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Investigations into the preparation of sila-β-diketones via 2-trimethylsilyl-1,3-dithianes: structural characterization of a second polymorph of bis(2,2,6,6-tetramethyl-2-sila-3,5-heptanedionato)copper(II)

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Abstract

The sila-β-diketone, 2,2,6,6-tetramethyl-2-silaheptane-3,5-dione (tmshdH), was synthesized by the condensation of the anion of 2-trimethylsilyl-1,3-dithiane with 1-bromo-3,3-dimethylbutan-2-one, followed by unmasking of the latent carbonyl moiety with HgO/HgCl$_2$. A monoclinic polymorph of the known copper(II) complex, Cu(tmshd)$_2$, was crystallized and studied by X-ray diffraction methods and found to be disordered like the orthorhombic one. Attempts to synthesize the disilylated β-diketone, 2,2,6,6-tetramethyl-2,6-disilaheptane-3,5-dione and monosilylated 4,4-dimethyl-4-sila-3-oxo-pentanal using the dithiane method were not successful. However, the 1,3-dithianyl precursors, along with the impurity 2,2′-bis(trimethylsilyl)-2,2′-bi-1,3-dithiane, were studied crystallographically. Large stereoelectronic and steric effects on the solid-state bonding parameters were observed for these molecules.
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Keywords: Copper(II) complexes; Sila-β-diketonate; Chemical vapor deposition; Volatility; Crystal structures; Dithianes

1. Introduction

The search for new volatile copper complexes, which are suitable for metal-organic chemical vapor deposition (MOCVD), has been an area of ongoing research [1–7]. Recently, we have reported on efforts to increase the volatility of homoleptic Cu(II) β-diketonate complexes by the incorporation of trialkylsilyl substituents in the supporting ancillary ligands [8–11]. In particular, the complex Cu(tmshd)$_2$ (where tmshd is the anion of 2,2,6,6-tetramethyl-2-silaheptane-3,5-dione) sublimes at a significantly lower temperature than its carbon analogue, Cu(tmhd)$_2$ (where tmhd is the anion of 2,2,6,6-tetramethylheptane-3,5-dione) [9] and is a viable, non-fluorinated candidate for MOCVD [8]. Further, the silylated Cu(II) compounds generally show greater stability than the corresponding non-silylated complexes [9–11]; the larger differences between the sublimation and decomposition temperatures should allow for the ability to attenuate the properties of the complex to fit a specific MOCVD application.

One method for the preparation of α-silylketones involves the silylation of the anion of 1,3-dithiane, followed by unmasking of the carbonyl moiety with suitable deprotection reagents [12,13]. As part of our investigations on the synthesis of sila-β-diketones, we report here on the utilization of this approach, combined with the umpolung afforded by 1,3-dithiane anions [12–16], to provide an alternative synthesis for 2,2,6,6-tetramethyl-2-sila-heptane-3,5-dione (tmshdH; **2**). The major byproduct of

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this procedure, 2, 2′-bis(trimethylsilyl)-2, 2′-bi-1,3-dithiane (**3**), as well as a second polymorph of Cu(tmshd)$_2$ (**4**), were characterized by X-ray diffraction methods. The 1,3-dithiane protocol was also explored for the preparations of the disilylated β-diketone, 2,2,6,6-tetramethyl-2,6-disilaheptane-3,5-dione, and the silylated β-ketoaldehyde, 4,4-dimethyl-4-sila-3-oxo-pentanal. While satisfactory deprotection to provide the corresponding dicarbonyl compounds could not be effected in these latter two cases, the silylated methylene-bis(1,3-dithianyl) precursors **5** and **6** were both crystallographically characterized in the solid-state.

2. Experimental

2.1. Materials and physical measurements

Commercial reagents and solvents were of reagent grade and were used as received, unless otherwise noted. All experiments, performed under dry inert gas, utilized standard Schlenk techniques or a vacuum atmospheres drybox filled with dinitrogen. Anhydrous diethyl ether and tetrahydrofuran (THF) were distilled from sodium-benzophenone ketyl under a dinitrogen atmosphere prior to use. Hexane was distilled from sodium-benzophenone-diglyme under dinitrogen. Column chromatography was performed using silica gel (40 μm, J.T. Baker).

^{1}H- and ^{13}C-NMR spectra were recorded on a Gemini-300 NMR spectrometer at 300 and 75.43 MHz, respectively, with CDCl$_3$ as solvent. ^{1}H and ^{13}C chemical shifts are reported relative to the residual signals of the CDCl$_3$ solvent, taken as δ 7.24 for ^{1}H and δ 77.00 for ^{13}C, relative to Me$_4$Si.

2.2. Preparation of 3,3-dimethyl-1-(2-trimethylsilyl-1,3-dithian-2-yl)-butan-2-one (1)

Under dry dinitrogen, a mixture of 2-trimethylsilyl-1,3-dithiane (3.84 g, 20 mmol; Lancaster Research Chemicals) and n-BuLi (8.0 ml, 20 mmol, 2.5 M in hexanes) in dry diethyl ether (20 ml) was stirred overnight at −30 °C. The solution of the substituted 1,3-dithiane anion was then added slowly to a solution of CuBr · Me$_2$S (2.06 g, 10 mmol) in Me$_2$S (10 ml) and dry diethyl ether (14 ml) held at −60 °C; after the addition was complete, stirring was continued for 1 h. 1-Bromo-3,3-dimethylbutan-2-one (1.79 g, 10 mmol) in dry diethyl ether (5 ml) was added to the cuprate solution over 1 h at −60 °C. After stirring for 5 h, the reaction mixture was allowed to warm to −30 °C and was kept stirring at that temperature overnight. After extraction with hexane and workup with aqueous NH$_4$Cl/NH$_4$OH and brine, the combined organic phase was dried over Na$_2$SO$_4$ and concentrated in vacuo. Column chromatography on silica gel using hexane:diethyl ether

(100:1 → 30:1) provided **1** as a colorless oil (1.63 g, 56% yield). ^{1}H NMR (CDCl$_3$): δ 3.51 (s, 2H, ^{t}BuC(O)CH_2), 2.4–3.1 (complex m, 4H, S–CH_2CH$_2$), 1.7–2.1 (complex m, 2H, S–CH$_2$CH_2), 1.17 (s, 9H, ^{t}Bu–CH_3), 0.23 (s, 9H, Si–CH_3).

