

Tuning the Lewis Acidity of Neutral Silanes Using Perfluorinated Aryl- and Alkoxy Substituents

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The emerging field of Lewis acidic silanes demonstrates the versatility of molecular silicon compounds for catalytic applications. Nevertheless, when compared to the multifunctional boron Lewis acid $B(C_6F_5)_3$, silicon derivatives still lack in terms of reactivity. In this regard, we demonstrate the installation of perfluorotolyl groups (Tol^f) on neutral silicon atoms to obtain the respective tetra- and trisubstituted silanes $Si(Tol^f)_4$ and $HSi(Tol^f)_3$. These compounds were fully characterized including SC-XRD analysis but unexpectedly showed no significant Lewis

acidity. By using strongly electron-withdrawing perfluorocresolato groups ($OTol^f$) the tetrasubstituted silane $Si(OTol^f)_4$ was obtained, bearing an 8% increased $\Delta\delta(^{31}P)$ shift when applying the Gutmann-Beckett method, compared to literature-known $Si(OPh^f)_4$. Ultimately the heteroleptic $Si(Ph^f)_2pin^f$ was successfully synthesized and fully characterized including SC-XRD analysis, introducing a highly Lewis acidic silicon atom holding two silicon-carbon bonds.

Introduction

Main-group element-based Lewis acids for catalytic applications have been intensively researched in the past decades.^[1] Especially tris(pentafluorophenyl)borane and its structural derivatives like the Piers borane (bis(pentafluorophenyl)borane) have demonstrated outstanding catalytic potential for a variety of organic transformations.^[2] Moving to group-14 elements, highly Lewis acidic Si(IV)- and Si(II) cations were investigated to efficiently catalyze reactions including Diels-Alder additions, C–F hydrodefluorinations, sila-Friedel-Crafts reactions, carbonyl- and even olefin hydrosilylation.^[1b,3] The utilization of silicon as a potential catalyst is most favorable, regarding its earth abundance and easy accessibility.^[4] By the implementation of perfluorinated aryl- and alkyl substituents, the groups of Tilley, Bergman and Hoge synthesized highly Lewis acidic but neutral silanes that were efficiently used for reactions including the catalytic hydrosilylation of electron-deficient carbonyls or transfer hydrogenation of 1,3,5-trimethylcyclohexa-2,4-diene.^[5] By the use of less π -back-donating perchloro-catecholato substituents,^[6] the Greb group furnished the synthesis of the first stable Lewis superacidic silane.^[7] According to the

definition given by Krossing such Lewis superacids possess a higher fluoride ion affinity (FIA) than isolated SbF_5 .^[8] Following this finding further Si-based Lewis superacids were developed, based on perhalogenated catecholato substituents, and investigated for catalytic applications in carbonyl hydrosilylation, ketone defunctionalization, and depolymerization reactions, among others.^[9] Our group reported the Lewis superacidic (perfluoropinacolato)silane, which showed outstanding catalytic activity for the fragmentation of oligo ethers and activated hard substrates such as Et_3SiF .^[10] Since Lewis acidity is a complex interplay of substrate-specific attractive and repulsive interactions during adduct formation, Greb additionally gave a definition for soft Lewis superacids, referring to Pearson's HSAB principle.^[11]

Attempts to fine-tune the Lewis acidity of benchmark soft Lewis superacid $B(C_6F_5)_3$ by the Mitzel group outlined a significant impact on the Lewis acidity of the boron atom by exchanging *para*-F moieties with CF_3 -groups. The resulting $B(Tol^f)_3$ showed a 9% increased Lewis acidity by Gutmann-Beckett measurement and a 10% higher FIA value than $B(C_6F_5)_3$.^[12a] Additional investigations by the White group demonstrated a significant Lewis acidity change upon the installation of oxygen bridges onto $B(C_6F_5)_3$ derivatives. The obtained $B(OC_6F_5)_x(C_6F_5)_{3-x}$ compounds where stronger and harder Lewis acids the more polarizing oxygen bridges were installed.^[13] The respective silicon analogues of $B(C_6F_5)_3$ and $B(OC_6F_5)_3$ were already synthesized in the mid-20th century, but unlike for their boron counterparts, no catalytic applications were reported.^[12c,e] In this context, we investigated the suitability of perfluorotolyl (Tol^f) and perfluorocresolato ($OTol^f$) substituents for fine-tuning the Lewis acidity of tetra- and trisubstituted silanes. Additionally, a heteroleptic approach with one perfluoropinacolato- (pin^f) and two perfluorophenyl (Ph^f) groups was examined (Figure 1).

