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# Bi- and tridentate silicon-based acceptor molecules

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**Abstract:** Triethynylphenylsilane (**1**), trivinylphenylsilane (**2**), diethynyldiphenylsilane (**3**) and diphenyldivinylsilane (**4**) were reacted with chlorodimethylsilane yielding the corresponding hydrosilylation products. To increase their Lewis acidity, the Si–Cl functions were directly transferred into Si–$C_6F_5$ units by salt elimination reactions leading to the (semi-) flexible molecules **5–8** bearing two or three Lewis-acidic sidearms. With the aim of providing host-guest complexes, the air-stable and readily soluble compounds **5–8** were converted with N- and O-Lewis bases of different size and geometry. In all cases, NMR spectroscopic investigations reveal no formation of Lewis acid-base complexes. X-ray diffraction experiments of host compounds **5–7** show intermolecular aryl...perfluoroaryl interactions of dispersion nature in the solid state. By hydrosilylation of **1** with trichlorosilane the more Lewis-acidic all-*trans*-tris[(trichlorosilyl)vinyl]phenylsilane (**9**) was obtained. Its Lewis acidity was further increased by fluorination to yield all-*trans*-tris[(trifluorosilyl)vinyl] phenylsilane (**10**); the conversion with nitrogen containing Lewis bases ends up in the formation of insoluble precipitates.

**Keywords:** dispersion interactions; poly-Lewis acids; X-ray diffraction experiments.

## 1 Introduction

Molecules containing multiple Lewis-acidic receptor moieties are also known as poly-Lewis acids. They can be considered as the direct opposite of poly-Lewis bases, however, the chemistry of the latter compounds (the most prominent examples are crown ethers, cryptands, etc.) are much better explored and well understood. Nevertheless, the chemistry of poly-Lewis acids became a rapidly growing field within the last years and various compounds have been described in the literature [1–7].

Prominent examples of bidentate Lewis acids are, for instance, 1,2-bis(difluoroboranyl)ethane [8], being able to form complexes with methanolate ions, or the rigid 1,2-bis(organostannyl)benzene [9] host and the fluorinated *ortho*-disilylbenzenes [10]. The latter compounds have been demonstrated to be excellent fluoride ion acceptors. Other well-known examples of bidentate Lewis hosts contain aluminium [11–14], gallium [13–18], indium [19, 20] or mercury [21, 22] as Lewis acid functions. Important contributions in the field of cyclic tridentate tin- or silicon-based Lewis acids stem from Jurkschat and co-workers [23–25], as well as from Jung and Xia [26] or Wong Chi Man et al. [27]. Tridentate Lewis acids in which the active sites are embedded in noncyclic structures are often generated by hydroalumination [14] or hydrogallation reactions [15]. In the course of our investigations in the field of polydentate Lewis acids we synthesized a wide range of compounds containing two [28–30], three [31–35], four [30, 36] and six [33, 37] Lewis-acidic functionalities. Common to all examples are Lewis-acid functions attached to a more or less rigid organic framework like alkynyl-anthracenes, -tribenzotriquinacenes or -trisilacyclohexanes. Very recently, we reported bidentate Si- and Ga-Lewis-acidic host structures with just one silicon atom as core unit, being able to form – in part polymeric – host-guest adducts with fluoride ions or neutral N-donor molecules [38, 39].

## 2 Results and discussion

Trichlorophenylsilane was converted with ethynyl- or vinyl magnesium bromide to yield the corresponding trisubstituted phenylsilanes **1** and **2** (Scheme 1), according to our previously published procedures for the generation of the doubly ethynyl- and vinyl-substituted compounds **3**

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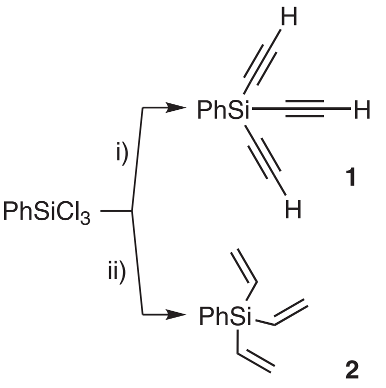


**Scheme 1:** Synthesis of the organic backbones **1** and **2**. Reagents and conditions: i) ethynylmagnesium bromide, THF, 0°C to r.t., 14 h, 80%; ii) vinylmagnesium chloride, THF, r.t., 16 h, 74%.

and **4** [38]. The products were isolated as colourless crystalline material (**1**) or as colourless liquid (**2**). Their identity was proven by multinuclear NMR spectroscopy as well as by mass spectrometry or elemental analysis.

Single crystals of triethynylphenylsilane (**1**), suitable for X-ray diffraction experiments, were grown from *n*-hexane at room temperature; the molecular structure in solid state is depicted in Fig. 1. The Si(1)–C(1) bond [1.848(3) Å] to the phenyl substituent is slightly longer than the Si(1)–C bonds to the ethynyl substituents, which are all of the same lengths within experimental errors [Si(1)–C(7) 1.821(3) Å, Si(1)–C(9) 1.827(3) Å and Si(1)–C(11) 1.830(3) Å]. The central silicon atom is tetrahedrally coordinated as it is indicated by the C–Si(1)–C angles ranging from 108.0(1)° [C(9)–Si(1)–C(11)] to 111.0(2)° [C(1)–Si(1)–C(9)]. All ethynyl units are close to linearity [Si(1)–C(7)–C(8) 176.5(3)° to Si(1)–C(11)–C(12) 178.5(3)°].