A white solid (0.50 g) was isolated during the column chromatography separation; recrystallization from hexane provided crystals of 2, 2′-bis(trimethylsilyl)-2, 2′-bi-1,3-dithiane (**3**) suitable for X-ray diffraction studies. ^{1}H NMR (CDCl$_3$): δ 3.66 (m, 4H, axial S–CH_2CH$_2$), 2.39 (m, 4H, equatorial S–CH_2CH$_2$), 2.16 (m, 2H, axial S–CH$_2$CH_2), 1.85 (m, 2H, equatorial S–CH$_2$CH_2), 0.37 (s, 18H, Si–CH_3).

2.3. Deprotection of 1 to form 2,2,6,6-tetramethyl-2-silaheptane-3,5-dione (tmshdH; 2); preparation of Cu(tmshd)$_2$ (4)

An adaptation of a literature method was employed [12]. A mixture of **1** (0.20 g, 0.70 mmol) with HgCl$_2$/HgO (0.29 g/0.33 g) in methanol/water (7 ml/0.7 ml) was stirred at room temperature for 2.5 h. The solids were filtered and washed with hot methanol (10 ml). The filtrate was diluted with water (70 ml) and extracted with diethyl ether (5 × 10 ml). The combined organic layers were dried over Na$_2$SO$_4$; removal of the volatiles on a rotary evaporator gave crude **2** as a colorless oil. ^{1}H- and ^{13}C-NMR data for **2** were essentially the same as our previously reported values for tmshdH prepared by another method [9,11]. ^{1}H NMR (CDCl$_3$): δ 14.78 (s, 1H, OH), 5.89 (s, 1H, =CH), 1.15 (s, 9H, ^{t}Bu–CH_3), 0.20 (s, 9H, Si–CH_3). ^{13}C NMR (CDCl$_3$): δ 210.00, 192.85, 104.26, 41.85, 26.99, −3.05.

Diketone **2** was of sufficient purity and was carried over for preparation of Cu(tmshd)$_2$ (**4**) from Cu(OAc)$_2$ · H$_2$O via our reported method [9,11]. The crude yield of **4** was 0.15 g (45% based on **1**). The electronic spectrum of **4** in n-hexane was identical to our reported spectrum [9]. Crystals of **4**, suitable for X-ray diffraction studies were grown from saturated diethyl ether solution.

2.4. Preparations of 2, 2′-methylenebis(2-trimethylsilyl-1,3-dithianyl) (5) and methylene-2-(1,3-dithianyl)-2′-(2-trimethylsilyl-1,3-dithianyl) (6)

Under dry argon, n-BuLi (2.64 ml, 6.6 mmol, 2.5 M in hexanes) was added dropwise to a solution of 2, 2′-methylenebis(1,3-dithiane) [17] (0.505 g, 2.00 mmol) in dry THF (10 ml) chilled in an ice-salt bath. The reaction mixture was stirred for 4 h, then cooled to −78 °C. HMPA (1.0 ml) was added and stirring was continued for an additional 2 h. Me$_3$SiCl (0.84 ml, 6.6 mmol) was added and the mixture was stirred for 1 h, whereupon aqueous NH$_4$Cl and hexane were added. The organic phase was separated, dried over MgSO$_4$, and concentrated in vacuo. Column chromatography on silica gel

using hexane:CH_2Cl_2 (100% hexane $\rightarrow$ 60:40) provided **5** as a white solid (0.325 g, 41% yield) in the bands where the eluent ratio was between 85:15 and 80:20, as well as monosilylated methylene-2-(1,3-dithiane)-2′-(2-trimethylsilyl-1,3-dithiane) (**6**) as a white solid (0.352 g, 54% yield) in the bands with eluent ratio between 80:20 and 60:40.

Monosilylated **6** could be selectively prepared if HMPA was omitted from the above procedure and with some further slight modifications. Thus, under dry argon, *n*-BuLi (3.0 ml, 7.5 mmol, 2.5 M in hexanes) was added dropwise to a solution of 2,2′-methylenebis(1,3-dithiane) (0.757 g, 3.00 mmol) in dry THF (15 ml) chilled in an ice-salt bath. The reaction mixture was stirred for 2 h. Me_3SiCl (0.84 ml, 6.6 mmol) was added and the mixture was stirred for 1.5 h. From this point, workup and purification proceeded as above to give **6** as a white solid (0.520 g, 83% yield). Crystals of **5** and **6** suitable for X-ray diffraction were obtained by slow evaporation of saturated hexane solutions. ^1H and ^{13}C NMR data for **5** and **6** follow. ^1H NMR for **5** (CDCl$_3$): δ 3.09 (m, 4H, axial S–C*H*$_2$CH$_2$), 2.77 (s, 2H, Me$_3$SiCC*H*$_2$CSiMe$_3$), 2.56 (m, 4H, equatorial S–C*H*$_2$CH$_2$), 2.03 (m, 2H, axial S–CH$_2$C*H*$_2$), 1.83 (m, 2H, equatorial S–CH$_2$C*H*$_2$), 0.37 (s, 18H, Si–C*H*$_3$). ^{13}C NMR for **5** (CDCl$_3$): δ 49.35, 36.22, 26.40, 23.99, -1.01. ^1H NMR for **6** (CDCl$_3$): δ 3.99 (t, 1H, Me$_3$SiCC*H*$_2$C*H*), 2.4–3.1 (complex m, 8H, S–C*H*$_2$CH$_2$), 2.44 (d, 2H, Me$_3$SiCC*H*$_2$CH), 1.7–2.1 (complex m, 4H, S–CH$_2$C*H*$_2$), 0.24 (s, 9H, Si–C*H*$_3$). ^{13}C NMR for **6** (CDCl$_3$): δ 44.97, 43.09, 38.33, 31.59, 25.10, 24.78, 23.64, -2.80.

