Supporting Information

**Coinage-metal Complexes of NHC-stabilized Silyliumylidene Ions**

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1. Experimental Section

1.1. General Methods and Instrumentation

All reactions were carried out under exclusion of water and oxygen in an atmosphere of argon 4.6 (≥99.996%) using standard Schlenk techniques or in a Labstar glovebox from MBraun with H₂O and O₂ levels below 0.5 ppm. Glassware was heat dried under vacuum prior to use. Acetonitrile and Acetonitrile-d₃ were refluxed over CaH₂, distilled under argon, deoxygenated by three freeze-pump-thaw cycles and stored over 3 Å molecular sieve in a glovebox. Diethylether was refluxed over sodium/benzophenone, distilled under argon, deoxygenated by three freeze-pump-thaw cycles and stored over 3 Å molecular sieve in a glovebox. All NMR samples were prepared under argon in J. Young PTFE valve NMR tubes. NMR spectra at ambient temperature (300 K) were recorded on a Bruker AV400US or DRX400 (¹H: 400.13 MHz, ¹³C: 100.62 MHz, ²⁹Si: 79.49 MHz), AVHD300 (¹H: 300.13 MHz) or AV500C (¹H: 500.36 MHz, ¹³C: 125.83 MHz, ²⁹Si: 99.41 MHz). Variable temperature NMR spectra were recorded on a Bruker DRX400 (¹H: 400.13 MHz, ¹³C: 100.62 MHz, ²⁹Si: 79.49 MHz) spectrometer. The ¹H, ¹³C and ²⁹Si NMR spectroscopic chemical shifts δ are reported in ppm relative to tetramethylsilane. ¹H and ¹³C NMR spectra are calibrated against the residual proton and natural abundance carbon resonances of the respective deuterated solvent as internal standard (CD₃CN: δ(¹H) = 1.94 ppm and δ(¹³C) = 118.3 ppm). ²⁹Si NMR spectra are referenced to the resonance of tetramethylsilane (δ = 0 ppm) as external standard. The following abbreviations are used to describe signal multiplicities: s = singlet, d = doublet, t = triplet, sept = septet, bs = broad signal, m = multiplet. Quantitative elemental analyses (EA) were carried out using a HEKAtech EURO EA instrument equipped with a CHNS combustion analyzer at the Laboratory for Microanalysis at the TUM Catalysis Research Center. Melting Points (M.P.) were determined in sealed glass capillaries under inert gas by a Büchi M-565 melting point apparatus. ESI-MS spectra were recorded on a Bruker HCT Instrument with a dry gas temperature of 300 °C and an injection speed of 240 µLS⁻¹. Samples were prepared in a glovebox and spectra were visualized using OriginPro 2018. Unless otherwise stated, all commercially available chemicals were purchased from abcr or Sigma-Aldrich and used without further purification. The compounds [m-Terphenyl-Si(Ime₄)₂]Cl (1a)⁵¹ and [Tipp-Si(Ime₄)₂]Cl (1b)⁵¹ were prepared as described in the literature.
1.2 Synthesis of [m–Terphenyl–Si(IME$_4$)$_2$–MCl]X (2a, 3a, 4a)

General procedure:

$[m$-Terphenyl-$Si(IME_4)_2]Cl$ (1a) (100.0 mg, 159.9 μmol, 1.0 eq) was dissolved in 3 mL acetonitrile and the coinage metal precursor (CuCl (2a)/AgOTf (3a)/(SMe$_2$)AuCl (4a), 159.9 μmmol, 1.0 eq) was added in one portion at room temperature while stirring (under exclusion of light for 3a). After stirring for 5 minutes the solution was filtered, concentrated under vacuum until incipient precipitation and Et$_2$O (4-5 mL) was added. After storing the solution at –40 °C for 48 hours the microcrystalline precipitate was collected by filtration, washed with Et$_2$O (2 × 2 mL) and after drying under vacuum the products 2a, 3a and 4a were obtained as colorless air-, (light-) and moisture-sensitive solids. The compounds are stable in the solid state and in acetonitrile solution at room temperature but decompose slowly upon heating to 90 °C in acetonitrile.
[m-Terphenyl–Si(IME$_4$)$_2$–CuCl]Cl (2a)

Yield = 92%.

