Supporting Information

DMAP-stabilized bis(silyl)silylenes as versatile synthons for organosilicon compounds

Richard Holzner,† Dominik Reiter,† Philipp Frisch, and Shigeyoshi Inoue*

Department of Chemistry, WACKER-Institute of Silicon Chemistry, Technische Universität München, Lichtenbergstraße 4, 85748 Garching bei München (Germany) *E-mail: s.inoue@tum.de
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1. Experimental Section

1.1. General Methods and Instrumentation

All manipulations were carried out under exclusion of water and oxygen under an atmosphere of argon 4.6 (≥99.996%) using standard Schlenk and glovebox techniques. The glassware used was heat dried under fine vacuum prior to use. All solvents were refluxed over sodium/benzophenone, freshly distilled under argon and deoxygenated prior to use. PTFE-based grease (Triboflon III from Freudenberg & Co. KG) was used as sealant. Deuterated benzene (C$_6$D$_6$) was obtained from Sigma-Aldrich, dried over Na/K alloy, flask-to-flask condensed, deoxygenated by three freeze-pump-thaw cycles and stored over 3 Å molecular sieves in a glovebox. All NMR samples were prepared under argon in J. Young PTFE valve NMR tubes. The NMR spectra were recorded on a Bruker DRX400 (1H: 400.13 MHz, 13C: 100.62 MHz, 29Si: 79.49 MHz), AV500 (1H: 500.13 MHz) or AV500C (1H: 500.36 MHz, 13C: 125.83 MHz, 29Si: 99.41 MHz) spectrometer at ambient temperature (300 K), unless otherwise stated. The 1H, 13C{1H} and 29Si{1H} NMR spectroscopic chemical shifts δ are reported in ppm relative to tetramethylsilane. 1H and 13C{1H} NMR spectra are calibrated against the residual proton and natural abundance carbon resonances of the respective deuterated solvent as internal standard (C$_6$D$_6$: δ(1H) = 7.16 ppm and δ(13C) = 128.1 ppm).

The following abbreviations are used to describe signal multiplicities: s = singlet, d = doublet, dd = doublet of doublets, m = multiplet, br = broad. In some NMR spectra, signals from silicone oil (C$_6$D$_6$: δ(1H) = 0.29 ppm, δ(13C) = 1.4 ppm and δ(29Si) = -21.8 ppm), originating from the cannulas used (B. Braun Melsungen AG Sterican®), can be observed. EPR spectra were recorded on a Jeol jes-Fa200 esr spectrometer with a spectrometer frequency of 9.267 GHz (X-band). Quantitative elemental analyses (EA) were measured with a EURO EA (HEKAtech) 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. Unless otherwise stated, all commercially available chemicals were purchased from abcr GmbH or Sigma-Aldrich and used without further purification. Hydrogen (H$_2$) 5.0 (≥99.999%) and ethylene 3.5 (≥99.95%) were purchased from Westfalen AG and used as received. The compounds ((TMS)$_3$Si)$_2$SiBr$_2$,[(Bu$_2$MeSi)$_2$SiBr$_2$, (Bu$_3$Si)$_2$SiBr$_2$] and ((TMS)$_2$Si)(Bu$_3$Si)Si—DMAP (1a) were prepared as described in the corresponding references. Potassium graphite (KC$_8$) was synthesized following a literature reported procedure upon heating a 1:8 mixture of potassium and graphite in a thick-walled, PTFE-capped pressurize-able Schlenk flask to 500 °C until a homogenous bronze powder was obtained.
1.2. (tBu₂MeSi)₂Si:—DMAP (1b)

THF (10 mL) was added to a mixture of (tBu₂MeSi)₂SiBr₂ (300 mg, 597 µmol, 1.0 eq.), KC₈ (169 mg, 1.25 mmol, 2.1 eq.) and DMAP (72.9 mg, 597 µmol, 1.0 eq.) at ambient temperature. After stirring for 3 hours, the solvent was removed under reduced pressure and the residue was extracted with toluene (3 × 2 mL) to remove KBr and graphite. The solvent was evaporated in vacuo and compound 1b was obtained as red-brown, crystalline solid (233 mg, 551 µmol, 92%). Crystals suitable for SC-XRD analysis were obtained from a cooled (-35 °C) toluene solution of 1b.

m.p. = 140 °C (decomposition; color change from red-brown to black)

¹H NMR (500 MHz, C₆D₆, 300 K): δ [ppm] = 8.66 (d, ³J = 7.5 Hz, 2H, o-DMAPH), 5.42 (d, ³J = 7.5 Hz, 2H, m-DMAPH), 1.76 (s, 6H, N(CH₃)₂), 1.41 (s, 36H, C(CH₃)₃), 0.42 (s, 6H, Si(CH₃)).

