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-*d*₃ were refluxed over CaH₂, distilled under argon, deoxygenated by three freezepump-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 ($\delta = 0$ 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**)^{S1} and $[Tipp-Si(IMe_4)_2]Cl$ (**1b**)^{S1} were prepared as described in the literature.

1.2 Synthesis of [m–Terphenyl–Si(IMe₄)₂–MCl]X (2a, 3a, 4a)



General procedure:

[*m*-Terphenyl-Si(IMe₄)₂]Cl (**1a**) (100.0 mg, 159.9 μ mol, 1.0 eq) was dissolved in 3 mL acetonitrile and the coinage metal precursor (CuCl (**2a**)/AgOTf (**3a**)/(SMe₂)AuCl (**4a**), 159.9 μ mmol, 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 Et₂O (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_2O (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(IMe₄)₂-CuCl]Cl (2a)

Yield = 92%.

Single crystals suitable for XRD analysis were obtained by slow diffusion of Et_2O into a concentrated acetonitrile solution of **2a** at -40 °C.

¹H NMR (400 MHz, CD₃CN, 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_{NHC}CH₃), 2.89 (bs, 6H, N_{NHC}CH₃), 2.19 (s, 6H, C_{mes}CH_{3,para}), 2.06 (bs, 24H, C_{mes}CH_{3,ortho} + C_{NHC}CH₃).

¹³C NMR (126 MHz, CD₃CN, 300 K): δ [ppm] = 150.7, 150.4, 140.5, 138.1, 135.7, 134.7, 131.7, 131.7, 130.4, 129.8, 129.2, 36.3, 22.8, 21.4, 21.1, 9.2.

²⁹Si NMR (99 MHz, CD₃CN, 300 K): δ [ppm] = -46.6.

EA: C₃₈H₄₉CuCl₂N₄Si calculated: C (63.01), H (6.82), N (7.73). measured: C (62.85), H (7.13), N (7.49).

ESI-MS: calculated: 687.27 (C₃₈H₄₉ClCuN₄Si⁺).

measured: 687.2 (**2a** – Cl[−]).

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







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 CD₃CN (bottom: −40 °C, middle: 0 °C, top: +60 °C).

[m-Terphenyl-Si(IMe₄)₂-AgCl]OTf (3a)

Yield = 86%.

Single crystals suitable for XRD analysis were obtained by slow diffusion of Et_2O into a concentrated acetonitrile solution of **3a** at -40 °C.

¹**H NMR** (300 MHz, CD₃CN, 300 K): δ [ppm] = 7.66 (t, *J* = 7.6 Hz, 1H, C_{ar}*H*_{para}), 7.16 (d, *J* = 7.6 Hz, 2H, C_{ar}*H*_{meta}), 6.82 (bs, 4H, C_{mes}*H*), 3.64 (bs, 6H, N_{NHC}CH₃), 2.83 (bs, 6H, N_{NHC}CH₃), 2.21 (s, 6H, C_{mes}CH_{3,para}), 2.06 (bs, 24H, C_{mes}CH_{3,ortho} + C_{NHC}CH₃).

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, ¹J_{SiAg} = 352.6 Hz), -44.1 (d, ¹J_{SiAg} = 408.1 Hz).

EA: C₃₉H₄₉AgClF₃N₄O₃SSi 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 ($C_{38}H_{49}CIAgN_4Si^+$).

measured: 731.2 (**3a** – Cl[–]).

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





Fig. S7 ¹³C NMR spectrum of [m-Terphenyl-Si(IMe₄)₂-AgCl]OTf (3a) in CD₃CN 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(IMe₄)₂-AuCl]Cl (4a)

Yield = 94%.

Single crystals suitable for XRD analysis were obtained by slow diffusion of Et_2O into a concentrated acetonitrile solution of **4a** at -40 °C.

¹H NMR (400 MHz, CD₃CN, 300 K): δ [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}CH₃), 2.81 (bs, 6H, N_{NHC}CH₃), 2.20 (s, 6H, C_{mes}CH_{3,para}), 2.08 (bs, 24H, C_{mes}CH_{3,ortho} + C_{NHC}CH₃).

¹³C NMR (126 MHz, CD₃CN, 300 K): δ [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.

²⁹Si NMR (79 MHz, CD₃CN, 300 K): δ [ppm] = -34.6.

EA: C₃₈H₄₉Cl₂AuN₄Si 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 ($C_{38}H_{49}CIAuN_4Si^+$).

measured: 821.3 (**4a** – Cl[−]).

