ELSEVIER

Journal of Organometallic Chemistry 651 (2002) 15–21

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Non-catalyzed addition reactions of $Cl_3SiSiCl_3$ with 1,2-diketones, 1,2-quinones and with a 1,4-quinone

Jinchao Yang, John G. Verkade *

Department of Chemistry, Iowa State University, Gilman Hall, Ames, IA 50011-3111, USA

Received 1 October 2001; received in revised form 15 January 2002; accepted 23 January 2002

Dedicated to Academician Mikhail Voronkov on the occasion of his eightieth birthday

---

Abstract

The first uncatalyzed reactions of a disilane with 1,2-diketones, 1,2-quinones and with a 1,4-quinone are reported. Thus, Si_2Cl_6 reacts under mild conditions with such substrates to give bis-trichlorosiloxy addition compounds. The structure of the corresponding addition compound of benzyl, namely, *cis*-$PhC(OSiCl_3)$=$C(OSiCl_3)Ph$ was structured by X-ray diffraction analysis. Evidence for the intermediacy of five-coordinate species in these reactions is discussed. A reaction of Si_2Cl_6 with LiNMeC(O)Et aimed at making a hypercoordinate silicon complex led to the disproportionation product *cis*-$Cl_2Si[NMeC(O)Et]_2$ (whose structure was also determined by X-ray diffraction analysis) in which the amide ligands chelate the silicon via the nitrogen and oxygen to form five-membered rings whose bond lengths suggest substantial electron delocalization. © 2002 Published by Elsevier Science B.V.

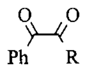
Keywords: 1,2-Diketones; 1,2-Quinones; 1,4-Quinone; Disilane; Addition reactions

---

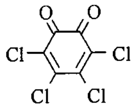
1. Introduction

Organosilicon compounds are important because of their versatile synthetic utility and their unique physical and chemical properties [1]. One method for their preparation involves the transition metal-catalyzed addition of disilanes [2] to unsaturated compounds such as acetylenes, olefins, dienes, allenes, a diyne, 1,2-unsaturated ketones, quinones, an α-keto ester, aldehydes, isocyanides and imines [1]. Although the formation of *p*-bis(dimethylfluorosiloxy)benzene from *p*-benzoquinone and $FMe_2SiSiMe_2F$ is known [2], this reaction is the only example involving an activated disilane. Moreover, this reaction required the presence of $Pd(PPh_3)_2Cl_2$ or $Pd(PPh_3)_4$ as a catalyst. To our knowledge, no disilane–1,2-diketone; disilane–1,4-quinone or disilane–1,2-quinone reactions not catalyzed by a transition metal catalyst have been reported.

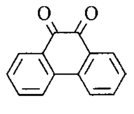
In earlier publications, we showed that alkynes are trimerized to benzene derivatives at ca. 200 °C in the presence of Si_2Cl_6 (**1**) as a catalyst [3]. In the past, such reactions of alkynes have been universally carried out with the aid of transition metal catalysts. We report here the use of the activated disilane Si_2Cl_6 (**1**) for the double silylation of α,β-diketones (**2a**,**b**); the *ortho*-quinones (**3a**,**b**) and the *para*-quinone (**4**). All of these reactions proceed well in the absence of a catalyst to give the corresponding products **5a**,**b**; **6a**,**b** and **7**. Whereas, alkyne trimerization catalyzed by **1** at ca. 200 °C occurs by a free radical mechanism [3], the



2a: R = Ph
2b: R = Me

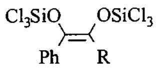


3a

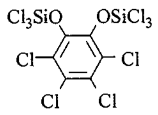


3b

4



5a: R = Ph
5b: R = Me



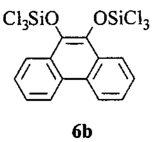
6a

---

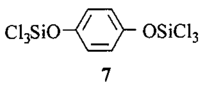
* Corresponding author. Tel.: + 1-515-294-5023; fax: + 1-515-294-0105.

E-mail address: jverkade@iastate.edu (J.G. Verkade).