Single crystals suitable for XRD analysis were obtained by slow diffusion of Et$_2$O into a concentrated acetonitrile solution of 2a at –40 °C.

$^1$H NMR (400 MHz, CD$_3$CN, 300 K): δ [ppm] = 7.63 (t, $J = 7.6$ Hz, 1H, C$_{ar}$H$_{para}$), 7.14, (d, $J = 7.6$ Hz, 2H, C$_{ar}$H$_{meta}$), 6.80 (bs, 4H, C$_{mes}$H), 3.73 (bs, 6H, N$_NNHCCH_3$), 2.89 (bs, 6H, N$_NNHCCH_3$), 2.19 (s, 6H, C$_{mes}$CH$_3$para), 2.06 (bs, 24H, C$_{mes}$CH$_3$,ortho + C$_{NHCCH_3}$).


$^{29}$Si NMR (99 MHz, CD$_3$CN, 300 K): δ [ppm] = –46.6.

EA: C$_{38}$H$_{49}$CuCl$_2$N$_4$Si calculated: C (63.01), H (6.82), N (7.73).

measure: C (62.85), H (7.13), N (7.49).

ESI-MS: calculated: 687.27 (C$_{38}$H$_{49}$ClCuN$_4$Si$^+$).

measured: 687.2 (2a – Cl$^-$).

M.P.: 125-126 °C (decomposition, color change to orange).

![Fig. S1 $^1$H NMR spectrum of [m-Terphenyl-Si(IME$_4$)$_2$-CuCl]Cl (2a) in CD$_3$CN at 300 K.](image-url)
**Fig. S2** $^{13}$C NMR spectrum of [m-Terphenyl-Si(IME)$_2$-CuCl]Cl (2a) in CD$_3$CN at 300 K.

**Fig. S3** $^{29}$Si NMR spectrum of [m-Terphenyl-Si(IME)$_2$-CuCl]Cl (2a) in CD$_3$CN at 300 K.

**Fig. S4** ESI-MS spectrum (detail view) of 2a (positive mode, 300 °C, −4000 V; line: measured spectrum; bars: simulated spectrum).
Fig. S5 Variable temperature NMR spectra of 2a in CD$_3$CN (bottom: $-40\,^\circ$C, middle: $0\,^\circ$C, top: $+60\,^\circ$C).
[m-Terphenyl–Si(IMe₄)₂–AgCl]OTf (3a)

Yield = 86%.

Single crystals suitable for XRD analysis were obtained by slow diffusion of Et₂O into a concentrated acetonitrile solution of 3a at -40 °C.

**¹H NMR** (300 MHz, CD₃CN, 300 K): δ [ppm] = 7.66 (t, J = 7.6 Hz, 1H, CarH₉para), 7.16 (d, J = 7.6 Hz, 2H, CarH₉meta), 6.82 (bs, 4H, CmesH), 3.64 (bs, 6H, NNH₂CH₃), 2.83 (bs, 6H, NNH₂CH₃), 2.21 (s, 6H, CmesCH₃para), 2.06 (bs, 24H, CmesCH₃ortho + NNH₂CH₃).

**¹³C NMR** (126 MHz, CD₃CN, 300 K): δ [ppm] = 151.3, 150.4, 150.3, 140.4, 138.6, 136.1, 133.6, 133.5, 132.2, 132.1, 130.6, 129.6, 36.5, 35.9, 22.8, 21.5, 21.2, 9.2.

**²⁹Si NMR** (99 MHz, CD₃CN, 300 K): δ [ppm] = -44.1 (d, JSiAg = 352.6 Hz), -44.1 (d, JSiAg = 408.1 Hz).

**EA:** C₃₉H₄₉AgClF₃N₄O₃Si calculated: C (53.09), H (5.60), N (6.35), S (3.63).

measured: C (53.41), H (5.70), N (6.40), S (3.41).

**ESI-MS:** calculated: 731.25 (C₃₈H₄₉ClAgN₄Si⁺).

measured: 731.2 (3a – Cl⁻).

