**Supported Silyl Cations**

**Silyl Cations Stabilized by Pincer Type Ligands with Adjustable Donor Atoms**

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Dedicated to Professor Klaus Jurkschat on the occasion of his retirement from the Technical University of Dortmund.

Abstract: Novel E,C,E′-pincer supported silyl cations (E, E′ = O, S, Se, Au) were prepared in three steps starting from 2,6-F2C6H3SiMe2H(3a–c) and 2,6-Br2C6H3SiMe2H(4b), which were first converted in two complementary ways into 2,6-(Ph2PE)2C6H3SiMe2H (2). The oxidation of 2 with H2O2/urea, 5c; and 2-(Ph2PE)-6-(Ph2PE)-C6H3SiMe2H (4c; E = S), which were reacted to the E,C,E-supported silyl cations [2-(Ph2P=O)C6H3SiMe2]+ (5a, E = O, countering Br5; 5b, E = S, counterion B(C6F5)4–), were isolated as well as the E,C,Au-supported silyl cations [2-(Ph2PAuC6F5)-6-(Ph2P=O)C6H3SiMe2]+ (7b, E = S, counterion B(C6F5)4–; 8b, E = S, counterion [B{3,5-(CF3)2C6H3}4]–) using Br2, O2, SPh, (tht)AuC6F5, Ph3Cl[B(C6F5)4] and Ph3Cl[B{3,5-(CF3)2C6H3}4]. All compounds were characterized by multinuclear 1H, 13C, 19F, 29Si, 31P, 77Se NMR spectroscopy, ESI MS spectrometry and X-ray crystallography (2, 3a–c, 4b, 5a, 5c, 7, 8b, 8c). The gas phase structures of 2, 3a–c, 5a–c (fully optimized) and 8b, 8c (single-point calculations) were studied at the B3PW91/6–311+G(d,f,p) level of theory. A set of real-space binding indicators (RSBIs) derived from the theoretically calculated electron and pair densities were analyzed utilizing the atoms-in-molecules (AIM) and electron-localizability indicator (ELI-D) space partitioning schemes.

Introduction

The isolation of tricoordinate silyl cations posed an exceptional challenge for several decades.[1] So far only two genuinely tricoordinate silyl cations [R3Si]+[A]– (I, namely [Mes2Si]+[HCBI1Me3Br9]–,[2] and [Pemp2Si]+[B2Cl3(C2H5)2]–[3]–[5] have successfully been prepared by the judicious choice of bulky and electron rich substituents and weakly coordinating anions (Mes = mesityl; Pemp = pentamethylyphenyl). The difficult preparation can arguably be attributed to the extreme Lewis acidity of tricoordinate silyl cations and their high reactivity towards almost all σ and π-donors, including many counterions and solvent molecules.[1] The presence of coordinating anions (A–) and neutral donors (D) inevitably increases the coordination number of the silicon atoms from CN = 3 in [R3Si]+[A]– (I) to CN = 3 + 1 in [R3Si]+[A–] (II) and ([R3Si–D]–[A]– (IV) or even CN = 3 + 2 in [R3Si]+[A–]– (VII) and ([R3Si–D2]–[A]– (V), respectively, and dramatically reduces the Lewis acidity (Scheme 1).[1] The prerequisite of kinetically stabilizing bulky substituents and weakly coordinating anions for the stabilization of tricoordinate silyl cations [R3Si]+[A]– (I) can be nicely deduced by inspection of a series of published compounds. In the absence of bulky substituents, contact ion pairs [R3Si]+[A–]– (II) were obtained as illustrated in [Mes2Si]+[RCBI1F11]– (R = H, Me),[6] ([R5Si]+–[B2Cl2(2,2)–] (R = Me, Et, iPr),[6] and [Et5Si]+[HCBI1H3Cl8]–[6] although weakly coordinating borane or carbane anions have been employed. The recently reported [H3Si]+[HCBI11H3Br6]– is a straightforward example of the type [R5Si]+[A–]– (III) in which the substituted carbane anions bridged between the parent H3Si+ (Scheme 1).[6]
In the presence of (substituted) benzene (derivatives), Lewis pair complexes \([\text{[R}_3\text{Si}–\text{D}_2]^{+}[\text{A}^-]}\) (IV) such as \([\text{[Me}_2\text{Si}–\text{arene}]+[\text{B}_3\text{C}_3\text{F}_3\text{A}^-]}\) were isolated in which the arenes serve as π-donors (arene = benzene, toluene etc.). Some of these species may be even viewed as silyl-substituted arenium ions. The use of one bulky \(m\)-terphenyl substituent (occasionally decorated by halogen atoms at the flanking phenyl groups) gave rise to the formation of intramolecularly coordinated donor acceptor complexes, such as \([2,6-\text{Mes}_2\text{C}_6\text{H}_4\text{Me}_2\text{Si}][\text{B}_3\text{C}_3\text{F}_3\text{A}^-]}\). In the ferrocenyl-substituted silyl cation \([\text{FeCMe}_2\text{Si}^+]\)[\(\text{[B}_3\text{Cl}_1\text{C}_1^-}\)], the iron intramolecularly provides electron density to the electron deficient silicon atom \((\text{Fc} = \text{ferrocenyl})\). The vast majority of silyl cations have been prepared by a variation of the Bartlett–Condon–Schneider reaction using trityl salts of weakly coordinating anions \([\text{Ph}_3\text{C}^+][\text{A}^-]\) for the hydride abstraction from neutral \(\text{H-silanes R}_3\text{SiH}\). Quite often, these reactions produced hydride-bridged silyl cations \([\text{R}_3\text{Si}+[\text{H}]\text{SiR}_3]^+\) possessing three-center two electron (3c2e) bonds, rather than “free” silyl cations. Despite having a somewhat reduced Lewis acidities some of the higher-coordinated silyl cations show remarkable catalytic activities, including \(\text{C–F}^+\) bond activation/hydrodefluorination reactions and Diels–Alder reactions. The combination of silyl cations and bulky phosphines has been considered as frustrated Lewis pairs (FLPs) for the fixation and activation of carbon dioxide and dihydrogen.

Pentacoordinate silyl cations \([\text{[R}_3\text{Si}–\text{D}_2]^{+}[\text{A}^-]}\) (V) have also been prepared deliberately using intramolecularly coordinating substituents with donor atoms (so-called built in ligands). A prominent and significant example involves the \(\text{Me}_2\text{Si}^+\)[\(\text{[B}^\text{III}\text{Cl}_2\text{A}^-}\)] containing two intramolecularly coordinating phosphonium oxide groups (Scheme 2).