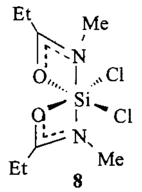
0022-328X/02/$ - see front matter © 2002 Published by Elsevier Science B.V.
PII: S0022-328X(02)01193-2



6b



7



8

reactions described herein, which proceed at room temperature, are likely to proceed via formation of a hypercoordinate intermediate followed by molecular rearrangement involving Si–Si bond cleavage. The notion that five-coordinate silicon intermediates possessing C=O → Si linkages are involved in these reactions is amply supported by the considerable number of reports of such complexes in recent years [4,5]. These complexes contain one chelate ring per silicon, and a six-coordinate silicon complex with a C=O → Si linkage in a six-membered ring has also been described recently [6]. Here we report the molecular structure of novel six-coordinate **8** in which two C=O → Si linkages are present, each in a four-membered ring.

2. Experimental

NMR spectra were measured on Bruker AC-200 (^{29}Si), Bruker DRX-400 (^{1}H and ^{13}C) and Bruker MSL-300 (solid ^{29}Si MAS) instruments. The NMR solvent was $CDCl_3$ unless otherwise noted. Chemical shifts were calibrated to $CDCl_3$ for ^{1}H- and ^{13}C-NMR spectra and to $SiMe_4$ for ^{29}Si-NMR spectra. High resolution mass spectral and elemental analyses were performed at Iowa State University by the Chemistry Department Instrument Services Unit.

Diethyl ether and THF were dried with Na, DMF was distilled under nitrogen, after stirring with CaH_2, and were stored over molecular sieves. Hexachlorodisilane (**1**) was purchased from Aldrich and was used as received. Benzyl (**2a**), 1-phenyl-1,2-propanedione (**2b**), tetrachloro-1,2-benzoquinone (**3a**), phenanthrenequinone (**3b**), *p*-benzoquinone (**4**) *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda), *N*-methylpropionamide and *N*-methyltrimethylacetamide were purchased from Aldrich Chemical Co. and were used as received unless otherwise noted.

2.1. General description of reactions

Reactions of hexachlorodisilane (**1**) with DMF and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine were carried out at room temperature (r.t.) in Et_2O or C_5H_{12} under nitrogen. Each reaction of **1** with a quinone was carried out in an NMR tube under nitrogen either at r.t. in $CHCl_3$ or at 80–120 °C without a solvent. The conversions in all the reactions were quantitative unless otherwise noted. Products were analyzed by ^{1}H-, ^{13}C-, ^{29}Si-NMR and HRM spectroscopies.

2.2. Adduct formation of 1 with *N*,*N*,*N*′,*N*′-tetramethylethylenediamine

In a 50 ml flask pre-flushed with nitrogen and equipped with a magnetic stirrer, Et_2O (ca. 20 ml) was added with a syringe, followed by *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (2.32 g, 20.0 mmol). Disilane **1** (2.69 g, 10.0 mmol) was then introduced dropwise with stirring at r.t. whereupon a white precipitate was observed to form immediately which was accompanied by a mild exotherm. The reaction mixture was stirred for 2 h and then the precipitate was filtered off and washed with 3 × 10 ml of Et_2O. Drying the precipitate under vacuum gave 4.70 g of product as a white powder in 93% yield assuming a 1:1 adduct had formed. The product was analyzed as a hypercoordinated silicon adduct of **1** with *N*,*N*,*N*′,*N*′-tetramethylethylenediamine by ^{29}Si-NMR spectroscopy. ^{29}Si MAS-NMR (solid, hexamethylcyclotrisiloxane) for the adduct: δ −79.24; ^{1}H-NMR ($CDCl_3$): δ 2.87 (s, 4H), 2.61 (s, 12H); ^{13}C-NMR ($CDCl_3$); δ 55.14, 46.57. Mass spectra revealed only the presence of decomposition products. Efforts to obtain crystals of this adduct failed.