**M.P.:** 170–171 °C (decomposition, color change to black).

![Fig. S6 ¹H NMR spectrum of [m-Terphenyl–Si(IMe₄)₂–AgCl]OTf (3a) in CD₃CN at 300 K.](image)
Fig. S7 $^{13}$C NMR spectrum of [m-Terphenyl-Si(IMe$_4$)$_2$-AgCl]OTf (3a) in CD$_3$CN at 300 K.

Fig. S8 $^{29}$Si NMR spectrum of [m-Terphenyl-Si(IMe$_4$)$_2$-AgCl]OTf (3a) in CD$_3$CN at 300 K.
Fig. S9 ESI-MS spectrum (detail view) of 3a (positive mode, 300 °C, −4000 V; line: measured spectrum; bars: simulated spectrum).
[m–Terphenyl–Si(IMe$_4$)$_2$–AuCl]Cl (4a)

Yield = 94%.

Single crystals suitable for XRD analysis were obtained by slow diffusion of Et$_2$O into a concentrated acetonitrile solution of 4a at –40 °C.

$^1$H NMR (400 MHz, CD$_3$CN, 300 K): $\delta$ [ppm] = 7.68 (t, $J$ = 7.6 Hz, 1H, C$_{ar}$H$_{para}$), 7.17 (d, $J$ = 7.6 Hz, 2H, C$_{ar}$H$_{meta}$), 6.80 (s, 4H, C$_{mes}$H), 3.89 (bs, 6H, N$_{NHC}$CH$_3$), 2.81 (bs, 6H, N$_{NHC}$CH$_3$), 2.20 (s, 6H, C$_{mes}$CH$_3$), 2.08 (bs, 24H, C$_{mes}$CH$_3$,ortho + C$_{NHC}$CH$_3$).

$^{13}$C NMR (126 MHz, CD$_3$CN, 300 K): $\delta$ [ppm] = 151.5, 148.6, 140.7, 138.4, 132.7, 132.6, 131.1, 129.5, 129.2, 37.4, 36.1, 23.0, 21.8, 21.2, 17.9, 9.3.

$^{29}$Si NMR (79 MHz, CD$_3$CN, 300 K): $\delta$ [ppm] = –34.6.

EA: C$_{38}$H$_{49}$Cl$_2$AuN$_4$Si calculated: C (53.21), H (5.76), N (6.53).

measured: C (52.99), H (5.86), N (6.42).

ESI-MS: calculated: 821.31 ([C$_{38}$H$_{49}$ClAuN$_4$Si]$^+$).

measured: 821.3 (4a – Cl$^-$).

M.P.: 234–235 °C (decomposition, color change to dark red).

Fig. S10 $^1$H NMR spectrum of [m-Terphenyl–Si(IMe$_4$)$_2$–AuCl]Cl (4a) in CD$_3$CN at 300 K.
Fig. S11 $^{13}$C NMR spectrum of [m-Terphenyl-Si(IMe$_4$)$_2$-AuCl]Cl (4a) in CD$_3$CN at 300 K.

Fig. S12 $^{29}$Si NMR spectrum of [m-Terphenyl-Si(IMe$_4$)$_2$-AuCl]Cl (4a) in CD$_3$CN at 300 K.
**Fig. S13** ESI-MS spectrum (detail view) of 4a (positive mode, 300 °C, −4500 V; line: measured spectrum; bars: simulated spectrum).
1.3 Synthesis of \([\text{Tipp–Si(IMe}_4\text{)}_2–\text{MCl}]\text{X (2b, 3b, 4b)}\)

General procedure:

\([\text{Tipp–Si(IMe}_4\text{)}_2\text{]}\text{Cl (1b) (50.0 mg, 97.1 \mu mol, 1.0 eq) was dissolved in 1.5 mL acetonitrile and cooled to –40 °C. The coinage metal precursor (MX = CuCl (2b)/AgOTf (3b)/(SMe}_2\text{)}\text{AuCl (4b), 97.1 \mu mol, 1.0 eq) was added in one portion while stirring (under exclusion of light for 3b). The solution was quickly filtered and Et}_2\text{O (10 mL) was added to precipitate a colorless solid. The solid was collected by filtration, washed with Et}_2\text{O (2 × 2 mL) and after drying under vacuum the products 2b and 3b were obtained as colorless air-, (light-), moisture-sensitive solids. The complexes are stable in the solid state but decompose rapidly in solution. Due to the rapid decomposition, no satisfactory analytical data could be obtained for complex 4b.}

\[
\begin{array}{c|cc}
2b & Cu & Cl \\
3b & Ag & OTf \\
4b & Au & Cl \\
\end{array}
\]
[Tipp–Si(IME₄)₂–CuCl]Cl (2b)

Yield = 71%.

¹H NMR (500 MHz, CD₃CN, 300 K): δ [ppm] = 7.12 (s, 2H, Caryl), 3.60 (hept, J = 6.8 Hz, 2H, CorthoH(CH₃)₂), 3.55 (s, 12H, NNHCCH₃), 2.88 (hept, J = 6.9 Hz, 1H, CparaH(CH₃)₂), 2.20 (s, 12H, CNHCCH₃), 1.22 (d, J = 6.9 Hz, 6H, CparaH(CH₃)₂), 1.02 (d, J = 6.8 Hz, 12H, CorthoH(CH₃)₂).

¹³C NMR (126 MHz, CD₃CN, 300 K): δ [ppm] = 157.4, 153.6, 152.2, 129.9, 129.2, 123.3, 36.4, 35.0, 34.8, 25.0, 24.0, 9.2.

²⁹Si NMR (99 MHz, CD₃CN, 300 K): δ [ppm] = -48.8.

EA: C₂₉H₄₇Cl₂CuN₄Si calculated: C (56.71), H (7.71), N (9.12).

measured: C (56.89), H (7.92), N (9.01).

M.P.: 132-134 °C (decomposition, color change to yellow-orange).

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Fig. S14 ¹H NMR spectrum of [Tipp–Si(IME₄)₂–CuCl]Cl (2b) in CD₃CN at 300 K. Residual C₆H₆ (7.36 ppm) stems from the crystallization of starting material 1b. NMR spectra were recorded immediately after mixing the starting materials due to rapid decomposition.
Fig. S15 $^{13}$C NMR spectrum of [Tipp-Si(IMes)$_2$-CuCl]Cl (2b) in CD$_3$CN at 300 K.

Fig. S16 $^{29}$Si NMR spectrum of [Tipp-Si(IMes)$_2$-CuCl]Cl (2b) in CD$_3$CN at 300 K.
[Tipp–Si(IMe₄)₂–AgCl]OTf (3b)

Single crystals suitable for XRD analysis were obtained by slow diffusion of Et₂O into a concentrated solution of 3b in acetonitrile:toluene (2:1) at −40 °C.

Yield = 89%.

¹H NMR (500 MHz, CD₃CN, 300 K): δ [ppm] = 7.16 (s, 2H, Caryl), 3.49 (s, 12H, NHC₃H₃), 3.29 (hept, J = 6.8 Hz, 2H, CorthoH(CH₃)₂), 2.90 (hept, J = 6.9 Hz, 1H, CparaH(CH₃)₂), 2.21 (s, 12H, CNHC₃H₃), 1.23 (d, J = 6.9 Hz, 6H, CparaH(CH₃)₂), 1.05 (d, J = 6.7 Hz, 12H, CorthoH(CH₃)₂).

¹³C NMR (126 MHz, CD₃CN, 300 K): δ [ppm] = 157.1, 153.4, 150.4, 131.0, 127.1, 123.9, 122.0 (q, JCF = 321.0 Hz) 36.7, 34.8, 35.1, 24.8, 23.9, 9.1.

²⁹Si NMR (99 MHz, CD₃CN, 300 K): δ [ppm] = −46.6 (d, ¹JSiAg = 355.8 Hz), −46.6 (d, ¹JSiAg = 410.1 Hz).

EA: C₃₀H₄₇AgClF₃N₄O₃Si calculated: C (46.66), H (6.14), N (7.26), S (4.15).

measured: C (46.29), H (5.99), N (7.38), S (4.04).