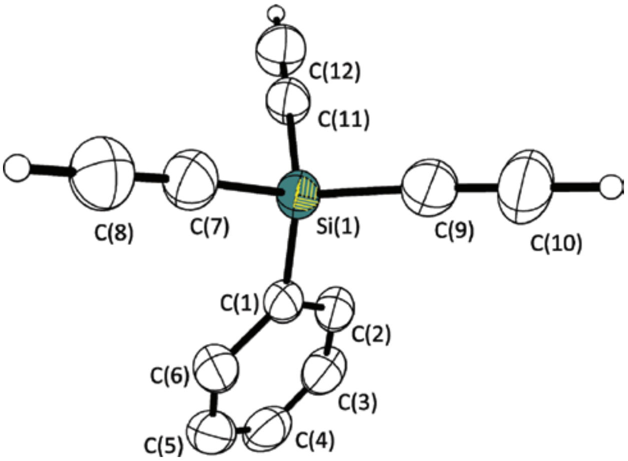
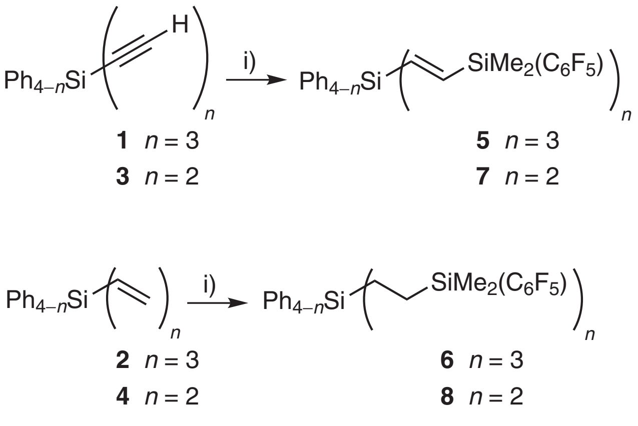


**Fig. 1:** Molecular structure of triethynylphenylsilane (**1**) in the solid state. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms of the phenyl substituent are omitted for clarity. Selected bond lengths (Å) and angles (deg): Si(1)–C(1) 1.848(3), Si(1)–C(7) 1.821(3), Si(1)–C(9) 1.827(3), Si(1)–C(11) 1.830(3), C(7)–C(8) 1.173(4), C(9)–C(10) 1.176(4), C(11)–C(12) 1.174(4); C(1)–Si(1)–C(7) 110.0(1), C(1)–Si(1)–C(9) 111.0(1), C(1)–Si(1)–C(11) 110.1(1), C(7)–Si(1)–C(9) 109.5(1), C(7)–Si(1)–C(11) 108.0(1), C(9)–Si(1)–C(11) 108.1(1), Si(1)–C(7)–C(8) 176.5(3), Si(1)–C(9)–C(10) 177.3(3), Si(1)–C(11)–C(12) 178.5(3).

As it is displayed in Scheme 2, the di- and triethynylsilanes **1** and **3** as well as the di- and trivinylsilanes **2** and **4** were converted with chloro(dimethyl)silane in the presence of Karstedt's catalyst to generate the corresponding hydrosilylation all-*trans*-products. These were directly reacted with (pentafluorophenyl)magnesium bromide to yield the desired perfluorophenyl-substituted bi- and tridentate silanes **5–8** (yields about 90%) as air- and moisture-stable compounds [40].

We also used trichlorosilane and dichloromethylsilane to transform compounds **1–4** to the corresponding hydrosilylated species. However, the subsequent reaction with the perfluoroaryl Grignard compound led to an undefined mixture of products – in part of extremely low solubility – which could not be separated successfully. Besides the NMR spectroscopic and mass spectrometric characterization of the $C_6F_5$-substituted silylsilanes, the molecular structures of all solid products **5–7** (compound **8** is of oily consistency) were elucidated by X-ray diffraction experiments (Figs. 2–4).

Due to intermolecular dispersive-type $C_6H_5\cdots C_6F_5$ interactions and H···F contacts, all pentafluorophenyl substituents of **5**, **6** and **7** are directed to the same side. Compounds **5** and **6** form strands (Figs. 2b and 3b), in which the electron rich phenyl substituent is interacting with pentafluorophenyl groups of another molecule. The shortest centroid($C_6F_5$)···centroid($C_6H_5$) distances to a



**Scheme 2:** Synthesis of the bi- and tridentate Lewis acids **5–8**. Reagents and conditions: i) 1. $HSiMe_2Cl$ (neat), Karstedt's catalyst, r.t., 1 h; 2. $BrMgC_6F_5$, THF, r.t. to reflux, 2 h, 85% to 92% over all.

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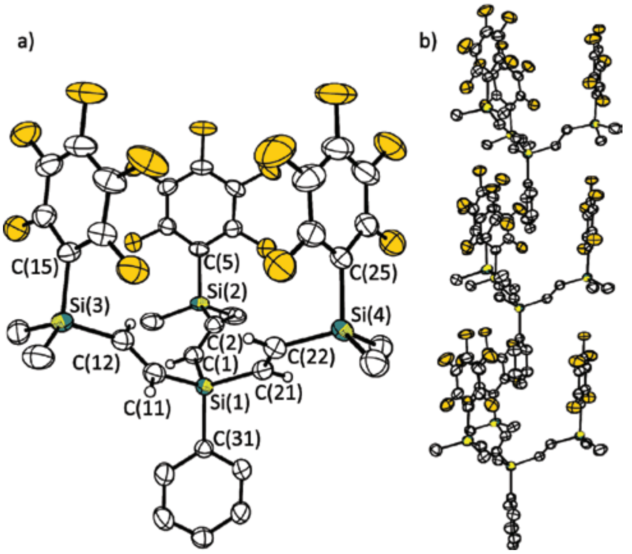

**Fig. 2:** Molecular structure of all-*trans*-tris[(pentafluorophenyl)-dimethylsilylvinyl]phenylsilane (**5**) (a) and a representative strand (b) in the solid state. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms of the phenyl substituents are omitted for clarity. Selected bond lengths (Å) and angles (deg): Si(1)–C(1) 1.859(2), Si(1)–C(11) 1.867(3), Si(1)–C(21) 1.867(3), Si(1)–C(31) 1.882(2), C(1)–C(2) 1.331(3), C(11)–C(12) 1.345(4), C(21)–C(22) 1.331(4), C(2)–Si(2) 1.859(3), C(12)–Si(3) 1.865(3), C(22)–Si(4) 1.872(3), Si(2)–C(5) 1.909(2), Si(3)–C(15) 1.904(2), Si(4)–C(25) 1.902(2); Si(1)–C(1)–C(2) 128.6(2), C(1)–C(2)–Si(2) 122.5(2), Si(1)–C(11)–C(12) 122.3(2), C(11)–C(12)–Si(3) 129.2(2), Si(1)–C(21)–C(22) 126.2(2), C(21)–C(22)–Si(4) 123.8(2), C(2)–Si(2)–C(5) 106.7(1), C(12)–Si(3)–C(15) 106.1(1), C(22)–Si(4)–C(25) 105.7(1).