It is nowadays understood that phosphonium oxides are best described by bipolar single bonds \(+\text{P}–\text{O}^-\) rather than \(\text{P}–\text{O}\) double bonds. At present, there is a vivid debate how to present donor acceptor interactions within main group complexes and it has been pleaded to avoid extreme resonance formulas for marketing reasons. In the centre of this debate are often low-coordinate cations, which are stabilized by phosphine ligands or \(\text{N}\)-heterocyclic carbens (NHCs). Although this work is not concerned with these compound classes, the question for the most significant resonance structure for the description of silyl cations, such as VI, also requires clarification and will be discussed below. Like the tricoordinate silyl cations \([\text{Mes}_2\text{Si}]^{+}[\text{HCB}_{\text{III}}\text{Me}_2\text{Br}]^-\) and \([\text{Pemp}_2\text{Si}]^{+}[\text{R}_3\text{Cl}_{\text{III}}]^2^-\), VI possesses a trigonal planar base consisting of three C atoms. In addition to the tricoordinate silyl cations VI comprises two axial O atoms that compensate the electron deficiency of the Si atom. For both tricoordinate silyl cations \([\text{R}_3\text{Si}–\text{D}_2]^{+}[\text{A}^-}\) and pentacoordinate silyl cations \([\text{R}_3\text{Si}–\text{D}_2]^{+}[\text{A}^-]\) (V), a simplistic “valence bond (VB) model” might attribute the bonding of the three equatorial substituents to three sp\(^3\)-orbitals. It might further describe the axial substituents D of the pentacoordinate silyl cations \([\text{R}_3\text{Si}–\text{D}_2]^{+}[\text{A}^-]\) (V) as three-center four electron (3c4e) bonds involving the \(\text{p}_2-\text{orbital} of the Si atom. In the tricoordinate silyl cations \([\text{R}_3\text{Si}]^{+}[\text{A}^-]\) (I) the \(\text{p}_2-\text{orbital} remains vacant. Most recent computational work attributes the high affinity of Si for O to the high electronegativity differences and emphasizes the strongly polar or even ionic bond character of the Si–O bond, which questions strong covalent contributions for the axial bonding in pentacoordinate silyl cations such as V. We became interested in the preparation of new \(\text{E,C,E}'\)-pincer supported silyl cations with a number of different donor atoms \(\text{E, E}' = \text{O, S, Se}, \text{Au}\) including also those with a smaller affinity and electronegativity difference between Si and O. The established synthetic route for the preparation of the \(\text{O,C,O}'\)-pincer supported silyl cation VI starts from the dibromo benzene VII, which was converted into the diphosphonate VIII by a transition metal catalyzed Arbusov reaction, which restricts the donor atoms of this pincer ligand to O atoms. We note in passing that efforts were undertaken to prepare related \(\text{O,C,S}'\)-pincer ligands, which, however, rely on the Arbusov reaction. The selective C–H metallaion of VIII prior to the reaction with \(\text{Ph}_3\text{SiHCl}\) gives rise to the formation of the \(\text{H-silane IX}\). Hydride abstraction from IX via the Bartlett–Condon–Schneider reaction eventually provided the silyl cation VI. In this work we present an alternative route that first introduces the Si moiety and avoids Arbusov type reactions, which allows setting up more versatile pincer type ligands. Using this route, a number of new \(\text{E,C,E}'\)-pincer supported silyl cations with various potential donor atoms \((\text{E, E}' = \text{O, S, Se}, \text{Au})\) have been prepared.
and fully characterized. The nature of the bonds within these compounds was determined by analysis of a set of topological and integrated real-space bonding indicators (RSBIs) derived from the theoretically calculated electron densities (ED) and electron pair densities utilizing the atoms-in-molecules (AIM)\(^\text{[23]}\) and electron-localizability-indicator (ELI-D)\(^\text{[24]}\) space partitioning schemes which divide space in basins of atoms and paired electrons, respectively. A combination of these two methods provides quantitative information about the strength and nature of a bond and is very well suited to straightforwardly detect also weak atomic interactions, which is not the case for sole inspection of molecular orbitals (MOs) and/or natural bond orbitals (NBOs).

### Results and Discussion

#### Synthetic Aspects

2,6-Difluorodimethylsilylbenzene, 2,6-F\(_2\)C\(_6\)H\(_3\)SiMe\(_2\)H (1\(\text{a}\)), was prepared by the reaction of 2,6-difluorophenyllithium, 2,6-F\(_2\)C\(_6\)H\(_3\)Li,\(^\text{[25]}\) with HSiMe\(_2\)Cl, adapting a literature procedure published for 2,6-F\(_2\)C\(_6\)H\(_3\)SiMe\(_3\).\(^\text{[26]}\) 2,6-Dibromodimethylsilylbenzene, 2,6-Br\(_2\)C\(_6\)H\(_3\)SiMe\(_2\)H (1\(\text{b}\)), was obtained similarly as already described.\(^\text{[27]}\) The preparation of 2,6-bis(diphenylphosphino)dimethylsilylbenzene, 2,6-(Ph\(_2\)P)\(_2\)C\(_6\)H\(_3\)SiMe\(_2\)H (2), was achieved in two complementary ways, namely, the reaction of 1\(\text{a}\) with two equivalents of Ph\(_2\)PLi and the double lithiation of 1\(\text{b}\) with nBuLi/TMEDA prior to the reaction with two equivalents of Ph\(_2\)PCl, respectively (Scheme 3). The former reaction entails a nucleophilic substitution at the aromatic ring, while the latter involves a nucleophilic substitution at the P atom. The oxidation of 2 with a slight excess of H\(_2\)O\(_2\)-urea, S\(_8\), and Se\(_8\) provided the 2,6-bis(diphenylphosphinchalcogenido)dimethylsilylbenzenes 2,6-(Ph\(_2\)PE)\(_2\)C\(_6\)H\(_3\)SiMe\(_2\)H (3\(\text{a}\), E = O; 3\(\text{b}\), E = S; 3\(\text{c}\), E = Se).

The reaction of 2 with one equivalent of S\(_8\) and Se\(_8\) gave 2-(diphenylphosphinchalcogenido)-6-(diphenylphosphino)dimethylsilylbenzene, 2-(Ph\(_2\)PE)-6-(Ph\(_2\)P)-C\(_6\)H\(_3\)SiMe\(_2\)H (4\(\text{a}\), E = S; 4\(\text{c}\), E = Se), in good selectivity (Scheme 3). The precursors 2–4 were purified by crystallization and obtained as air-stable crystalline materials. The preparation of the O,C,O-pincer supported silyl cation [2,6-(Ph\(_2\)PO)\(_2\)C\(_6\)H\(_3\)SiMe\(_2\)]\(^+\) (5\(\text{a}\); counterion Br\(_3^-\)) was achieved by the simple oxidation of 2,6-(Ph\(_2\)PO)\(_2\)C\(_6\)H\(_3\)SiMe\(_2\)H (3\(\text{a}\)) with an excess bromine (Scheme 4). Attempts to prepare the same O,C,O-pincer supported silyl cation 5\(\text{a}\) by the established Bartlett–Condon–Schneider reaction using [Ph\(_3\)C\(^+\)][B(C\(_6\)F\(_5\))\(_4\)] proved unsuccessful and afforded an unaccounted mixture of products. In one experiment a small crop of Ph\(_3\)COOCPh\(_3\) was isolated, however, it is unclear if it is related to the preferred reaction, or simply a side-product formed by traces of molecular oxygen (see ESI for details).

The Bartlett–Condon–Schneider reaction of the heavier analogs 3\(\text{b}\) and 3\(\text{c}\) afforded in each case two organometallic products. The product distribution was inferred by integration of the

![Scheme 3. Formation and selected NMR data of the precursors 2–4.](image-url)

![Scheme 4. Formation and selected NMR data of the O,C,O-supported silyl cation 5\(\text{a}\).](image-url)
31P NMR resonances. The 31P NMR spectra of the crude reaction mixtures are shown in Figure 1.

The reaction of 2,6-(Ph2PS)2C6H3SiMe2H (3b) and [Ph3C][B(C6F5)4] gave a mixture of the desired S,C,S-supported silyl cation [2,6-(Ph2PS)2C6H3SiMe2]+ (5b, 10 %), the unexpected S,C-supported silyl cation [2-(Ph2PS)-6-(Ph2P)C6H3SiMe2]+ (6b, 74 %), and the starting material 3b (9 %) that was not separated (Scheme 5). The side-product of the formation of 6b, tritylthiol Ph3CSH was isolated from the mother liquor by column chromatography and unambiguously identified by comparison with an authentic sample. The reaction of 2,6-(Ph2PSe)2C6H3SiMe2H (3c) and [Ph3C][B(C6F5)4] gave a mixture of the desired Se,C,Se-supported silyl cation [2,6-(Ph2PSe)2C6H3SiMe2]+ (5c, 90 %) and the unexpected Se,C-supported silyl cation [2-(Ph2PSe)-6-(Ph2P)C6H3SiMe2]+ (6c, 10 %) from which the former was isolated (Scheme 5).