¹³C{¹H} NMR (126 MHz, C₆D₆, 300 K): δ [ppm] = 154.3 (p-DMAP), 153.0 (o-DMAP), 105.2 (m-DMAP), 38.1 (N(CH₃)₂), 31.2 (C(CH₃)₃), 22.9 (Q(CH₃)₃), -3.7 (Si(CH₃)).

²⁹Si{¹H} NMR (99 MHz, C₆D₆, 300 K): δ [ppm] = 61.5 (∑Si), 11.8 (∑/tBu₂Me).

Note: The chemical shifts of DMAP-stabilized silylenes 1 and silaimines 7 are dependent on the concentration of the NMR sample.

EA: Si₃C₂₅H₅₂N₂  Calculated [%]:  C (64.58), H (11.27), N (6.03)
Experimental [%]:  C (64.34), H (11.33), N (5.98)
Fig. S1: $^1$H NMR spectrum (500 MHz) of compound 1b in C$_6$D$_6$ at 300 K.

Fig. S2: $^{13}$C NMR spectrum (126 MHz) of compound 1b in C$_6$D$_6$ at 300 K.
Fig. S3: $^{29}\text{Si}$ NMR spectrum (99 MHz) of compound 1b in C$_6$D$_6$ at 300 K.

Fig. S4: $^1\text{H}/^{29}\text{Si}$ HMBC NMR spectrum of compound 1b in C$_6$D$_6$ at 300 K.
1.3. Bis(hypersilyl)silylene DMAP complex (1c)

THF (10 mL) was added to a mixture of \((\text{TMS})_3\text{Si}_2\text{SiBr}_2\) (300 mg, 439 µmol, 1.0 eq.), KC₈ (125 mg, 922 µmol, 2.1 eq.) and DMAP (53.7 mg, 439 µmol, 1.0 eq.) at ambient temperature. After stirring for 3 hours, the solvent was removed under reduced pressure and the residue was extracted with toluene (3 × 2 mL) to remove KBr and graphite. The solvent was evaporated in vacuo and compound 1c was obtained as dark-brown solid.

Note: During the synthesis of 1c, the concomitant formation of hexakis(trimethylsilyl)trisilirane (4) and Si(TMS)₄ was observed. Therefore, no sample of 1c with sufficient purity for elemental analysis was obtained and the yield was not determined.

\(^1\text{H}\) NMR (500 MHz, C₆D₆, 300 K): \(\delta\) [ppm] = 8.65 (d, \(^3J = 7.1\) Hz, 2H, \(\alpha\)-DMAP-H), 5.67 (d, \(^3J = 6.6\) Hz, 2H, \(m\)-DMAP-H), 1.73 (s, 6H, N(CH₃)₂), 0.48 (s, 54H, Si(CH₃)₃).

\(^{29}\text{Si}(\text{H})\) NMR (99 MHz, C₆D₆, 300 K): \(\delta\) [ppm] = 72.5 (Si), -9.7 (Si(CH₃)₃), -121.8 (Si(TMS)₃).

![Fig. S5: \(^1\text{H}\) NMR spectrum (500 MHz) of compound 1c in C₆D₆ at 300 K. Signals labeled with * and # belong to Si(TMS)₄ and hexakis(trimethylsilyl)trisilirane (4), respectively.](image-url)
Fig. S6: $^{29}$Si NMR spectrum (99 MHz) of compound 1c in C$_6$D$_6$ at 300 K. Signals labeled with * belong to hexakis(trimethylsilyl)trisilirane (4).
1.4. Silyl Radical 2