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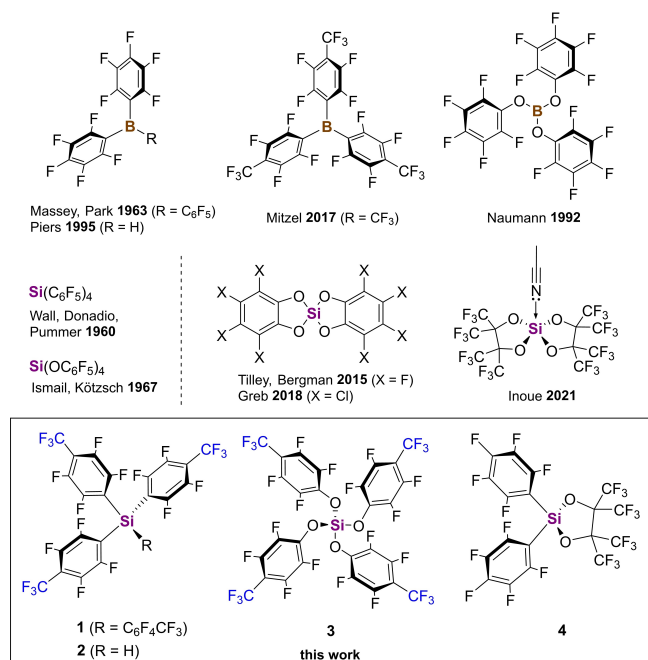
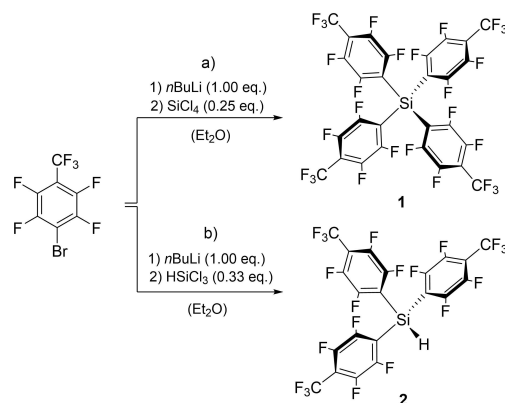


Figure 1. Boron Lewis acids holding C_6F_5 , $p-C_6F_4CF_3$ (Tol^F) and $p-OC_6F_4CF_3$ (OTol^F) substituents as well as related silicon-centered Lewis acids presented in the literature.^[2c,5a,7,10a,12] Bottom: Neutral silicon-based Lewis acids **1**, **2**, and **3** with OTol^F substituents and heteroleptic silane **4** presented in this work.

Results and Discussion

Tilley and Bergman *et al.* demonstrated that unlike $B(C_6F_5)_3$, $Si(C_6F_5)_4$ does not catalyze the hydrosilylation of electron-deficient carbonyls with Et_3SiH .^[5a] The reduced activity can be explained by the insufficient Lewis acidity of the tetravalent silane, compared to the electron-deficient, trivalent, boron compound.^[14] This is supported by the Gutmann-Beckett assessment of $Si(C_6F_5)_4$ where only a chemical shift of $\Delta\delta(^{31}P) = 15.2$ ppm is measured, which is significantly lower than that of $B(C_6F_5)_3$ ($\Delta\delta(^{31}P) = 30.1$ ppm).^[13] In analogy to the recently reported boron derivative, we synthesized $Si(Tol^F)_4$ to increase the Lewis acidity of the silicon atom by exploiting the inductive effect of the additional $p-CF_3$ groups.^[12a] According to the Hammett theory this should yield a more pronounced electron withdrawal on the silicon atom, thus resulting a stronger Lewis acid.^[15] Consequently, we synthesized **1** from $SiCl_4$ and perfluorotoluene in an adapted procedure given for the boron derivative.^[12a] In the case of silicon, however, no transmetalation with copper was required and compound **1** was directly synthesized in 77% yield using $p-BrC_6F_4CF_3$ via lithiation with $nBuLi$ (Scheme 1, a).