2.3. Adduct formation of 1 with DMF

To a 50 ml flask pre-flushed with nitrogen, Et_2O (ca. 20 ml) was added by syringe, followed by DMF (1.46 g, 20.0 mmol). Disilane **1** (2.69 g, 10 mmol) was then introduced dropwise at r.t., whereupon a white precipitate was observed which was accompanied by a mild exotherm. The reaction mixture was stirred for 3 h and then the precipitate was filtered and washed with 5 × 10 ml of Et_2O. Drying the precipitate under vacuum afforded 3.10 g product (90% yield) assuming the formation of a 1:1 adduct. The product analyzed as a hypercoordinated adduct of **1** with DMF by ^{29}Si-NMR spectroscopy. ^{29}Si MAS-NMR (solid hexamethylcyclotrisiloxane): δ −184.71, −192.10; ^{1}H-NMR ($CDCl_3$): δ 8.02 (s, 1H), 2.95 (s, 3H), 2.87 (s, 3H); ^{13}C-NMR ($CDCl_3$) δ 162.69, 36.68, 31.61. Mass spectra revealed only the presence of decomposition products. Efforts to purify the product failed and no crystals were obtained.

2.4. Reaction of 1 with 2a (method A: at 100 °C without a solvent)

A nitrogen-flushed NMR tube was charged with **2a** (42.0 mg, 0.200 mmol) followed by the introduction of **1** (64.0 mg, 0.240 mmol). The NMR tube was stoppered with a septum and the mixture was heated to 100 °C for 1 h. After cooling to r.t., a yellow solution was obtained which when analyzed by ^{1}H-, ^{13}C-, ^{29}Si-NMR and HR mass spectroscopies revealed the product **5a** in which a vinylic fragment had formed. ^{1}H-NMR ($CDCl_3$): δ 7.25 (m, 10H); ^{13}C-NMR ($CDCl_3$): δ 136.60, 133.04, 129.46, 129.01, 128.27. ^{29}Si-NMR ($CDCl_3$, $SiMe_4$): δ -21.27. HRMS (EI): Calc. for $C_{14}H_{10}Cl_6O_2Si_2$: 475.83506. Found: 475.83527. Purifying the product (to remove **1**) by evaporation under vacuum afforded pure **5a**. Anal. Calc. for $C_{14}H_{10}Cl_6O_2Si_2$: C, 35.07; H, 2.08; Cl, 44.46; Si, 11.69. Found: C, 35.84; H, 2.16; Cl, 44.19; Si, 11.65%.

2.5. Reaction of **1** with **2a** (method B: at r.t. in $CHCl_3$)

In a nitrogen-flushed NMR tube was charged with **2a** (42.0 mg, 0.200 mmol) followed by the introduction of **1** (64.0 mg, 0.240 mmol). The NMR tube was stoppered with a septum and 0.70 ml of $CDCl_3$ was added with a syringe. A light yellow solution was obtained after **2a** had dissolved. Taking the NMR spectra immediately after adding the $CDCl_3$ showed the absence of starting material **2a**. ^{1}H- and ^{13}C-NMR spectroscopies confirmed that methods A and B both gave **5a**.

2.6. Reaction of **1** with **2a** at 0 °C

In a glass tube equipped with a magnetic stirrer, and cooled by an ice bath was charged with **2a** (0.42 g, 2.0 mmol) followed by the introduction of (0.64 g, 2.4 mmol) of **1**. The tube was then cooled with liquid nitrogen and flame sealed under vacuum. The mixture was then allowed to warm to 0 °C in an ice bath and stirred until a homogeneous mixture was obtained. Shaking the reaction mixture occasionally was essential to ensure good mixing. The tube was then left undisturbed for 2 days at 0 °C, during which time colorless crystals of **5a** formed which were suitable for X-ray diffraction studies.

2.7. Reaction of **1** with **2b**

In a nitrogen-flushed NMR tube, **2b** (30.0 mg, 0.200 mmol) was added by a syringe. The NMR tube was cooled to 0 °C by an ice bath and then disilane **1** (64.0 mg, 0.240 mmol) was introduced. The reaction was exothermic judging from the boiling of the mixture and the warm-up of the tube. The product analyzed by ^{1}H-, ^{13}C-, ^{29}Si-NMR and HRMS spectroscopies as **5b**. Formation of the *cis*-isomer was inferred from the analogous reaction of **1** with **2a** to give **5a** whose structure was determined by X-ray diffraction analysis. ^{1}H-NMR ($CDCl_3$): δ 7.40 (m, 5H), 2.07 (s, 3H); ^{13}C-NMR ($CDCl_3$): δ 134.70, 134.15, 133.07, 129.22, 129.10, 128.41, 17.70; ^{29}Si-NMR ($CDCl_3$, $SiMe_4$): δ -21.79, -22.74. MS (70 eV, EI): *m*/*z* (relative intensity, ion) 418.0 [8.97, M^+(2 ^{37}Cl, 4 ^{35}Cl)], 416.0 [11.13, M^+(^{37}Cl, 5 ^{35}Cl)], 265.0 (4.50, $[M-OSiCl_3]^+$). HRMS (EI): Calc. for $C_9H_8Cl_6O_2Si_2$: 413.81941. Found: 413.81935. Attempts to purify the product were unsuccessful.