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













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 [Tipp-Si(IMe₄)₂-MCI]X (2b, 3b, 4b)



General procedure:

[Tipp-Si(IMe₄)₂]Cl (**1b**) (50.0 mg, 97.1 μ 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**)/(SMe₂)AuCl (**4b**), 97.1 μ mol, 1.0 eq) was added in one portion while stirring (under exclusion of light for **3b**). The solution was quickly filtered and Et₂O (10 mL) was added to precipitate a colorless solid. The solid was collected by filtration, washed with Et₂O (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**.

[Tipp-Si(IMe₄)₂-CuCl]Cl (2b)

Yield = 71%.

¹H NMR (500 MHz, CD₃CN, 300 K): δ [ppm] = 7.12 (s, 2H, C_{ar}H), 3.60 (hept, J = 6.8 Hz, 2H, C_{ortho}H(CH₃)₂), 3.55 (s, 12H, N_{NHC}CH₃), 2.88 (hept, J = 6.9 Hz, 1H, C_{para}H(CH₃)₂), 2.20 (s, 12H, C_{NHC}CH₃), 1.22 (d, J = 6.9 Hz, 6H, C_{para}H(CH₃)₂), 1.02 (d, J = 6.8 Hz, 12H, C_{ortho}H(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).



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.



[Tipp-Si(IMe₄)₂-AgCl]OTf (3b)

Single crystals suitable for XRD analysis were obtained by slow diffusion of Et_2O into a concentrated solution of **3b** in acetonitrile:toluene (2:1) at -40 °C.

Yield = 89%.

¹**H NMR** (500 MHz, CD₃CN, 300 K): δ [ppm] = 7.16 (s, 2H, C_{ar}H), 3.49 (s, 12H, N_{NHC}CH₃), 3.29 (hept, J = 6.8 Hz, 2H, C_{ortho}H(CH₃)₂), 2.90 (hept, J = 6.9 Hz, 1H, C_{para}H(CH₃)₂), 2.21 (s, 12H, C_{NHC}CH₃), 1.23 (d, J = 6.9 Hz, 6H, C_{para}H(CH₃)₂), 1.05 (d, J = 6.7 Hz, 12H, C_{ortho}H(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, ¹J_{CF} = 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, ¹*J*_{SiAg} = 355.8 Hz), -46.6 (d, ¹*J*_{SiAg} = 410.1 Hz). EA: C₃₀H₄₇AgClF₃N₄O₃SSi 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 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 ¹³C NMR spectrum of [Tipp-Si(IMe₄)₂-AgCl]OTf (3b) in CD₃CN at 300 K.



[Tipp-Si(IMe₄)₂-AuCl]Cl (4b)

¹H NMR (500 MHz, CD₃CN, 300 K): δ [ppm] = 7.19 (s, 2H, C_{ar}H), 3.63 (s, 12H, N_{NHC}CH₃), 3.38 (hept, J = 6.7 Hz, 2H, C_{ortho}H(CH₃)₂), 2.90 (hept, J = 6.8 Hz, 1H, C_{para}H(CH₃)₂), 2.24 (s, 12H, C_{NHC}CH₃), 1.23 (d, J = 6.7 Hz, 6H, C_{para}H(CH₃)₂), 1.06 (d, J = 6.8 Hz, 12H, C_{ortho}H(CH₃)₂).

CH groups of the 'Pr-substituents of **4b** overlap with CH groups of the 'Pr substituents of the decomposition products. ²⁹Si NMR (99 MHz, CD₃CN, 300 K): δ [ppm] = -38.0.



Fig. S20 ¹H NMR spectrum of [Tipp-Si(IMe₄)₂-AuCl]Cl (**4b**) in CD₃CN at 300 K. Residual C₆H₆ (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 *.



180 160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 **Fig. S21** ²⁹Si NMR spectrum of [Tipp-Si(IMe₄)₂-AuCl]Cl (**4b**) in CD₃CN at 300 K. Beginning decomposition is marked with *.

1.4 Decomposition of 4b



Fig. S22 ¹H NMR spectra of [Tipp-Si(IMe₄)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 ¹H NMR spectra of [Tipp-Si(IMe₄)₂-AuCl]Cl (**4b**) after 5 minutes, 30 minutes, 1 hour and 4 hours (left: $C_{ar}H$ region, middle: $N_{NHC}CH_3$ and $CH(CH_3)_2$ region, right: $C_{NHC}CH_3$ region).

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110	100	90	80	70	60	50	40	30	20	10	0	-10	-20	-30	-40	-50	-60	-70	-80	-90	-1

Fig. S24 ²⁹Si NMR spectrum of [Tipp-Si(IMe₄)₂-AuCl]Cl (**4b**) and thermal decomposition in CD₃CN 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 [(IMe₄)₂Au]Cl are marked with * (*cf.* Fig. S26).