The same synthetic procedure was applied starting from $HSiCl_3$ to synthesize the sterically less congested silane **2** in 26% yield (Scheme 1, b). Both compounds were fully characterized using multi-nuclear NMR spectroscopy, EA, melting point and SC-XRD. The Lewis acidity assessment of **1** using the Gutmann-Beckett method revealed no interaction of the silane with Et_3PO . Also, no interaction was observed with the softer Lewis base *trans*-crotonaldehyde by conducting the Childs



Scheme 1. Syntheses of $Si(Tol^F)_4$ (**1**) and $HSi(Tol^F)_3$ (**2**) starting from $p-BrC_6F_4CF_3$ and $SiCl_4$ (path a) or $HSiCl_3$ (path b). Both reactions were conducted at $-78^\circ C$ to minimize the risk of explosive LiF elimination.

method. The ^{29}Si NMR signal of **1** in $THF-d_8$ was found at $\delta = -40.7$ ppm, which is in the same region as for the $Si(C_6F_5)_4$ derivative ($\delta(^{29}Si) = -41.1$ ppm). This result was unexpected as the Hammett constant of CF_3 ($\sigma_p = 0.54$) should result in more electron withdrawal when compared to F ($\sigma_p = 0.06$).^[15a] SC-XRD structure analysis of **1** crystallized from saturated THF solution ultimately demonstrated the untypically low Lewis acidity of **1** (Figure 2). The perfluorotolyl substitutes arrange in a slightly distorted tetrahedral coordination with bond angles between $103.5(1)^\circ$ and $113.7(1)^\circ$. The unit cell additionally contains two THF molecules, that are not coordinating the silicon atom, displayed by Si–O distances of 4.247(2) Å (Si1–O1) and 4.249(2) Å (Si1–O2).

In contrast to the boron analogue, the introduction of Tol^F groups quenched the Lewis acidity of the obtained silane completely. A potential explanation for this observation could be given by the enhanced steric bulk of the additional $p-CF_3$ groups. Consequently, less bulky silane **2** should show enhanced Lewis acidity due to the more accessible silicon site. The ^{29}Si NMR analysis of **2** revealed a singlet at $\delta = -54.3$ ppm, which is slightly shifted, but still in the same range as for **1**

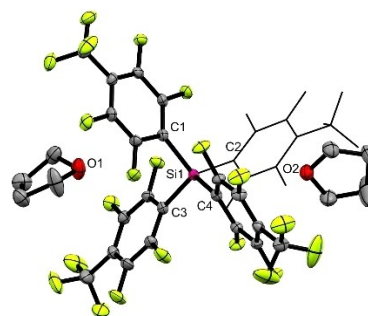


Figure 2. SC-XRD structure of $Si(Tol^F)_4$ (**1**) with thermal vibration ellipsoids plotted at 50% probability level. The structure additionally contains two non-coordinating THF molecules. For clarity reasons, hydrogens are omitted and one Tol^F group is depicted in wireframe model. Selected bond lengths (Å) and angles ($^\circ$): Si1–C1 1.878(2), Si1–C2 1.879(2), Si1–C3 1.879(2), Si1–C4 1.880(2); C2–Si1–C1 113.2(1), C2–Si1–C3 111.0(1), C2–Si1–C4 103.5(1), C1–Si1–C3 104.4(1), C1–Si1–C4 111.4(1), C3–Si1–C4 113.7(1).^[16]

holding four perfluorotolyl substituents. The Gutmann-Beckett analysis with one equivalent of Et_3PO revealed a slight shift of $\Delta\delta(^{31}\text{P})=0.60$ ppm with respect to free Et_3PO . Only a chemical shift of $\Delta(^1\text{H}^3)=0.01$ ppm was observed in case of the Childs method when *trans*-crotonaldehyde was applied in dichloromethane- d_2 solution. The observed low Lewis acidity remained unexpected as the silicon atom of **2** is easily accessible, which was validated by SC-XRD (Figure 3). A potential explanation could be intermolecular coordination of the CF_3 groups to the neighboring silicon site in solution. Nonetheless, no intermolecular adduct formation is seen in solid state.

Instead, compound **2** shows a slightly distorted tetrahedral geometry with a sum of angles of $330.2(6)^\circ$. The silicon-carbon distances are 1.879(5) Å for Si1–C1, 1.892(6) Å for Si1–C2, and 1.878(5) Å for Si1–C3. As demonstrated in case of boron, the installation of oxygen bridges heavily affects the Lewis acidity of the central boron atom.^[13] The strong polarization leads to “harder” and strongly Lewis acidic boron sites with respect to the HSAB theory.^[17] This effect is also true for $\text{Si}(\text{OC}_6\text{F}_5)_4$ where an increased Gutmann-Beckett shift of $\Delta\delta(^{31}\text{P})=26.9$ ppm was observed. Consequently, the respective perfluorotolyl substituted orthosilicate **3** was synthesized. The synthetic strategy started from perfluorinated cresol, which was lithiated using *n*BuLi. The subsequent conversion with SiCl_4 furnished the desired product **3** in 72% yield (Scheme 2). Due to the enhanced Lewis acidity of the obtained silane, residual acetonitrile could not be completely removed by multiple washing attempts in hexanes.