2.8. Reaction of **1** with **3a**

An NMR tube pre-flushed with nitrogen was charged with **3a** (49.0 mg, 0.200 mmol). Disilane **1** (60.0 mg, 0.220 mmol) was introduced with a syringe and then the tube was stoppered with a septum and heated to 80 °C for 2 h, during which time a homogenous light brown solution was obtained. The ^{1}H-, ^{13}C-, ^{29}Si-NMR and HR mass spectra of the product were consistent with the formation of **6a**. ^{13}C-NMR ($CDCl_3$): δ 140.18, 129.51, 129.97, 125.97; ^{29}Si ($CDCl_3$, $SiMe_4$): δ -20.17. MS (70 eV, EI): *m*/*z* (relative intensity, ion) 518.0 [4.48, M^+(4 ^{37}Cl, 6 ^{35}Cl)], 516.0 [8.67, M^+(3 ^{37}Cl, 7 ^{35}Cl)], 514.0 [9.66, M^+(2 ^{37}Cl, 8 ^{35}Cl)], 344.0 [8.16, $M-(SiCl^3+Cl)]^+$. HRMS (EI): Calc. for $C_6Cl_{10}O_2Si_2$: 509.63222. Found: 509.63227. Efforts to purify the product were unsuccessful.

2.9. Reaction of **1** with **3b**

This procedure is the same as that of the reaction of **1** with **3a**, so only the characterization of the product **6b** is given. ^{1}H-NMR ($CDCl_3$): δ 8.67–8.69 (m, 2H), 8.21–8.23 (m, 2H), 7.70–7.71 (m, 4H); ^{13}C-NMR ($CDCl_3$): δ 134.88, 128.87, 127.43, 127.03, 126.66, 122.91, 122.84; ^{29}Si-NMR ($CDCl_3$, $SiMe_4$): δ -20.09. MS (70 eV, EI): *m*/*z* (relative intensity, ion) 482.0 [1.18, M^+(4 ^{37}Cl, 2 ^{35}Cl)], 480.0 [4.23, M^+(3 ^{37}Cl, 3 ^{35}Cl)], 478.0 [9.55, M^+(4 ^{37}Cl, 2 ^{35}Cl)], 476.0 [12.38, M^+(^{37}Cl, 5 ^{35}Cl)], 474.0 [6.18, M^+(6 ^{35}Cl)], 135.0 (6.64, $SiCl_3$). HRMS (EI): Calc. for $C_{14}H_8Cl_6O_2Si_2$: 473.81941. Found: 473.81953. Attempts to purify the product were unsuccessful.

2.10. Reaction of **1** with **4**

Compound **4** (purified by recrystallization from C_6H_{14} (22.0 mg, 0.220 mmol) was introduced by syringe into an NMR tube. The tube was closed with a septum and then it was heated to 80 °C for 2 h, during which time the reaction mixture became a clear light yellow solution. The product analyzed by ^{1}H-, ^{13}C-, ^{29}Si-NMR and HR mass spectroscopies as **7**. ^{1}H-NMR ($CDCl_3$): δ 7.04 (s, 4H); ^{13}C-NMR ($CDCl_3$): δ 147.62, 121.00; ^{29}Si-NMR ($CDCl_3$): δ -22.02. MS (70 eV, EI): *m*/*z* (relative intensity, ion) 380.0 [5.34, M^+(4 ^{37}Cl, 2 ^{35}Cl)], 378.0 [11.75, M^+(3 ^{37}Cl, 3 ^{35}Cl)], 376.0 [17.21, M^+(2 ^{37}Cl, 4 ^{35}Cl)], 241.0 [1.01, $[M-SiCl_3]^+$]. HRMS (EI): Calc. for $C_6H_4Cl_6O_2Si_2$: 373.7881. Found: 373.78780. This reaction was also carried out in $CHCl_3$ at r.t., giving **7** in 100% conversion immediately after mixing **1** and **4**. Purification of the product by removal of **1** under vacuum afforded pure product. Anal. Calc. for $C_6H_4Cl_6O_2Si_2$: C, 19.09; H, 1.19; Cl, 56.49; Si, 14.77. Found: C, 19.31; H, 1.19; Cl, 56.01; Si, 14.48%.