M.P.: 190-191 °C (decomposition, color change to black).

![Fig. S17](image-url) ¹H NMR spectrum of [Tipp–Si(IMe₄)₂–AgCl]OTf (3b) in CD₃CN at 300 K. Residual C₆H₆ (7.36 ppm) stems from the crystallization of starting material 1b. NMR spectra were recorded immediately after mixing the starting materials due to rapid decomposition.
Fig. S18 $^{13}$C NMR spectrum of [Tipp-Si(IMe$_4$)-AgCl]OTf (3b) in CD$_3$CN at 300 K.

Fig. S19 $^{29}$Si NMR spectrum of [Tipp-Si(IMe$_4$)-AgCl]OTf (3b) in CD$_3$CN at 300 K.
[Tipp–Si(IMe$_4$)$_2$–AuCl]Cl (4b)

$^1$H NMR (500 MHz, CD$_3$CN, 300 K): $\delta$ [ppm] = 7.19 (s, 2H, C$_{ar}$H), 3.63 (s, 12H, N$_{NHC}$CH$_3$), 3.38 (hept, $J = 6.7$ Hz, 2H, C$_{ortho}$H(CH$_3)_2$), 2.90 (hept, $J = 6.8$ Hz, 1H, C$_{para}$H(CH$_3)_2$), 2.24 (s, 12H, C$_{NHC}$CH$_3$), 1.23 (d, $J = 6.7$ Hz, 6H, C$_{para}$H(CH$_3)_2$), 1.06 (d, $J = 6.8$ Hz, 12H, C$_{ortho}$H(CH$_3)_2$).

CH groups of the iPr-substituents of 4b overlap with CH groups of the iPr substituents of the decomposition products.

$^{29}$Si NMR (99 MHz, CD$_3$CN, 300 K): $\delta$ [ppm] = −38.0.

Fig. S20 $^1$H NMR spectrum of [Tipp–Si(IMe$_4$)$_2$–AuCl]Cl (4b) in CD$_3$CN at 300 K. Residual C$_6$H$_6$ (7.36 ppm) stems from the crystallization of starting material 1b. NMR spectra were recorded immediately after dissolution of the complex. Because of the rapid decomposition even at low temperature, no satisfactory NMR data was obtained. Decomposition products are marked with *.

Fig. S21 $^{29}$Si NMR spectrum of [Tipp–Si(IMe$_4$)$_2$–AuCl]Cl (4b) in CD$_3$CN at 300 K. Beginning decomposition is marked with *.
1.4 Decomposition of 4b

Fig. S22 $^1$H NMR spectra of [Tipp-Si(IMe$_4$)$_2$-AuCl]Cl (4b) after 5 minutes, 30 minutes, 1 hour and 4 hours. Initially fast formation of intermediate decomposition products can be observed that slowly change to the final product mixture. After around 3 hours no further changes could be observed. (cf. Fig. S23 for detailed view)
Fig. S23 Detailed look at the changing signals observed in the $^1$H NMR spectra of [Tipp-Si[IMe$_4$]$_2$-AuCl]Cl (4b) after 5 minutes, 30 minutes, 1 hour and 4 hours (left: $C_2H$ region, middle: $N_{Het}CH_3$ and $CH(CH_3)_2$ region, right: $C_{Het}CH_3$ region).

Fig. S24 $^{29}$Si NMR spectrum of [Tipp-Si[IMe$_4$]$_2$-AuCl]Cl (4b) and thermal decomposition in CD$_3$CN at 300 K immediately after mixing of the starting materials (top) and after complete decomposition (bottom). Signals at $-38.0$ (4b) and intermediates (8.4 & 1.4 ppm) vanish completely over a period of 4 hours and signals at $+40.5$ and $+64.0$ emerge.
Fig. S25 $^1$H/$^{29}$Si HMBC NMR spectrum of the decomposition products of complex 4b. Clear correlation between the minor species in the $^1$H NMR and the Si resonance at +40.5 ppm as well as the major species in the $^1$H NMR and the Si resonance at +64.0 ppm can be observed. Signals corresponding to [(IMe$_4$)Au]Cl are marked with *. (cf. Fig. S26).
$[(\text{IMe}_4)_2\text{Au}]\text{Cl}$

$^1\text{H NMR (500 MHz, CD}_3\text{CN, 300 K)}$: $\delta$ [ppm] = 3.73 (s, 6H, NCH$_3$), 2.16 (s, 6H, CCH$_3$).