Various attempts to remove the dithiane protecting groups from **5** and **6**, including the usage of HgCl$_2$/HgO, copper(II) halides, I$_2$, CH$_3$I, or NCS [18] led invariably to complex mixtures as determined by ^1H NMR spectroscopy.

2.5. X-ray crystallography

X-ray data for compounds **3**, **4**, and **6** were collected at ambient temperature using a Bruker R3m diffractometer in the $\omega/2\theta$ mode for **3** and **6**, $\theta/2\theta$ mode for **4** with variable scan speed (3–20 deg min^{-1} for **3** and **6**, 2–20 deg min^{-1} for **4**) and graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Check reflections were measured every 200 reflections during data collection and gave no indication of crystal decay. Data were corrected for background, attenuators, Lorentz and polarization effects, but not for absorption, in the usual fashion [19].

X-ray intensity data for **5** were measured at 173(2) K (Bruker KRYO-FLEX) on a Bruker SMART APEX CCD-based X-ray diffractometer system equipped with a Mo-target X-ray tube ($\lambda = 0.71073$ Å) operated at 1800 W power. The detector was placed at a distance of 6.14 cm from the crystals. A total of 1850 frames was

collected with a scan width of 0.3° in ω and an exposure time of 20 s/frame. The frames were integrated with the Bruker SAINT software package using a narrow-frame integration algorithm. The final unit cell constants are based upon the refinement of the XYZ-centroids of 7791 reflections above $20\sigma(I)$.

All structures were solved by direct methods and refined by full matrix least-squares procedures on $|F^2|$ with SHELXTL 97, version 6.12 [20]. All non-hydrogen atoms were refined anisotropically except for **4**. For **4**, only the heteroatoms and the methyl carbon atoms of the chelate ligand were refined anisotropically, due to the poor quality of the crystals. Also for **4**, the peripheral Me$_3$Si and *t*-Bu substituents of the unique chelate of the centrosymmetric structure were distributed amongst the two possible sites. The occupancy of the position labelled Si(1) was modelled as 65% Si/35% C, while the position labelled C(4) was modelled with complementary occupancies. We chose not to attempt to model the rotational disorder of the peripheral substituents in **4**, due to the relatively small amount of data. Attempts to collect data at low temperature were unsuccessful; crystals of **4** diffracted even more poorly at low temperature, due to an apparent partial loss of crystallinity. Hydrogen atom positions were calculated geometrically and fixed at a C–H distance of 0.96 Å and were not refined, except for the hydrogen atoms of the methylene carbon, C(2), in **5** and **6**, which were located and refined. Crystal data and further data collection parameters are summarized in Table 1.

2.6. Theoretical calculations

Compounds **3**, **5**, and **6** were constructed using Titan (version 1.0.5; 2000; Wavefunction, Inc./Schrodinger, Inc.) on a Dell Dimension 4500 desktop computer. Each molecule was given angular and torsion constraints for the major bond deviations and specific conformations observed in the solid-state structures. They were then minimized in energy with the constraints active prior to the molecular orbital surface calculations. The HOMO for each molecule was calculated using a single algorithm, consisting of the B3LYP/6-31G** basis set in Titan.

3. Results and discussion

As we have previously discussed [10,11], retrosynthetic analysis of the sila-β-diketone framework (Fig. 1) suggests that there are three possible disconnections. Disconnection between the α-trialkylsilyl group and β-carbonyl carbon requires the nucleophilic attack by a trialkylsilyl anion at an electron deficient center, such as those found in substituted diketenes [21], ketoesters [22], or in more exotic reagents [23,24]. Yields of the desired sila-β-diketones were generally low.

Table 1
Crystallographic data and parameters for **3–6**

	3	**4**	**5**	**6**
Formula	$C_{14}H_{30}S_4Si_2$	$C_{20}H_{38}CuO_4Si_2$	$C_{15}H_{32}S_4Si_2$	$C_{12}H_{24}S_4Si$
Formula weight	382.8	462.2	396.8	324.6
Crystal color, habit	Colorless, plate	Olive green, prism	Colorless, prism	Colorless, prism
Crystal dimensions (mm)	$0.20 \times 0.40 \times 0.90$	$0.06 \times 0.20 \times 0.30$	$0.06 \times 0.13 \times 0.14$	$0.60 \times 0.70 \times 0.80$
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P2/c (No. 13)	P2$_1$/n (No. 14)	C2/c (No. 15)	P2$_1$/c (No. 14)
a (Å)	13.739(5)	10.183(3)	18.4358(13)	8.981(2)
b (Å)	9.048(3)	12.302(3)	13.1165(9)	22.175(5)
c (Å)	16.637(7)	11.651(4)	17.4949(12)	8.481(2)
α (°)	90	90	90	90
β (°)	104.32(3)	110.31(3)	97.1970(10)	95.32(2)
γ (°)	90	90	90	90
V (Å^3)	2003.9(13)	1368.8(7)	4197.2(58)	1681.7(7)
Z	4	2	8	4
D_{calc} (g cm^{-3})	1.269	1.121	1.256	1.282
μ (Mo Kα) (mm^{-1})	0.584	0.904	0.560	0.616
$F(000)$	824	494	1712	696
2θ max (°)	45.0	40.0	56.5	55.0
Reflections collected	2733	1344	17 558	4120
Independent reflections	2620 ($R_{int} = 2.48\%$)	1267 ($R_{int} = 9.18\%$)	4880 ($R_{int} = 5.61\%$)	3842 ($R_{int} = 1.90\%$)
Observed reflections	2075 ($I > 2.0\sigma (I)$)	528 ($I > 2.0\sigma(I)$)	3368 ($I > 2.0\sigma(I)$)	2840 ($I > 2.0\sigma(I)$)
Number of parameters	181	99	198	154
R_1[a], wR_2[b] ($I > 2.0\sigma(I)$)	0.0569, 0.1400	0.0790, 0.1378	0.0393, 0.0827	0.0407, 0.0899
R_1[a], wR_2[b] (all data)	0.0721, 0.1476	0.2164, 0.1858	0.0685, 0.0901	0.0663, 0.1027
GOF[c]	1.147	0.984	0.933	1.030

[a] $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$.