*2.11. Synthesis of hexacoordinated bicyclic silicon compound **8***

In a 250 ml flask equipped with a magnetic stirrer, Et_2O (100 ml) was added under nitrogen, followed by *N*-methylpropionamide (2.61 g, 30.0 mmol). The solution was cooled to 0 °C, and *tert*-butyllithium (1.7 M in pentane, 18.0 ml) was added dropwise under nitrogen with a syringe. A white suspension was observed to form during the addition of *t*-BuLi. After the addition of *t*-BuLi solution, the reaction mixture was stirred at 0 °C for 1 h, and then at r.t. for another 2 h. Then the reaction mixture was re-cooled to 0 °C and **1** (2.01 g, 7.50 mmol) or $SiCl_4$ (2.55 g, 15 mmol) was added dropwise to the suspension. The reaction mixture was allowed to warm to r.t. where it was stirred for another 2 h and then refluxed overnight. The reaction mixture was filtered, and colorless crystals of **8** (3.13 g) suitable for X-ray diffraction were observed to form in the filtrate during filtration. ^{1}H-NMR ($CDCl_3$): δ 2.99 (s, 3H), 2.40–2.47 (q, 2H), 1.17–1.22 (t, 3H); ^{13}C-NMR ($CDCl_3$): δ 183.31, 29.27, 21.09, 8.02; ^{29}Si MAS-NMR (solid hexamethylcyclotrisiloxane): δ −159.89. MS (EI) *m*/*z* (intensity, ion): 270.9 (19.46, M^+).

3. X-ray molecular structure solution of 5a and 8

A colorless crystal with approximate dimensions $0.43 \times 0.31 \times 0.14$ mm^3 was selected from oil under ambient conditions and was attached to the tip of a glass capillary. The crystal was mounted in a stream of cold nitrogen at 173(2) K and centered in the X-ray beam by using a video camera. The crystal evaluation and data collection were performed on a Bruker CCD-1000 diffractometer with Mo–K$_\alpha$ ($\lambda = 0.71073$ Å) radiation and the diffractometer to crystal distance of 5.08 cm.

The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 20 frames at intervals of 0.3° in a 6° range about ω with the exposure time of 10 s per frame. A total of 43 reflections were obtained. The reflections were successfully indexed by an automated indexing routine built in the SMART program. The final cell constants were calculated from a set of 6921 strong reflections from the actual data collection.

The data were collected by using the hemisphere data collection routine. The reciprocal space was surveyed to the extent of 1.8 hemisphere to a resolution of 0.80 Å. A total of 22 002 (for **5a**) and 11 557 (for **8**) data were harvested by collecting three sets of frames with 0.3° scans in ω with an exposure time 30 (for **5a**) and 20 s (for **8**) per frame. These highly redundant data sets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements [7].

The systematic absences in the diffraction data were uniquely consistent for the space groups $P2_1/c$ (for **5a**) and $P2_1/n$ (for **8**) that yielded chemically reasonable and computationally stable results of refinement [8]. A successful solution by the direct methods provided the positions of most atoms from the *E*-map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. Crystallographic data and pertinent bond lengths and angles are given in Tables 1 and 2, respectively.