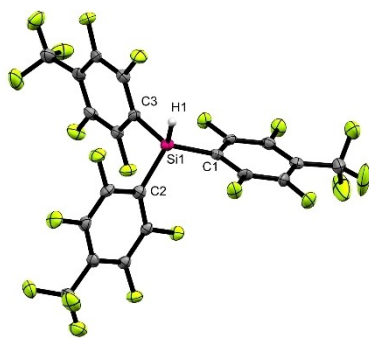
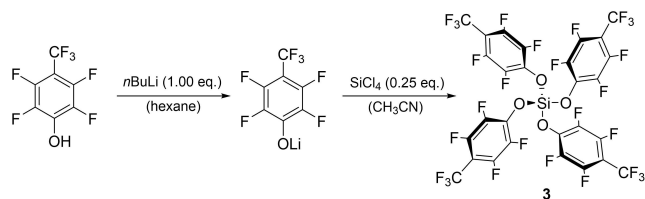


Figure 3. SC-XRD structure of $\text{HSi}(\text{ToI}^{\text{F}_3})_2$ (**2**) with thermal vibration ellipsoids plotted at 50% probability level. The unit cell contains a second molecule **3**, which is omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): Si1–H1 1.31(5), Si1–C1 1.879(5), Si1–C2 1.892(6), Si1–C3 1.878(5); C1–Si1–H1 119(2), C1–Si1–C2 112.4(2), C2–Si1–H1 113(2), C3–Si1–H1 105(2), C3–Si1–C1 111.3(2), C3–Si1–C2 105.8(2).^[16]



Scheme 2. Syntheses of $\text{Si}(\text{OTol}^{\text{F}_3})_4$ (**3**) starting with the lithiation of perfluorocresolato using *n*BuLi and subsequent reaction with SiCl_4 .

Moreover, ^{19}F NMR analysis revealed the presence of little amounts of unidentified side-products that could not be avoided by improved reaction parameters. For this reason, no elemental analysis and melting point measurement were performed for compound **3**. Nevertheless, successful product formation was proven by LIFDI-MS analysis (see SI). The ^{29}Si NMR signal was observed at $\delta=-153.4$ in $\text{THF}-d_3$ and $\delta=-153.2$ in acetonitrile- d_3 solution which corresponds to octahedral coordinated silicon species reported in the literature.^[18] A similar shift was obtained for oxygen-bridged $\text{Si}(\text{OC}_6\text{F}_5)_4$ (Table 1). The strong coordination of acetonitrile indicates an enhanced Lewis acidity, as it was already reported for the donor-coordinated Lewis superacid $\text{Si}(\text{pin}^{\text{F}})_2\cdot\text{MeCN}$.^[10a] The Gutmann-Beckett analysis revealed a change in the ^{31}P NMR shifts of $\Delta\delta(^{31}\text{P})=29.2$ ppm and $\Delta\delta(^{31}\text{P})=8.8$ ppm for the mono- and double-coordinated silane **3**. Double coordination was also observed in the case of $\text{Si}(\text{OC}_6\text{F}_5)_4$ ($\Delta\delta(^{31}\text{P})=6.9$ ppm for twofold-coordinated product) with excess of Et_3PO present. The obtained shifts are in the range of strong Lewis acids and the increased electrophilicity of **3** matches the results reported for the boron derivative.^[12a] In the case of **3**, the installation of *p*- CF_3 groups leads to an 8% increase of the Gutmann-Beckett shift, when referenced to $\text{Si}(\text{OC}_6\text{F}_5)_4$ (for mono-coordinated products).

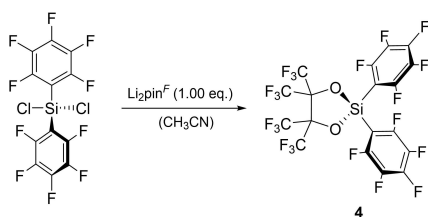
An additional strategy to synthesize a strongly Lewis acidic silane with a less polarized silicon atom is the installation of heteroleptic systems with the strongly electron-withdrawing perfluoropinacolato group (pin^{F}). A direct synthesis of such a species starting from SiCl_4 was not possible, due to inevitable tetrasubstitution with one substituent type. Consequently, a synthetic approach was adapted from the literature, using $\text{Si}(\text{C}_6\text{F}_5)_2\text{Cl}_2$ as a reaction intermediate, that is synthesized from Ph_2SiCl_2 .^[19] The subsequent conversion with $\text{Li}_2\text{pin}^{\text{F}}$ in acetonitrile solution yielded the desired heteroleptic product **4** in 66% yield. (Scheme 3).