Scheme 5. Formation and selected NMR data of the E,C,E- and E,C-supported silyl cations 5b, 5c, 6b and 6c (E = S, Se).
Since all 2,6-bis(diphenylphosphinoalkyl)dimethylsilylbenzenes 2,6-(Ph₂PE)₂C₆H₃SiMe₂H (3a, E = O; 3b, E = S; 3c, E = Se) gave evidence for the partial dechalcogenation during the Bartlett–Condon–Schneider reaction, the same reaction was also extended to the unsymmetric species 2-(Ph₂PE)-6-(Ph₂P)C₆H₃SiMe₂H (4b, E = S; 4c, E = Se) and [Ph₃C][B(3,5-CF₃)₂C₆H₃]₄, which gave the E,C-supported silyl cations [2-(Ph₂PS)-6-(Ph₂P)C₆H₃SiMe₂]⁺ (6b, E = S; 6c, E = Se) as sole products in solution with sufficient purity (Scheme 6). No indication for the dechalcogenation reaction was observed during the synthesis of 6b. However, when 6c was prepared by reacting 4c with [Ph₃C][B(3,5-CF₃)₂C₆H₃]₄ in C₆D₆ a mixture of 6c (major product), 5c, and an unidentified side-product was obtained (see ESI for details). The ratio between the products of this reaction remained constant for at least 12 h. The same reaction had a different outcome when it was carried out in fluorobenzene (see ESI for details). Shortly after the start of the reaction (its progress was monitored by ³¹P NMR) a mixture of 6c, 5c and an unidentified product was obtained. The starting material was consumed in less than 13 minutes, and after this time the concentration of 5c and the unknown product decreased rapidly. Within 60 minutes the molar ratio between 6c and 5c became 1:1.02. While this solvent dependence is still not fully understood, the observation shows that the reaction mechanism might be quite complex. The E,C-supported silyl cations [2-(Ph₂PS)-6-(Ph₂P)C₆H₃SiMe₂]⁺ (6b, E = S; 6c, E = Se)
are fairly reactive and all attempts to isolate these species were impeded by decomposition. However, the clean formation of silyl cations 6b and 6c was unambiguously confirmed by 31P, 29Si and 77Se NMR spectroscopy (see below). Freshly prepared samples of 6b and 6c were used for all subsequent reactions. Exposed to the air, 6b reacted rapidly with molecular oxygen to give the O,C,S-supported silyl cation [2-(Ph2PS)-6-(Ph2PO)-C6H3SiMe2]+ (7). The reaction of 6b with sulfur proceeded at a slower pace (6 d), but eventually produced the S,C,S-supported silyl cation [2,6-(Ph2PS)2C6H3SiMe2]+ (5b).

The E,C,E′-supported silyl cations 5a, 5b, 5c and 7 (E, E′ = O, S, Se) were isolated by crystallization and obtained as crystalline materials that can be handled in air for short periods of time. When solutions of 6b and 6c were treated with (tht)AuC6F5, the corresponding E,C,Au-supported silyl cations [2-(Ph2PAuC6F5)-6-(Ph2PE)C6H3SiMe2]+ (8b, E = S, 8c, E = Se; counterion [B(3,5-(CF3)2C6H3)4]–) were obtained as crystalline air-sensitive materials in good yields (Scheme 6).

**Solid-State and Solution Structure**

The molecular structures of the precursors 2, 3a·H2O, 3b, 3c and 4b, the E,C,E′-pincer supported silyl cations 5a, 5c and 7 (E, E′ = O, S, Se) as well as the E,C,Au-pincer supported silyl
cations $8b$ and $8c$ ($E = S, Se$) are shown in Figure 2, 3 and 4. Selected bond parameters are collected in Table 1. The spatial arrangement of the Si atoms of the precursors $2, 3a$·$H_2O, 3b, 3c$ and $4$ is distorted tetrahedral. Only $3a$ shows an intramolecular Si···O contact (3.024(8) Å) significantly longer than that of $\text{VIII}$ (2.738(2) Å), which is indicative to weak $\sigma$-hole bonding.\cite{28} The tetrahedral geometry of the Si atoms is unaffected by this additional coordination as the sum of C–Si–C angles steadily increases in the series $2$ (338.1(3)°), $3a$ (339.9(4)°), $3b$ (341.5(1)°) and $3c$ (343.6(4)°). The spatial arrangement of the Si atoms of the silyl cations $5a, 5c$ and $7$ is distorted trigonal bipyramidal (type $\text{IV}$, Chart 1), whereby the three C atoms and chalcogen atoms $E, E' = O, S, Se$ adopt the equatorial and axial positions, respectively. The distortion is reflected in the O-Si-O angle of $5a$ (168.9(2)°), which deviates remarkably from linearity. The Si–O bond lengths of $5a$ (1.902(4) and 1.963(4) Å) compare well with those of $\text{V}$ (1.923(1) and 1.931(1) Å). The Si–O bond length of $7$ (1.825(2) Å) is significantly smaller, albeit still larger than Si–O single bonds. The Si–Se bond lengths of $5c$ (2.597(3) and 2.823(3) Å) are uneven. The Si–S bond length of $7$ (2.635(1) Å) lies about midway between those values. The Se–Si–Se angles of $5b$ (178.2(1)°) and the O-Si–S angle of $7$ (174.4(1)°) are essentially linear. The sum of C–Si–C angles of the trigonal bipyramidal silyl cations $5a$ (360.0(3)°), $5c$ (359.6(5)°) and $7$ (358.9(1)°) is significantly higher than those of the tetrahedral precursors $2$ (see above).

Figure 3. ORTEP view of the X-ray molecular structure of $5a, 5c$ and $7$ showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.
Due to the intramolecular coordination, the P–O bond lengths of 5a (1.525(4) and 1.525(4) Å) and 7 (1.532(2) Å) are longer than those of 3a (1.445(6) and 1.450(6) Å). The elongation of the P–S and P–Se bonds upon intramolecular coordination is less pronounced. The spatial arrangement of the Si atoms of the silyl cations 8b and 8c is distorted tetrahedral (type III, Chart 1). The Si–S bond length of 8b (2.216(1) Å) is significantly shorter than that of 7 (2.635(1) Å) and only slightly longer than typical Si–S single bonds. Similarly, the Si–Se bond length of 8c (2.350(3) Å) is significantly shorter than those of 5c (2.597(3), 2.823(3) Å) and nearly matches typical Si–Se single bonds. The Si--Au distances of 8b (3.678(2) Å) and 8c (3.612(5) Å) are significantly longer than the sum of van der Waals radii (approx. 3.46 and 3.56 Å),[29] which apparently suggests that there is no Si--Au interaction.