4. Results and discussion

4.1. Si–Si bond cleavage during adduct formation

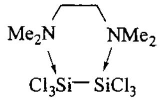
In an effort to detect silyl radicals in our alkyne trimerization reactions catalyzed by **1** [3], 1,2-quinones and 1,4-quinones (which are commonly used as efficient radical traps [9]) were utilized in the reactions reported herein. When benzil (**2a**) was introduced in the reactions of **1** with alkynes, no cyclotrimerizations product was detected, however, the new product **5a** was formed as a viscous liquid. Lowering the reaction temperature to 80 °C, or by simply mixing **1** and **2a** in $CHCl_3$ (or toluene) at room temperature gave **5a** in quantitative conversion, as confirmed by ^{1}H-, ^{13}C- and ^{29}Si-NMR spectroscopies. The 1,2-diones **2b** and **3a**,**b** also resulted in the formation of the corresponding products **5b** and **6a**,**b** in quantitative conversions. Similarly, the 1,4-quinone **4** led to the quantitative formation of **7** whether the reaction was carried out at 100 °C or by mixing the reagents in $CHCl_3$ at room temperature. Although this compound was reported in 1940 [10], it had been synthesized from the reaction of *para*-cresol with $SiCl_4$, and only a density, index of refraction and a partial elemental analysis (Cl and Si) was reported.

The strength of Si–Si linkage in disilanes is expected to be weakened when electron withdrawing substituents are present, thus facilitating the generation of $SiCl_3$ radicals at elevated temperatures (ca. 200 °C) [3]. We therefore suspected that the radical generation might account for the occurrence of the reaction of **2a** with **1** to form **5a** at 100 °C. However, the following observation militates against this possibly. When **1** and **2a** were mixed in chloroform or toluene, we observed immediate formation of **5a** even under ambient conditions, at which temperature the concentration of $SiCl_3$ radicals, if any, would be expected to be too low to cause the reaction to occur so rapidly.

We suggest that the disilane–1,2-diketones, –quinone and –1,4-quinone reactions reported herein are probably initiated by the formation of pentacoordinated silicon species, the presence of which becomes more prominent when electron withdrawing groups such as halogens are attached to the silicon. Although hypercoordinated silicon compounds have been extensively investigated [11], similar compounds formed from disilanes are lacking. In an effort to elucidate the pathway for the reactions reported here, we now describe some observations that lend credence to the formation of hypercoordinate species with **1**.

4.2. Si_2Cl_6 adduct formation with tmeda and DMF

Silanes such as methyltrichlorosilane have long been known to be able to form adducts with compounds possessing electron lone pairs [11,12]. Formation of the adducts was detected in solution by ^{29}Si-NMR and supported by characteristic catalytic reactions [11,12]. When Si_2Cl_6 was added to a solution of tmeda in Et_2O at room temperature (or at −78 °C), a white precipitate formed immediately. Filtering off the solvent and drying the product under vacuum afforded a white powdery material in 93% yield based on the assumed formation of a 1:1 adduct. Only slight changes in the ^{1}H- and ^{13}C-NMR spectra were observed upon adduct formation but evidence for the presence of hypercoordinated silicon species was obtained from the solid state ^{29}Si-NMR spectrum, in which only a strong upfield signal at δ −79.24 ppm was observed. The lack of other ^{29}Si peaks was consistent with the idea of a stoichiometric reaction. The presence of a single ^{29}Si-NMR chemical shift suggests the possibility of a six-membered ring structure for this adduct as shown below.



The reaction of Si_2Cl_6 with DMF further supports the notion of the formation of hypercoordinated disilane species. In this case, although we could not obtain pure

Table 1
Crystal data and structure refinement for **5a** and **8**

Empirical formula	$C_{28}H_{20}Cl_{18}O_4Si_6$	$C_8H_{16}Cl_2N_2O_2Si$
Formula weight	1227.08	271.22
Temperature (K)	173(2)	173(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
Unit cell dimensions		
a (Å)	19.5119(10)	10.3238(5)
b (Å)	5.9456(5)	9.0982(5)
c (Å)	22.7893(12)	14.3632(7)
α (°)	90	90
β (°)	110.493(1)	103.822(1)
γ (°)	90	90
V (Å^3)	2476.5(3)	1310.04(12)
Z	2	4
D_{calc} (mg m^{-3})	1.646	1.375
Absorption coefficient (mm^{-1})	1.173	0.572
F(000)	1220	568
Crystal size (mm^3)	0.43 × 0.31 × 0.14	0.45 × 0.45 × 0.45
θ range for data collection (°)	1.11–26.37	2.67–26.36
Index ranges	$-24 \leq h \leq 22$, $0 \leq k \leq 7$, $0 \leq l \leq 28$	$-12 \leq h \leq 12$, $0 \leq k \leq 11$, $0 \leq l \leq 17$
Reflections collected	22 002	11 557
Independent reflections	5077 [$R_{int} = 0.0385$]	2669 [$R_{int} = 0.0170$]
Completeness to $\theta = 26.37°$	99.8%	99.9%
Absorption correction	Empirical with SADABS	Empirical with SADABS
Max/min transmission	0.8530 and 0.6324	0.7830 and 0.7830
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	5077/0/253	2669/0/140
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0397$, $wR_2 = 0.1122$	$R_1 = 0.0250$, $wR_2 = 0.0914$
R indices (all data)	$R_1 = 0.0574$, $wR_2 = 0.1247$	$R_1 = 0.0288$, $wR_2 = 0.0948$
Goodness-of-fit on F^2	1.081	1.006
Largest difference peak and hole (e Å^{-3})	0.694 and −0.543	0.239 and −0.219