Precooled THF (10 mL, -78 °C) was added to a mixture of (Bu$_3$Si)$_2$SiBr$_2$ (100 mg, 170 µmol, 1.0 eq.) and KC$_8$ (92.2 mg, 682 µmol, 3.5 eq.). The reaction mixture was allowed to warm to room temperature over 16 hours and the solvent was subsequently removed under reduced pressure. Concomitantly formed KBr and graphite were separated by extracting the residue with toluene (3 × 4 mL). Evaporation of the solvent in vacuo and subsequent washing of the residue with n-hexane (3 × 2 mL) afforded compound 2 as orange-brown solid (54.1 mg, 88.5 µmol, 52%). Crystals suitable for SC-XRD analysis were obtained from a cooled (-35 °C) solution of 2 in toluene.

m.p. = 60 °C (decomposition; color change to dark red)

**EPR** (toluene, 286 K) \( g = 2.0056, a(\alpha-^{29}\text{Si}) = 2.92 \text{ mT} \)

Note: Compound 2 is completely NMR silent. Elemental analysis was not matching, presumably because an unquantifiable amount of coordinating toluene was removed during drying compound 2 in fine vacuum. Due to its extreme air and moisture sensitivity and the fact, that it is not stable in toluene, no satisfactory spectroscopic data of 2 was obtained before addition of crown ether (18-C-6). With crown ether however, one signal in the EPR spectrum was observed (Fig. S7). Hyperfine coupling with the β-^{29}\text{Si} nuclei was not visible.

**Fig. S7:** X-band EPR spectrum of compound 2 + crown ether (18-C-6) in toluene (1×10⁻⁴M, 286 K).
1.5. Azasilepin 3

[Chemical structure image]

A solution of DMAP-stabilized silylene 1b (36.0 mg, 85.1 µmol) in benzene (2 mL) was heated to 65 °C for 16 h. The color changed from deep-brown to yellow. Evaporation of the solvent, afforded compound 3 as yellow solid (36.0 mg, 85.1 µmol, quant.). Crystals suitable for SC-XRD analysis were obtained from a cooled (-35 °C) solution of 3 in n-hexane.

$^1$H NMR (500 MHz, C$_6$D$_6$, 300 K): $\delta$ [ppm] = 8.34 (d, $^3$J = 4.7 Hz, 1H, NCH$_3$), 6.27 (dd, $^3$J = 15.5 Hz, $^4$J = 2.5 Hz, 1H, SiCH$_2$H), 6.01 (d, $^3$J = 15.5 Hz, 1H, SiCH$_3$), 4.68 (dd, $^3$J = 4.7 Hz, $^4$J = 2.5 Hz, 1H, NCH$_2$H), 2.27 (s, 6H, N(CH$_3$)$_2$), 1.29 (s, 18H, C(CH$_3$)$_3$), 1.19 (s, 18H, C(CH$_3$)$_3$), 0.37 (s, 6H, Si(CH$_3$)$_3$).

$^{13}$C($^1$H) NMR (126 MHz, C$_6$D$_6$, 300 K): $\delta$ [ppm] = 165.4 (SiNCH), 156.2 (CNMe$_2$), 138.2 (NCHCH), 137.4 (SiCHCH), 105.8 (SiCH$_2$CH), 40.3 (N(CH$_3$)$_2$), 30.4 (Si(C(CH$_3$)$_3$), 30.1 (Si(C(CH$_3$)$_3$), 22.5 (Si(C(CH$_3$)$_3$), 21.6 (Si(C(CH$_3$)$_3$), -4.9 (Si(CH$_3$)$_3$).

$^{29}$Si($^1$H) NMR (99 MHz, C$_6$D$_6$, 300 K): $\delta$ [ppm] = 2.0 (Si$_2$Bu$_2$Me), -28.1 (SiN).

EA: $\text{Si}_3\text{C}_{25}\text{H}_{52}\text{N}_2$ Calculated [%]: C (64.58), H (11.27), N (6.03)
Experimental [%]: C (64.62), H (11.47), N (5.99)
Fig. S8: $^1$H NMR spectrum (500 MHz) of compound 3 in C$_6$D$_6$ at 300 K.

Fig. S9: $^{13}$C NMR spectrum (126 MHz) of compound 3 in C$_6$D$_6$ at 300 K.
Fig. S10: $^{29}\text{Si}$ NMR spectrum (99 MHz) of compound 3 in C$_6$D$_6$ at 300 K.