For the precursor IX (Scheme 2) the presence of hydrogen bridges of the Si–H–O–P type have been claimed.[17] A similar Si–H–O contact seems to be present in 3a, as evidenced by the H···O bond length (2.826(7) Å). The other precursors 3b, 3c and 4b show no evidence for contacts of the type Si–H--E interactions (E = S, Se). In the solid-state, the precursors 3a, 3b and 3c each adopt different conformations regarding the position of the chalcogen atoms relative to the central C₆H₃Si plane. In 3a·H₂O, the O atoms are situated on the opposite side of the plane (transoid), whereas in 3b and 3c and the S and Se atoms lie on the same sides of the plane (cisoid). In 3a·H₂O the transoid conformation might be related to the presence of PO···H-OH hydrogen bridges. The O···O donor acceptor distances (2.844(7) and 2.907(8) Å) are indicative of medium to weak hydrogen bonding.[30] While there appears to be no Si--Au contact in 8b and 8c, both compounds show two intramolecular hydrogen bonds of the type C--H···Au. The H···Au bond lengths of 8b (2.772(1) Å, 2.962(1) Å) and 8c (2.816(2) Å, 2.891(2) Å) and the C···Au distances of 8b (3.539(3) Å, 3.701(3) Å) and 8c (3.555(1) Å, 3.614(1) Å) fully consistent with parameters collected for a recent survey on H···Au contacts.[31]

In the O,C,O-pincer supported silyl cation (5a), the O atoms are nearly coplanar with the central C₆H₃Si plane (largest deviation from the ideal plane 0.083(3) Å for O1). The same holds also for the O,C,S-pincer supported silyl cation 7 (largest deviation from the ideal plane 0.080(1) Å for S2). However, in the Se,C,Se-pincer supported silyl cation 5c, the dimethylsilyl...
moiety is twisted to accommodate the large Se atoms that are situated above and below the central C₆H₅Si plane (largest deviation from the ideal plane 0.353(3) Å for Se1). Similar twists are also observed for the E,C,Au-supported silyl cations 5a and 8c.

29Si NMR spectroscopy is a sensitive probe to determine the coordination number of the Si atom in solution. While truly tricordinate silyl cations [Si(R₃)]⁺[(A⁻)] show typical δ 38.5 ppm, E = Se) reveal the largest δ 41.9 ppm. The coordination of the P(III) atom to the Au(C₆F₅) moiety, gives rise to apparent quintets in 31P NMR caused by coupling of 31P with four 19F nuclei.

**Gas-Phase and Electronic Structures**

Using the coordinates of the X-ray structures as starting point the gas-phase structures of the E,C,E-pincer supported silyl cations 5a and 8c were fully optimized at the B3PW91/6-311+G(2df,p) level of theory. Due to the size and issues related to relativistic effects for the E,C,Au-pincer supported silyl cations 8b and 8c only single point calculations were carried out at the same level of theory. In general there is good agreement between experimental and calculated bond parameters (see ESI for details). For the precursor 3a, both the cisoid and the transoid conformers were preliminary calculated, however, as their relative stability differs only by about 6 kJ mol⁻¹ only the transoid conformer of 3a resembling the solid-state structure most was taken into fur-

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**Table 1. Comparison of selected bond lengths (in Å) and angles (in deg) determined by X-ray single-crystal analyses of 2, 3a–3c, 4b, 5a, 5c, 7, 8b and 8c.**

| Bond lengths | 2 | 3a | 3b | 3c | 4b | 5a | 5c | 7 | 8b | 8c |
|--------------|---|----|----|----|----|----|----|---|----|----|
| E1–Si1       | – | –  | –  | –  | –  | 1.963(4) | 2.823(3) | 1.825(2) | – | –  |
| E2–Si1       | – | –  | –  | –  | –  | 1.902(4) | 2.597(3) | 2.635(1) | 2.216(1) | 2.350(3) |
| C1–Si1       | 1.891(7) | 1.864(9) | 1.869(2) | 1.857(7) | 1.864(4) | 1.860(6) | 1.847(9) | 1.861(2) | 1.847(3) | 1.835(11) |
| C2–Si1       | 1.850(7) | 1.867(9) | 1.864(2) | 1.835(8) | 1.875(4) | 1.850(6) | 1.864(9) | 1.860(2) | 1.840(3) | 1.846(10) |
| C10–Si1      | 1.908(5) | 1.921(7) | 1.931(2) | 1.936(5) | 1.922(4) | 1.906(5) | 1.926(7) | 1.926(2) | 1.899(3) | 1.906(9) |
| E1–P1        | – | 1.450(6) | 1.956(1) | 2.105(2) | – | 1.525(4) | 2.130(2) | 1.532(2) | – | –  |
| E2–P2        | – | 1.445(6) | 1.955(1) | 2.107(2) | – | 1.525(4) | 2.144(2) | 1.966(1) | 2.031(1) | 2.178(2) |
| C1–P1        | 1.840(5) | 1.816(7) | 1.837(2) | 1.836(5) | 1.849(4) | 1.790(6) | 1.838(7) | 1.793(2) | 1.828(3) | 1.835(9) |
| C2–P2        | 1.848(5) | 1.829(7) | 1.844(2) | 1.836(5) | 1.825(4) | 1.792(6) | 1.809(7) | 1.810(2) | 1.799(3) | 1.800(9) |
| C10–P2       | 1.841(6) | 1.819(8) | 1.808(6) | 1.837(4) | 1.793(6) | 1.810(8) | 1.776(2) | 1.816(1) | 1.816(3) | 1.806(10) |
| C3–P2        | 1.832(6) | 1.811(8) | 1.818(2) | 1.824(5) | 1.825(4) | 1.795(5) | 1.791(8) | 1.771(2) | 1.819(3) | 1.801(9) |
| C4–P2        | 1.853(6) | 1.814(7) | 1.822(4) | 1.831(4) | 1.876(6) | 1.821(8) | 1.821(2) | 1.790(3) | 1.788(10) |
| C5–P2        | 1.827(6) | 1.807(8) | 1.821(2) | 1.810(7) | 1.814(2) | 1.781(6) | 1.806(8) | 1.814(2) | 1.789(3) | 1.797(10) |
| C60–Au1      | – | –  | –  | –  | –  | –  | –  | –  | 2.045(3) | 2.074(9) |
| P1–Au1       | – | –  | –  | –  | –  | –  | –  | –  | 2.277(11) | 2.282(20) |

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For 3b and 3c the cisoid conformers were calculated. The bond topology according to the AIM theory and isosurface representations of the ELI-D localization domains are shown in Figure 5, Figure 6, and Figure 7. Selected bond lengths and AIM bond topological parameters are collected in Table 2, whereas topological and integrated ELI-D bond descriptors are listed in Table 3. Since similar bonds exhibit similar topological and integrated RSBIs only one example is given each (see ESI for all data). The considered RSBIs include: $\rho(r)$ – the electron density at the bond critical point (bcp) – and its corresponding Laplacian ($\nabla^2 \rho_{\text{bcp}}$), $\varepsilon$ – the bond ellipticity ($\varepsilon = (\lambda_1/\lambda_2)^{-1}$; $\lambda_1$ and $\lambda_2$ are the curvatures perpendicular to the bond axis), $d_1/d$ – the ratio of the atom-bcp distance over the atom-atom distance, $G/\rho_{\text{bcp}}$ and $H/\rho_{\text{bcp}}$ – the kinetic and total energy density over $\rho_{\text{bcp}}$ ratios, $V_{001}^{\text{ELI}}$ – the volume and electron population of the ELI-D basin, $\text{ELI}_{\text{max}}$ – the ELI-D value at the attractor position, $\Delta_{\text{ELI}}$ – the distance of the attractor position perpendicular to the atom-atom axis and $RJI$ – the Raub-Jansen index, which provides the number of electrons (and also percentage contributions) of an bonding or lone pair ELI-D basin distributed between the adjacent AIM atoms which form a bond. The delocalization index $\delta(A,B)$ is also calculated, which is a direct measure for electron sharing between two AIM atoms. In 3a–c no Si–E (E = O, S, Se) bond paths were observed in the AIM topology which rules out such types of interactions in these compounds, although the Si···S distances (< 3.7 Å) and Si···Se distances (< 3.8 Å) are shorter than the sum of the Van der Waals radii of 3.9 Å and 4.0 Å, respectively. This result is supported by the AIM atomic charges (see below). However, a Si–H···O bond path was observed in 3a indicating a weak interaction between the hydridic H atom and the also negatively

