub>, 4 H), 1.48–1.58 (m, CH/CH<sub>2</sub>, 17 H), 2.06 (s, 18 H, *m*-CH<sub>3</sub>), 2.13 (s, 9 H, *p*-CH<sub>3</sub>), 2.22 (s, 18 H, *o*-CH<sub>3</sub>).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.71 MHz, C<sub>6</sub>D<sub>6</sub>, 305 K):  $\delta$  15.7 (s, CH<sub>3</sub>), 16.3 (s, CH<sub>3</sub>), 23.0 (s, CH<sub>3</sub>), 24.5 (s, CH<sub>3</sub>), 25.9 (d, 12 Hz, CH<sub>2</sub>), 26.0 (d, 3.3 Hz, CH<sub>2</sub>), 26.2 (d, 3.5 Hz, CH<sub>2</sub>), 26.3 (d, 3.5 Hz, CH<sub>2</sub>), 27.3 (s, CH<sub>2</sub>), 30.5 (d, 31.5 Hz, CH), 133.3 (s), 133.9 (s), 138.1 (s), 138.9 (s), 157.7 (d,  $^1J_{P-C}$  = 108.9 Hz, PC=O).  $^{29}\text{Si}\{^1\text{H}\}$  NMR (99.32 MHz, C<sub>6</sub>D<sub>6</sub>, 305 K):  $\delta$  -1.84 (s).  $^{31}\text{P}\{^1\text{H}\}$  NMR (202.35 MHz, C<sub>6</sub>D<sub>6</sub>, 305 K):  $\delta$  46.57 (s). IR (ATR, neat):  $\nu$  (cm<sup>-1</sup>) 1714 (C=O).

## ■ ASSOCIATED CONTENT

### Supporting Information

Figures and tables giving experimental, computational, and analytical details and data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

Financial support by the Deutsche Forschungsgemeinschaft (DFG) is gratefully acknowledged (Mu1440/7-1). The High End Computing Resource Oldenburg (HERO) at the CvO University is thanked for computer time.

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