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# Ferrocene-Stabilized Silicon Cations as Catalysts for Diels–Alder Reactions: Attempted Experimental Quantification of Lewis Acidity and ReactIR Kinetic Analysis

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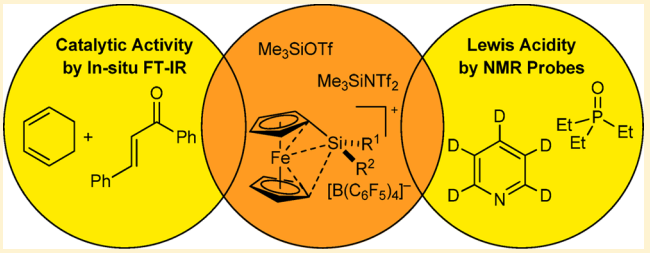
Supporting Information

**ABSTRACT:** The $^{29}$Si NMR chemical shifts of ferrocene-stabilized silicon cations span a wide range depending on the substituents at the silicon atom. These pronounced differences in deshielding of the silicon atom do not translate into significant differences in their catalytic activity in Diels–Alder reactions. It was shown by Lewis pair formation with Lewis base probes ($Et_3PO$ and pyridine-$d_5$) that there is hardly any difference between these silicon cations after coordination to a Lewis base. This finding not only thwarts experimental quantification of the Lewis acidity of the free Lewis acids but also demonstrates that the reactivity differences are largely due to steric effects for a given counteranion. These observations are further verified by a ReactIR kinetic analysis. The Lewis acidity of silicon cations and their performance as catalysts cannot be correlated with $^{29}$Si NMR chemical shifts as well as resonances of adducts with Lewis base probes, not even for a subset of silicon Lewis acids.

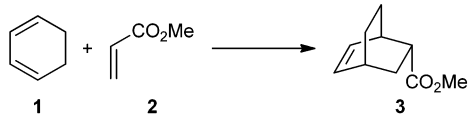



## INTRODUCTION

The performance of tetracoordinate silicon-based Lewis acids of the general formula $R_3SiX$ as catalysts largely depends on the X group (typically Cl, OTf, and $NTf_2$) and, to lesser extent, on the R groups (usually alkyl or aryl groups).[1,2] A particularly striking example is the reactivity difference of $Me_3SiOTf$ (**4**) and $Me_3SiNTf_2$ (**5**) in low-temperature Diels–Alder reactions. It was Ghosez and co-workers who demonstrated that **5** catalyzes Diels–Alder reactions at 0 °C where conventional **4** is not sufficiently potent (e.g., **1** + **2** → **3**, Scheme 1).[3] Sawamura and co-workers later showed that $[Et_3Si(toluene)]^+[B(C_6F_5)_4]^-$ (**6**) is an even better catalyst for the same transformation (**1** + **2** → **3**, Scheme 1).[4] The coordinating ability order of the involved counteranions $X^-$ is $TfO^- > Tf_2N^- > [B(C_6F_5)_4]^-$, and that greatly enhances the Lewis acidity at the silicon atom in reverse order.[2] Also, the silicon atom in **6** is cationic, and the neutral arene solvent lends stabilization to an otherwise tricoordinate, tetravalent silicon cation. Such solvent-stabilized silylium ions are nevertheless exceptionally strong Lewis acids.[2,5] Although it is not allowed to directly correlate the $^{29}$Si NMR chemical shift with the Lewis acidity of the silicon atom, the degree of deshielding is still believed to be a good qualitative measure of its Lewis acidity (43.5 ppm for **4** < 55.9 ppm for **5** < 81.8 ppm for **6**).[6]

Our laboratory had introduced the ferrocene-stabilized silicon cation **7a**,[7] which emerged as an excellent catalyst for the above and other challenging Diels–Alder reactions (**1** + **2** → **3**, Scheme 1).[8] We were recently able to prepare and characterize 10 additional new members of this family (**7b**–**7k**, Figure 1).[9] These span a relatively wide chemical shift range of 77.4–120.9 ppm. We assumed that a maximum $\Delta\delta$ value of 43.5 ppm would also be reflected in different Lewis acidities

**Scheme 1. Diels–Alder Reaction Catalyzed by Silicon-Based Lewis Acids**




| Ghosez (**1997**) | | Sawamura (**2005**) | Oestreich (**2009**) |
|---|---|---|---|
| $Me_3SiOTf$ **4** | $Me_3SiNTf_2$ **5** | $[Et_3Si(toluene)]^+[B(C_6F_5)_4]^-$ **6** | **7a** |
| 10 mol % | 10 mol % | 1.0 mol % | 1.0 mol % |
| toluene | toluene | toluene | $CH_2Cl_2$ |
| 0 °C, 1 h | 0 °C, 1 h | 0 °C, 1 h | −78 °C, 16 h |
| 0% | 92%, 98% *endo* | 97%, 98% *endo* | 95%, >99% *endo* |
| $^{29}$Si NMR: | $^{29}$Si NMR: | $^{29}$Si NMR: | $^{29}$Si NMR: |
| $\delta$ 43.5 ppm | $\delta$ 55.9 ppm | $\delta$ 81.8 ppm | $\delta$ 114.5 ppm |

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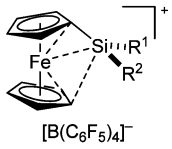



| | R1 | R2 | 29Si NMR (ppm) |
|---|---|---|---|
| 7a | tBu | Me | 114.4 |
| 7b | iPr | Me | 113.4 |
| 7c | Me | Me | 110.7 |
| 7d | tBu | tBu | 120.9 |
| 7e | iPr | iPr | 114.7 |
| 7f | Ph | tBu | 98.6 |
| 7g | Ph | Me | 93.8 |
| 7h | Fc | Fc | 91.3 |
| 7i | Fc | Me | 88.3 |
| 7j | Ph | Ph | 81.0 |
| 7k | Fc | Ph | 77.4 |

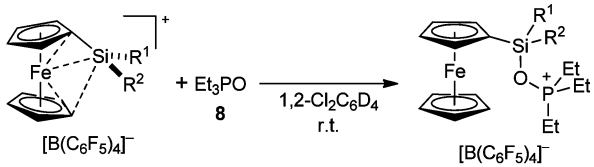
**Figure 1.** The family of ferrocene-stabilized silicon cations: $^{29}$Si NMR chemical shifts.

and, hence, catalytic activity. We, therefore, embarked on an experimental verification of the Lewis acidities of ferrocene-stabilized silicon cations **7** in comparison with **4**–**6** by adduct formation with Lewis base probes and by kinetic measurements of a selected Diels–Alder reaction.[10]

## RESULTS AND DISCUSSION

**Quantification of Lewis Acidity.** To assess the Lewis acidity of **7**,[12] we chose the established Gutmann–Beckett method where Lewis pair formation with triethylphosphine oxide **8** as Lewis base is used to determine relative Lewis acidities.[13] The degree of deshielding in the $^{31}$P NMR spectrum related to free **8** ($\delta$ 47.6 ppm in 1,2-$Cl_2C_6D_4$) is a measure of the Lewis acidity. The $^{29}$Si and $^{31}$P{$^1$H} NMR chemical shifts of selected adducts **9**[14] are summarized in Table 1 (entries 1–6;