![Figure 5](image1.png)

![Figure 6](image2.png)

![Figure 7](image3.png)
polarized O atom. In contrast, the molecular gas-phase structures of 5a–c show such Si–E bond paths and the electronic parameters determined at the Si–E bcps unravel the respective nature of the interaction. The positive (or very close to zero) values of Laplacian at the Si–E bcps indicate polarized interactions for all three types of contacts (Table 2). As anticipated, the Si–O contacts are the shortest, leading to the highest electron density value (0.46 e/Å³) and only in this case the Laplacian is negative values of corresponding Laplacian, and a H/ρ_{bcps} value close to –1 he⁻¹. The delocalization index unravels that more electron pairs are shared between C and P atoms (δ = 0.67–0.84, R/λ = 71–78 %) than for C and Si atoms (δ = 0.39–0.53, R/λ = 83–89 %). Aforementioned properties of C–P bond are in proper agreement with our recent results for peri-substituted (ace)naphthylphosphinoboranes where such type of bonds were also evaluated using both AIM and EII-D approaches.[37]

Similarly, as it was found for the solid-state structures, the E–P bond lengths are also longer in the gas-phase E,C,E-pincer supported silyl cations (5a–5c) in comparison to those of the precursors (2, 3a–3c), especially in case of the P–O bond where the elongation is more pronounced due to the relatively small size of the O atom in comparison to other chalcogen atoms (S and Se). Such elongation is reflected in the topological parameters of these bonds; for example the electron density is lower in the pincer-type structures. As mentioned above, the P–O bonds are highly polarized covalent bonds with significant ionic contributions, which is consistent with findings from combined experimental and theoretical studies.[38] Herein, two parame-

Table 2. Bond length (in Å) and AIM bond topological parameters[a] for selected bonds to phosphorus and silicon atoms of 2, 3a–3c, 5a–5c, 8b and 8c.

| Bond     | d   | ρ_{bcps} | ∇^2ρ_{bcps} | d/d | ϵ  | G/ρ_{bcps} | H/ρ_{bcps} |
|----------|-----|----------|-------------|-----|----|------------|------------|
| C1–Si1   | 1.8785 | 0.83    | 2.9        | 0.61 | 0.02 | 0.95       | –0.70      |
| 8b       | 1.8473(3) | 0.89   | 3.0        | 0.61 | 0.02 | 0.97       | –0.73      |
| 8c       | 1.835(11) | 0.90  | 3.4        | 0.61 | 0.03 | 0.99       | –0.73      |
| C10–Si1  | 1.9155 | 0.78    | 3.1        | 0.62 | 0.03 | 0.95       | –0.67      |
| 8b       | 1.899(3) | 0.80   | 3.3        | 0.61 | 0.03 | 0.97       | –0.68      |
| 8c       | 1.906(9) | 0.79  | 2.8        | 0.61 | 0.03 | 0.96       | –0.68      |
| C11–P1   | 1.8460 | 1.07    | –6.7       | 0.59 | 0.10 | 0.52       | –0.96      |
| 8b       | 1.828(3) | 1.11   | –6.4       | 0.60 | 0.08 | 0.59       | –1.00      |
| 8c       | 1.835(9) | 1.10  | –6.7       | 0.60 | 0.09 | 0.57       | –0.99      |
| C20–P1   | 1.8385 | 1.08    | –6.0       | 0.60 | 0.18 | 0.58       | –0.97      |
| 8b       | 1.816(3) | 1.14   | –7.3       | 0.60 | 0.09 | 0.56       | –1.01      |
| 8c       | 1.806(10) | 1.16  | –7.1       | 0.60 | 0.07 | 0.59       | –1.02      |
| 3a       | 1.4884 | 1.62    | 28.6       | 0.60 | 0.00 | 2.16       | –0.93      |
| 5a       | 1.5323 | 1.47    | 21.7       | 0.60 | 0.06 | 1.93       | –0.90      |
| 3b       | 1.9544 | 1.13    | 6.2        | 0.54 | 0.01 | 0.36       | –0.74      |
| 3c       | 1.9941 | 1.08    | 6.2        | 0.55 | 0.08 | 0.31       | –0.72      |
| 3c       | 2.1103 | 0.93    | –2.4       | 0.50 | 0.02 | 0.41       | –0.59      |
| 3c       | 2.1422 | 0.91    | –2.9       | 0.50 | 0.08 | 0.35       | –0.57      |
| 3c       | 2.031(11) | 1.02  | –5.9       | 0.55 | 0.08 | 0.29       | –0.70      |
| 3c       | 2.178(2) | 0.87   | –3.0       | 0.51 | 0.09 | 0.31       | –0.55      |
| 5a       | 2.4968 | 0.35    | –0.2       | 0.63 | 0.05 | 0.43       | –0.47      |
| 5b       | 2.6454 | 0.33    | –0.5       | 0.61 | 0.07 | 0.31       | –0.41      |
| 8b       | 2.216(1) | 0.57  | 1.1        | 0.64 | 0.04 | 0.74       | –0.61      |
| 8c       | 2.350(3) | 0.53   | –0.6       | 0.65 | 0.04 | 0.55       | –0.62      |
| 8b       | 2.271(1) | 0.80   | 2.3        | 0.52 | 0.02 | 0.67       | –0.47      |
| 8c       | 2.280(2) | 0.79   | 2.2        | 0.51 | 0.01 | 0.66       | –0.47      |
| 8b       | 2.045(3) | 0.92   | 3.9        | 0.54 | 0.04 | 0.78       | –0.48      |
| 8c       | 2.074(9) | 0.88   | 3.6        | 0.54 | 0.03 | 0.75       | –0.46      |

[a] Electron density ρ_{bcps} in e Å⁻³ and its corresponding Laplacian ∇²ρ_{bcps} in e Å⁻⁵, d/d – longer distance from bond critical point to nucleus over distance ratio, ϵ – the bond ellipticity, G/ρ_{bcps} and H/ρ_{bcps} – kinetic and total energy density over ρ_{bcps} ratios in he⁻¹.
Table 3. Topological[a] and integrated[b] ELI-D bond descriptors for selected bonds to phosphorus and silicon atoms of 2, 3a–3c, 5a–5c, 8b and 8c.