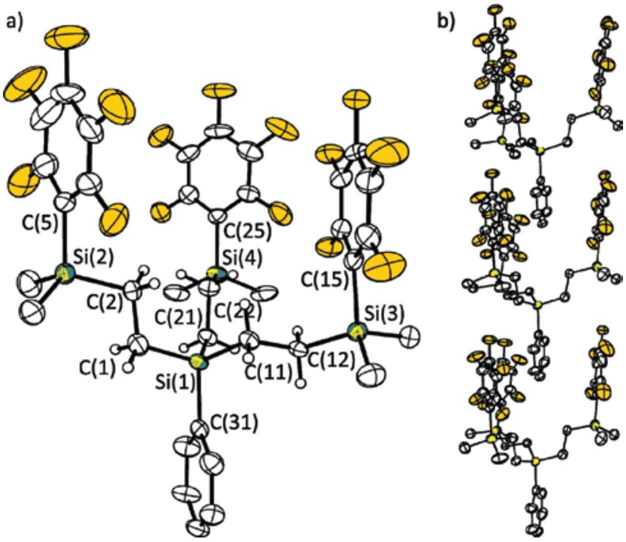

**Fig. 3:** Molecular structure of tris[(pentafluorophenyl)dimethylsilylethyl]phenylsilane (**6**) (a) and a representative strand (b) in the solid state. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms of the phenyl substituents are omitted for clarity. Selected bond lengths (Å) and angles (deg): Si(1)–C(1) 1.886(8), Si(1)–C(11) 1.868(9), Si(1)–C(21) 1.872(9), Si(1)–C(31) 1.910(9), C(1)–C(2) 1.543(12), C(11)–C(12) 1.511(12), C(21)–C(22) 1.530(11), C(2)–Si(2) 1.880(8), C(12)–Si(3) 1.870(9), C(22)–Si(4) 1.867(8), Si(2)–C(5) 1.926(10), Si(3)–C(15) 1.943(9), Si(4)–C(25) 1.931(8); Si(1)–C(1)–C(2) 112.0(5), C(1)–C(2)–Si(2) 113.1(6), Si(1)–C(11)–C(12) 114.0(6), C(11)–C(12)–Si(3) 117.1(6), Si(1)–C(21)–C(22) 113.8(5), C(21)–C(22)–Si(4) 115.8(5), C(2)–Si(2)–C(5) 106.6(4), C(12)–Si(3)–C(15) 109.6(4), C(22)–Si(4)–C(25) 111.7(4).

molecule generated by the glide plane in **5** are 3.936(2) Å, whereas in **6** six crystallographically independent strands can be obtained all generated by translation along the crystallographic *a* axis showing centroid–centroid distances in the range from 3.817(5) to 4.893(6) Å. In **7**, in which the pentafluorophenyl substituents show interactions with two different molecules, the shortest centroid($C_6F_5$)···centroid($C_6H_5$) distances in the solid state were found with 3.685(1) Å to the neighbouring molecule generated by the glide plane and 3.740(1) Å to the one generated by translation along the *a* axis, resulting in the formation of crosslinked strands. In co-crystals containing phenyl substituents and $C_6F_6$, the length of such π–π interactions falls over a range from 3.5 to 3.8 Å [41, 42]. In this case, the hexafluorobenzene enables shorter aryl···perfluoroaryl contacts than the substituted ones of **5**, **6** and **7**.

Within the scope of our project, we reacted products **5–8** with equimolar amounts of some neutral N- and O-containing Lewis bases. To cover a wide range of different sizes as well as of various kinds, numbers and orientations of the donor atoms, we used pyridine, 1,3,5-triazine, 4,4′-bipyridine and 1,3,5-trimethoxybenzene as Lewis basic guest species. However, in neither case the formation of host-guest complexes could be revealed by NMR spectroscopy, as the resonances of host- and guest compounds in the mixture are not shifted compared to the pure species.

Inspired by the solid state structures of compounds **5–7**, showing dispersion intermolecular $C_6H_5$···$C_6F_5$ interactions, we explored the option whether the (semi-) flexible (perfluoroaryl)silylsilanes **5–8** can serve as two- or three-fold π-acceptor substrates. To investigate a potential co-crystallisation of external electron-rich aryl systems, we added tolane (diphenylacetylene), anthracene, triptycene or triphenylsilane to solutions of **5–8** in dichloromethane and *n*-hexane [41]. Despite numerous attempts, we found no evidence for the formation of such dispersion-driven complexes, neither by crystallization nor by NMR spectroscopic techniques.

As already mentioned above, triethynylphenylsilane (**1**) was also reacted with trichlorosilane to form all-*trans*-tris(trichlorosilylvinyl)phenylsilane (**9**). As shown in Scheme 3, the corresponding tris(trifluorosilyl) species **10**

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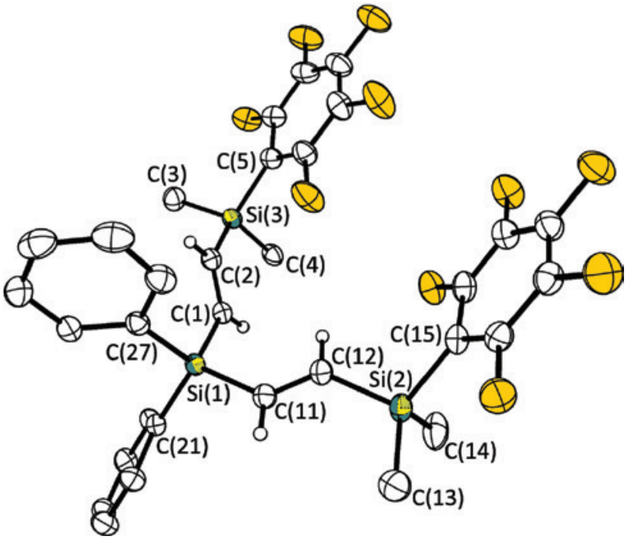


**Fig. 4:** Molecular structure of bis[(pentafluorophenyl)dimethylsilylvinyl]diphenylsilane (**7**) in the solid state. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms of the phenyl substituents are omitted for clarity. Selected bond lengths (Å) and angles (deg): Si(1)–C(1) 1.858(2), Si(1)–C(11) 1.873(2), Si(1)–C(21) 1.872(2), Si(1)–C(27) 1.872(2), C(1)–C(2) 1.332(2), C(11)–C(12) 1.340(2), C(2)–Si(3) 1.854(2), C(12)–Si(2) 1.866(2), Si(2)–C(15) 1.905(2), Si(3)–C(5) 1.911(2); Si(1)–C(1)–C(2) 123.7(1), C(1)–C(2)–Si(3) 124.7(1), Si(1)–C(11)–C(12) 123.3(1), C(11)–C(12)–Si(2) 125.4(1), C(2)–Si(3)–C(5) 108.3(1), C(12)–Si(2)–C(15) 107.9(1).