[b] $wR_2 = \left[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2 \right]^{1/2}$.

[c] $GOF = \left[\sum w(F_o^2 - F_c^2)^2 / (N_{obs} - N_{params}) \right]^{1/2}$.
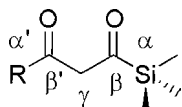

Fig. 1. Schematic drawing with labeling of carbon atoms for a general sila-β-diketone, R'C(O)CH$_2$C(O)SiR$_3$.

We have already reported on the extensive utilization of the disconnection between the γ-carbon atom and the β'-carbonyl carbon bearing the non-silylated substituent (Fig. 1) in order to prepare a wide variety of sila-β-diketones [8–11]. In general, this method employs the condensation of the lithium salt of an acetyltrialkylsilane with an activated carbonyl compound, such as an acyl chloride [8–11]. However, attempts to prepare a *di*silylated β-diketone using this protocol proved unsuccessful, which prompted us to explore a synthetic strategy involving 1,3-dithiane chemistry [12,13], based upon disconnection between the γ-carbon atom and the β-carbonyl carbon (Fig. 1).

Our first attempts to employ this method involved the condensation of the 2-trimethylsilyl-1,3-dithiane anion with 1-bromo-3,3-dimethylbutan-2-one (Scheme 1). The lithium salt of the substituted 1,3-dithiane proved to be too reactive; its usage provided a complex mixture of

products, that included low yields of **1**, as well as significant amounts of 2, 2'-bis(trimethylsilyl)-2, 2'-bi-1,3-dithiane (**3**). Consequently, the lithium salt was converted to the lithium cuprate salt in order to enhance the selectivity of the reaction with the bromoketone to provide **1** in acceptable yield, with minimal formation of **3**.

The instability of the trialkylsilyl substituent under acidic conditions precluded the use of the common acidic reagents to unmask the protected carbonyl group [18] in order to obtain 2,2,6,6-tetramethyl-2-silaheptane-3,5-dione (**2**). Neutral or basic methods, including metal salts [12,18,25,26], DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) [27], alkylation of the dithiane moiety [28], as well as mildly acidic conditions with Amberlyst resin [29] were tried out. All methods gave either complex product mixtures or yields that were inferior to the standard HgO/HgCl$_2$ procedure. Hence, the latter was employed to give **2** in reasonable yield and sufficient purity to carry on in further synthesis.

Cu(tmshd)$_2$ (**4**) could be prepared directly from **2** using our published method [9,11]. Curiously, crystals of **4** grown from diethyl ether solution were a monoclinic polymorph, as compared to the previously reported orthorhombic polymorph [9], the crystals of which were grown from *n*-hexane solution. Unfortunately, the
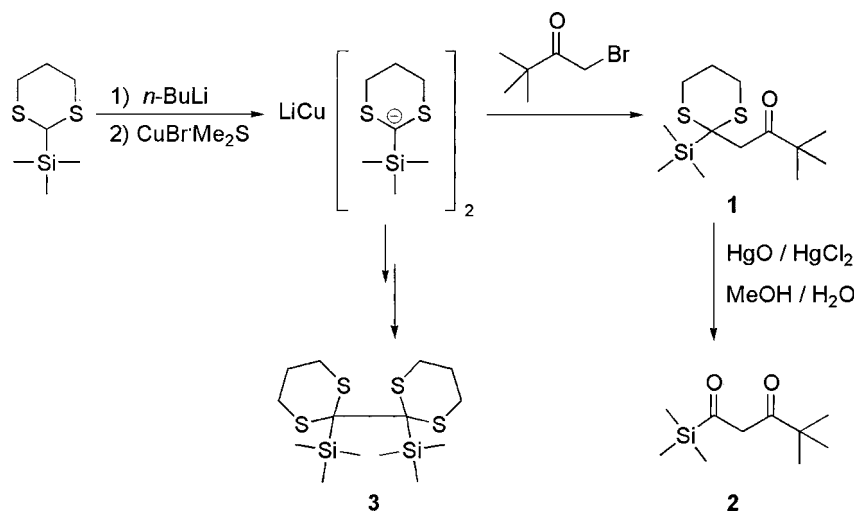
Scheme 1. Preparation of tmshdH (**2**) via the dithiane method.

monoclinic polymorph was found to be disordered about a center of symmetry, just as the orthorhombic polymorph was [9]. Several crystallization attempts resulted in well-shaped, but poorly diffracting crystals of **4**; hence the discussion of this structure must necessarily be limited due to inherent unreliability of the data. The monoclinic polymorph is also essentially square planar (Fig. 2); the dihedral angle between the nearly planar chelate ring and the symmetry enforced plane of the four oxygen donor atoms is 3.8(6)°. Bond distances and angles within the coordination sphere are close to those observed for the orthorhombic modification [9] and to those found in structurally ordered Cu(II) complexes containing silylated β-diketonate ligands [10,11].