Even though this compound was synthesized in acetonitrile solution, no remaining solvent coordination was observed in the ^1H NMR spectrum. The ^{29}Si NMR analysis in benzene- d_6 revealed a signal at $\delta=-5.25$ ppm. Interestingly, in more polar $\text{THF}-d_8$ the ^{29}Si signal was found at $\delta=-19.5$ ppm, indicating a geometry change, most likely caused by THF coordination. The

Table 1. Collected Lewis acidity data, obtained from ^{29}Si NMR, Gutmann-Beckett, and Childs method.

Compound	^{29}Si NMR signal [ppm] ^[a]	Gutmann-Beckett $\Delta\delta(^{31}\text{P})$ [ppm] ^[b]	Childs $\Delta\delta(^1\text{H}^3)$ [ppm] ^[c]
1	−40.7	0.0	0.00
2	−54.3	0.6	0.01
3	−153.2	29.2	0.04
4	−19.5	27.2	0.01
$\text{Si}(\text{OPh}^{\text{F}})_4$	−152.1	26.9	0.04
$\text{Si}(\text{Ph}^{\text{F}})_4$	−41.1	15.2	0.00

[a] ^{29}Si NMR measured in $\text{THF}-d_6$, [b] Et_3PO mono-coordination in CD_2Cl_2 . [c] shift of H^3 -proton of *trans*-crotonaldehyde in CD_2Cl_2 .



Scheme 3. Syntheses of $\text{Si}(\text{Ph}^{\text{F}})_2\text{pin}^{\text{F}}$ (**4**) starting from preformed $\text{Si}(\text{C}_6\text{F}_5)_2\text{Cl}_2$ and $\text{Li}_2\text{pin}^{\text{F}}$ in acetonitrile.

Gutmann-Beckett assessment of **4** revealed a change in ^{31}P NMR shift of $\Delta\delta = 27.2$ ppm, which is slightly smaller than that for compound **3**, but lies in the same range as for the perfluorophenyl substituted $\text{Si}(\text{OC}_6\text{F}_5)_4$. This high observed Lewis acidity renders remarking, as compound **4** holds two silicon-carbon bonds and only two directly bound oxygen atoms (Figure 4). According to the results obtained for boron by Britovsek *et al.* this should lead to a less hard Lewis acid. However, subsequent acidity determination by the Childs method did not show any coordination of *trans*-crotonaldehyde. This reflects the results obtained from all investigated Lewis acids in this study (Table 1). Single crystals suitable for XRD analysis were obtained from a saturated MeCN/DCM solution. The unit cell does not contain any MeCN molecules. Instead, a slightly distorted tetrahedral silicon central element was observed that is coordinated by one perfluoropinacolato group and two perfluorophenyl groups. The Si1–O1 and Si1–O2 bond lengths of 1.648(3) Å and 1.654(3) Å are in the same range as for $\text{Si}(\text{pin}^{\text{F}})_2\text{MeCN}$ (Si–O bond lengths: 1.675(1)–1.723(1) Å).^[10a] With Si1–C1 and Si1–C7 bond lengths of 1.859(4) and 1.857(4) reflect the results obtained for homoleptic $\text{Si}(\text{C}_6\text{F}_5)_4$ (Si–O bond length: 1.886(1) Å).^[20]

The GB and Childs shifts, as well as the ^{29}Si NMR signals obtained in this study are summarized in Table 1.

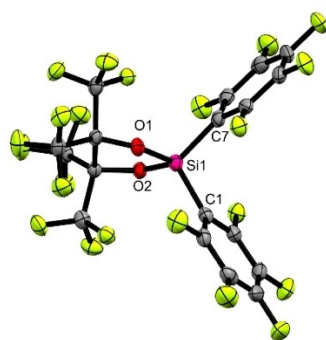


Figure 4. SC-XRD structure of $\text{Si}(\text{Ph}^{\text{F}})_2\text{pin}^{\text{F}}$ (**4**) with thermal vibration ellipsoids plotted at 50% probability level. The unit cell additionally contains a second molecule **4**, which is omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): Si1–O1 1.648(3), Si1–O2 1.654(3), Si1–C1 1.857(4), Si1–C7 1.859(4); O1–Si1–O2 95.5(1), C1–Si1–C7 108.0(2), O1–Si1–C1 113.5(2), O1–Si1–C7 113.2(2), O2–Si1–C1 113.1(2), O2–Si1–C7 113.1(2).^[16]