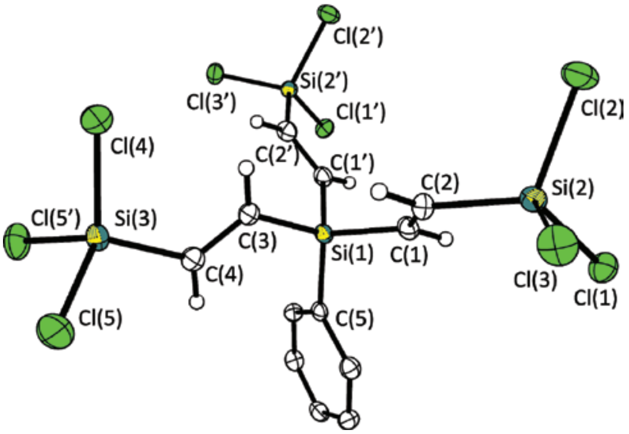
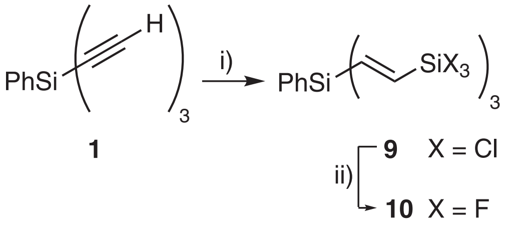


**Fig. 5:** Molecular structure of tris(trichlorosilylvinyl)phenylsilane (**9**) in the solid state. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms of the phenyl substituent are omitted for clarity. Selected bond lengths (Å) and angles (deg): Si(1)–C(1) 1.874(3), Si(1)–C(3) 1.874(4), Si(1)–C(5) 1.863(3), C(1)–C(2) 1.332(4), C(3)–C(4) 1.337(5), C(2)–Si(2) 1.840(3), C(4)–Si(3) 1.844(4), Si(2)–Cl(1) 2.026(1), Si(2)–Cl(2) 2.032(1), Si(2)–Cl(3) 2.029(1), Si(3)–Cl(4) 2.018(2), Si(3)–Cl(5) 2.033(2); Si(1)–C(1)–C(2) 124.9(2), Si(1)–C(3)–C(4) 124.4(3), C(1)–C(2)–Si(2) 124.4(2), C(3)–C(4)–Si(3) 122.9(3), Cl(1)–Si(2)–Cl(2) 107.6(1), Cl(2)–Si(2)–Cl(3) 108.0(1), Cl(1)–Si(2)–Cl(3) 108.7(1), Cl(4)–Si(3)–Cl(5) 108.9(1), Cl(5)–Si(3)–Cl(5′) 106.6(1). Symmetry equivalent atoms are generated by the operation 1 – *x*, *y*, *z*.



**Scheme 3:** Synthesis of the tridentate Lewis acids **9–10**. Reagents and conditions: i) $HSiCl_3$ (neat), Karstedt's catalyst, r.t., 1 h, 97%; ii) $SbF_3$, pentane, r.t., 25 h, 90%.

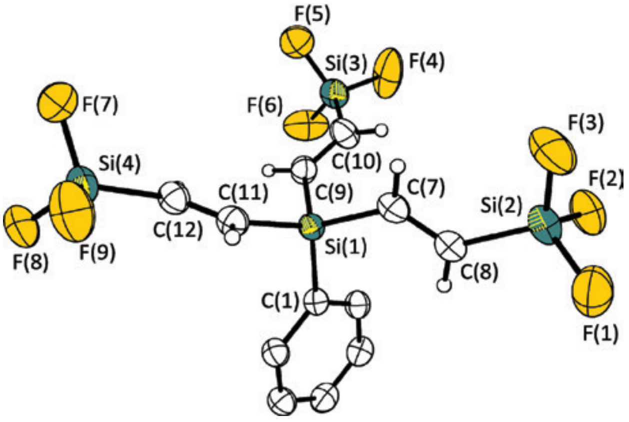


**Fig. 6:** Molecular structure of tris(trifluorosilylvinyl)phenylsilane (**10**) in the solid state. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms of the phenyl substituent are omitted for clarity. Selected bond lengths (Å) and angles (deg): Si(1)–C(1) 1.862(3), Si(1)–C(7) 1.878(3), Si(1)–C(9) 1.873(3), Si(1)–C(11) 1.868(3), C(7)–C(8) 1.330(4), C(9)–C(10) 1.324(4), C(11)–C(12) 1.323(4), C(8)–Si(2) 1.817(3), C(10)–Si(3) 1.816(3), C(12)–Si(4) 1.819(3), Si(2)–F(1) 1.566(2), Si(2)–F(2) 1.569(2), Si(2)–F(3) 1.557(2), Si(4)–F(9) 1.551(2); Si(1)–C(7)–C(8) 124.6(2), C(7)–C(8)–Si(2) 124.5(2), Si(1)–C(9)–C(10) 125.7(3), C(9)–C(10)–Si(3) 123.8(3), Si(1)–C(11)–C(12) 123.7(2), C(11)–C(12)–Si(4) 124.6(2), F(1)–Si(2)–F(2) 105.4(2), F(5)–Si(3)–F(6) 103.3(2), F(7)–Si(4)–F(9) 108.5(2).

is accessible by conversion of **9** with $SbF_3$ in pentane at ambient temperature avoiding Si–C bond cleavage [43].