**Table 1. Gutmann–Beckett Analysis: Adducts with Triethylphosphine Oxide (8) as Lewis Base Probe**[a,b]




| entry | compound | R1 | R2 | 29Si NMR (ppm) | 31P{1H} NMR (ppm) |
|---|---|---|---|---|---|
| 1 | **9a** | tBu | Me | 27.2[c] | 88.7 |
| 2 | **9d** | tBu | tBu | 25.0[c] | 87.9 |
| 3 | **9e** | iPr | iPr | 24.3[c] | 88.4 |
| 4 | **9f** | Ph | tBu | 14.3[c] | 90.5 |
| 5 | **9h** | Fc | Fc | 13.5[d] | 88.0 |
| 6 | **9i** | Fc | Me | 17.8[c] | 89.0 |
| 7 | **6′·8** | | | 35.8[d] | 88.8 |
| 8 | **5·8** | | | 32.5[c] | 91.0 |
| 9 | **4·8** | | | 32.3[c] | 92.5 |

[a]Lewis pairs generated according to General Procedures 1 (for **9** and **6′·8**) and 2 (for **5·8** and **4·8**). [b]$^{31}$P{$^1$H} NMR chemical shift of **8** in 1,2-$Cl_2C_6D_4$: $\delta$ 47.6 ppm. [c]$^{29}$Si DEPT NMR. [d]$^1$H,$^{29}$Si HMQC NMR.

for the NMR spectroscopic characterization of **9b**–**9c**, **9g**, and **9j**–**9k**, see the Supporting Information). The $^{29}$Si NMR chemical shifts $\delta$ 13.5–27.2 ppm of adducts **9** are clear evidence for the formation of a tetracoordinated silicon atom, and the $^2J_{Si,P}$ coupling constants ranging from 12.5 to 21.1 Hz obtained from $^{29}$Si DEPT NMR spectra are further proof of Lewis pair formation. The $^{31}$P{$^1$H} NMR chemical shifts of **9** indicate coordination of a strong Lewis acid to the oxygen atom of **8**, but absolute values are almost identical ($\delta$ 89.5 ± 1.5 ppm). The adduct of $[Et_3Si(1,2\text{-}Cl_2C_6H_4)]^+[B(C_6F_5)_4]^-$ **6′·8** ($^{29}$Si NMR: $\delta$ 101.3 ppm) with the same counteranion fits also into this scale (Table 1, entry 7). Even the chemical shifts found for **5·8** and **4·8** generated from nonionic **5** and **4** are of the same order of magnitude (Table 1, entries 8 and 9). This is in stark contrast to the large range of $^{29}$Si NMR chemical shifts of silicon cations **7** ($\delta$ 77.4–120.9 ppm, cf. Figure 1). The $^{31}$P{$^1$H} NMR chemical shifts show no correlation with other spectroscopic or structural data. Hence, determination of the Lewis acidity by the Gutmann–Beckett method is not applicable within our family of silylium ions. Differences in the $^{29}$Si NMR chemical shift as well as in the Lewis acidity are largely controlled by the degree of interaction between the cationic silicon atom and the ferrocene backbone. Coordination of phosphine oxide **8** (or any other Lewis base) cancels that interaction, and the thus-formed cations with a tetracoordinated silicon atom do not show pronounced differences in the $^{31}$P{$^1$H} NMR chemical shifts, as the substituent effects alone are relatively minor.

As a consequence of the poor validity of the Gutmann–Beckett method, we moved to Lewis base probes **10**-$d_1$ and **11**-$d_5$ for the quantification of Lewis acidity, which were introduced by Hilt (Figure 2).[15,16] Coordination of either the

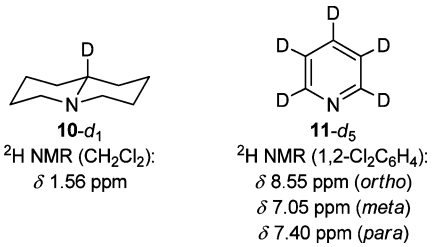



**Figure 2.** Lewis base probes **10**-$d_1$[15] and **11**-$d_5$[16] introduced by Hilt.

tertiary amine or the pyridine nitrogen atom to the Lewis acid had been shown to result in deshielding of $^2$H resonance signals depending on the strength of the Lewis acid.

Amine **10**-$d_1$ was too sterically hindered to form stable adducts with ferrocene-stabilized silicon cations **7**. Decomposition was usually observed, and that was in agreement with previous findings from our laboratory.[8b] The use of non-hindered **11**-$d_5$ was more promising, as Manners and co-workers had already reported the preparation of stable pyridine adducts of **7** ($^{29}$Si NMR: $\delta$ 36.2 ppm in $CD_2Cl_2$ for **12e** and $\delta$ 25.2 ppm in $CD_2Cl_2$ for **12h**).[11] Moreover, Hilt and Nödling had employed **11**-$d_5$ to quantify the Lewis acidities of several triorganosilyl triflates and had found a qualitative correlation between the deshielding of the $^2H_{para}$ nucleus and the rate constants of a Diels–Alder reaction catalyzed by these silicon Lewis acids.[16] Not surprisingly, the targeted adducts **12** cleanly formed with six selected silicon cations **7**[14] (Table 2, entries 1–6). $^{29}$Si NMR chemical shifts were again diagnostic of Lewis pair formation. However, the $\Delta\delta$ values, particularly those of the $^2H_{para}$ nucleus, obtained from the $^2$H NMR measurements did not show the same trends as seen for the aforementioned screening of triorganosilyl triflates.[16] $\Delta\delta(^2H_{para})$ values are within less than 0.1 ppm, even for **6′·11**-$d_5$ and **5·11**-$d_5$ (Table 2, entries 7 and 8). Also, $\Delta\delta(^2H_{ortho})$ values were not positive throughout; negative values correspond to a shielding of the $^2H_{ortho}$ nucleus. The $\Delta\delta(^2H_{meta})$ values were distinguishable but


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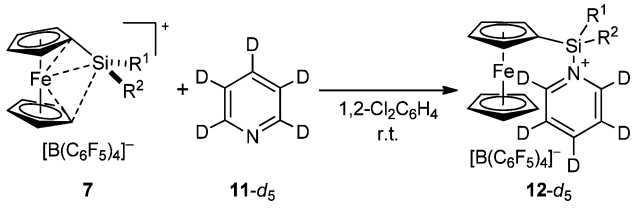
**Table 2. Adducts with Pyridine-$d_5$ (11-$d_5$) as Lewis Base Probe**[a]



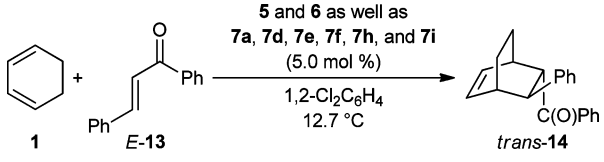

| | | | | Δδ in $^2$H NMR[b,c] | | | |
|---|---|---|---|---|---|---|---|
| entry | compound | $R^1$ | $R^2$ | *ortho* | *meta* | *para* | $^{29}$Si NMR (ppm) |
| 1 | **12a**-$d_5$ | *t*Bu | Me | −0.41 | 0.38 | 0.60 | 36.8[d] |
| 2 | **12d**-$d_5$ | *t*Bu | *t*Bu | 0.57 | 0.65 | 0.67 | 35.0[d] |
| 3 | **12e**-$d_5$ | *i*Pr | *i*Pr | −0.36 | 0.44 | 0.57 | 34.5[d] |
| 4 | **12f**-$d_5$ | Ph | *t*Bu | −0.37 | 0.38 | 0.60 | 23.4[d] |
| 5 | **12h**-$d_5$ | Fc | Fc | 0.62 | 0.60 | 0.61 | 22.8[d] |
| 6 | **12i**-$d_5$ | Fc | Me | 0.03 | 0.47 | 0.58 | 26.8[d] |
| 7 | **6′**·**11**-$d_5$ | | | −0.40 | 0.54 | 0.61 | 42.6[d] |
| 8 | **5**·**11**-$d_5$ | | | −0.04 | 0.67 | 0.64 | 41.9[e] |
| 9 | **4**·**11**-$d_5$ | | | −0.07 | 0.24 | 0.28 | 42.7[e] |