Table 2
Bond lengths (Å) and angles (°) for **5a** and **8**

5a		**8**	
Bond lengths			
Cl(1)–Si(1)	2.0061(12)	Si–N(1)	1.8303(11)
Cl(2)–Si(1)	2.0096(12)	Si–N(2)	1.8345(11)
Cl(3)–Si(1)	2.0086(12)	Si–O(2)	1.8850(10)
Cl(4)–Si(2)	1.9914(13)	Si–O(1)	1.8859(10)
Cl(5)–Si(2)	2.0107(13)	Si–Cl(1)	2.1447(5)
Cl(6)–Si(2)	2.0085(14)	Si–Cl(2)	2.1542(5)
Si(1)–O(1)	1.603(2)	Si–C(5)	2.2886(14)
Si(2)–O(2)	1.614(2)	Si–C(1)	2.2896(14)
O(1)–C(1)	1.397(3)		
O(2)–C(2)	1.400(3)		
Bond angles			
Cl(1)–Si(1)–Cl(3)	109.59(6)	N(1)–Si–N(2)	158.86(6)
O(1)–Si(1)–Cl(2)	108.72(9)	N(1)–Si–O(2)	94.50(5)
Cl(1)–Si(1)–Cl(2)	110.08(6)	N(2)–Si–O(2)	69.14(5)
Cl(3)–Si(1)–Cl(2)	108.20(6)	N(1)–Si–O(1)	69.48(5)
Cl(4)–Si(2)–Cl(6)	111.34(7)	N(2)–Si–O(1)	95.47(5)
O(2)–Si(2)–Cl(5)	111.63(9)	O(2)–Si–O(1)	86.76(4)
Cl(4)–Si(2)–Cl(5)	110.29(7)	N(1)–Si–Cl(1)	98.00(4)
Cl(6)–Si(2)–Cl(5)	106.58(6)	N(2)–Si–Cl(1)	96.92(4)
C(1)–O(1)–Si(1)	130.39(18)	O(2)–Si–Cl(1)	165.49(3)
C(2)–O(2)–Si(2)	127.41(18)	O(1)–Si–Cl(1)	90.74(3)
C(2)–C(1)–O(1)	118.5(3)	N(1)–Si–Cl(2)	95.97(4)
		N(2)–Si–Cl(2)	97.45(4)
		O(2)–Si–Cl(2)	90.58(4)
		O(1)–Si–Cl(2)	164.92(4)
		Cl(1)–Si–Cl(2)	95.40(2)
		N(1)–Si–C(5)	128.07(5)
		N(2)–Si–C(5)	34.57(5)
		O(2)–Si–C(5)	34.58(4)
		O(1)–Si–C(5)	91.95(4)
		Cl(1)–Si–C(5)	131.43(4)
		Cl(2)–Si–C(5)	94.26(4)
		C(1)–O(1)–Si	89.72(8)
		C(5)–O(2)–Si	89.96(6)

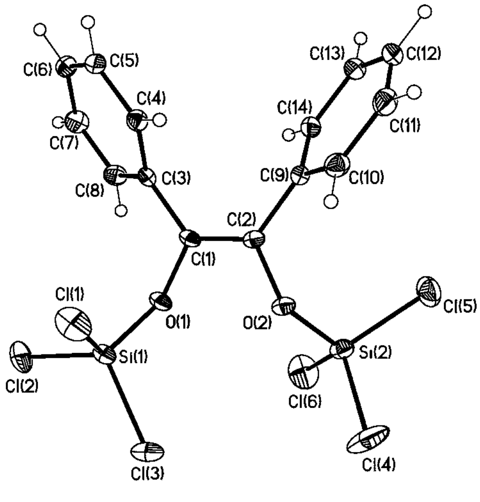
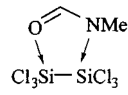