Single crystals of the tridentate silicon Lewis acids **9** and **10**, suitable for X-ray diffraction experiments, were grown from $Et_2O$ at room temperature; the molecular structures in the solid state are shown in Figs. 5 and 6. In contrast to **10**, the solid state structure of **9** displays a mirror plane through the phenyl substituent and the vinylic sidearm Si(1)–C(3)–C(4)–Si(3). The C=C double bonds of **9** and **10** are all of the same length within their experimental errors [1.330(4) Å]. The C–Si bond lengths to the trifluorosilyl groups [C(10)–Si(3) 1.816(3) Å to

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C(12)–Si(4) 1.819(3) Å] are slightly shorter than the corresponding ones to the trichlorosilyl groups [C(2)–Si(2) 1.840(3) Å and C(4)–Si(3) 1.844(4) Å]. This agrees well with the increased Lewis acidity of **10**. Due to the electron-withdrawing character of fluorine, the Si–Cl bond lengths [Si(3)–Cl(4) 2.018(2) Å to Si(3)–Cl(5) 2.033(2) Å] are remarkably longer than the Si–F bonds [Si(4)–F(9) 1.551(2) Å to Si(2)–F(2) 1.569(2) Å].

We tried to convert the air and moisture sensitive tridentate Lewis acids **9** and **10** with equimolar amounts of some neutral Lewis bases. Oxygen-containing Lewis bases like diethyl ether, 1,4-dioxane, 1,3,5-trioxane and 1,3,5-trimethoxybenzene show no reaction, neither observed in NMR spectra nor by crystallisation. The absence of an adduct formation is also obvious from the fact that donor-free crystals of **9** and **10** were grown from $Et_2O$ solutions. Nitrogen containing Lewis bases like pyridine, 1,4-diazabicyclo[2.2.2]octane, TMEDA or 1,3,5-triazine led to the formation of colourless precipitates. These solid compounds were insoluble in any common solvents. The conversion of **10** with pyridine gave crystals of tetrafluorobispyridinesilicon(IV) after a week, indicating a decomposition of the Lewis acid [44].

## 3 Conclusion

The triply unsaturated silicon-centred species triethynylphenylsilane (**1**) and trivinylphenylsilane (**2**) were synthesized *via* salt-elimination reactions. Compounds **1** and **2** and the bidentate analogues diethynyldiphenylsilane (**3**) and divinyldiphenylsilane (**4**) were converted into the two- and three-fold pentafluorophenyl substituted species **5–8** *via* hydrosilylation and salt elimination reactions. These air stable bi- and tridentate Lewis acids show no reaction to nitrogen and oxygen containing Lewis bases. In the solid state, **5**, **6** and **7** display dispersion-driven intermolecular $Ar\cdots Ar_f$ interactions. **5** and **6** crystallize in strands with centroid($C_6F_5$)···centroid($C_6H_5$) distances ranging from 3.817(5) to 4.893(6) Å, whereas the strands of **7** are crosslinked by $C_6H_5\cdots C_6F_5$ distances of 3.685(1) and 3.740(1) Å. However, no interactions of compounds **5–8** with any electron rich aryl compounds could be observed. The more Lewis-acidic tris(trifluorosilylvinyl)phenylsilane (**10**) was synthesized by fluorination of the tris(trichlorosilyl) compound **9**, which was generated by hydrosilylation of **1** with trichlorosilane. The conversion of **10** with nitrogen containing Lewis bases leads to insoluble precipitates, whereas oxygen containing bases show no interactions.

## 4 Crystal structure determinations

Suitable crystals of the compounds **1**, **5**, **6** and **7** were obtained by evaporating saturated solutions of *n*-hexane, **9** and **10** from $Et_2O$ solutions. They were coated with paratone-N oil, selected, mounted on a glass fibre and transferred onto the goniometer and into the cryostream of the diffractometer. Data collections were performed at 100.0(2) K on a SuperNova diffractometer, using monochromated Cu-Kα radiation for **1**, **5**, **6** and **10** and monochromatized Mo-Kα radiation for **7** and **9**.

Using OLEX2, the structures were solved by Direct Methods and refined by full-matrix least-squares cycles (program SHELX-97) [45, 46]. Crystal and refinement details, as well as the CCDC numbers for each structure determination are provided in Table 1.

CCDC 1531692-15316697 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.ac.uk/data_request/cif.

## 5 Experimental section

### 5.1 General

All reactions using organometallic reagents were carried out under an anhydrous, inert atmosphere of nitrogen or argon using standard Schlenk and glovebox techniques. THF (dried over potassium) and pentane (dried over $LiAlH_4$) were freshly distilled before use. Ethynylmagnesium bromide (0.5 M in THF) and vinylmagnesium chloride (1.9 M in THF) were purchased from Acros Organics. Trichlorophenylsilane (from FLUKA), trichlorosilane (FLUKA) and chloro(dimethyl)silane (FLUKA) were condensed before use. Karstedt's catalyst (from ABCR) and bromopentafluorobenzene (Fluorochem) were used without further purifications. The syntheses of diethynyldiphenylsilane (**3**) and divinyldiphenylsilane (**4**) as well as the procedure of hydrosilylation are described elsewhere [38]. NMR spectra were recorded on a Bruker DRX 500 and a Bruker Avance III 500 HD instrument. The chemical shifts (δ) were measured in ppm with respect to the solvent ($C_6D_6$: $^1$H NMR, $\delta = 7.16$ ppm, $^{13}$C NMR, $\delta = 128.06$ ppm) or referenced externally ($^{29}$Si: $SiMe_4$, $^{19}$F: $CFCl_3$). EI mass spectra were recorded using an Autospec Xmagnetic sector mass spectrometer with EBE geometry (Vacuum Generators, Manchester, UK) equipped with a standard EI source. Samples were introduced by push

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**Table 1:** Crystallographic data for **1**, **5**, **6**, **7**, **9** and **10**.