| Bond      | δ       | V001 ELI | ELI pop | ELImax | ΔELI | RJI [e] | RJI [%] |
|-----------|---------|----------|---------|--------|------|--------|--------|
| 2         | C1–Si1  | 0.50     | 5.79    | 2.00   | 1.98 | 0.041  | 1.71   | 85     |
| 8b        | C1–Si1  | 0.52     | 5.67    | 2.01   | 1.95 | 0.006  | 1.68   | 84     |
| 8c        | C1–Si1  | 0.53     | 5.57    | 2.01   | 1.94 | 0.012  | 1.69   | 84     |
| 2         | C10–Si1 | 0.45     | 8.14    | 2.32   | 2.07 | 0.021  | 2.06   | 89     |
| 8b        | C10–Si1 | 0.45     | 7.89    | 2.33   | 2.07 | 0.076  | 2.06   | 88     |
| 8c        | C10–Si1 | 0.46     | 7.81    | 2.32   | 2.06 | 0.066  | 2.04   | 88     |
| 2         | C11–P1  | 0.84     | 4.99    | 2.14   | 1.89 | 0.038  | 1.64   | 77     |
| 8b        | C11–P1  | 0.77     | 5.10    | 2.19   | 1.94 | 0.006  | 1.70   | 77     |
| 8c        | C11–P1  | 0.77     | 5.13    | 2.19   | 1.94 | 0.015  | 1.69   | 77     |
| 2         | C20–P1  | 0.84     | 4.86    | 2.14   | 1.89 | 0.065  | 1.67   | 78     |
| 8b        | C20–P1  | 0.80     | 5.29    | 2.20   | 1.91 | 0.040  | 1.65   | 75     |
| 8c        | C20–P1  | 0.80     | 5.19    | 2.21   | 1.92 | 0.040  | 1.66   | 75     |
| 3a        | P1–O1   | 0.86     | 2.02    | 1.59   | 1.45 | 0.144  | 1.21   | 76     |
| 5a        | P1–O1   | 0.72     | 1.74    | 1.53   | 1.49 | 0.038  | 1.25   | 81     |
| 3b        | P1–S1   | 1.36     | 4.38    | 2.00   | 1.53 | 0.026  | 1.13   | 56     |
| 5b        | P1–S1   | 1.17     | 4.15    | 1.93   | 1.59 | 0.065  | 0.98   | 51     |
| 3c        | P1–Se1  | 1.39     | 5.61    | 2.15   | 1.53 | 0.060  | 1.39   | 65     |
| 5c        | P1–Se1  | 1.21     | 5.12    | 2.03   | 1.59 | 0.104  | 1.22   | 60     |
| 8b        | S2–P2   | 1.05     | 3.89    | 1.84   | 1.62 | 0.050  | 0.98   | 53     |
| 8c        | Se2–P2  | 1.11     | 4.76    | 1.92   | 1.62 | 0.069  | 1.08   | 56     |
| 5a        | Si1–O1  | 0.22     | 1.82    | 1.41   | 1.56 | 0.022  | 1.34   | 95     |
| 5b        | Si1–S1  | 0.27     | 3.97    | 1.42   | 1.64 | 0.069  | 1.25   | 88     |
| 5c        | Si1–Se1 | 0.30     | 4.31    | 1.38   | 1.50 | 0.025  | 1.17   | 85     |
| 8b        | Si1–S2  | 0.41     | 4.41    | 1.70   | 1.68 | 0.044  | 1.47   | 86     |
| 8c        | Si1–Se2 | 0.45     | 5.01    | 1.73   | 1.62 | 0.030  | 1.43   | 83     |
| 8b        | P1–Au1  | 0.98     | 8.27    | 2.13   | 1.63 | 0.392  | 1.60   | 75     |
| 8c        | P1–Au1  | 0.96     | 8.09    | 2.11   | 1.61 | 0.309  | 1.57   | 74     |
| 8b        | C60–Au1 | 0.93     | 7.63    | 2.05   | 1.65 | 0.088  | 1.67   | 62     |
| 8c        | C60–Au1 | 0.91     | 7.24    | 1.99   | 1.66 | 0.026  | 1.63   | 62     |

[a] ELI max – ELI-D value at the attractor position, ΔELI = the distance in Å of the attractor position perpendicular to the atom-atom axis. [b] δ – the delocalization index, V001 ELI – the volume of the ELI-D basin in Å³ cut at 0.001 au, ELI pop – the electron population within the ELI-D basin in e, and RJI – the Raub-Jansen index in e %.

...ters: H/ρbcp and the Raub-Jansen index, showing the degree of covalency, are very similar for the P–O bond type. The values 1.93 and 2.16 Å³ e⁻¹ of the parameter G/ρbcp, the highest observed for all structures analyzed, indicate the high degree of ionicity for such type of bond. Based on DFT studies combined with AIM and ELI-D approaches, P–S and P–Se bonds can be classified as shared-shell interactions with a negative value of the Laplacian and a negative H/ρbcp ratio. The P–Se bonding shows only a slight polarization towards the phosphorus atom which is reflected by RJI = 60–65 %. In both cases a delocalization index higher than 1 indicates that the P and S/Se atoms share more than one but less than two electron pairs. The ionic contribution described by G/ρbcp is very small and comparable to those found for P–C bonds. In the E,C,Au-pincher supported silyl cations 8b and 8c the nature of the C–Si/C–P/E–P bonds remains unchanged in comparison to the E,C,E supported silyl cations 5a–5c, which is confirmed by the very similar real-space bonding indicators characteristic for polar-covalent interactions. Interestingly, the Si–E (E = S, Se) bond lengths are significantly shorter in 8b and 8c (up to 0.3 Å) in comparison to the related gas-phase structures of the E,C,E-pincher supported silyl cations 5b and 5c. This discrepancy is not an effect of different computational techniques used (single point calculation vs. geometry optimization) since the X-ray analysis revealed the same tendency for experimental distances of 5c and 8c. Such a difference in bond lengths, however, has a considerable impact on topological (G/ρbcp, G/ρbcp, H/ρbcp, and integrated (δ) parameters, however the Laplacian values still remain close to zero. Considering the ELI-D bonding indicators of Si–Se contact in 8c, it is interesting to note that the electrons within its ELI-D basin are more localized (values of ELI max and ELI pop increased) than in structure 5c. It is reflected in the graphical representation of ELI-D isosurfaces of 8c and 5c. In the former case (Figure 7) the Si1–Se2 basin is clearly visible in contrast to the latter case (Figure 6) where the corresponding basin is not observed at Y = 1.5 (but becomes visible at smaller ELI-D values). For the related Si–S basins of 5b and 8b the enhancement of electron localization is not so clearly pronounced. Interestingly in all studied S, Se-pincer supported cations, the RJIs remain comparable (above 80 %) confirming the polar covalent character of studied Si–E (E = S, Se) contacts. The AIM analysis confirmed the existence of intramolecular C–H···Au interactions found in the crystal structures of 8b and 8c. The topological properties determined at the Au–H bond critical points clearly show that these interactions are weak with electron density close to zero (0.06–0.09 e Å⁻³), the associated Laplacian below 1e Å⁻³, and the kinetic energy density dominates the potential energy density (|V|/G = 0.85–0.88).[33]
Table 4. Selected atomic charges (in e) of 2, 3a–3c, 5a, 5c, 8b and 8c.

|      | E1 | E2 | Si  | P1  | P2  | (Si)H | Σ(Ph,P1) | Σ(Ph,P2) | Σ(Ph|10–15) |
|------|----|----|-----|-----|-----|-------|----------|----------|----------|
| 2    |    |    | 2.77| 1.47| 1.46| –0.67 | 0.48     | 0.47     | –1.65     |
| 3a   | E = O| –1.49| –1.48| 2.77| 2.93| 2.91  | –0.67    | 1.97     | 1.97     | –1.66     |
| 3b   | E = S| –0.74| –0.73| 2.76| 2.02| 1.99  | –0.67    | 1.15     | 1.12     | –1.52     |
| 3c   | E = Se| –0.47| –0.47| 2.76| 1.72| 1.69  | –0.67    | 0.87     | 0.85     | –1.48     |
| 5a   | E = O| –1.54| –1.54| 2.91| 2.92| 2.92  | –        | 2.08     | 2.08     | –1.66     |
| 5b   | E = S| –0.78| –0.78| 2.65| 2.16| 2.16  | –        | 1.40     | 1.40     | –1.58     |
| 5c   | E = Se| –0.48| –0.48| 2.56| 1.89| 1.89  | –        | 1.14     | 1.14     | –1.56     |
| 8b   | E2 = S| – | –0.88| 2.77| 1.75| 2.23  | –        | 0.93     | 1.50     | –1.61     |
| 8c   | E2 = Se| – | –0.59| 2.70| 1.79| 1.99  | –        | 0.94     | 1.26     | –1.60     |