[a]Lewis pairs generated according to General Procedures 3 (for **12**-$d_5$ and **6′**·**11**-$d_5$) and 4 (for **5**·**11**-$d_5$ and **4**·**11**-$d_5$). [b]Δδ values relative to free **11**-$d_5$ (for $^2$H NMR chemical shifts, see Figure 2). [c]Line widths were determined for the resonance signal of the deuteron in the *meta* position (*ortho* for **4**·**11**-$d_5$): 17.7 Hz (average) for **12**-$d_5$ and 4.8 Hz (average) for **4**·**11**-$d_5$–**6′**·**11**-$d_5$. [d]$^1$H,$^{29}$Si HMQC NMR. [e]$^{29}$Si DEPT NMR.

did not allow for any correlation with kinetic data (*vide infra*). As with the Gutmann–Beckett analysis, these results are inconclusive.

**Kinetic Analysis.** The marked chemical shift differences in the $^{29}$Si NMR spectra of ferrocene-stabilized silicon cations **7** did not translate into meaningful trends in the Lewis pair formation with $^{31}$P{$^1$H} NMR (Table 1) or $^2$H NMR (Table 2) probes.[12] We had observed though that Lewis acids **7** catalyze Diels–Alder reactions at slightly different rates, and it therefore appeared reasonable to evaluate the reactivity of selected **7** in a kinetic analysis of a representative Diels–Alder reaction. The C=O group in the various dienophiles tested in the past[8] suggested *in situ* IR spectroscopy with a ReactIR as a suitable tool for monitoring these air- and moisture-sensitive reactions. We chose the Diels–Alder reaction of cyclohexa-1,3-diene (**1**) and chalcone (*E*-**13**) as a model reaction (**1** + *E*-**13** → *trans*-**14**, Scheme 2). The carbonyl stretching bands of *E*-**13** and *trans*-**14**

**Scheme 2. Model Diels–Alder Reaction for the ReactIR Analysis**




were sufficiently separated, and this rather difficult Diels–Alder reaction would not be catalyzed by protons[8b] at the reaction temperature (approximately 15 °C) required for our ReactIR measurements.

The reaction progress was constantly monitored until no further increase in the absorption intensity of the carbonyl band of *trans*-**14** was observed (Figure 3). It is apparent that full conversion is usually reached within half an hour. Neither the

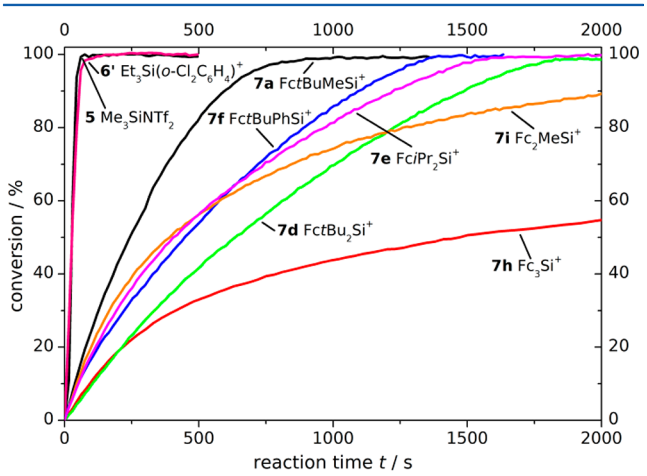



**Figure 3.** Comparison of the kinetic profiles of the model Diels–Alder reaction catalyzed by various silicon Lewis acids.

technical equipment nor the solvent (1,2-$Cl_2C_6H_4$ solidifies at −18 °C, and **7** are not stable above −40 °C in $CH_2Cl_2$) allowed running these reactions at lower temperature. The setup was extremely sensitive toward minor variations of the temperature. The cycloaddition even occurs instantaneously with $Me_3SiNTf_2$ (**5**) and $[Et_3Si(1,2\text{-}Cl_2C_6H_4)]^+[B(C_6F_5)_4]^-$ (**6′**), and **5** and **6′** are better catalysts than **7** at 12.7 °C.[17] The kinetic profiles of the catalyses with ferrocene-stabilized silicon cations **7** are all different and might be grouped into those of silicon cations with and without additional ferrocenyl groups (**7h** and **7i** versus **7a**, **7d**, **7e**, and **7f**). Within this family, the steric demand of $R^1$ and $R^2$ might account for the different kinetic profiles: **7a** ($R^1$ = *t*Bu and $R^2$ = Me) is by far the best catalyst. As discussed above, the initial deshielding of the silicon atom is canceled by coordination of a Lewis base, here dienophile *E*-**13**. **7f** ($R^1$ = *t*Bu and $R^2$ = Ph, δ 98.6 ppm) is the better catalyst than more hindered **7d** ($R^1$ = *t*Bu and $R^2$ = *t*Bu, δ 120.9 ppm) but significantly less deshielded. Currently, we cannot explain the course of the curve for catalysts **7h** and **7i** with more than one ferrocenyl substituent but speculate that the excellent stabilization and secondary effects[9] exerted by the electron-rich ferrocenyl groups makes them poorer Lewis acids.

No simple overall reaction order could be deduced from these kinetic profiles.[18] We think that this is a reflection of the unclear mechanism of Diels–Alder reactions catalyzed by highly Lewis acidic silicon cations. Our group proved that the Diels–Alder reaction is indeed stepwise and diastereoconvergent; both *E*-**13** and *Z*-**13** yield *trans*-**14** with d.r. = 99:1.[19] Moreover, Prakash, Olah, and co-workers had shown for the silylcarboxonium/silyloxycarbenium ion of cyclohex-2-enone that the positive charge accumulates at the β-position.[20] We interpret these findings in support of a polar stepwise rather than a concerted mechanism.[3] We exclude here the intermediacy of pentacoordinate silicon cations, as there was no $^{29}$Si NMR spectroscopic evidence when treating **7a** with excess Lewis base (benzophenone or acetonitrile).