Conclusions

In this work we demonstrate the use of perfluorotolyl (ToI^{F}) and perfluorocresolato (OToI^{F}) substitutes for the synthesis of Lewis acidic silanes. It was shown that a direct bound oxygen bridge is essential to form strongly Lewis acidic silicon atoms as compounds **1** and **2** did not show considerable coordination by donor molecules. By the installation of (OToI^{F}) groups the Gutmann-Beckett shift of the respective silane **3** was 8% increased, when compared to $\text{Si}(\text{Ph}^{\text{F}})_4$. Additionally, a heteroleptic silane was synthesized by employing one perfluoropinacolato and two perfluorophenyl groups. The Gutmann-Beckett shift of obtained compound **4** was in the same range as for tetra-oxo substituted $\text{Si}(\text{OPh}^{\text{F}})_4$ and $\text{Si}(\text{OToI}^{\text{F}})_4$ (**3**). In stark contrast to boron species, the additional *p*- CF_3 group had only a minor beneficial effect on the overall Lewis acidity but caused significant steric bulk. While the Childs method proved to be an effective tool for the assessment of boron Lewis acids, no reliable results were obtained in case of the portrayed silanes.

Experimental Section

Materials and Chemicals: All mentioned reactions were performed under argon 4.6 atmosphere. For sealing of glass connections *Triboflon III* grease from *Freudenberg* was used. Plastic materials like syringes or cannulas were flushed with argon before use. All chemicals for this project were purchased from commercial distributors: *Sigma-Aldrich*, *ABCR*, and *TCl*. *p*-Heptafluorocresol was dried over molecular sieves (4 Å) prior to use. Synthetic precursors $\text{Li}_2\text{pin}^{\text{F}}$,^[10a] *p*- $\text{Br}(\text{C}_6\text{F}_4)\text{CF}_3$,^[12a] and $\text{Si}(\text{C}_6\text{F}_5)_2\text{Cl}_2$ were synthesized according to literature procedures. Solvents were distilled from mixtures with elemental sodium/benzophenone (Et_2O) or calcium hydride (acetonitrile, chloroform) and stored over molecular sieves (4 Å).

Synthesis and characterization of $p\text{-LiOToI}^{\text{F}}$: The title compound was synthesized according to an adapted procedure for LiOPh^{F} given in the literature.^[21] In this case 3.00 g *p*-heptafluorocresol (12.82 mmol, 1.00 equiv.) were dissolved in 50 ml hexane and 5.13 ml 2.5 M *n*BuLi solution in hexane (12.82 mmol, 1.00 equiv.) were added dropwise while stirring vigorously. After addition, the reaction mixture was stirred for 30 more minutes at 25 °C. After filtration, the obtained off-white residue was washed two times with 5 ml hexane. After drying in vacuum, the colorless product was obtained in 94% yield. ^{13}C NMR (126 MHz, acetonitrile- d_3 , 298 K) δ (ppm) = 153.55–150.71 (m, 1 C, C^1), 145.10 (dm, $^1J_{\text{C-F}}$ = 246.7 Hz, 2 C, ArC), 141.07 (dm, $^1J_{\text{C-F}}$ = 247.6 Hz, 2 C, ArC), 123.15 (q, $^1J_{\text{C-F}}$ = 269.8 Hz, 1 C, CF_3), 88.66–87.40 (m, 1 C, C^4). ^{19}F NMR (471 MHz, acetonitrile- d_3 , 298 K) δ (ppm) = –54.13 (t, $^4J_{\text{F-F}}$ = 20.9 Hz, 3F, CF_3), –151.03––151.40 (m, 2F, ArF), –167.45––167.66 (m, 2F, ArF).

Synthesis and characterization of $\text{Si}(\text{ToI}^{\text{F}})_4$ (1**):** To 100 ml Et_2O were added 7.30 g of *p*-bromoheptafluorotoluene (24.58 mmol, 1.00 equiv.). The solution was cooled to –78 °C and 9.8 ml of 2.5 M *n*-BuLi solution in hexane (24.58 mmol, 1.00 equiv.) were added drop by drop. After complete addition 14.1 ml (1.04 g, 6.15 mmol, 0.25 equiv.) of a 0.436 M SiCl_4 solution in Et_2O were added. The obtained solution was stirred overnight whilst warming up to room temperature. After removal of the solvents in vacuum, a sublimation was carried out at 190 °C and 0.03 mbar. Compound **1** was obtained as a slightly off-white solid in a 77% yield. Single crystals suitable for SC-XRD analysis were obtained from a saturated THF solution at –30 °C. The obtained unit cell additionally contains two