$^{13}\text{C NMR (126 MHz, CD}_3\text{CN, 300 K)}$: $\delta$ [ppm] = 183.0, 127.1, 35.8, 9.0.

EA: $(\text{C}_{14}\text{H}_{24}\text{AuClN}_4)$ calculated: C (34.97), H (5.03), N (11.65).

measured: C (34.84), H (5.24), N (11.73).

Fig. S26 $^1\text{H NMR spectrum of } [(\text{IMe}_4)_2\text{Au}]\text{Cl (5)} \text{ in CD}_3\text{CN at 300 K}$.

Fig. S27 $^{13}\text{C NMR spectrum of } [(\text{IMe}_4)_2\text{Au}]\text{Cl (5)} \text{ in CD}_3\text{CN at 300 K}$.
2. X-ray Crystallographic Data

General Information

The X-ray intensity data of 4a was collected on an X-ray single crystal diffractometer equipped with a CMOS detector (Bruker Photon-100), an IMS microsource with MoKα radiation (λ = 0.71073 Å) and a Helios mirror optic by using the APEX III software package. The X-ray intensity data of 2a, 3a, 3b and 5 were collected on an X-ray single crystal diffractometer equipped with a CMOS detector (Bruker Photon-100), a rotating anode (Bruker TXS) with MoKα radiation (λ = 0.71073 Å) and a Helios mirror optic by using the APEX III software package. The measurements were performed on single crystals coated with the perfluorinated ether Fomblin® Y. The crystals were fixed on the top of a micro sampler, transferred to the diffractometer and frozen under a stream of cold nitrogen. A matrix scan was used to determine the initial lattice parameters. Reflections were merged and corrected for Lorenz and polarization effects, scan speed, and background using SAINT. Absorption corrections, including odd and even ordered spherical harmonics were performed using SADABS. Space group assignments were based upon systematic absences, E statistics, and successful refinement of the structures. Structures were solved by direct methods with the aid of successive difference Fourier maps, and were refined against all data using the APEX III software in conjunction with SHELXL-2014 and SHELXLE. All H atoms were placed in calculated positions and refined using a riding model, with methylene and aromatic C–H distances of 0.99 and 0.95 Å, respectively, and $U_{iso}(H) = 1.2 \cdot U_{eq}(C)$. Full-matrix least-squares refinements were carried out by minimizing $\Delta w(F_o^2 - F_c^2)^2$ with SHELXL-97 weighting scheme. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from International Tables for Crystallography. The images of the crystal structures were generated by Mercury. The CCDC numbers CCDC-1870254 (2a), CCDC-1870256 (3a), CCDC-1870258 (3b), CCDC-1870255 (4a) and CCDC-1870257 (5) contain the supplementary crystallographic data for the structures. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/structures/.
2.1 SC-XRD structure of \([m\text{-}\text{Ter}–\text{Si}$(\text{IME}_4)_2$–\text{Cu}]\text{Cl} \ (2a)\)

![Ellipsoid plot (50% probability level) of the molecular structures of complex 2a.](image)

Fig. S28 Ellipsoid plot (50% probability level) of the molecular structures of complex 2a. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1–C1 1.916(3), Si1–C25 1.939(2), Si1–C32 1.938(2), Si1–Cu1 2.238(2), Cu1–Cl1 2.1477(6), Si1–Cu1–Cl1 169.3(1), C25–Si1–C32 95.5(2), C1–Si1–Cu1 119.4(2).