As mentioned in Section 1, Cu(tmshd)$_2$ (**4**) is significantly more volatile than the unsilylated analogue, Cu(tmhd)$_2$ (Table 2) [9]. We have speculated that the former complex has higher volatility as a result of less efficient packing in the solid-state due to the presence of the trialkylsilyl substituents [9]. Indeed, the orthorhombic modification of Cu(tmshd)$_2$ (**4**) has a lower calculated density (1.117 g cm^{-1}) than the temperature-dependent calculated densities (1.149–1.213 g cm^{-1}) found for Cu(tmhd)$_2$ [30–32], even though **4** has a *higher*
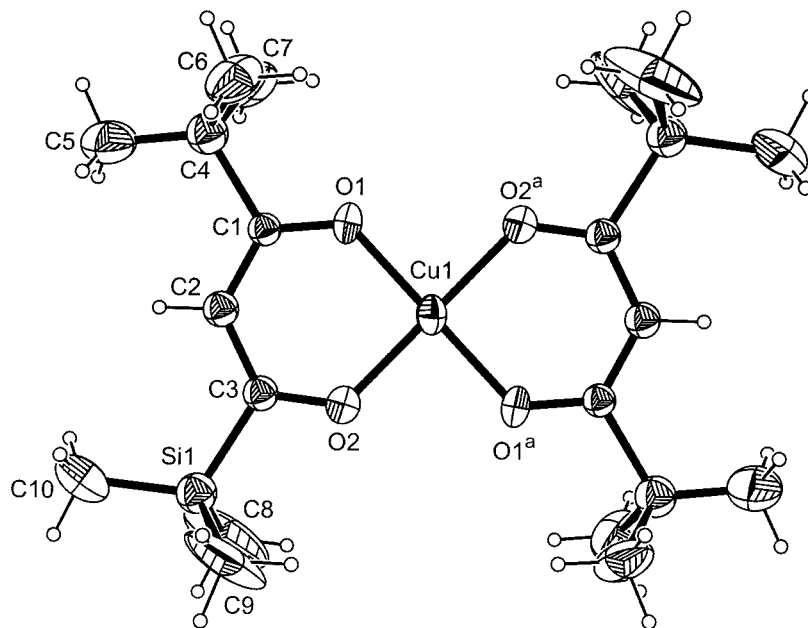

Fig. 2. Molecular structure and atom numbering scheme for Cu(tmshd)$_2$ (**4**). Atoms related by the symmetry transformation $(-x, -y, -z)$ are designated by 'a'. Thermal ellipsoids are drawn at 20% probability.

Table 2
Selected bond lengths (Å) and angles (°) for both polymorphs of Cu(tmshd)$_2$ (**4**)

	Monoclinic	Orthorhombic[a]
Cu(1)–O(1)	1.878(7)	1.880(9)
Cu(1)–O(2)	1.906(9)	1.897(9)
O(1)–Cu(1)–O(2)	92.9(4)	91.9(4)
O(1)–Cu(1)–O(2a)	87.1(4)[b]	88.1(4)[b]
O(1)–Cu(1)–O(1a)	180[b,c]	180[b,c]
O(2)–Cu(1)–O(a)	180[b,c]	180[b,c]

[a] Ref. [9].
[b] Symmetry transformation $(-x, -y, -z)$.
[c] Symmetry enforced.

molecular mass. The calculated density of the monoclinic polymorph of **4** is 1.121 g cm^{-1}, which is virtually the same as for the orthorhombic phase. Thus, the inefficiency of solid-state packing does not seem to depend on the identity of the solid-state crystal system.

As noted above, a main byproduct in the formation of **1** was determined to be 2,2′-bis(trimethylsilyl)-2,2′-bi-1,3-dithiane (**3**). Presumably, **3** forms as a result of oxidative dimerization of the 1,3-dithiane carbanion [14,15,33], possibly initiated by Cu(II) impurities in the preparation of the cuprate salt of the anion. It is known that coupling of dithiane carbanions can occur under the influence of the Cu(II) ion [15]. Compound **3** has been observed as an apparent oxidative byproduct in the reaction of the 2-trimethylsilyl-1,3-dithiane carbanion with 4-nitrobenzenesulfonyl azide [34] or with

2,3,4,5-tetraphenylcyclopentadieneone [35], and has been prepared in modest yield by oxidation of the same carbanion with molecular iodine in THF [36]. Alternatively, it is possible that the formation of **3** is due to a halophilic reaction mechanism as has been proposed for the reaction of silylated 1,3-dithiane carbanions with 1,2-dihaloalkanes [37].

X-ray crystallographic analysis of **3** showed that, though the molecules do not possess crystallographic symmetry, they have approximate two-fold rotational symmetry. Each dithiane ring adopts the chair conformation with the two rings in the *cis* rotational conformation with respect to the C(1)–C(8) bond (Fig. 3). The SiMe$_3$ groups both assume equatorial positions on the respective dithiane rings at carbon atoms C(1) and C(8); consequently, the substituted dithiane ring, which constitutes the other half of the molecule, is in the axial position at these carbon atoms. The overall *cis*-axial,axial conformation of the dithiane rings in **3** contrasts with the *trans*-equatorial,equatorial geometry found for 2,2′-diphenyl-2,2′-bi-1,3-dithiane [38]. Presumably, the larger steric demand of the SiMe$_3$ groups in **3**, as compared to the phenyl substituents in the latter compound, is responsible for the reversal in equatorial/axial preferences (Table 3).

Torsion angles X–C(1)–C(8)–Y around the highly crowded C(1)–C(8) bond for various (X;Y) combinations in **3** are: 89.2(4)° (Si(1);Si(2)), −156.6(4)° (Si(1);S(3)), −30.2(4)° (Si(1);S(4)), −29.5(5)° (S(1);Si(2)), 84.6(4)° (S(1);S(3)), −148.9(4)° (S(1);S(4)), −156.9(4)° (S(2);Si(2)),
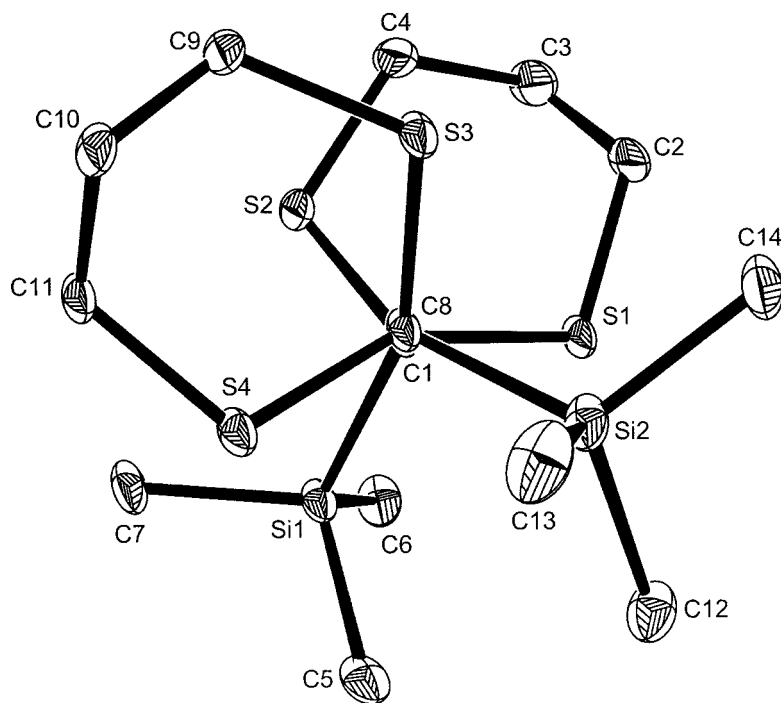

Fig. 3. Molecular structure and atom numbering scheme for **3**. The view is down the C(1)–C(8) bond. Hydrogen atoms are omitted for clarity; thermal ellipsoids are drawn at 20% probability.