As quantification of the reactivity of **7** from rate constants was not possible, we determined the initial rates (Figure 4 and Table 3) and turnover frequencies (TOFs) at 50% and 95% conversion (Table 3) to establish a reactivity order. Comparison of the initial rates results in a relative order **7a**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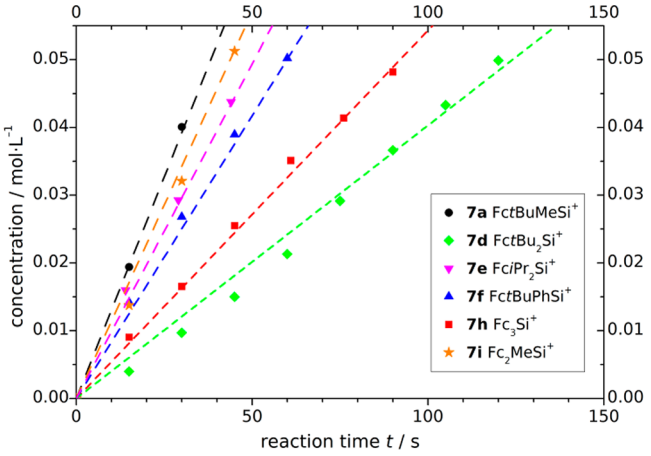


**Figure 4.** Determination of the initial rates (cf. Scheme 2).

≈ **7i** > **7e** ≈ **7f** > **7h** ≈ **7d** (column 3). Similar trends are seen with the TOFs at different conversion: **7a** > **7i** ≈ **7e** ≈ **7f** > **7d** > **7h** (column 4) and **7a** > **7f** ≈ **7e** ≈ **7d** > **7i** (column 5). We interpret these data to mean that the different reactivities of **7** are largely due to steric effects. The performance of catalysts **7h** and **7i** with multiple ferrocenyl substituents at higher conversion is not understood. It is worthy of note that **7a** ($R^1$ = *t*Bu and $R^2$ = Me), which we selected almost arbitrarily when we had started this chemistry five years ago,[8a] indeed is the best catalyst within the family of ferrocene-stabilized silicon cations.

## CONCLUSION

The initial purpose of this study was an experimental quantification of the Lewis acidity of our ferrocene-stabilized silicon cations **7**[12] by Lewis pair formation utilizing the methods established by Gutmann and Beckett[13] (with $Et_3PO$ as a $^{31}P$ NMR probe) and Hilt[16] (with pyridine-$d_5$ as a $^2H$ NMR probe). We soon learned that the wide range of $^{29}Si$ NMR chemical shifts of **7** does not translate into significant differences in the $^{31}P$ NMR and $^2H$ NMR chemical shifts, respectively, in the Lewis pairs **9** (Table 1) and **12** (Table 2). The adduct formation cancels the interaction between the cationic silicon atom and the ferrocene backbone, thereby reducing pronounced to minor differences that are simply due to the steric environment around the silicon atom. When applying **7** as catalysts in Diels–Alder reactions, it is the dienophile that slips into the role of the Lewis base. For that reason, it now comes as no surprise that Lewis acids **7** display similar catalytic activity in Diels–Alder reactions despite markedly different deshielding of the silicon atom in the free Lewis acid (Figure 1). Steric and to a lesser extent electronic effects govern the reactivity, as verified by ReactIR kinetic measurements. The key finding of this work is that the Lewis acidity of silicon cations and their performance as catalysts cannot be correlated with $^{29}Si$ NMR chemical shifts nor with those of adducts with various Lewis base NMR probes, not even for a small subset of silicon Lewis acids.

## EXPERIMENTAL SECTION

**General Remarks.** All reactions were performed in flame-dried glassware using a glovebox ($O_2$ < 0.5 ppm, $H_2O$ < 0.5 ppm) or conventional Schlenk techniques under a static pressure of argon or nitrogen. Solvents and solutions were transferred with syringes. Benzene was purified and dried using a solvent system. Toluene was dried over $CaH_2$ and stored over molecular sieves. 1,2-$Cl_2C_6H_4$ and 1,2-$Cl_2C_6D_4$ were dried over $CaH_2$ prior to use and stored over molecular sieves in a glovebox. Cyclohexa-1,3-diene (**1**) was distilled from $NaBH_4$. *E*-Chalcone (*E*-**13**) was recrystallized from ethanol and dried by azeotropic distillation with benzene or toluene. Ferrocenyl-substituted silanes, i.e., precursors of silylium ions **7a**–**7k**, were prepared according to previously reported procedures and dried by azeotropic distillation with benzene.[9] Triethylsilane and allyltrimethylsilane were distilled from $CaH_2$ or $LiAlH_4$ and stored over molecular sieves. $[Ph_3C]^+[B(C_6F_5)_4]^-$ was prepared according to a reported procedure, recrystallized from $CH_2Cl_2$/*n*-pentane, and stored in a glovebox.[21] Triethylphosphine oxide (**8**) was used as received and stored in a glovebox. Quinolizidine-$d_1$ (**10**-$d_1$) was prepared according to a reported procedure,[15] and pyridine-$d_5$ (**11**-$d_5$) was dried over $CaH_2$; both were stored over molecular sieves. $Me_3SiOTf$ (**4**) was purified by fractional distillation under an inert atmosphere in the presence of $Me_4Si$. $Me_3SiNTf_2$ (**5**) was obtained from commerical sources or prepared according to a known procedure from allyltrimethylsilane[3b] and used immediately thereafter. $^1H$, $^2H$, $^{11}B$, $^{19}F$, $^{29}Si$, and $^{31}P\{^1H\}$ NMR spectra were recorded in 1,2-$Cl_2C_6H_4$ and 1,2-$Cl_2C_6D_4$ at the Westfälische Wilhelms-Universität Münster, the Technische Universität Berlin, and the Philipps-Universität Marburg. Chemical shifts are reported in parts per million (ppm) and are referenced to the residual solvent resonance as the internal standard (1,2-$Cl_2C_6D_3H$: $\delta$ 6.94 and 7.20 ppm for $^1H$ NMR; 1,2-$Cl_2C_6DH_3$: $\delta$ 6.94 and 7.20 ppm for $^2H$ NMR). Data are reported as follows: chemical shift, multiplicity (br s = broad singlet, s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, br m = broad multiplet, m = multiplet, $m_c$ = centrosymmetric multiplet), coupling constants (Hz), and integration. $^1H$,$^{29}Si$ HMQC NMR spectra are measured with a coupling constant of 7.0 Hz for the $^3J_{H,Si}$ coupling. The peak intensities in the $^1H$,$^{29}Si$ HMQC NMR spectra cannot be correlated to the amount of compound. Gas liquid chromatography (GLC) was performed on a capillary column (30 m × 0.32 mm, 0.25 $\mu$m film thickness) using the following programs: $N_2$ carrier gas, injection temperature 240 or 250 °C, detector temperature 300 °C, flow rate 1.74 mL/min or 1.70 mL/min; temperature program: start temperature 40 °C, heating rate 10 °C/min, end temperature 280 °C for 10 min. *In situ* FT-IR spectroscopy was performed using a ReactIR with

**Table 3. Average Initial Rates and Turnover Frequencies (cf. Scheme 2 and Figure 4)[18]**

| entry | Lewis acid | initial rate (mol·$L^{-1}$·$s^{-1}$) | TOF at 50% conv ($s^{-1}$) | TOF at 95% conv ($s^{-1}$) |
|---|---|---|---|---|
| 1 | **7a** | (1.23 ± 0.10) × $10^{-3}$ | (4.08 ± 0.29) × $10^{-2}$ | (2.86 ± 0.20) × $10^{-2}$ |
| 2 | **7d** | (0.43 ± 0.10) × $10^{-3}$ | (1.45 ± 0.29) × $10^{-2}$ | (1.07 ± 0.26) × $10^{-2}$ |
| 3 | **7e** | (0.86 ± 0.13) × $10^{-3}$ | (2.32 ± 0.25) × $10^{-2}$ | (1.22 ± 0.19) × $10^{-2}$ |
| 4 | **7f** | (0.84 ± 0.22) × $10^{-3}$ | (2.18 ± 0.27) × $10^{-2}$ | (1.46 ± 0.28) × $10^{-2}$ |
| 5 | **7h** | (0.53 ± 0.03) × $10^{-3}$ | (0.69 ± 0.17) × $10^{-2}$ | [a] |
| 6 | **7i** | (1.17 ± 0.16) × $10^{-3}$ | (2.82 ± 0.37) × $10^{-2}$ | (0.63 ± 0.27) × $10^{-2}$ |
| 7 | **6′** | n.d. | 37.2 × $10^{-2}$ | 32.0 × $10^{-2}$ |
| 8 | **5** | n.d. | 37.6 × $10^{-2}$ | 39.3 × $10^{-2}$ |

[a]Full conversion required 16 h at room temperature. n.d. = not determined.