non-attached solvent molecules (Figure S5, SI). **m.p.**: 232.0–234.2 °C. ¹³C NMR (126 MHz, THF-*d*₈, 298 K) δ (ppm) = 150.38 (dm, ¹J_{C-F} = 247.6 Hz, 6 C, C^{3,5}), 145.33 (dd, ¹J_{C-F} = 263.0, ¹J_{C-F} = 18.2 Hz, 8 C, C^{2,6}), 121.79 (q, ¹J_{F-C} = 275.3 Hz, 4 C, CF₃), 115.48–114.30 (m, 8 C, C⁴), 112.62 (t, ¹J_{C-F} = 27.0 Hz, 4 C, C¹). ¹⁹F NMR (471 MHz, THF-*d*₈, 298 K) δ (ppm) = -57.88 (t, ⁴J_{F-F} = 21.6 Hz, 12F, CF₃), -125.86–126.0 (m, 8F, ArF), -139.43–139.71 (m, 8F, ArF). ²⁹Si NMR (99 MHz, THF-*d*₈, 298 K) δ (ppm) = -40.68 (s). **Elemental analysis:** calculated (%): C (37.52), H (0.00), N(0.00), S(0.00); found (%): C (37.50) H (0.00), N(0.00), S(0.00).

Synthesis and characterization of HSi(Tol^f)₃ (2): To suspension of 0.165 g (6.73 mmol, 3.00 equiv.) magnesium turnings in 10 ml Et₂O were added 2.00 g (6.73 mmol, 3.00 equiv.) *p*-bromoheptafluorotoluene at room temperature until the start of the exothermic reaction was noticed by slight color change. Subsequently an ice bath was used to cool the reaction mixture to 0 °C. After complete reaction, the Grignard reagent was filtered into a solution of 0.23 ml (2.24 mmol, 1.00 equiv.) HSiCl₃ in 8 ml Et₂O. The resulting reaction mixture was stirred for 16 h and afterwards filtrated. The obtained solid was recrystallized from hexane solution, giving compound **2** as an off-white solid in 26% yield. Single crystals suitable for SC-XRD analysis were obtained from a saturated DCM solution at -30 °C (Figure S6, SI). **m.p.**: 97.2–101.2 °C. ¹H NMR (500 MHz, chloroform-*d*, 298 K) δ (ppm) = 6.00 (h, *J*_{H-F} = 3.9 Hz, 1H, Si-H). ¹³C NMR (126 MHz, chloroform-*d*, 298 K) δ (ppm) = 149.41 (dm, ¹J_{C-F} = 249.0 Hz, 6 C, C^{3,5}), 144.12 (dd, ¹J_{C-F} = 265.2, ²J_{C-F} = 18.3 Hz, 6 C, C^{2,6}), 120.45 (q, ¹J_{C-F} = 275.0 Hz, 3 C, CF₃), 114.70–113.68 (m, 3 C, C⁴), 110.79 (t, ¹J_{H-C} = 27.9 Hz, 3 C, C¹). ¹⁹F NMR (471 MHz, chloroform-*d*, 298 K) δ (ppm) = -56.87 (t, ⁴J_{F-F} = 21.8 Hz, 9F, CF₃), -122.85–125.19 (m, 8F, ArF), -135.60–138.81 (m, 8F, ArF). ²⁹Si NMR (99 MHz, chloroform-*d*, 298 K) δ (ppm) = -53.78 (s). ²⁹Si NMR (99 MHz, THF-*d*₈, 298 K) δ (ppm) = -153.43 (s). **Elemental analysis:** calculated (%): C (37.08), H (0.15), N(0.00), S(0.00); found (%): C (37.31) H (0.18), N(0.00), S(0.00).

Synthesis and characterization of Si(OTol^f)₄ (3): To a solution of 200 mg *p*-LiOTol^f (0.83 mmol, 4.00 equiv.) in 20 ml of acetonitrile were added 0.48 ml (0.21 mmol, 1.00 eq.) of a 0.456 M SiCl₄ solution. The reaction was stirred at room temperature for four days and afterwards filtered. The crude product was then washed with hexane and the volatiles were removed under vacuum. Product **3** was obtained as an oily, off-white solid in a 72% yield. ¹³C NMR (126 MHz, acetonitrile-*d*₃, 298 K) δ (ppm) = 145.61 (dm, ¹J_{C-F} = 251.3 Hz, 8 C, C^{3,5}), 142.02 (dm, ¹J_{C-F} = 248.3 Hz, ³J_{C-F} = 14.5 Hz, 8 C, C^{2,6}), 140.92–140.66 (m, 4 C, C¹), 122.58 (q, ²J_{C-F} = 272.0 Hz, 4 C, CF₃), 100.7 (qt, ²J_{C-F} = 34.4, 13.1 Hz, 4 C, C⁴). ¹⁹F NMR (471 MHz, acetonitrile-*d*₃, 298 K) δ (ppm) = -56.17 (t, ⁴J_{F-F} = 21.5 Hz, 12F, CF₃), -146.55–146.78 (m, 8F, *m*-ArF), -157.63 (d, ³J_{F-F} = 11.5 Hz, 8F, *o*-ArF). ²⁹Si NMR (99 MHz, acetonitrile-*d*₃, 298 K) δ (ppm) = -153.24 (s). ²⁹Si NMR (99 MHz, THF-*d*₈, 298 K) δ (ppm) = -153.43 (s). The obtained LIFDI-MS pattern for compound **3** can be found in the SI (Figure S1).