Table 3
Selected bond lengths (Å) and angles (°) for **3**

S(1)–C(1)	1.828(4)
S(2)–C(1)	1.788(6)
Si(1)–C(1)	1.969(5)
S(3)–C(8)	1.830(5)
S(4)–C(8)	1.828(5)
Si(2)–C(8)	1.974(6)
C(1)–C(8)	1.563(7)
S(1)–C(1)–C(8)	110.7(3)
S(2)–C(1)–C(8)	115.5(3)
S(3)–C(8)–S(4)	110.3(2)
S(3)–C(8)–C(1)	115.7(4)
S(4)–C(8)–C(1)	110.8(3)
Si(1)–C(1)–C(8)	117.0(3)
S(1)–C(1)–S(2)	106.0(2)
Si(1)–C(1)–S(1)	103.9(2)
Si(1)–C(1)–S(2)	97.5(3)
Si(2)–C(8)–C(1)	118.0(3)
Si(2)–C(8)–S(3)	97.0(2)
Si(2)–C(8)–S(4)	103.8(3)

−42.7(4)° (S(2);S(3)), and 83.7(4)° (S(2);S(4)). Molecular orbital calculations suggest that the unusual torsion angles result in large part from repulsive interactions between lone pairs on the sulfur atoms in the HOMO, especially S(2) and S(3) (Fig. 4(a)). The calculations indicate that the stereoelectronic effect between sulfur lone pairs is minimized in the experimentally observed *cis* conformation. While the C(1)–C(8) bond length (1.563(7) Å) in **3** is slightly *shorter* than the corresponding bond length in the two crystallographically independent

molecules of 2, 2′-diphenyl-2, 2′-bi-1,3-dithiane (1.592(4) and 1.593(4) Å) [38], the Si(1)–C(1) and Si(2)–C(8) bonds (1.969(5) and 1.974(6) Å) are significantly longer than similar ones in related silylated mono-1,3-dithianes (1.938(4) and 1.925(3) Å) [39,40]. There is also a marked flattening of the tetrahedra around the C(1) and C(8) atoms. Thus, the combination of steric congestion, due to the presence of the two SiMe$_3$ substituents, and stereoelectronic effects from the sulfur atom lone pairs leads to the structural distortions observed for **3**.

Having enjoyed modest success in the employment of the 1,3-dithiane method for the preparation of tmshdH (**2**), we proceeded to explore its application for the preparation of disilylated β-diketones, such as 2,2,6,6-tetramethyl-2,6-disilaheptane-3,5-dione. It was suggested in the literature that lithiation of 2, 2′-methylenebis(1,3-dithiane), followed by treatment with chlorotrimethylsilane, provided quantitative yields of 2, 2′-methylenebis (2-trimethylsilyl-1,3-dithianyl) (**5**) [17]; however, no experimental details were provided. Under the reaction conditions that we employed (see Section 2), we obtained a mixture of **5** and methylene-2-(1,3-dithianyl)-2′-(2-trimethylsilyl-1,3-dithianyl) (**6**). The two compounds were easily separated by column chromatography. Later, we discovered that **6** could be obtained exclusively by omitting HMPA from the synthetic procedure (Scheme 2).

The preparations of **5** and **6** were not optimized further, because we found no success in the isolation of the desired β-dicarbonyl compounds by any of several
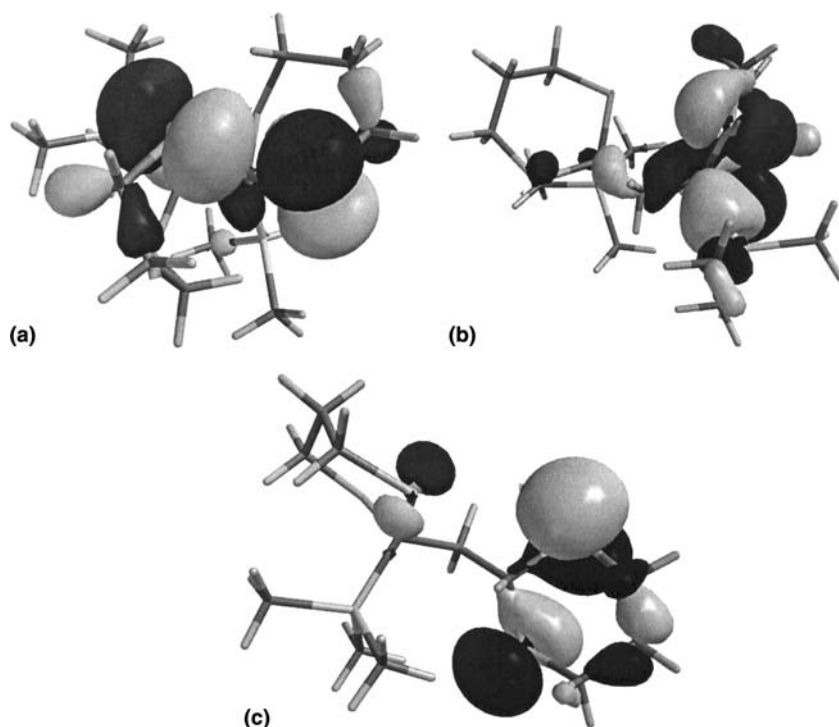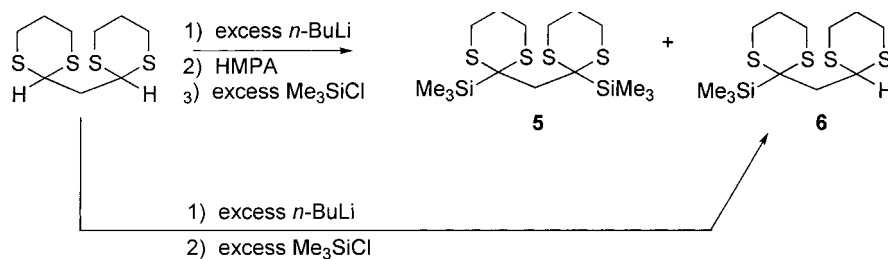

Fig. 4. Molecular orbital contour plots for the HOMO of compounds (a) **3**, (b) **5**, and (c) **6**.