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DS AgX FiberConduit technology applying DiComp diamond-based ATR sensors. The probe head was cleaned before every use by sonication at 40 °C in distilled toluene followed by rinsing with distilled $CH_2Cl_2$ afterward.

**General Procedure 1: Preparation of Triethylphosphine Oxide Adducts 6′·8 and 9 of Silylium Ions 6′ and 7.** In a glovebox, a solution of the requisite silane (1.00 equiv) in 1,2-$Cl_2C_6D_4$ (0.25 mL) was added to a suspension of $[Ph_3C]^+[B(C_6F_5)_4]^-$ (1.00 equiv) in 1,2-$Cl_2C_6D_4$ (0.15 mL) in an 8 mL vial equipped with a magnetic stir bar. The resulting red-brown solution was stirred for 1 min, and a solution of triethylphosphine oxide (**8**, 0.870−0.980 equiv) in 1,2-$Cl_2C_6D_4$ (0.25 mL) was added. The sample was transferred to an NMR tube and directly subjected to NMR spectroscopic analysis.

**General Procedure 2: Preparation of Triethylphosphine Oxide Adducts 4·8 and 5·8 of Trimethylsilyl Precursors 4 and 5.** In a glovebox, triethylphosphine oxide (**8**, 0.806−0.895 equiv) was weighed into a vial equipped with a magnetic stir bar and sealed with a septum. The vial was transferred out of the glovebox and connected to a Schlenk line, and 1,2-$Cl_2C_6D_4$ (0.60 mL) was added. **4** or **5** (1.00 equiv) was added, and the solution was stirred for 1 min. The sample was transferred to an NMR tube, the vial was washed with 1,2-$Cl_2C_6H_4$ (0.20 mL), and the washings were transferred to the NMR tube. The sample was directly subjected to NMR spectroscopic analysis.

**General Procedure 3: Preparation of Pyridine-$d_5$ Adducts 6′·11-$d_5$ and 12-$d_5$ of Silylium Ions 6′ and 7.** In a glovebox, a solution of the requisite silane (1.00 equiv) in 1,2-$Cl_2C_6H_4$ (0.40 mL) was added to a suspension of $[Ph_3C]^+[B(C_6F_5)_4]^-$ (1.00 equiv) in 1,2-$Cl_2C_6H_4$ (0.30 mL) in an 8 mL vial equipped with a magnetic stir bar. The resulting red-brown solution was stirred for 1 min and transferred to a vial containing pyridine-$d_5$ (**11**-$d_5$, 0.639−0.661 equiv). The sample was transferred to an NMR tube, the vials were washed with 1,2-$Cl_2C_6H_4$ (0.30 mL), and the washings were transferred to the NMR tube. The sample was directly subjected to NMR spectroscopic analysis.

**General Procedure 4: Preparation of Pyridine-$d_5$ Adducts 4·11-$d_5$ and 5·11-$d_5$ of Trimethylsilyl Precursors 4 and 5.** A septum-sealed screw-cap NMR tube was charged with pyridine-$d_5$ (**11**-$d_5$, 0.602−0.624 equiv), and a solution of **4** or **5** (1.00 equiv) in 1,2-$Cl_2C_6H_4$ (1.00 mL) was added. The sample was directly subjected to NMR spectroscopic analysis.

**General Procedure 5: ReactIR Analysis of the Model Diels−Alder Reaction.** Stock solutions in 1,2-$Cl_2C_6H_4$ of all reactants were used: silanes (0.1 M), $[Ph_3C]^+[B(C_6F_5)_4]^-$ (62.5 mM), and *E*-**13** (1.67 M). The stock solutions of $[Ph_3C]^+[B(C_6F_5)_4]^-$ and *E*-**13** were prepared for a maximum of 10 measurements and used for at least two different catalysts to eliminate errors. A 10 mL two-neck flask with a magnetic stir bar was equipped with the ReactIR probe head and connected to a Schlenk line through a rubber septum. The joint for the probe head was air tightened using a PTFE sleeve and the ReactIR PTFE adapter. The flask was heated under inert atmosphere, evacuated, and flushed with inert gas after cooling to room temperature at least five times. Appropriate amounts of the stock solutions were transferred into vials sealed with rubber septa inside the glovebox before being connected to a Schlenk line outside the glovebox. The flask was cooled to 12.7 °C (*para*-xylene/$CO_2$ cooling bath), an aliquot of the stock solution of $[Ph_3C]^+[B(C_6F_5)_4]^-$ (0.40 mL, 0.025 mmol, 5.0 mol %) was added, and the measurement was initiated. An aliquot of the silane stock solution (0.30 mL, 0.030 mmol, 6.0 mol %) was added. After 1 min, an aliquot of the stock solution of *E*-**13** (0.30 mL, 0.50 mmol, 1.0 equiv) was added, and the solution was stirred for approximately 4 min. Precooled **1** (0.10 mL, 1.0 mmol, 2.0 equiv) was added. The reaction progress was monitored until no further increase of the carbonyl band absorption of *trans*-**14** at 1687 $cm^{-1}$ was observed (8 h was required for **7h** as full conversion was reached after more than 16 h at room temperature). To confirm full conversion, a sample was hydrolyzed with saturated aqueous $NaHCO_3$ solution (2 mL) and extracted with *tert*-butyl methyl ether (2 mL). An aliquot of the organic phase (100 μL) was eluted over a small pad of silica gel with *tert*-butyl methyl ether and subjected to GLC analysis; triphenylmethane formed in silicon cation generation was used as internal standard.

***tert*-Butylferrocenylmethylsilylium Tetrakis(pentafluorophenyl)borate Triethylphosphine Oxide Adduct (9a).** This was prepared from *tert*-butylferrocenylmethylsilane (5.00 mg, 17.5 μmol, 1.00 equiv), $[Ph_3C]^+[B(C_6F_5)_4]^-$ (16.1 mg, 17.5 μmol, 1.00 equiv), and triethylphosphine oxide (**8**, 2.30 mg, 17.1 μmol, 0.980 equiv) according to General Procedure 1. $^1$H NMR (300 MHz, 1,2-$Cl_2C_6D_4$): δ 0.38 (s, 3H), 0.80 (dt, $J_{H,P}$ = 19.5 Hz, $J$ = 7.7 Hz, 9H), 0.99 (s, 9H), 1.57 (dq, $J_{H,P}$ = 11.5 Hz, $J$ = 7.7 Hz, 6H), 3.90 (m$_c$, 1H), 4.01 (s, 5H), 4.04 (m$_c$, 1H), 4.41 ppm (m$_c$, 2H). $^{11}$B NMR (96 MHz, 1,2-$Cl_2C_6D_4$): δ −16.5 ppm. $^{19}$F NMR (282 MHz, 1,2-$Cl_2C_6D_4$): δ −166.3, −162.2, −132.0 ppm. $^{29}$Si DEPT NMR (60 MHz, 1,2-$Cl_2C_6D_4$): δ 27.2 ppm (d, $J_{Si,P}$ = 17.5 Hz). $^{31}$P{$^1$H} NMR (162 MHz, 1,2-$Cl_2C_6D_4$): δ 88.7 ppm.