[(IMe₄)₂Au]Cl

¹H NMR (500 MHz, CD₃CN, 300 K): δ [ppm] = 3.73 (s, 6H, NCH₃), 2.16 (s, 6H, CCH₃). ¹³C NMR (126 MHz, CD₃CN, 300 K): δ [ppm] = 183.0, 127.1, 35.8, 9.0. EA: (C₁₄H₂₄AuClN₄) calculated: C (34.97), H (5.03), N (11.65). measured: C (34.84), H (5.24), N (11.73).



20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -: Fig. S27 ¹³C NMR spectrum of [(IMe₄)₂Au]Cl (5) in CD₃CN 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 MoK α radiation (λ = 0.71073 Å) and a Helios mirror optic by using the APEX III software package.⁵² 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 MoK α radiation (λ = 0.71073 Å) and a Helios mirror optic by using the APEX III software package.⁵² 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.^{S3} Absorption corrections, including odd and even ordered spherical harmonics were performed using SADABS.⁵³ 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-2014⁵⁴ and SHELXLE.⁵⁵ 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 $U_{iso}(H) = 1.2 \cdot U_{eq}(C)$. Fullmatrix least-squares refinements were carried out by minimizing $\Delta w (F_o^2 - F_c^2)^2$ with SHELXL-97 weighting scheme.⁵⁶ Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from International Tables for Crystallography.⁵⁷ The images of the crystal structures were generated by Mercury.^{S8} 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*-Ter–Si(IMe₄)₂–CuCl]Cl (2a)



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*-Ter–Si(IMe₄)₂–AgCl]OTf (3a)



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(IMe₄)₂-AuCl]Cl (4a)



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(IMe₄)₂-AgCl]OTf]₂ (3b)



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 $[(IMe_4)_2Au]CI$ (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.