Fig. S11: $^1\text{H}/^{29}\text{Si}$ HMBC NMR spectrum of compound 3 in C$_6$D$_6$ at 300 K.
Fig. S12: $^1$H/$^{13}$C HSQC NMR spectrum of compound 3 in C$_6$D$_6$ at 300 K.
1.6. Hexakis(trimethylsilyl)trisilirane (4)

A toluene solution of crude silylene 1c (50 mg) was heated to 65 °C for 16 hours. After cooling down to ambient temperature, liberated DMAP was separated by precipitation with SiBr₄ (26.9 mg, 77.5 µmol, 1.0 eq.) and subsequent filtration. The resulting solution was concentrated under reduced pressure and compound 4 was obtained by crystallization at -35 °C as colorless solid (30.1 mg).

Note: Compound 4 has already been reported by Klinkhammer et al. from the attempted synthesis of the free silylene ((TMS)₃Si)₂Si::[S7] Therefore, we did not analyze it further. DMAP forms an unidentified adduct with SiBr₄ which is insoluble in common organic solvents. Thus, this adduct was not further analyzed.

¹H NMR (500 MHz, C₆D₆, 300 K): δ [ppm] = 0.43 (s, 54H, Si(CH₃)₃).

¹³C(¹H) NMR (126 MHz, C₆D₆, 300 K): δ [ppm] = 4.7 (Si(CH₃)₃).

²⁹Si(¹H) NMR (99 MHz, C₆D₆, 300 K): δ [ppm] = -6.5 (Si(CH₃)₃), -168.6 (Si(TMS)₂).

Fig. S13: ¹H NMR spectrum (500 MHz) of compound 4 in C₆D₆ at 300 K.
**Fig. S14:** $^{13}$C NMR spectrum (126 MHz) of compound 4 in C$_6$D$_6$ at 300 K.

**Fig. S15:** $^{29}$Si NMR spectrum (99 MHz) of compound 4 in C$_6$D$_6$ at 300 K.
1.7. Hydrosilanes 5a-c

In a pressurizable Schlenk flask, a solution of the respective DMAP-stabilized silylenes 1a-c (100 µmol, 1.0 eq.) in toluene (5 mL) was frozen in liquid nitrogen, degassed and exposed to dihydrogen (1 bar). The reaction mixture was subsequently heated to 65 °C for 2 hours. Decolorization indicated full conversion. Concomitantly formed free DMAP was separated by precipitation with SiBr₄ (100 µmol, 1.0 eq.) and filtration. The solvent was removed under reduced pressure to afford hydrosilanes 5 as colorless solids in quantitative yields. Compounds 5a-c were identified by comparison of NMR spectral data with corresponding literature reports (5a,[S5] 5b,[S2] 5c[S3]).
1.8. Siliranes 6

The synthesis of siliranes 6 was conducted by a similar procedure than that for hydrosilanes 5 (vide supra). Instead of H₂, the DMAP-silylene complexes 1a and 1b were exposed to ethylene (1 bar). The compounds 6 were obtained as colorless solids. Silirane 6a was identified by comparison of NMR spectral data with literature reports.\textsuperscript{[S5]} Compound 6b was identified by multinuclear NMR spectroscopy.

6b

\textsuperscript{1}H NMR (500 MHz, C\textsubscript{6}D\textsubscript{6}, 300 K): δ [ppm] = 1.10 (s, 36H, C(CH\textsubscript{3})\textsubscript{3}), 0.81 (s, 4H, CH\textsubscript{2}), 0.10 (s, 6H, Si(CH\textsubscript{3})).

\textsuperscript{13}C NMR (126 MHz, C\textsubscript{6}D\textsubscript{6}, 300 K): δ [ppm] = 29.9 (C(CH\textsubscript{3})\textsubscript{3}), 21.8 (C(CH\textsubscript{3})\textsubscript{3}), -0.7 (CH\textsubscript{2}), -6.3 (SiCH\textsubscript{3})

\textsuperscript{29}Si\{\textsuperscript{1}H\} NMR (99 MHz, C\textsubscript{6}D\textsubscript{6}, 300 K): δ [ppm] = 11.2 (Si\textsubscript{t}Bu\textsubscript{2}Me), -174.5 (SiCH\textsubscript{3}).
1.9. Silaimine 7a

Trimethylsilyl azide (11.6 mg, 100 µmol, 1.0 eq.) was added to a solution of silylene 1a (60.0 mg, 100 µmol, 1.0 eq.) in benzene (2 mL) at ambient temperature. Decolorization from dark-brown to yellow and concomitant N₂ evolution was observed. After stirring the mixture for 1 hour, evaporation of the solvent under reduced pressure afforded compound 7a as yellow solid (53.8 mg, 78.6 µmol, 78%). Crystals suitable for SC-XRD analysis were obtained from a cooled (-35 °C) n-hexane solution of 7a.