2.2 SC-XRD structure of \([m\text{-}\text{Ter}–\text{Si}$(\text{IME}_4)_2$–\text{Ag}]\text{ClO}_4 \ (3a)\)

![Ellipsoid plot (50% probability level) of the molecular structures of complex 3a.](image)

Fig. S29 Ellipsoid plot (50% probability level) of the molecular structures of complex 3a. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1–C1 1.911(4), Si1–C25 1.936(3), Si1–C32 1.938(4), Si1–Ag1 2.379(1), Ag1–Cl1 2.366(1), Si1–Ag1–Cl1 171.8(1), C25–Si1–C32 95.8(1), C1–Si1–Ag1 114.8(1).
2.3 SC-XRD structure of $[m$-Ter–Si(IME)$_4$–AuCl]Cl (4a)

![Diagram of complex 4a](image.png)

Fig. S30 Ellipsoid plot (50% probability level) of the molecular structures of complex 4a. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1–C1 1.916(2), Si1–C25 1.942(2), Si1–C32 1.941(2), Si1–Au1 2.281(1), Au1–Cl1 2.354(1), Si1–Au1–Cl1 176.8(1), C25–Si1–C32 96.5(1), C1–Si1–Au1 119.0(1).

2.4 SC-XRD structure of $[[Tipp–Si(IME)$_4$–AgCl]OTf]_2$ (3b)

![Diagram of complex 3b](image.png)

Fig. S31 Ellipsoid plot (50% probability level) of the molecular structure of complex 3b. Hydrogen atoms are omitted for clarity. Only one triflate anion is shown and the Tipp substituents are depicted as wireframes. Selected bond lengths [Å] and angles [°]: Si1–C1 1.919(2), Si1–C16 1.935(2), Si1–C23 1.931(2), Si1–Ag1 2.398(1), Ag1–Cl1 2.562(1), Si1–Ag1–Cl1 141.2(1), C16–Si1–C23 100.8(1), C1–Si1–Ag1 118.0(1).
2.5 SC-XRD structure of [(IMe$_4$)$_2$Au]Cl (5)

Fig. S32 Ellipsoid plot (50% probability level) of the molecular structure of complex 5. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Au1–C1 2.030(4), Au1–C8 2.022(4), C1–Au–C8 176.9(2).
Table S1 Crystal data and structural refinement parameters for compounds 2a, 3a, 3b, 4a and 5.