| | **1** | **5** | **6** | **7** | **9** | **10** |
|---|---|---|---|---|---|---|
| Empirical formula | $C_{12}H_8Si$ | $C_{36}H_{29}F_{15}Si_4$ | $C_{36}H_{35}F_{15}Si_4$ | $C_{32}H_{26}F_{10}Si_3$ | $C_{12}H_{11}Cl_9Si_4$ | $C_{12}H_{11}F_9Si_4$ |
| $M_r$ | 180.27 | 858.95 | 865.00 | 684.80 | 586.62 | 438.57 |
| $F(000)$, $e$ | 376 | 1744 | 5304 | 1400 | 584 | 1760 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic | Monoclinic | Orthorhombic | Orthorhombic |
| Space group | $Pc$ | $P2_1/c$ | $P2_1$ | $P2_1/n$ | $Pmn2_1$ | $Pbca$ |
| $a$, Å | 12.3799(13) | 10.7869(3) | 10.04213(9) | 9.3040(2) | 16.3606(4) | 6.7112(2) |
| $b$, Å | 11.7758(6) | 18.5948(5) | 55.8944(7) | 17.7490(4) | 6.38123(13) | 17.6920(6) |
| $c$, Å | 7.3475(4) | 19.3875(5) | 21.0381(2) | 19.8628(5) | 11.3405(2) | 30.4841(10) |
| $\beta$, deg | 96.593(8) | 100.516(2) | 93.3013(9) | 101.787(3) | 90 | 90 |
| $V$, Å$^3$ | 1064.06(14) | 3823.41(17) | 11789.1(2) | 3210.93(14) | 1183.95(4) | 3619.5(2) |
| $Z$ | 4 | 4 | 12 | 4 | 2 | 8 |
| $\rho_{calcd.}$, g cm$^{-3}$ | 1.13 | 1.49 | 1.46 | 1.42 | 1.65 | 1.61 |
| $\mu$, mm$^{-1}$ | 1.5 | 2.4 | 2.3 | 0.2 | 1.3 | 3.9 |
| $\theta_{max}$, deg | 133.0 | 144.0 | 134.0 | 60.0 | 55.0 | 144.3 |
| Index ranges $h$, $k$, $l$ | $-14 \le h \le 14$ | $-13 \le h \le 13$ | $-11 \le h \le 11$ | $-13 \le h \le 13$ | $-21 \le h \le 21$ | $-8 \le h \le 8$ |
| | $-14 \le k \le 14$ | $-22 \le k \le 21$ | $-66 \le k \le 59$ | $-24 \le k \le 24$ | $-8 \le k \le 8$ | $-21 \le k \le 21$ |
| | $-8 \le l \le 8$ | $-23 \le l \le 23$ | $-25 \le l \le 25$ | $-27 \le l \le 27$ | $-14 \le l \le 14$ | $-37 \le l \le 37$ |
| Reflexes collected | 15 686 | 71 866 | 17 8151 | 53 339 | 20 030 | 64 007 |
| Independent reflexes | 3587 | 7514 | 39 725 | 9348 | 2801 | 3566 |
| $R_{int}$ | 0.0467 | 0.0818 | 0.0628 | 0.0486 | 0.0337 | 0.1063 |
| Observed refl. ($I > 2\,\sigma(I)$) | 3335 | 6182 | 37404 | 7633 | 2742 | 2994 |
| Parameters | 235 | 502 | 3010 | 410 | 124 | 227 |
| $R_1$, ($I > 2\,\sigma(I)$) | 0.0367 | 0.0541 | 0.0741 | 0.0447 | 0.0201 | 0.0470 |
| $wR_2$, ($I > 2\,\sigma(I)$) | 0.0970 | 0.1493 | 0.1966 | 0.1194 | 0.0510 | 0.1115 |
| $R_1$ (all data) | 0.0401 | 0.0638 | 0.0775 | 0.0571 | 0.0207 | 0.0570 |
| $wR_2$ (all data) | 0.1005 | 0.1583 | 0.2006 | 0.1299 | 0.0514 | 0.1183 |
| $GoF$ | 1.038 | 1.062 | 1.030 | 1.053 | 1.049 | 1.045 |
| $\rho_{max}/\rho_{min}$, $e$ Å$^{-3}$ | 0.37/−0.16 | 0.46/−0.84 | 1.80/−0.58 | 0.53/−0.34 | 0.33/−0.19 | 0.49/−0.37 |
| CCDC No. | 1531692 | 1531693 | 1531694 | 1531695 | 1531696 | 1531697 |
| Remarks | a) | – | b) | – | c) | – |

a) Flack parameter 0.05(3); b) merohedral twin (BASF 0.62); c) Flack parameter −0.02(3).

rod in aluminum crucibles. Ions were accelerated by 8 kV. Elemental analyses were performed with CHNS elemental analyzer HEKAtech EURO EA.

## 5.2 Triethynylphenylsilane (1)

Trichlorophenylsilane (4.0 mL, 25 mmol) was added dropwise to a mixture of ethynylmagnesium bromide solution (160 mL, 80 mmol) in THF (50 mL) at 0°C. The mixture was warmed to ambient temperature, stirred for 14 h and all volatile compounds were removed *in vacuo*. The remaining brownish solid was washed with diethyl ether (25 mL), the solvent was removed from the organic filtrate and the colourless residue was purified by distillation (80°C, $10^{-2}$ mbar) to yield triethinylphenylsilane as crystalline material. Yield: 3.6 g (20 mmol, 80%). – $^1$H NMR (500 MHz, $C_6D_6$): $\delta = 7.91$ (m, 2H, *o*-Ph*H*), 7.11 (m, 3H, *m*-/*p*-Ph*H*), 1.99 (s, 3H, C*H*) ppm. – $^{13}$C{$^1$H} NMR (125 MHz, $C_6D_6$): $\delta = 134.7$, 131.3, 130.3, 128.6, 97.3, 82.2 ppm. – $^{29}$Si{$^1$H} NMR (99 MHz, $C_6D_6$): $\delta = -70.2$ ppm. – EI-MS (70 eV): $m/z = 179.1$, 154.1, 129.1, 103.0, 77.0. – Elemental analysis calcd. (%) for $C_{12}H_8Si$ ($M_r = 180.28$): C 79.95, H 4.47; found C 80.10, H 4.53.