Note: Compound 7a decomposes in solution under liberation of DMAP. Presumably, the donor-free silaimine is formed that decomposes further to an unidentified mixture of products.

¹H NMR (500 MHz, C₆D₆, 300 K): δ [ppm] = 9.42 (br. s, 1H, o-CDMAPH), 8.50 (br. s, 1H, o-CDMAPH), 6.06 (d, 3J = 6.9 Hz, 2H, m-CDMAHP), 1.83 (s, 6H, N(CH₃)₂), 1.41 (s, 27H, Si(C(CH₃)₃)), 0.69 (s, 9H, NSi(C(CH₃)₃)), 0.47 (s, 27H, Si(Si(C(CH₃)₃)₃)).

¹³C NMR (126 MHz, C₆D₆, 300 K): δ [ppm] = 155.9 (p-CDMAAP), 150.6 (o-CDMAAP), 106.9 (m-CDMAAP), 38.3 (N(CH₃)₂), 33.3 (C(CH₃)₃), 25.1 (O(CH₃)₃), 7.7 (NSi(CH₃)), 5.3 (Si(Si(CH₃)₃)).

²⁹Si¹H NMR (99 MHz, C₆D₆, 300 K): δ [ppm] = 2.0 (Si(tBu)₃), -9.4 (Si(SiMe₃)₃), -25.1 (N(SiMe₃)), -25.9 (Si=N), -121.3 (Si(SiMe₃)₃).
1.10. Silaimine 7b

Analog to the synthesis of 7a (vide supra) silylene 1b (25 mg, 53.8 µmol, 1.0 eq.) was treated with trimethylsilyl azide (6.19 mg, 53.8 µmol, 1.0 eq.) to afford silaimine 7b as yellow, crystalline solid (28.4 mg, 51.4 mmol, 96%).

Fig. S16: $^1$H NMR spectrum (500 MHz) of compound 7b in C$_6$D$_6$ at 300 K.
**Fig. S17:** $^{13}$C NMR spectrum (126 MHz) of compound 7b in C$_6$D$_6$ at 300 K.

**Fig. S18:** $^{29}$Si NMR spectrum (99 MHz) of compound 7b in C$_6$D$_6$ at 300 K.
Fig. S19: $^1$H/$^29$Si HMBC NMR spectrum of compound 7b in C$_6$D$_6$ at 300 K.
2. X-ray Crystallographic Data

2.1. General Information

The X-ray intensity data of 2 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 (\(\lambda = 0.71073 \ \text{Å}\)) and a Helios mirror optic by using the APEX III software package.\[S8\] The X-ray intensity data of 1b and 7a were collected on an X-ray single crystal diffractometer equipped with a CMOS detector (Bruker Photon-100), an IMS microsource with MoKα radiation (\(\lambda = 0.71073 \ \text{Å}\)) and a Helios mirror optic by using the APEX III software package.\[S8\] The X-ray intensity data of 3 was collected on an X-ray single crystal diffractometer equipped with a CCD detector (Apex II CCD), a fine-focus sealed tube with MoKα radiation (\(\lambda = 0.71073 \ \text{Å}\)) and a Triumph monochromator by using the APEX II/III software package.\[S8\] The measurements were performed on single crystals coated with the perfluorinated ether Fomblin® Y. The crystal was 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.\[S9\] Absorption corrections, including odd and even ordered spherical harmonics were performed using SADABS.\[S9\] 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\[S10\] and SHELXLE\[S11\]. 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 \(\Delta w(F_o^2-F_c^2)\)\[S9\] with SHELXL-97 weighting scheme.\[S12\] Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from International Tables for Crystallography.\[S13\] The images of the crystal structures were generated by Mercury.\[S14\] The CCDC numbers CCDC-1967942 (1b), CCDC-1967943 (2), CCDC-1967944 (3) and CCDC-1967945 (7a) 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/.
2.2 SC-XRD structures

Fig. S20: SC-XRD structure of silylene 1b with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity, tBu- and Me-groups are simplified as wireframes. Selected bond lengths [Å] and angles [°]: Si1–N1 1.937(5), Si1–Si2 2.390(3), Si1–Si3 2.378(3), Si2–Si1–Si3 123.1(1), Si2–Si1–N1 96.2(2), Si3–Si1–N1 98.8(2).