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<th>3b</th>
<th>4a</th>
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<td>100(2) K</td>
<td>100(2) K</td>
<td>100(2) K</td>
<td>100(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
<td>0.161 Å</td>
<td>0.164 Å</td>
<td>0.170 Å</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.106 × 0.146 × 0.218 mm</td>
<td>0.182 mm</td>
<td>0.184 mm</td>
<td>0.245 mm</td>
<td>0.209 mm</td>
</tr>
<tr>
<td>Unit cell</td>
<td>monoclinic</td>
<td>monoclinic</td>
<td>monoclinic</td>
<td>monoclinic</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P 1</td>
<td>C 1 2/c 1</td>
<td>P 1</td>
<td>P 1</td>
<td>P 1</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.223 g/cm³</td>
<td>1.324 g/cm³</td>
<td>2.385 g/cm³</td>
<td>1.494 g/cm³</td>
<td>1.785 g/cm³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.715 mm⁻¹</td>
<td>0.594 mm⁻¹</td>
<td>3.713 mm⁻¹</td>
<td>3.713 mm⁻¹</td>
<td>7.722 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>800</td>
<td>4000</td>
<td>900</td>
<td>952</td>
<td>1016</td>
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<tr>
<td>Diffractometer</td>
<td>Bruker D8 Venture</td>
<td>Bruker D8 Venture</td>
<td>Bruker D8 Venture</td>
<td>Bruker D8 Venture</td>
<td>Bruker D8 Venture</td>
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<tr>
<td>Radiation source</td>
<td>TXS rotating anode (Mo)</td>
<td>TXS rotating anode (Mo)</td>
<td>TXS rotating anode (Mo)</td>
<td>TXS rotating anode (Mo)</td>
<td>TXS rotating anode (Mo)</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>2.21 to 25.68°</td>
<td>2.21 to 25.68°</td>
<td>2.27 to 25.35°</td>
<td>2.20 to 25.35°</td>
<td>2.15 to 25.68°</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-14&lt;=h&lt;=14, all data: R1 = 0.0138, wR2 = 0.0346</td>
<td>-34&lt;=h&lt;=34, all data: R1 = 0.0389, wR2 = 0.0832</td>
<td>-18&lt;=l&lt;=18, all data: R1 = 0.0403, wR2 = 0.0698</td>
<td>-11&lt;=l&lt;=11, all data: R1 = 0.0610, wR2 = 0.1024</td>
<td>-18&lt;=l&lt;=18, all data: R1 = 0.0610, wR2 = 0.1024</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>73871 [R(int) = 0.0633]</td>
<td>9197 [R(int) = 0.0734]</td>
<td>12800 [R(int) = 0.0857]</td>
<td>16395 [R(int) = 0.0935]</td>
<td>12800 [R(int) = 0.0857]</td>
</tr>
<tr>
<td>Coverage of independent reflections</td>
<td>100.0%</td>
<td>100.0%</td>
<td>100.0%</td>
<td>100.0%</td>
<td>100.0%</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Multi-Scan</td>
<td>Multi-Scan</td>
<td>Multi-Scan</td>
<td>Multi-Scan</td>
<td>Multi-Scan</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.6820 and 0.7461</td>
<td>0.6782 and 0.7454</td>
<td>0.7063 and 0.7464</td>
<td>0.7063 and 0.7464</td>
<td>0.4181 and 0.7454</td>
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<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
<td>Full-matrix least-squares on F²</td>
<td>Full-matrix least-squares on F²</td>
<td>Full-matrix least-squares on F²</td>
<td>Full-matrix least-squares on F²</td>
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<td>Refinement program</td>
<td>SHELXL-2014/7</td>
<td>SHELXL-2014/7</td>
<td>SHELXL-2014/7</td>
<td>SHELXL-2014/7</td>
<td>SHELXL-2014/7</td>
</tr>
<tr>
<td>Function minimized</td>
<td>Σ w F² - F²</td>
<td>Σ w f² - f²</td>
<td>Σ w F² - F²</td>
<td>Σ w F² - F²</td>
<td>Σ w F² - F²</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>7896 / 0 / 458</td>
<td>9197 / 0 / 548</td>
<td>8606 / 0 / 512</td>
<td>97351</td>
<td>7652 / 75 / 514</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.025</td>
<td>1.065</td>
<td>1.061</td>
<td>1.100</td>
<td>1.006</td>
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<tr>
<td>Δ/σmax</td>
<td>0.001</td>
<td>0.001</td>
<td>0.002</td>
<td>0.006</td>
<td>0.001</td>
</tr>
<tr>
<td>Final R indices</td>
<td>6967 data; 1720(7): R1 = 0.0326, wR2 = 0.0801</td>
<td>7530 data; 1720(7): R1 = 0.0403, wR2 = 0.0951</td>
<td>7908 data; 1720(7): R1 = 0.0261, wR2 = 0.0823</td>
<td>7541 data; 1720(7): R1 = 0.0135, wR2 = 0.0344</td>
<td>6833 data; 1720(7): R1 = 0.0255, wR2 = 0.0698</td>
</tr>
<tr>
<td>Weighting scheme</td>
<td>all data: R1 = 0.0389, wR2 = 0.0832</td>
<td>all data: R1 = 0.0559, wR2 = 0.1024</td>
<td>all data: R1 = 0.0289, wR2 = 0.0640</td>
<td>all data: R1 = 0.0289, wR2 = 0.0346</td>
<td>all data: R1 = 0.0273, wR2 = 0.0711</td>
</tr>
<tr>
<td>R.m.s. deviation from mean</td>
<td>0.763 and -0.374 e Å⁻³</td>
<td>1.012 and -0.678 e Å⁻³</td>
<td>0.807 and -0.630 e Å⁻³</td>
<td>0.305 and -0.745 e Å⁻³</td>
<td>2.385 and -0.961 e Å⁻³</td>
</tr>
</tbody>
</table>

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3. References

S2  APEX suite of crystallographic software, APEX 3 version 2015.5-2; Bruker AXS Inc.: Madison, Wisconsin, USA, 2015.