## 5.3 Trivinylphenylsilane (2)

Trichlorophenylsilane (4.8 mL, 30 mmol) was added dropwise to a mixture of vinylmagnesium chloride solution (50 mL, 95 mmol) with THF (100 mL) at ambient temperature and stirred for 16 h. Ice (50 g) was added and all volatile compounds were removed *in vacuo*. The remaining brownish solid was washed with DCM (60 mL), the solvent was removed from the organic filtrate and the colourless residue was purified by distillation (68°C, 3 mbar) to yield trivinylphenylsilane as oily liquid. Yield: 4.1 g (22 mmol, 74%). – $^1$H NMR (500 MHz, $CDCl_3$): $\delta = 7.55$ (m, 2H, *o*-Ph*H*), 7.39 (m, 3H, *m*-/*p*-Ph*H*), 6.34 (dd, $J = 20.1$, 14.6 Hz, 3H, $\alpha$-*H*), 6.21 (dd, $J = 14.6$, 4.0 Hz, 3H, β-*Z*-*H*), 5.83 (dd,

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$J = 20.1$, 4.0 Hz, 3H, $\beta$-*E*-*H*) ppm. – $^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$): $\delta = 136.1$, 135.2, 134.6, 133.9, 129.6, 128.0 ppm. – $^{29}$Si{$^1$H} NMR (99 MHz, $CDCl_3$): $\delta = -23.9$ ppm. – EI-MS (70 eV): *m*/*z* = 186.1, 158.1, 107.1, 82.1, 67.0.

## 5.4 all-*trans*-Tris[(pentafluorophenyldimethylsilyl)vinyl]phenylsilane (5)

Magnesium turnings (120 mg, 5.1 mmol) and bromopentafluorobenzene (0.60 mL, 4.8 mmol) were refluxed in $Et_2O$ (20 mL) for 45 min. At ambient temperature, tris(chlorodimethylsilylvinyl)phenylsilane (0.74 g, 1.2 mmol), dissolved in THF (20 mL) was added and the mixture was refluxed for 2 h, quenched with sat. aqueous $NH_4Cl$ solution (10 mL) and extracted with *n*-hexane (20 mL). All volatiles of the combined organic phases were removed *in vacuo*. Recrystallisation (*n*-hexane) afforded tris[(pentafluorophenyldimethylsilyl)vinyl] phenylsilane as crystalline solid. Yield: 0.95 g (1.1 mmol, 92%). – $^1$H NMR (500 MHz, $CDCl_3$): $\delta = 7.47$ (m, 2H, *o*-Ph*H*), 7.40 (m, 3H, *m*-/*p*-Ph*H*), 6.86 (s, 6H, PhSiC*H*C*H*), 0.51 (s, 18H, C$H_3$) ppm. – $^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$): $\delta = 152.2$, 149.0, 146.4, 142.4, 137.5, 135.3, 133.6, 129.9, 128.2, –1.9 ppm. – $^{19}$F NMR (282 MHz, $CDCl_3$): $\delta = -126.4$ (dd, 6F, $J = 24.6$, 10.6 Hz), –151.5 (tt, 3F, $J = 20.0$, 3.4 Hz), –161.3 (m, 6F) ppm. – $^{29}$Si{$^1$H} NMR (99 MHz, $CDCl_3$): $\delta = -26.7$ (Ph*Si*), –11.2 (*Si*$Me_2$) ppm. – EI-MS (70 eV): *m*/*z* = 858.2, 843.2, 633.2, 607.2, 523.1, 472.1, 371.1, 309.1, 225.1, 145.1, 139.1, 135.1, 125.1, 77.1. – HRMS (EI, 70 eV): Calcd. for $C_{36}H_{29}F_{15}Si_4Na^+$: 881.09990; found 881.10229; deviation [ppm]: 2.71, deviation [mmu]: 2.39.

## 5.5 Tris[(pentafluorophenyldimethylsilyl)-ethyl]phenylsilane (6)

Magnesium turnings (75 mg, 3.1 mmol) and bromopentafluorobenzene (0.25 mL, 2.0 mmol) were refluxed in $Et_2O$ (13 mL) for 2 h. At 0°C, tris(chlorodimethylsilylethyl) phenylsilane (0.24 g, 0.5 mmol), dissolved in THF (13 mL), was added and the mixture was warmed to ambient temperature, quenched with sat. aqueous $NH_4Cl$ solution (5 mL) and extracted with DCM (10 mL). All volatiles of the combined organic phases were removed *in vacuo*. Recrystallisation (*n*-hexane) afforded tris[(pentafluorophenyldimethylsilyl)ethyl]phenylsilane as crystalline solid. Yield: 0.39 g (0.45 mmol, 90%). – $^1$H NMR (500 MHz, $CDCl_3$): $\delta = 7.36$ (m, 5H, *o*-/*m*-/*p*-Ph*H*), 0.72 (s, 12H, PhSiC$H_2$C$H_2$), 0.39 (s, 18H, C$H_3$) ppm. – $^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$): $\delta =$ 149.1, 142.0, 137.3, 135.9, 134.2, 129.4, 128.0, 109.9, 8.3, 3.1, –2.3 ppm. – $^{19}$F NMR (282 MHz, $CDCl_3$): $\delta = -127.6$ (dd, 6F, $J = 25.0$, 9.8 Hz), –151.7 (tt, 3F, $J = 20.4$, 3.4 Hz), –161.2 (m, 6F) ppm. – $^{29}$Si{$^1$H} NMR (99 MHz, $CDCl_3$): $\delta = 2.2$ (*Si*$Me_2$), 2.9 (Ph*Si*) ppm. – EI-MS (70 eV): *m*/*z* = 864.2, 849.2, 787.2, 759.2, 685.2, 611.2, 461.1, 371.2, 309.1, 287.1, 249.1, 225.1, 187.1, 135.1, 121.1, 77.1.