Fig. S21: SC-XRD structure of silyl radical 2 with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity, tBu-groups and toluene molecules are simplified as wireframes. Selected bond lengths [Å] and angles [°]: Si1–Si2 2.3936(14), Si1–K1 3.315(2), K1–Si1–Si2 114.91(2), Si2–Si1–Si2* 130.19(3).
**Fig. S22:** SC-XRD structure of azasilepin 3 with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity, 'Bu- and Me-groups are simplified as wireframes. Selected bond lengths [Å] and angles [°]: Si1–N1 1.750(1), Si1–C19 1.878(1), Si1–Si2 2.4144(6), Si2–Si1–Si3 113.74(2), Si2–Si1–N1 109.08(4), N1–Si1–C19 104.71(5).

**Fig. S23:** SC-XRD structure of silaimine 7a with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity, 'Bu- and Me-groups are simplified as wireframes. Selected bond lengths [Å] and angles [°]: Si1–Si2 2.453(1), Si1–N1 1.928(2), Si1–N3 1.616(2), N3–Si7 1.660(2), Si2–Si1–Si3 125.08(3), N1–Si1–N3 106.08(8), Si1–N3–Si7 177.1(1).
### 2.3 Crystal data and structural refinement parameters

#### Table S1: Crystal data and structural refinement parameters for compounds 1, 3, 4 and 7a.

| Compound # | 1b | 2 | 3 | 7a |
|------------|----|---|---|----|
| CCDC #     | 1967942 | 1967943 | 1967944 | 1967945 |
| Chemical formula | C_{20}H_{20}N_{25}SiS | C_{20}H_{20}KSiS | C_{20}H_{20}N_{25}SiS | C_{20}H_{20}N_{25}SiS |
| Formula weight | 464.96 | 650.31 | 464.96 | 684.55 |
| Temperature | 100(2) K | 100(2) K | 100(2) K | 100(2) K |
| Wavelength | 0.7107 Å | 0.7107 Å | 0.7107 Å | 0.7107 Å |
| Crystal size | 0.209 × 0.235 × 0.373 mm | 0.176 × 0.299 × 0.302 mm | 0.268 × 0.342 × 0.398 mm | 0.059 × 0.153 × 0.213 mm |
| Crystal habit | clear dark red-brown fragment | clear yellow fragment | clear yellow fragment | clear yellow fragment |
| Crystal system | monoclinic | monoclinic | monoclinic | orthorhombic |
| Space group | C 2/c | C 2/c | C 2/c | P -1 |
| Unit cell dimensions | | | | |
| a = 28.128(4) Å, α = 90° | b = 15.312(2) Å, β = 110.180(4)° | c = 17.567(3) Å, γ = 90° | a = 11.9770(13) Å, α = 90° |
| Volume | 5933.4(14) Å³ | 4048(3) Å³ | 5809.6(11) Å³ | 8 |
| Density (calculated) | 1.041 g/cm³ | 1.067 g/cm³ | 1.063 g/cm³ | 1.073 g/cm³ |
| Absorption coefficient | 0.174 mm⁻¹ | 0.243 mm⁻¹ | 0.178 mm⁻¹ | 0.246 mm⁻¹ |
| Diffractometer | Bruker D8 Venture Duo IMS | Bruker D8 Venture | Bruker D8 Venture | Bruker D8 Venture Duo IMS |
| Radiation source | Mo | Mo | Mo | Mo |
| Theta range for data collection | 1.94 to 25.35° | 2.28 to 25.68° | 2.20 to 26.37° | 2.03 to 25.35° |
| Index ranges | -33<o<33, -18<e<18, -17<e<17 | -25<e<25, -15<e<15, 21<e<21 | -14<e<14, -21<e<21, -35<e<35 | -13<e<13, -14<e<14, -18<e<19 |
| Refinements collected | 36869 | 68411 | 188411 | 90933 |
| Independent reflections | 5424 [R(int) = 0.0913] | 3797 [R(int) = 0.0742] | 5931 [R(int) = 0.0304] | 7757 [R(int) = 0.0458] |
| Coverage of independent reflections | 99.8% | 98.6% | 99.8% | 99.9% |
| Absorption correction | Multi-Scan | Multi-Scan | Multi-Scan | Multi-Scan |
| Refinement method | Full-matrix least-squares on F² | Full-matrix least-squares on F² | Full-matrix least-squares on F² | Full-matrix least-squares on F² |
| Function minimized | Σ w(F₂ - F₁)² | Σ w(F₂ - F₀)² | Σ w(F₂ - F₁)² | Σ w(F₂ - F₀)² |
| Data / restraints / parameters | 5424 / 6 / 328 | 3797 / 0 / 202 | 5931 / 0 / 287 | 7757 / 0 / 393 |
| Goodness-of-fit on F² | 1.172 | 1.040 | 1.045 | 1.123 |
| Final R indices | R1 = 0.1217, wR2 = 0.2651 | R1 = 0.0305, wR2 = 0.0855 | R1 = 0.0289, wR2 = 0.0771 | R1 = 0.0402, wR2 = 0.0992 |
| all data: R1 = 0.1445, wR2 = 0.2786 | all data: R1 = 0.0341, wR2 = 0.0886 | all data: R1 = 0.0334, wR2 = 0.0802 | all data: R1 = 0.0439, wR2 = 0.1016 |
| Weighting scheme | w = 1/[σ(F²)⁺(0.108245P⁺)] | w = 1/[σ(F²)⁺(0.0477P⁺)+2.4242P⁺] | w = 1/[σ(F²)⁺(0.0388P⁺)+3.2781P⁺] | w = 1/[σ(F²)⁺(0.0445P⁺)+1.7142P⁺] |
| Largest diff. peak and hole | 0.560 and -0.742 eÅ⁻³ | 0.263 and -0.218 eÅ⁻³ | 0.366 and -0.261 eÅ⁻³ | 0.634 and -0.258 eÅ⁻³ |
| R.M.S. deviation from mean | 0.104 eÅ⁻³ | 0.040 eÅ⁻³ | 0.042 eÅ⁻³ | 0.056 eÅ⁻³ |
3. References