Scheme 2. Preparations of **5** and **6**.

deprotection methods, including the use of HgO/HgCl$_2$, CuCl$_2$, MeI, NCS, or I$_2$. In all cases, starting material was consumed, but ^{1}H NMR analysis indicated the formation of complex product mixtures with none of the target compounds evident. It is not clear whether our inability to deprotect **5** and **6** is due to an inherent instability of the disilylated 1,3-dicarbonyl products or that we just did not identify appropriate deprotection reaction conditions. We note that 1,4- and 1,5-bis(acylsilane) compounds have been successfully prepared by deprotection of the corresponding bis(dithianyl) compounds [24,37,41–43].

In addition to spectroscopic means, **5** and **6** were characterized by X-ray diffraction methods, in order to make structural comparisons to **3**. For **5** (Fig. 5), both SiMe$_3$ groups occupy equatorial positions on the chair-like 1,3-dithiane rings, while methylene group C(2) is in an axial position with respect to each of the 1,3-dithiane rings. The Si(1)–C(1) and Si(2)–C(3) bonds in **5** are slightly shorter than the corresponding bond lengths in

3, but are still slightly longer than those in silylated mono-1,3-dithianes [39,40], though perhaps not significantly so (Table 4). The tetrahedra around trimethylsilyl-substituted C(1) and C(3) atoms are not as severely flattened as for the corresponding atoms in **3**.

Strikingly, however, the C(1)–C(2)–C(3) bond angle in **5** opens to 126.1(2)°, while the C(1)–C(2) and C(2)–C(3) bond lengths remain normal. The hydrogen atoms bonded to C(2) were located and refined successfully. The C–H bond lengths appear to be normal (0.96(2) Å for each), while H–C–H bond angles range from 101.2° to 109.5°. Molecular orbital calculations in this case indicate that a strong stereoelectronic effect involving repulsive interactions of sulfur lone pairs in the HOMO (Fig. 4(b)) helps to lead to the observed distortion from tetrahedral geometry at C(2). Although there are no direct links of the distortions to steric effects, the desire of the SiMe$_3$ groups to occupy equatorial sites on the dithiane rings undoubtedly helps cause the situation encountered here, where the dithiane rings find it difficult to avoid repulsive
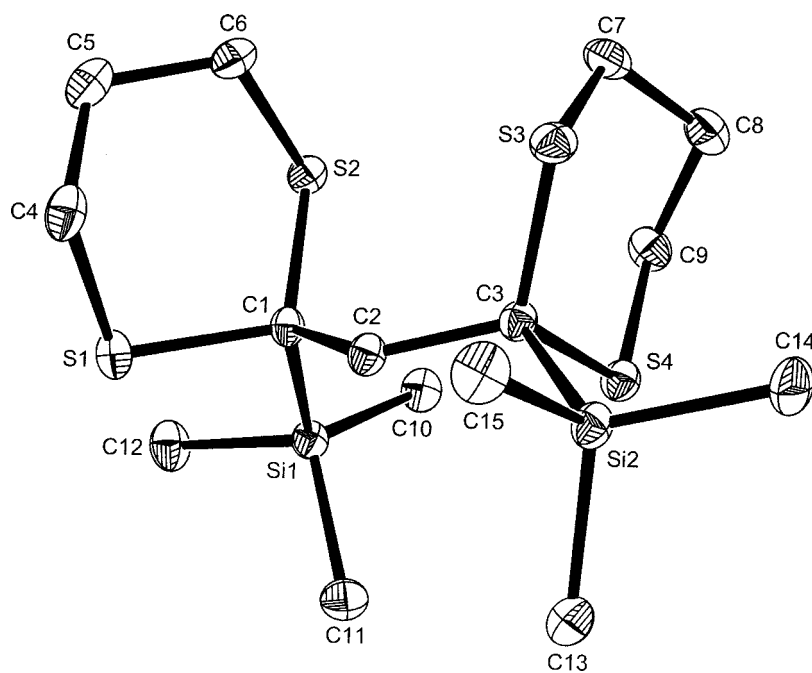

Fig. 5. Molecular structure and atom numbering scheme for **5**. Hydrogen atoms are omitted for clarity; thermal ellipsoids are drawn at 30% probability.

Table 4
Selected bond lengths (Å) and angles (°) for **5** and **6**

	5	**6**
S(1)–C(1)	1.850(2)	1.819(2)
S(2)–C(1)	1.814(2)	1.824(2)
Si(1)–C(1)	1.949(2)	1.922(2)
S(3)–C(3)	1.830(2)	1.804(2)
S(4)–C(3)	1.820(2)	1.804(2)
Si(2)–C(3)	1.942(2)	–
C(1)–C(2)	1.558(3)	1.550(3)
C(2)–C(3)	1.541(3)	1.529(3)
S(1)–C(1)–S(2)	110.3(1)	111.5(1)
S(1)–C(1)–C(2)	105.4(1)	112.6(2)
S(2)–C(1)–C(2)	116.3(1)	108.5(2)
S(3)–C(3)–S(4)	114.9(1)	111.6(1)
S(3)–C(3)–C(2)	113.9(1)	108.8(2)
S(4)–C(3)–C(2)	116.4(1)	110.6(2)
Si(1)–C(1)–C(2)	117.5(1)	114.8(2)
Si(1)–C(1)–S(1)	101.5(1)	105.9(1)
Si(1)–C(1)–S(2)	104.9(1)	103.1(1)
Si(2)–C(3)–C(2)	107.0(1)	–
Si(2)–C(3)–S(3)	100.0(1)	–
Si(2)–C(3)–S(4)	102.0(1)	–
C(1)–C(2)–C(3)	126.1(2)	115.6(2)

contact between the sulfur lone pairs. We note that in the case of bis[2-(1,3-dithianyl)]methanol, for which the bis-1,3-dithianyl-substituted methylene group is in an equatorial site with respect to both dithiane rings and in which the two dithiane ring moieties are well separated, the C–C–C bond angle around the methylene carbon is close to tetrahedral at 111.7(3)° [44].