Compound #	2a	За	3b	4a	5		
Chemical formula	$C_{40}H_{52}Cl_2CuN_5Si$	C43H55AgCIF3N6O3SSi	C ₃₇ H ₅₅ AgClF ₃ N ₄ O ₃ SSi	C ₄₂ H ₅₅ AuCl ₂ N ₆ Si	$C_{32}H_{54}Au_2Cl_2N_{10}$		
Formula weight	765.39 g/mol	964.39 g/mol	864.32	939.88 g/mol	1043.68		
Temperature	100(2) K	100(2) K	100(2) K	100(2) K	100(2) K		
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å		
Crystal size	0.106 × 0.146 × 0.218 mm	0.161 × 0.164 × 0.182 mm	0.084 × 0.194 × 0.245 mm	0.135 × 0.318 × 0.433 mm	0.120 × 0.294 × 0.402 mm		
Crystal habit	clear colorless fragment	clear colorless fragment	clear colorless fragment	clear colorless fragment	clear colorless fragment		
Crystal system	triclinic	monoclinic	triclinic	triclinic	triclinic		
Space group	P -1	C 1 2/c 1	P -1	P -1	P -1		
Unit cell dimensions	a = 11.7503(10) Å, α = 89.784(4)°	a = 28.241(2) Å, α = 90°	a = 9.2078(5) Å, α = 86.901(2)°	a = 11.8414(17) Å, α = 89.739(6)°	a = 9.656(2) Å, α = 76.210(7)°		
	b = 12.5328(11) Å, β = 88.660(4)°	b = 24.601(2) Å, β = 125.378(2)°	b = 15.2562(7) Å, β = 74.733(2)°	b = 12.5689(19) Å, β = 88.886(5)°	b = 10.844(3) Å, β = 79.390(8)°		
	c = 15.2070(14) Å, γ = 68.230(4)°	c = 17.0773(13) Å, γ = 90°	c = 17.3518(8) Å, γ = 74.546(2)°	c = 15.180(2) Å, γ = 68.401(5)°	c = 19.427(5) Å, γ = 88.399(7)°		
Volume	2079(3) ų	9673.8(13) ų	2266.13(19) Å ³	2100.3(8) Å ³	1941.5(8) ų		
Z	2	12	2	4	2		
Density (calculated)	1.223 g/cm ³	1.324 g/cm ³	g/cm ³	1.494 g/cm ³	1.785 g/cm ³		
Absorption coefficient	0.715 mm ⁻¹	0.594 mm ⁻¹	mm ⁻¹	3.713 mm ⁻¹	7.722 mm ⁻¹		
F(000)	808	4000	900	952	1016		
Diffractometer	Bruker D8 Venture	Bruker D8 Venture	Bruker D8 Venture	Bruker D8 Venture Duo IMS	Bruker D8 Venture		
Radiation source	TXS rotating anode (Mo)	TXS rotating anode (Mo)	TXS rotating anode (Mo)	IMS microsource (Mo)	TXS rotating anode (Mo)		
Theta range for data collection	2.21 to 25.68°	2.21 to 25.68°	2.37 to 25.68°	2.20 to 25.35°	2.15 to 25.68°		
Index ranges	-14<=h<=14, -15<=k<=15, -18<=l<=18	-34<=h<=34, -30<=k<=30, -20<=l<=20	-11<=h<=11, -18<=k<=18, -21<=l<=21	-14<=h<=14, -15<=k<=15, -18<=l<=18	-11<=h<=11, -12<=k<=12, -23<=l<=23		
Reflections collected	45489	141925	97351	78718	59756		
Independent reflections	7896 [R(int) = 0.0424]	9197 [R(int) = 0.0734]	8606 [R(int) = 0.0385]	7652 [R(int) = 0.0224]	7387 [R(int) = 0.0633]		
Coverage of independent	00.00/	100.0%	100.0%	00.00/	100.00/		
reflections	99.9%	100.0%	100.0%	99.9%	100.0%		
Absorption correction	Multi-Scan	Multi-Scan	Multi-Scan	Multi-Scan	Multi-Scan		
Max. and min. transmission	0.6820 and 0.7461	0.6782 and 0.7454	0.5713 and 0.7464	0.7063 and 0.7466	0.4181 and 0.7454		
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²		
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)	SHELXL-2014/7 (Sheldrick, 2014)	SHELXL-2014/7 (Sheldrick, 2014)	SHELXL-2014/7 (Sheldrick, 2014)	SHELXL-2014/7 (Sheldrick, 2014)		
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	$\Sigma w(F_o^2 - F_c^2)^2$	$\Sigma w(F_o^2 - F_c^2)^2$	$\Sigma w(F_o^2 - F_c^2)^2$	$\Sigma w(F_o^2 - F_c^2)^2$		
Data / restraints / parameters	7896 / 0 / 458	9197 / 0 / 548	8606 / 0 / 512	7652 / 75 / 514	7387 / 0 / 434		
Goodness-of-fit on F ²	1.025	1.065	1.061	1.100	1.066		
Δ/σmax	0.001	0.001	0.002	0.006	0.001		
Final R indices	6967 data; I>2σ(I): R1 = 0.0326,	7530 data; I>2σ(I): R1 = 0.0403,	7908 data; I>2σ(I): R1 = 0.0261,	7541 data; I>2σ(I): R1 = 0.0135,	6833 data; I>2σ(I): R1 = 0.0255,		
	wR2 = 0.0801	wR2 = 0.0951	wR2 = 0.0625	wR2 = 0.0344	wR2 = 0.0698		
	all data: R1 = 0.0389, wR2 = 0.0832	all data: R1 = 0.0559, wR2 = 0.1024	all data: R1 = 0.0297, wR2 = 0.0640	all data: R1 = 0.0138, wR2 = 0.0346	all data: R1 = 0.0273, wR2 = 0.0711		
Weighting scheme	w=1/[$\sigma^2(F_o^2)$ +(0.0330P) ² +2.4865P]	$w=1/[\sigma^2(F_o^2)+(0.0483P)^2+33.9538P]$	w=1/[$\sigma^2(F_o^2)$ +(0.0280P) ² +2.1058P]	$w = 1/[\sigma^2(F_o^2)+(0.0171P)^2+1.6279P]$	$w = 1/[\sigma^2(F_o^2)+(0.0411P)^2+2.0259P]$		
	where $P=(F_o^2+2F_c^2)/3$	where $P = (F_0^2 + 2F_c^2)/3$	where $P=(F_o^2+2F_c^2)/3$	where $P=(F_o^2+2F_c^2)/3$	where $P = (F_o^2 + 2F_c^2)/3$		
Largest diff. peak and hole	0.763 and -0.374 eÅ ⁻³	1.012 and -0.678 eÅ ⁻³	0.807 and -0.630 eÅ ⁻³	0.305 and -0.745 eÅ ⁻³	2.385 and -0.961 eÅ ⁻³		
R.M.S. deviation from mean	0.060 eÅ ⁻³	0.088 eÅ ⁻³	0.056 eÅ ⁻³	0.064 eÅ ⁻³	0.154 eÅ ⁻³		

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