Analysis of AIM Charges

Selected atomic and fragmental charges obtained by integration of the AIM atomic basins are given in Table 4. As anticipated, the chalcogen atoms are negatively charged according to the relative electronegativities: O (–1.48 e to –1.54 e) > S (–0.73 e to –0.78 e) > Se (–0.47 e to –0.48 e) while the Si and P atoms are significantly positive (2.56 e to 2.91 e for Si, 1.47 e to 2.92 e for P). In the three precursors 3a–c the Si charges remain constant at about 2.76 e and the (Si)H charges remain constant at –0.67 e. The P atoms solely compensate the negative charges of the E atoms. Hence, in accordance with the geometrical and other real-space bonding indicators, Si–E interactions in the E,C,E-pincer supported silyl cations, high positive charges are also situated on the P atoms of 3a (2.92 e), 5a (2.16 e) and 5c (1.89 e), which can be accounted for the by use of bipolar single bonds “P–E” in the Lewis formula representations (Scheme 2, Scheme 3, Scheme 4, Scheme 5, and Scheme 6). In this way, both Si and P atoms are assigned formal positive charges. In light of the recent controversial debate of the appropriate description of donor acceptor bonds within main group compounds,[19] we deliberately used “arrows” to emphasize the strongly polar or even ionic bond character of the Si–O bond in 5a. Resonance structures involving “formal charges” suggesting a higher degree of covalence, are rather inadequate to describe the bond situation of the Si–O bonds of 5a. The same holds true for the Si–S bonds of 5b and the Si–Se bonds of 5c, albeit the bond polarity of these bonds is less pronounced. In an effort to contribute to this debate[19] we propose to generally write donor–acceptor complexes with predominantly covalent bond character using “lines and formal charges” and those with predominately ionic bond character using “arrows”.

Conclusions

A versatile route for the preparation of E,C,E-pincer supported silyl cations 5a–c distinct changes in the AIM atomic charges are observed in comparison to the corresponding precursors. Interestingly, in 5a the Si atom has 0.14 e less electrons compared to its precursor 3a, whereas an electron increase of 0.11 e and 0.20 e is found for the corresponding S- and Se-containing pincer molecules 5b and 5c.

Experimental Section

General. Reagents were obtained commercially and used as received. Dry solvents were collected from a SPS800 mBrAun solvent system. Triphenylcarbenium tetrais(pentafluorophenyl)borate,[8] triphenylcarbenium tetrakis(3,5-bistrifluoromethylphenyl)borate,[39] (tht)AuC6F5,[40] and dimethylsilyl-2,3-dibromobenzene[26] were prepared according to literature procedures. 1H, 13C, 29Si, 77Se and 31P-NMR spectra were recorded in CDCls unless otherwise stated at r.t. using Bruker Avance 360 and Bruker Avance DXP 200 spectrometers and are referenced to tetramethylsilane (1H, 13C, 29Si), phosphoric acid 85 % in water (31P), CFCl3 (19F), Ph2Se2 (77Se). Chemical shifts are reported in parts per million (ppm) and coupling constants (J) are given in Hertz (Hz). Electron impact mass spectroscopy (EIMS) was carried out using a Finnigan MAT 95. The ESI MS spectra were obtained with a Bruker Esquire-LC MS. Methanol solutions (unless otherwise stated, c = 1 × 10–6 mol L–1) were injected directly into the spectrometer at a flow rate of 3 μL min–1. Nitrogen was used both as a drying gas and for nebulization with flow rates of approximately 5 L min–1 and a pressure of 5 psi, respectively. Pressure in the mass analyzer region was usually about 1 × 10–5 mbar. Spectra were collected for one minute and averaged.

Synthesis of 2,6-F2C6H3SiMe2H (1a). A 2.5-M solution of n-butyl-lithium (21.9 mmol, 8.8 mL) in THF (40 mL) and n-hexane (18 mL)
was cooled down to -78 °C and diisopropylamine (2.2 g, 21.9 mmol) and 1,3-difluorobenzene (2.5 g, 21.9 mmol) was successively added. The mixture was stirred 1 h at -78 °C then dimethyldichlorosilane (2.1 g, 21.9 mmol) in THF (10 ml) was added dropwise. After 1 h stirring at -78 °C the reaction was quenched with distilled water. The layers were separated, the aqueous layer was extracted with CH₂Cl₂ and the combined organic layers were dried with MgSO₄. The solvents were removed at reduced pressure to leave a yellow oil. Vacuum trap to trap condensation afforded 1a as colorless oil (2.6 g, 15.1 mmol, 96%).

**Method B.** A suspension of lithium granule (0.21 g, 30 mmol) in THF (20 mL) and diphenyl(t, 3\(^{19}F\)-29Si) = 8 Hz). IR (KBr): ν\(_{\text{Si-H}}\) = 2171 cm\(^{-1}\). MS (ESI\(^+\)): \[M\] = 172 [M - Si]. **Synthesis of 2,6-(Ph\(_2\)P)\(_2\)C\(_6\)H\(_3\)SiMe\(_2\)H (2). Method A.** A solution of lithium granule (0.21 g, 30 mmol) in THF (20 mL) and diphenyl(t, 3\(^{19}F\)-29Si) = 8 Hz). IR (KBr): ν\(_{\text{Si-H}}\) = 2171 cm\(^{-1}\). MS (ESI\(^+\)): \[M\] = 172 [M - Si]. **Synthesis of 2-(Ph\(_2\)P)-6-(Ph\(_2\)P)-C\(_6\)H\(_3\)SiMe\(_2\)H (2b). Method A.** A suspension of lithium granule (0.21 g, 30 mmol) in THF (20 mL) and diphenyl(t, 3\(^{19}F\)-29Si) = 8 Hz). IR (KBr): ν\(_{\text{Si-H}}\) = 2171 cm\(^{-1}\). MS (ESI\(^+\)): \[M\] = 172 [M - Si]. **Synthesis of 2-(Ph\(_2\)P)-6-(Ph\(_2\)P)-C\(_6\)H\(_3\)SiMe\(_2\)H (2b). Method A.** A suspension of lithium granule (0.21 g, 30 mmol) in THF (20 mL) and diphenyl(t, 3\(^{19}F\)-29Si) = 8 Hz). IR (KBr): ν\(_{\text{Si-H}}\) = 2171 cm\(^{-1}\). MS (ESI\(^+\)): \[M\] = 172 [M - Si]. **Synthesis of 2-(Ph\(_2\)P)-6-(Ph\(_2\)P)-C\(_6\)H\(_3\)SiMe\(_2\)H (2b). Method A.** A suspension of lithium granule (0.21 g, 30 mmol) in THF (20 mL) and diphenyl(t, 3\(^{19}F\)-29Si) = 8 Hz). IR (KBr): ν\(_{\text{Si-H}}\) = 2171 cm\(^{-1}\). MS (ESI\(^+\)): \[M\] = 172 [M - Si]. **Synthesis of 2-(Ph\(_2\)P)-6-(Ph\(_2\)P)-C\(_6\)H\(_3\)SiMe\(_2\)H (2b). Method A.** A suspension of lithium granule (0.21 g, 30 mmol) in THF (20 mL) and diphenyl(t, 3\(^{19}F\)-29Si) = 8 Hz). IR (KBr): ν\(_{\text{Si-H}}\) = 2171 cm\(^{-1}\). MS (ESI\(^+\)): \[M\] = 172 [M - Si].
NMR (50 MHz, CDCl3): δ = 152.6 (dd, J = 51, 17 Hz), 148.1 (apparent J, J = 14 Hz), 140.6 (dd, J = 78, 17 Hz), 138.4 (d, J = 3 Hz), 137.5 (d, J = 12 Hz), 134.1, 133.8, 133.1 (d, J = 18 Hz), 132.9 (d, J = 10 Hz), 132.1, 131.4 (Jd, J = 4 Hz, 128.7, 128.6, 128.5, 128.27, -0.4 (d, J = 20 Hz), 31P(H)-NMR (81 MHz, CDCl3): δ = 39.6 (d, J(31P-29Si) = 4 Hz, J(31P-77Se) = 729 Hz), -8.9 (d, J(31P-1H) = 4.0 Hz). 32Si(H)-NMR (72 MHz, CDCl3): δ = -22.5 (t, J(29Si-31P) = 11 Hz). 77Se-NMR: δ = -189.7 (d, J(31P-77Se) = 729 Hz). IR (KBr): 3056 (m, Si-H) ppm. MS (ESI+): m/z = 586.3 [M+1].