On the other hand for **6** (Fig. 6), there is clear evidence that steric strain is relieved by the removal of one SiMe₃ group. The remaining SiMe₃ substituent again occupies an equatorial position of a 1,3-dithiane ring; however, the methylene group C(2) now occupies an equatorial site on the 1,3-dithiane ring that lacks trimethylsilyl substitution, which allows for more conformational flexibility. The C(1)–Si(1) distance is in the range observed for silylated mono-1,3-dithianes [39,40] and the C(1)–C(2)–C(3) bond angle is considerably less distorted from tetrahedral at 115.6(2)°. Molecular orbital calculations show that repulsive interactions between sulfur lone pairs in the HOMO are greatly attenuated for **6** (Fig. 4(c)). Bond angles around C(1) and C(3) are also much less distorted from tetrahedral values (Table 4).

4. Conclusions

We have successfully applied the use of the 1,3-dithiane group as a masked carbonyl equivalent for the preparation of the known sila-β-diketone, 2,2,6,6-tetramethyl-2-silaheptane-3,5-dione (**2**; tmshdH) [9,11] in modest yield via the condensation of the 2-trimethylsilyl-1,3-dithiane anion with 1-bromo-3,3-dimethylbutan-2-one. This method presumably can be generalized by the utilization of differently substituted 2-trialkylsilyl-1,3-dithianes and/or 1-bromomethylketones. However, while it is clear that alkylation of 2-trialkylsilyl-1,3-
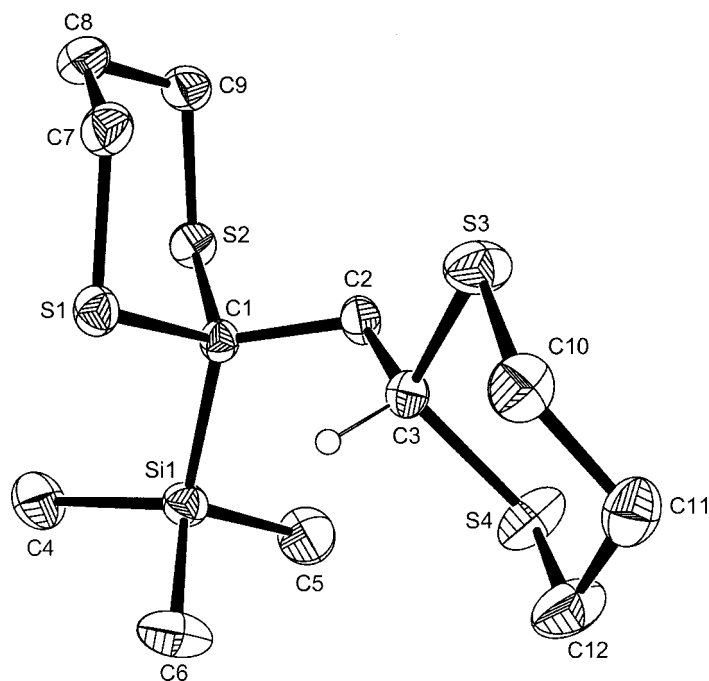

Fig. 6. Molecular structure and atom numbering scheme for **6**. Hydrogen atoms are omitted for clarity; thermal ellipsoids are drawn at 30% probability.

dithiane anions can be used to prepare sila-β-diketones, our previously reported method involving the condensation of the lithium salt of an acetyltrialkylsilane with an activated carbonyl compound, such as an acyl chloride, is far superior with regard to ease of preparation, yields, and the use of less toxic reagents [8–11].

During the investigation, we characterized a second structural polymorph of Cu(tmshd)$_2$ (**4**). This monoclinic polymorph was site disordered like the previously characterized, orthorhombic polymorph [9], and had similar bonding parameters in its coordination sphere. Also, the calculated density of the monoclinic modification, like the orthorhombic one, was lower than expected based on molecular mass considerations, probably due to inefficient packing of the molecules in the solid-state.

We made attempts to apply the 1,3-dithiane method for the synthesis of the disilylated β-diketone, 2,2,6,6-tetramethyl-2,6-disilaheptane-3,5-dione. We were able to prepare the desired precursor, 2,2′-methylenebis(2-trimethylsilyl-1,3-dithianyl) (**5**), as well as a monosilylated compound, methylene-2-(1,3-dithianyl)-2′-(2-trimethylsilyl-1,3-dithianyl) (**6**). However, neither **5** nor **6** could be deprotected by any of several deprotection protocols to give the corresponding β-dicarbonyl compound. The solid-state structures of **5** and **6** were determined and compared to that of bis(trimethylsilyl)-2,2′-bi-1,3-dithiane (**3**), an impurity that was isolated in the preparation of tmshdH by the 1,3-dithiane method. Strong stereoelectronic effects involving repulsions between sulfur atom lone pairs, as well as significant steric interactions, were apparent, particularly in the structures of **3** and **5**, which contain long C–Si bonds and severely distorted torsion and bond angles.

5. Supplementary material

Full lists of crystallographic data for **3** (CCDC-149097), **4** (CCDC-215184), **5** (CCDC-215185), and **6** (CCDC-215186), including atomic coordinates, bond lengths and angles, and anisotropic thermal parameters have been deposited with the Cambridge Crystallographic Data Centre. Copies of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1233-336033;e-mail: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk).

Acknowledgements

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