[S1] G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics* **2010**, *29*, 2176-2179.

[S2] T. Gross, H. Reinke, H. Oehme, *Can. J. Chem.* **2000**, *78*, 1399-1404.

[S3] A. Sekiguchi, T. Fukawa, M. Nakamoto, V. Y. Lee, M. Ichinohe, *J. Am. Chem. Soc.* **2002**, *124*, 9865-9869.

[S4] N. Wiberg, W. Niedermayer, H. Nöth, J. Knizek, W. Ponikwar, K. Polborn, D. Fenske, G. Baum, *Z. Anorg. Allg. Chem.* **2001**, *627*, 594-606.

[S5] D. Reiter, R. Holzner, A. Porzelt, P. J. Altmann, P. Frisch, S. Inoue, *J. Am. Chem. Soc.* **2019**, *141*, 13536-13546.

[S6] K. Fredenhagen, G. Cadenbach, *Z. Anorg. Allg. Chem.* **1926**, *158*, 249-263.

[S7] a) K. W. Klinkhammer, *Chem. Eur. J.* **1997**, *3*, 1418-1431.; b) K. W. Klinkhammer, *Organosilicon Chemistry III - From Molecules to Materials* (Eds.: N. Auner, J. Weis), Wiley-VCH, 1997.

[S8] *APEX suite of crystallographic software*, APEX 3 version 2015.5-2; Bruker AXS Inc.: Madison, Wisconsin, USA, 2015.

[S9] *SAINT*, Version 7.56a and SADABS Version 2008/1; Bruker AXS Inc.: Madison, Wisconsin, USA, 2008.

[S10] G. M. Sheldrick, SHELXL-2014, University of Göttingen, Göttingen, Germany, 2014.

[S11] C. B. Hübschle, G. M. Sheldrick, B. Dittrich, *J. Appl. Cryst.* **2011**, *44*, 1281-1284.

[S12] G. M. Sheldrick, SHELXL-97, University of Göttingen, Göttingen, Germany, 1998.

[S13] A. J. C. Wilson, *International Tables for Crystallography*, Volume C, Tables 6.1.1.4 (pp. 500-502), 4.2.6.8 (pp. 219-222), and 4.2.4.2 (pp. 193-199), Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992.

[S14] C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek, P. A. Wood, *J. Appl. Cryst.* **2008**, *41*, 466-470.