**Di-*tert*-butylferrocenylsilylium Tetrakis(pentafluorophenyl)borate Triethylphosphine Oxide Adduct (9d).** This was prepared from di-*tert*-butylferrocenylsilane (5.73 mg, 17.5 μmol, 1.00 equiv), $[Ph_3C]^+[B(C_6F_5)_4]^-$ (16.1 mg, 17.5 μmol, 1.00 equiv), and triethylphosphine oxide (**8**, 2.30 mg, 17.1 μmol, 0.980 equiv) according to General Procedure 1. $^1$H NMR (300 MHz, 1,2-$Cl_2C_6D_4$): δ 0.81 (dt, $J_{H,P}$ = 19.5 Hz, $J$ = 7.7 Hz, 9H), 1.06 (s, 18H), 1.60 (dq, $J_{H,P}$ = 12.1 Hz, $J$ = 7.7 Hz, 6H), 4.05 (m$_c$, 2H), 4.06 (s, 5H), 4.44 ppm (m$_c$, 2H). $^{11}$B NMR (96 MHz, 1,2-$Cl_2C_6D_4$): δ −15.9 ppm. $^{19}$F NMR (282 MHz, 1,2-$Cl_2C_6D_4$): δ −165.8, −161.9, −131.5 ppm. $^{29}$Si DEPT NMR (60 MHz, 1,2-$Cl_2C_6D_4$): δ 25.0 ppm (d, $J_{Si,P}$ = 21.1 Hz). $^{31}$P{$^1$H} NMR (162 MHz, 1,2-$Cl_2C_6D_4$): δ 87.9 ppm.

**Ferrocenyldiisopropylsilylium Tetrakis(pentafluorophenyl)borate Triethylphosphine Oxide Adduct (9e).** This was prepared from ferrocenyldiisopropylsilane (5.23 mg, 17.5 μmol, 1.00 equiv), $[Ph_3C]^+[B(C_6F_5)_4]^-$ (16.1 mg, 17.5 μmol, 1.00 equiv), and triethylphosphine oxide (**8**, 2.30 mg, 17.1 μmol, 0.980 equiv) according to General Procedure 1. $^1$H NMR (300 MHz, 1,2-$Cl_2C_6D_4$): δ 0.82 (dt, $J_{H,P}$ = 19.4 Hz, $J$ = 7.7 Hz, 9H), 1.06−1.20 (m, 14H), 1.53 (dq, $J_{H,P}$ = 11.6 Hz, $J$ = 7.6 Hz, 6H), 3.95 (m$_c$, 2H), 4.02 (s, 5H), 4.41 ppm (m$_c$, 2H). $^{11}$B NMR (96 MHz, 1,2-$Cl_2C_6D_4$): δ −15.9 ppm. $^{19}$F NMR (282 MHz, 1,2-$Cl_2C_6D_4$): δ −165.8, −161.9, −131.5 ppm. $^{29}$Si DEPT NMR (60 MHz, 1,2-$Cl_2C_6D_4$): δ 24.3 ppm (d, $J_{Si,P}$ = 17.6 Hz). $^{31}$P{$^1$H} NMR (162 MHz, 1,2-$Cl_2C_6D_4$): δ 88.4 ppm.

***tert*-Butylferrocenylphenylsilylium Tetrakis(pentafluorophenyl)borate Triethylphosphine Oxide Adduct (9f).** This was prepared from *tert*-butylferrocenyphenylsilane (6.08 mg, 17.5 μmol, 1.00 equiv), $[Ph_3C]^+[B(C_6F_5)_4]^-$ (16.1 mg, 17.5 μmol, 1.00 equiv), and triethylphosphine oxide (**8**, 2.30 mg, 17.1 μmol, 0.980 equiv) according to General Procedure 1. $^1$H NMR (300 MHz, 1,2-$Cl_2C_6D_4$): δ 0.78 (dt, $J_{H,P}$ = 19.4 Hz, $J$ = 7.7 Hz, 9H), 1.03 (s, 9H), 1.51 (dq, $J_{H,P}$ = 11.6 Hz, $J$ = 7.7 Hz, 6H), 3.89 (ddd, $J$ = 2.5 Hz, $J$ = 1.2 Hz, $J$ = 1.2 Hz, 1H), 4.17 (s, 5H), 4.22 (ddd, $J$ = 2.5 Hz, $J$ = 1.2 Hz, $J$ = 1.2 Hz, 1H), 4.45 (ddd, $J$ = 2.4 Hz, $J$ = 2.4 Hz, $J$ = 1.0 Hz, 1H), 4.50 (ddd, $J$ = 2.4 Hz, $J$ = 2.4 Hz, $J$ = 1.1 Hz, 1H), 7.44−7.50 (m, 3H), 7.75−7.79 ppm (m, 2H). $^{11}$B NMR (96 MHz, 1,2-$Cl_2C_6D_4$): δ −15.9 ppm. $^{19}$F NMR (282 MHz, 1,2-$Cl_2C_6D_4$): δ −165.8, −161.9, −131.5 ppm. $^{29}$Si DEPT NMR (60 MHz, 1,2-$Cl_2C_6D_4$): δ 14.3 ppm (d, $J_{Si,P}$ = 16.9 Hz). $^{31}$P{$^1$H} NMR (121 MHz, 1,2-$Cl_2C_6D_4$): δ 90.5 ppm.

**Triferrocenylsilylium Tetrakis(pentafluorophenyl)borate Triethylphosphine Oxide Adduct (9h).** This was prepared from triferrocenylsilane (10.2 mg, 17.5 μmol, 1.00 equiv), $[Ph_3C]^+[B(C_6F_5)_4]^-$ (16.1 mg, 17.5 μmol, 1.00 equiv), and triethylphosphine oxide (**8**, 2.30 mg, 17.1 μmol, 0.980 equiv) according to General Procedure 1. $^1$H NMR (300 MHz, 1,2-$Cl_2C_6D_4$): δ 0.84 (dt, $J_{H,P}$ = 19.4 Hz, $J$ = 7.7 Hz, 9H), 1.65 (dq, $J_{H,P}$ = 11.6 Hz, $J$ = 7.7 Hz, 6H), 4.08 (s, 15H), 4.44 (m$_c$, 6H), 4.56 ppm (m$_c$, 6H). $^{11}$B NMR (96 MHz, 1,2-$Cl_2C_6D_4$): δ −16.0 ppm. $^{19}$F NMR (282 MHz, 1,2-$Cl_2C_6D_4$): δ −165.8, −162.0, −131.6 ppm. $^1$H,$^{29}$Si HMQC NMR (99 MHz, 1,2-$Cl_2C_6D_4$): δ 13.5 ppm. $^{31}$P{$^1$H} NMR (202 MHz, 1,2-$Cl_2C_6D_4$): δ 88.0 ppm.