Synthesis and characterization of Si(Ph^f)₂pin^f (4): To a solution of 0.80 g Li₂pin^f (2.31 mmol, 1.00 equiv.) in 12 ml acetonitrile was dropwise added a solution of 1.00 g Si(C₆F₅)₂Cl₂ (2.31 mmol, 1.00 equiv.) in 6 ml acetonitrile while stirring vigorously. An off-white precipitate was formed, and the resulting mixture was heated 80 °C for 2.5 h. Afterwards the mixture was filtered, and all volatiles were removed in vacuum. The obtained off-white crude product was further purified by sublimation at 150 °C and 0.02 mbar to give product **4** as a colorless solid in 66% yield. Single crystals suitable for SC-XRD analysis were obtained from a saturated MeCN/DCM solution at -30 °C (Figure S7). **m.p.**: 95.3–104.7 °C. ¹³C-NMR (126 MHz, benzene-*d*₆, 298 K): δ (ppm) = 148.17 (dm, ¹J_{C-F} = 249.7 Hz, 4 C, ArC^{2,6}), 145.36 (dm, ¹J_{C-F} = 262.6 Hz, 2 C, ArC⁴), 137.37 (dm, ¹J_{C-F} = 258.2 Hz, 4 C, ArC^{3,5}), 121.01 (q, ¹J_{C(F)}} = 292.6 Hz, 4 C, CF₃), 101.00 (t,

²J_{C-F} = 28.6 Hz, 2 C, ArC¹), 85.66 (br, 2 C, OC(CF₃)₂). ¹⁹F-NMR (471 MHz, benzene-*d*₆, 298 K): δ (ppm) = -69.12 (s, 12F, CF₃), -126.9 (dm, 4F, *o*-ArF), -141.06 (tt, ³J_{F-F} = 21.2, ⁴J_{F-F} = 6.1 Hz, 2F, *p*-ArF), -157.14–157.38 (m, 4F, *m*-ArF). ²⁹Si-NMR (99 MHz, benzene-*d*₆, 298 K): δ (ppm) = -5.25 (s). ²⁹Si NMR (99 MHz, THF-*d*₈, 298 K) δ (ppm) = -19.47 (s). **Elemental analysis:** calculated (%): C (31.14), H (0.00), N(0.00), S(0.00); found (%): C (31.53) H (0.20), N(0.00), S(0.00).

Lewis acidity assessments by Gutmann-Beckett and Childs method: For the Lewis acidity assessment with the Gutmann-Beckett method, 12.0 μmol of the investigated Lewis acid **1**, **2**, **3**, **4**, or Si(Ph^f)₄ were placed together with 1.61 mg Et₃PO (12.0 μmol, 1.00 equiv.) in a *J-Young*-valved NMR tube and dissolved in 0.5 ml of dichloromethane-*d*₂. For compound Si(OPh^f)₄ the procedure was conducted using 36 μmol of the Lewis acid and Et₃PO. The obtained solution was then analyzed by ³¹P NMR spectroscopy, and the obtained ³¹P NMR shift was referenced to pure Et₃PO in dichloromethane-*d*₂ (Table S1, SI). Only in the case of compound **3** and Si(OPh^f)₄ double-coordination was observed when using 2.0 equiv. of Et₃PO (Figure S3, SI).

For the Childs assessment 6.00 mmol the respective Lewis acid **1**, **2**, **3**, **4**, Si(Ph^f)₄ or Si(OPh^f)₄ were first suspended in 0.5 ml of dichloromethane-*d*₂. Subsequently 0.5 μl *trans*-crotonaldehyde (0.42 mg, 6.00 mmol, 1.00 equiv.) were added with a precision pipette. The obtained mixture was shaken until complete dissolution and afterwards analyzed by ¹H NMR spectroscopy. The obtained signals of the H³ proton are summarized in the Table S1 (see SI). No significant change in the chemical shift was observed for the presented silanes.

Supporting Information

Supplementary information to this article is available in a separate file. The authors have cited additional references within the Supporting Information.^[22]

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Childs method · Gutmann-Beckett method · Lewis acids · perfluorotolyl ligands · silanes

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