Synthesis of [2-(Ph2PS)-6-(Ph2PO)C6H3SiMe2]+[B(C6F5)4]- (5b·B(C6F5)4).

A solid mixture of 3a (100 mg, 0.1 mmol) and 4b (19 mg, 0.04 mmol) in THF (10 mL) was stirred for 9 h at room temperature. The solvent was removed to give a red-brownish residue. Recrystallization from dichloromethane afforded red-brownish crystals of 5a·B(C6F5)4. 1H-NMR (200 MHz, CDCl3): δ = 8.0–7.5 (m, 23H), 0.9 (6H, s). 13C{1H}-NMR (50 MHz, CDCl3): δ = 124.8 (d, J(13C-31P) = 128 Hz), 138.3 (d of multiplet, J(13C-19F) = 242 Hz), 137.3 (d, J = 12 Hz), 136.3 (d, J = 2 Hz), 136.6 (d of multiplet, J(13C-19F) = 235 Hz), 133.7 (d, J = 2 Hz), 133.4 (d, J = 3 Hz), 132.4 (d, J = 4 Hz), 132.0 (d, J = 3 Hz), 130.4 (d, J = 14 Hz), 129.5 (d, J = 14 Hz), 128.9, 128.6, 128.4, 128.2, 127.0, 126.3, 123.3, 121.1, 7.7. 29Si(H)-NMR (72 MHz, CDCl3): δ = 5.9 (t, J(31P-29Si) = 3 Hz). 31P(H)-NMR (81 MHz, CDCl3): δ = 56.7 (s, J(13C-31P) = 12 Hz), 46.8 (s, J(13C-31P) = 11 Hz) ppm. MS (ESI+): m/z = 551.3 [M+].

Synthesis of [2-(Ph2PS)-6-(Ph2PO)C6H3SiMe2]+[BArF]– (6b·[BArF]–).

NMR monitored experiment. In the glovebox, an NMR tube was charged with 4b (78 mg, 0.145 mmol) and [Ph3C][BArF] (160 mg, 0.145 mmol). Anhydrous C6D6 (1 mL) was added to the solid mixture. The NMR tube was shaken occasionally for the next 3 h then was left standing for additional 9 h. Two layers formed. The dark red bottom layer was assessed by 1H NMR, 31P and 29Si NMR: a complete and clean conversion of 4b into 6b-[BArF]– was observed.

Isolation of 8b·[BArF]–. In the glovebox, a vial was charged with 4b (116 mg, 0.216 mmol) and trityl tetraakis[3,5-bis(trifluoromethyl)phenyl]borate (239 mg, 0.216 mmol). Anhydrous fluorobenzene (3 mL) was added. The mixture was stirred for 20 min then to the crude 6b-[BArF]– was added (tht)AuC6F5 (98 mg, 0.216 mmol) and stirring was continued for 10 additional minutes. The red solution was layered with n-hexane (approx. 7 mL) and the vial left standing for a week. After this time a red oily layer separated at the bottom of the vial. The vial was placed in a freezer at –30 °C for several days causing the precipitation of a crystalline solid. The solution was removed and the solid washed with n-hexane (3×0.5 mL) then dried. Compound 8b-[BArF]– was obtained as a tan solid (315 mg, 0.179 mmol, 83 %; Mp: 153–155 °C dec). Crystals suitable for X-ray diffraction were obtained by diffusion of n-hexane vapors into a concentrated solution of 8b-[BArF]– in CH2Cl2 (approx. 0.3 mL).

1H-NMR (200 MHz, CDCl3): δ = 8.30 (s, 8H, BArF2), 7.55 (s, 4H, BArF2) 7.30–6.67 (m, 23H), 0.62 (s, 6H, 13C(H)-NMR (50 MHz, CDCl3): δ = 162.8 (q, J(13C-19F) = 49 Hz, sept, J(13C-19F) = 17 Hz), 149.3 (ds of multiplet, J(13C-19F) = 224, J(13C-19F) = 24 Hz, 148.3 (t, J(13C-19F) = 248 Hz), 140.2 (d, J(13C-19F) = 248 Hz), 140.2–127.1 (multiple resonances overlapped), 122.5, 121.9, 120.2, 118.1, 117.1, 5.4. 31P(H)-NMR (81 MHz, CDCl3): δ = 57.6 (d, J(31P-29Si) = 1 Hz), 41.9 (apparent quintet, J = 8 Hz). 29Si(H)-NMR (72 MHz, CDCl3): δ = 41.2 (d, J = 8 Hz).

Synthesis of [2-(Ph2PS)-6-(Ph2PO)C6H3SiMe2]+[BArF]– (8c-[BArF]–). NMR monitored experiment. In the glovebox, an NMR tube was charged with 4c (85 mg, 0.145 mmol) and [Ph3C][BArF] (160 mg, 0.145 mmol). Anhydrous C6D6 (1 mL) was added to the solid mixture. The NMR tube was shaken occasionally for the next 3 h then was left standing for additional 9 h. Two layers formed. The dark yellow bottom layer was assessed by 1H, 31P and 29Si NMR.
NMR: a complete conversion of 4c was observed. The formation of 6c{[BArF]–}; 5c{[BArF]–}; and of an unidentified side-product in a 1.0:25:0.11 molar ratio was indicated by $^{31}$P-NMR.

$^{31}$P($^1$H)-NMR (81 MHz, C$_6$D$_6$): $\delta = 53.7$ (s, 1$^{1}$J($^3$P–$^{77}$Se) = 469 Hz, P=Se of 6c{[BArF]–}), 44.7 (s, 1$^{1}$J($^3$P–$^{77}$Se) = 470 Hz, P=Se of 5c{[BArF]–}), –4.2 (s, side-product), –7.6 (s, P of 6c{[BArF]–}). $^{77}$Se-NMR (72 MHz, C$_6$D$_6$): $\delta = 38.5$ (d, 1$^{3}$J($^3$P–$^{77}$Se) = 85 Hz, 6c{[BArF]–}). $^{77}$Se-NMR (69 MHz, C$_6$D$_6$): $\delta = --147.9$ (d, 1$^{3}$J($^3$P–$^{77}$Se) = 470 Hz).

The NMR tube was brought in the glovebox and to the crude mixture containing 6c{[BArF]–} was added (tht)AuC$_6$F$_5$ (65 mg, 0.145 mmol). The NMR tube was shaken for approximately 5 minutes. The upper layer removed and the bottom layer washed with C$_6$D$_6$ (6×0.35 mL). Complete conversion of the target product 8c{[BArF]–} was indicated by $^{31}$P- and $^{29}$Si NMR. Compound 5c{[BArF]–} was present in approximately the same amount with respect to 8c{[BArF]–}. The solvent was then evaporated in the glovebox and the remaining oil dissolved in fluorobenzene.

Crystals suitable for X-ray diffraction were obtained by diffusion of C$_6$D$_6$ (6×0.35 mL). Complete conversion of the target product 6c{[BArF]–} was indicated by $^{31}$P and $^{29}$Si NMR. Crystal structure determination.

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