**Diferrocenylmethylsilylium Tetrakis(pentafluorophenyl)borate Triethylphosphine Oxide Adduct (9i).** This was prepared from diferrocenylmethylsilane (7.23 mg, 17.5 μmol, 1.00 equiv),


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$[Ph_3C]^+[B(C_6F_5)_4]^-$ (16.1 mg, 17.5 μmol, 1.00 equiv), and triethylphosphine oxide (**8**, 2.30 mg, 17.1 μmol, 0.980 equiv) according to General Procedure 1. $^1$H NMR (300 MHz, 1,2-$Cl_2C_6D_4$): δ 0.75 (s, 3H), 0.89 (dt, $J_{H,P}$ = 19.3 Hz, $J$ = 7.7 Hz, 9H), 1.64 (dq, $J_{H,P}$ = 11.6 Hz, $J$ = 7.7 Hz, 6H), 4.05 (s, 10H), 4.06 ($m_c$, 4H), 4.42 (ddd, $J$ = 2.4 Hz, $J$ = 2.4 Hz, $J$ = 1.1 Hz, 2H), 4.45 ppm (ddd, $J$ = 2.4 Hz, $J$ = 2.4 Hz, $J$ = 1.2 Hz, 2H). $^{11}$B NMR (96 MHz, 1,2-$Cl_2C_6D_4$): δ −16.0 ppm. $^{19}$F NMR (282 MHz, 1,2-$Cl_2C_6D_4$): δ −165.9, −162.0, −131.6 ppm. $^{29}$Si DEPT NMR (60 MHz, 1,2-$Cl_2C_6D_4$): δ 17.8 ppm (d, $J_{Si,P}$ = 12.5 Hz). $^{31}$P{$^1$H} NMR (162 MHz, 1,2-$Cl_2C_6D_4$): δ 89.0 ppm.

**Triethylsilylium Tetrakis(pentafluorophenyl)borate Triethylphosphine Oxide Adduct (6′·8).** This was prepared from triethylsilane (11.6 mg, 100 μmol, 1.00 equiv), $[Ph_3C]^+[B(C_6F_5)_4]^-$ (92.2 mg, 100 μmol, 1.00 equiv), and triethylphosphine oxide (**8**, 12.7 mg, 95.0 μmol, 0.950 equiv) according to General Procedure 1 except for stirring the silylium ion solution for 24 h before the addition of **8**. The formation of **6′** was not entirely complete; thus the adduct of $[Ph_3C]^+[B(C_6F_5)_4]^-$ and **8** formed additionally. $^1$H NMR (300 MHz, 1,2-$Cl_2C_6D_4$): δ 0.51−0.56 (m, 6H), 0.75−0.81 (m, 9H), 0.91−0.99 (m, 9H), 1.69−1.81 ppm (m, 6H). $^{11}$B NMR (96 MHz, 1,2-$Cl_2C_6D_4$): δ −15.8 ppm. $^{19}$F NMR (282 MHz, 1,2-$Cl_2C_6D_4$): δ −165.8, −161.9, −131.4 ppm. $^1$H,$^{29}$Si HMQC NMR (99 MHz, 1,2-$Cl_2C_6D_4$): δ 35.8 ppm. $^{31}$P{$^1$H} NMR (202 MHz, 1,2-$Cl_2C_6D_4$): δ 88.8 ppm.

**Trimethylsilylium Bis(trifluoromethanesulfonyl)imide Triethylphosphine Oxide Adduct (5·8).** This was prepared from *N*-trimethylsilyl bis(trifluoromethanesulfonyl)imide (**5**, 49.4 mg, 32.0 μL, 139.7 μmol, 1.00 equiv) and triethylphosphine oxide (**8**, 16.8 mg, 125.1 μmol, 0.895 equiv) according to General Procedure 2. $^1$H NMR (400 MHz, 1,2-$Cl_2C_6D_4$): δ 0.23 (s, 9H), 1.03 (dt, $J_{H,P}$ = 19.3 Hz, $J$ = 7.7 Hz, 9H), 2.03 ppm (dq, $J_{H,P}$ = 11.7 Hz, $J$ = 7.7 Hz, 6H). $^{19}$F NMR (376 MHz, 1,2-$Cl_2C_6D_4$): δ −78.6 ppm. $^{29}$Si DEPT NMR (79 MHz, 1,2-$Cl_2C_6D_4$): δ 32.5 ppm (d, $J_{Si,P}$ = 14.5 Hz). $^{31}$P{$^1$H} NMR (162 MHz, 1,2-$Cl_2C_6D_4$): δ 91.0 ppm.

**Trimethylsilylium Trifluoromethanesulfonate Triethylphosphine Oxide Adduct (4·8).** This was prepared from trimethylsilyl trifluoromethanesulfonate (**4**, 29.5 mg, 24.0 μL, 132.7 μmol, 1.00 equiv) and triethylphosphine oxide (**8**, 14.4 mg, 107.3 μmol, 0.806 equiv) according to General Procedure 2. $^1$H NMR (400 MHz, 1,2-$Cl_2C_6D_4$): δ 0.25 (s, 9H), 1.05 (dt, $J_{H,P}$ = 19.2 Hz, $J$ = 7.6 Hz, 9H), 2.23 ppm (dq, $J_{H,P}$ = 12.0 Hz, $J$ = 7.6 Hz, 6H). $^{19}$F NMR (376 MHz, 1,2-$Cl_2C_6D_4$): δ −77.4 ppm. $^{29}$Si DEPT NMR (79 MHz, 1,2-$Cl_2C_6D_4$): δ 32.3 ppm (d, $J_{Si,P}$ = 14.4 Hz). $^{31}$P{$^1$H} NMR (162 MHz, 1,2-$Cl_2C_6D_4$): δ 92.5 ppm.

***tert*-Butylferrocenylmethylsilylium Tetrakis(pentafluorophenyl)borate Pyridine-$d_5$ Adduct (12a-$d_5$).** This was prepared from *tert*-butylferrocenylmethylsilane (22.9 mg, 80.0 μmol, 1.00 equiv), $[Ph_3C]^+[B(C_6F_5)_4]^-$ (73.8 mg, 80.0 μmol, 1.00 equiv), and pyridine-$d_5$ (**11**-$d_5$, 4.40 mg, 52.3 μmol, 0.654 equiv) according to General Procedure 3. $^2$H NMR (77 MHz, 1,2-$Cl_2C_6H_4$): δ 7.43, 8.00, 8.14 ppm. $^1$H,$^{29}$Si HMQC NMR (99 MHz, 1,2-$Cl_2C_6H_4$): δ 36.8 ppm.

**Di-*tert*-butylferrocenylsilylium Tetrakis(pentafluorophenyl)borate Pyridine-$d_5$ Adduct (12d-$d_5$).** This was prepared from di-*tert*-butylferrocenylsilane (26.3 mg, 80.0 μmol, 1.00 equiv), $[Ph_3C]^+[B(C_6F_5)_4]^-$ (73.8 mg, 80.0 μmol, 1.00 equiv), and pyridine-$d_5$ (**11**-$d_5$, 4.40 mg, 52.3 μmol, 0.654 equiv) according to General Procedure 3. $^2$H NMR (77 MHz, 1,2-$Cl_2C_6H_4$): δ 7.70, 8.07, 9.12 ppm. $^1$H,$^{29}$Si HMQC NMR (99 MHz, 1,2-$Cl_2C_6H_4$): δ 35.0 ppm.