## 5.6 all-*trans*-Bis[(pentafluorophenyldimethylsilyl)vinyl]diphenylsilane (7)

Magnesium turnings (90 mg, 3.8 mmol) and bromopentafluorobenzene (0.39 mL, 3.2 mmol) were refluxed in $Et_2O$ (5 mL) for 1 h. At ambient temperature, bis(chlorodimethylsilylvinyl)diphenylsilane (0.54 g, 1.3 mmol), dissolved in THF (5 mL), was added and the mixture was refluxed for 1 h, quenched with sat. aqueous $NH_4Cl$ solution (5 mL) and extracted with *n*-hexane (10 mL). All volatiles of the combined organic phases were removed *in vacuo*. Crystallisation from *n*-hexane afforded bis[(pentafluorophenyldimethylsilyl)vinyl]diphenylsilane as crystalline brownish solid. Yield: 0.72 g (1.1 mmol, 85%). – $^1$H NMR (500 MHz, $CDCl_3$): $\delta = 7.49$ (m, 4H, *o*-Ph*H*), 7.40 (m, 6H, *m*-/*p*-Ph*H*), 7.04 (d, $J = 22.5$ Hz, 2H, $Ph_2$SiC*H*), 6.89 (d, $J = 22.5$ Hz, 2H, $Ph_2$SiCHC*H*), 0.51 (s, 12H, C$H_3$) ppm. – $^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$): $\delta = 152.3$, 149.1, 146.8, 142.2, 137.4, 135.7, 133.7, 129.9, 128.2, 109.6, –1.8 ppm. – $^{19}$F NMR (282 MHz, $CDCl_3$): $\delta = -127.1$ (dd, 4F, $J = 24.9$, 10.3 Hz), –151.6 (tt, 2F, $J = 20.5$, 3.5 Hz), –161.3 (m, 4F) ppm. – $^{29}$Si{$^1$H} NMR (99 MHz, $CDCl_3$): $\delta = -22.2$ ($Ph_2$*Si*), –10.7 (*Si*$Me_2$) ppm. – EI-MS (70 eV): *m*/*z* = 684.2, 607.2, 534.1, 433.2, 349.1, 207.1, 201.1, 197.1, 183.1, 135.1, 105.1, 77.1.

## 5.7 Bis[(pentafluorophenyldimethylsilyl)-ethyl]diphenylsilane (8)

Magnesium turnings (30 mg, 3.8 mmol) and bromopentafluorobenzene (0.15 mL, 1.2 mmol) were refluxed in $Et_2O$ (10 mL) for 2 h. At ambient temperature, bis(chlorodimethylsilylethyl)diphenylsilane (0.17 g, 0.40 mmol), dissolved in THF (10 mL), was added and the mixture was refluxed for 1 h. The mixture was quenched with sat. aqueous $NH_4Cl$ solution (5 mL) and extracted with *n*-hexane (20 mL). All volatiles of the combined organic phases were removed *in vacuo* affording bis[(pentafluorophenyldimethylsilyl)vinyl]diphenylsilane as brownish oil. Yield: 0.25 g (0.36 mmol, 90%). – $^1$H NMR (500 MHz, $CDCl_3$): $\delta = 7.45$ (m, 4H, *o*-Ph*H*), 7.37 (m, 6H, *m*-/*p*-Ph*H*), 1.02 (m, 4H, $Ph_2$SiC$H_2$), 0.80 (m, 4H, $Ph_2$Si$CH_2$C$H_2$), 0.40 (s, 12H, C$H_3$) ppm. – $^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$): $\delta = 149.2$, 142.1,

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137.3, 135.4, 135.0, 129.5, 128.1, 110.0, 8.3, 3.9, –2.2 ppm. – $^{19}$F NMR (282 MHz, $CDCl_3$): $\delta = -127.5$ (dd, 4F, $J = 25.0$, 9.9 Hz), –151.8 (tt, 2F, $J = 20.5$, 3.4 Hz), –161.2 (m, 4F) ppm. – $^{29}$Si{$^1$H} NMR (99 MHz, $CDCl_3$): $\delta = -3.9$ ($Ph_2$*Si*), 2.1 (*Si*$Me_2$) ppm. – EI-MS (70 eV): $m/z = 688.2$, 673.2, 662.5, 647.5, 587.2, 583.2, 509.2, 435.2, 287.2, 253.1, 201.1, 183.1, 147.1, 105.1, 77.1.

## 5.8 all-*trans*-Tris[(trichlorosilyl)vinyl]phenylsilane (9)

Triethynylphenylsilane (64 mg, 0.36 mmol) was dissolved in trichlorosilane (0.5 mL, 5.0 mmol), one drop of Karstedt's catalyst (1 M in xylene) was added at ambient temperature and the pale yellow mixture was stirred for 1 h. Removing of all volatiles afforded tris[(trichlorosilyl)-vinyl]phenylsilane as a colourless solid. Yield: 205 mg (0.35 mmol, 97%). – $^1$H NMR (500 MHz, $CDCl_3$): $\delta = 7.50$ (m, 5H, *o*-/*m*-/*p*-Ph*H*), 7.30 (d, $J = 22.0$ Hz, 3H, PhSiC*H*), 6.69 (d, $J = 22.0$ Hz, 3H, PhSiCHC*H*) ppm. – $^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$): $\delta = 150.3$, 146.3, 135.40, 131.5, 129.0, 128.6 ppm. – $^{29}$Si{$^1$H} NMR (99 MHz, $CDCl_3$): $\delta = -24.4$ (Ph*Si*), –6.4 (*Si*$Cl_3$) ppm. – Elemental analysis calcd. (%) for $C_{12}H_{11}Cl_9Si_4$ ($M_r = 586.63$): C 24.57, H 1.89; found C 24.87, H 1.97.

## 5.9 all-*trans*-Tris[(trifluorosilyl)vinyl]phenylsilane (10)

Tris[(trichlorosilyl)vinyl]phenylsilane (60 mg, 0.10 mmol) and antimony trifluoride (210 mg, 1.2 mmol) were dissolved in pentane (2 mL) and stirred for 25 h at ambient temperature. Filtration, removing all volatiles from the filtrate and removing of antimony trichloride by sublimation (50°C, $10^{-2}$ mbar) afforded tris[(trifluorosilyl)vinyl]phenylsilane as a colourless solid. Yield: 40 mg (91 µmol, 90%). – $^1$H NMR (500 MHz, $CDCl_3$): $\delta = 7.48$ (m, 5H, *o*-/*m*-/*p*-Ph*H*), 7.47 (d, $J = 23.1$ Hz, 3H, PhSiC*H*), 6.45 (dq, $J = 23.1$, 3.3 Hz, 3H, PhSiCHC*H*) ppm. – $^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$): $\delta = 156.2$, 135.8 (q, $J = 25.6$ Hz), 135.3, 131.6, 131.5, 129.1 ppm. – $^{19}$F NMR (470 MHz, $CDCl_3$): $\delta = -141.3$ (d, $J = 3.3$ Hz) ppm. – $^{29}$Si{$^1$H} NMR (99 MHz, $CDCl_3$): $\delta = -24.2$ (Ph*Si*), –78.7 (q, $J = 268.4$ Hz, *Si*$F_3$) ppm.

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