**Ferrocenyldiisopropylsilylium Tetrakis(pentafluorophenyl)borate Pyridine-$d_5$ Adduct (12e-$d_5$).** This was prepared from ferrocenyldiisopropylsilane (24.0 mg, 80.0 μmol, 1.00 equiv), $[Ph_3C]^+[B(C_6F_5)_4]^-$ (73.8 mg, 80.0 μmol, 1.00 equiv), and pyridine-$d_5$ (**11**-$d_5$, 4.40 mg, 52.3 μmol, 0.654 equiv) according to General Procedure 3. $^2$H NMR (77 MHz, 1,2-$Cl_2C_6H_4$): δ 7.49, 7.97, 8.19 ppm. $^1$H,$^{29}$Si HMQC NMR (99 MHz, 1,2-$Cl_2C_6H_4$): δ 34.5 ppm.

***tert*-Butylferrocenylphenylsilylium Tetrakis(pentafluorophenyl)borate Pyridine-$d_5$ Adduct (12f-$d_5$).** This was prepared from *tert*-butylferrocenylphenylsilane (27.8 mg, 80.0 μmol, 1.00 equiv), $[Ph_3C]^+[B(C_6F_5)_4]^-$ (73.8 mg, 80.0 μmol, 1.00 equiv), and pyridine-$d_5$ (**11**-$d_5$, 4.30 mg, 51.1 μmol, 0.639 equiv) according to General Procedure 3. $^2$H NMR (77 MHz, 1,2-$Cl_2C_6H_4$): δ 7.43, 8.00, 8.18 ppm. $^1$H,$^{29}$Si HMQC NMR (99 MHz, 1,2-$Cl_2C_6H_4$): δ 23.4 ppm.

**Triferrocenylsilylium Tetrakis(pentafluorophenyl)borate Pyridine-$d_5$ Adduct (12h-$d_5$).** This was prepared from triferrocenylsilane (46.7 mg, 80.0 μmol, 1.01 equiv), $[Ph_3C]^+[B(C_6F_5)_4]^-$ (73.0 mg, 79.1 μmol, 1.00 equiv), and pyridine-$d_5$ (**11**-$d_5$, 4.40 mg, 52.3 μmol, 0.661 equiv) according to General Procedure 3. $^2$H NMR (77 MHz, 1,2-$Cl_2C_6H_4$): δ 7.65, 8.01, 9.17 ppm. $^1$H,$^{29}$Si HMQC NMR (99 MHz, 1,2-$Cl_2C_6H_4$): δ 22.8 ppm.

**Diferrocenylmethylsilylium Tetrakis(pentafluorophenyl)borate Pyridine-$d_5$ Adduct (12i-$d_5$).** This was prepared from diferrocenylmethylsilane (33.1 mg, 80.0 μmol, 1.01 equiv), $[Ph_3C]^+[B(C_6F_5)_4]^-$ (73.4 mg, 79.5 μmol, 1.00 equiv), and pyridine-$d_5$ (**11**-$d_5$, 4.40 mg, 52.3 μmol, 0.658 equiv) according to General Procedure 3 along with adduct **12h**-$d_5$. $^2$H NMR (77 MHz, 1,2-$Cl_2C_6H_4$): δ 7.52, 7.98, 8.58 ppm. $^1$H,$^{29}$Si HMQC NMR (99 MHz, 1,2-$Cl_2C_6H_4$): δ 26.8 ppm.

**Triethylsilylium Tetrakis(pentafluorophenyl)borate Pyridine-$d_5$ Adduct (6′·11-$d_5$).** This was prepared from triethylsilane (9.30 mg, 80.0 μmol, 1.00 equiv), $[Ph_3C]^+[B(C_6F_5)_4]^-$ (73.8 mg, 80.0 μmol, 1.00 equiv), and pyridine-$d_5$ (**11**-$d_5$, 4.40 mg, 52.3 μmol, 0.654 equiv) according to General Procedure 3. $^2$H NMR (77 MHz, 1,2-$Cl_2C_6H_4$): δ 7.59, 8.01, 8.15 ppm. $^1$H,$^{29}$Si HMQC NMR (99 MHz, 1,2-$Cl_2C_6H_4$): δ 42.6 ppm.

**Trimethylsilylium Bis(trifluoromethanesulfonyl)imide Pyridine-$d_5$ Adduct (5·11-$d_5$).** This was prepared from *N*-trimethylsilyl bis(trifluoromethanesulfonyl)imide (**5**, 28.3 mg, 80.0 μmol, 1.00 equiv) and pyridine-$d_5$ (**11**-$d_5$, 4.20 mg, 49.9 μmol, 0.624 equiv) according to General Procedure 4. $^2$H NMR (61 MHz, 1,2-$Cl_2C_6H_4$): δ 7.72, 8.04, 8.51 ppm. $^{29}$Si DEPT NMR (79 MHz, 1,2-$Cl_2C_6H_4$): δ 41.9 ppm.

**Trimethylsilylium Trifluoromethanesulfonate Pyridine-$d_5$ Adduct (4·11-$d_5$).** This was prepared from trimethylsilyl trifluoromethanesulfonate (**4**, 18.4 mg, 82.9 μmol, 1.00 equiv) and pyridine-$d_5$ (**11**-$d_5$, 4.20 mg, 49.9 μmol, 0.602 equiv) according to General Procedure 4. $^2$H NMR (61 MHz, 1,2-$Cl_2C_6H_4$): δ 7.29, 7.68, 8.46 ppm. $^{29}$Si DEPT NMR (79 MHz, 1,2-$Cl_2C_6H_4$): δ 42.7 ppm.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Experimental details, characterization data, as well as $^1$H, $^{11}$B, $^{19}$F, $^{29}$Si, and $^{31}$P NMR spectra. 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.

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(10) The obvious choice of ferrocenyl-substituted silicon Lewis acids **7** with $TfO^-$ and $Tf_2N^-$ as counteranions was thwarted by our inability to access these in pure form. We are aware that Manners and co-workers had prepared such triflates as well as their pyridine adducts.[11] While the data of the latter were a useful reference point for our purposes, we decided not to use impure Lewis acids in the kinetic analysis.

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(12) We had previously calculated fluoride ion affinities as a measure of the Lewis acidity of **7**, but these correlated poorly with the $^{29}Si$ NMR chemical shifts.[9] Likewise, there was no correlation of those numbers with the observed catalytic activities of **7** later obtained in the ReactIR kinetic analysis.

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(17) Interestingly, the Diels−Alder reaction outlined in Scheme 2 cannot be performed at temperatures below −25 °C when using $[Et_3Si(toluene)]^+[B(C_6F_5)_4]^-$ (**6**) as the catalyst because the solution began to solidify (cf. ref 4).

(18) We cannot exclude temporary catalyst inhibition by the Diels−Alder adduct formed during the course of the reaction. Also, the Lewis acid might undergo undesired side-reactions with the diene component. We, therefore, report TOF values in addition to the initial rates as a qualitative measure to compare and distinguish between the reactivity of the silicon cations at higher conversion (Table 3).

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