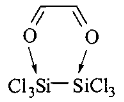
Fig. 1. Computer drawing of **5a**.

product from the reaction, two high-field signals (δ -184.71 and -192.10 ppm) were observed in the solid ^{29}Si-NMR spectrum (despite the similarity in the ^{1}H- and ^{13}C-NMR spectra of the adduct to DMF itself). The proposed structure of this adduct is shown below. Although five- and six-membered ring structures are shown for the DMF and tmeda adducts, respectively, we are unable to rule out a polymeric structure or a larger cyclic oligomer.



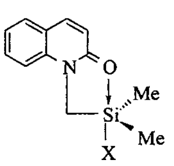
4.3. Si_2Cl_6 reactions with 1,2-diketones and a quinone

1,2-Diketones (**2a**,**b**) and (**3a**,**b**) and the quinone (**4**) react at moderate temperature (80 °C or below), to give **5a**,**b**; **6a**,**b** and **7**, respectively, in excellent conversions. We propose that adduct formation (as an unstable intermediate) between disilane **1** and a 1,2-diketone or a 1,2-quinone is the initial step for these reactions as depicted in the structure below. In an effort to obtain evidence for such an adduct, a mixture of **1** and **2a** (with **1** in 20% excess) was sealed in a glass tube. As described in Section 2, crystals were grown from this reaction mixture.



Analysis of these crystals by X-ray diffraction means, however, (Fig. 1) showed the compound to be *cis*-1,2-diphenyl-1,2-bis(trichlorosiloxy)ethylene **5a** (with **1** as an inclusion). Moreover, monitoring the reaction with ^{29}Si-NMR spectroscopy in toluene at -50 °C showed instant formation of **5a**. These results suggest that any intermediate adduct formed must be too short-lived to allow isolation or detection by NMR spectroscopy.

Examples of coordination of an acetyl group (via oxygen) to a silicon atom are well known [13]. It has been reported [12] that in **9**–**12** the Si–X as well as the Si–O bond distances vary with different X groups, with the shortest Si–O bond (1.74 Å) observed for X = SO_3CF_3. This bond distance (not unexpectedly) is longer than the Si–O bond in **5a** [1.609(2) Å, Fig. 1].



9: X = F
10: X = Cl
11: X = Br
12: X = SO_3CF_3

4.4. Synthesis of a new hexacoordinated silicon species

When we performed the reaction between **1** and four equivalents of the lithium salt of *N*-methylpropionamide (obtained by reacting equimolar amounts of

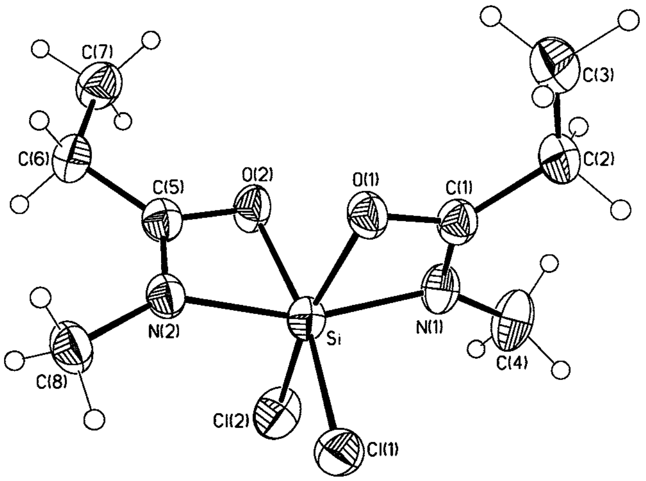


Fig. 2. Computer drawing of **8**.

N-methylpropionamide and *t*-BuLi in Et_2O) we obtained the novel hexacoordinated silicon compound **8** (Fig. 2). It is interesting to note that the Si–N and Si–O bond lengths in this compound [1.8324(11) and 1.8855(11) Å, respectively] are fairly similar, and that the O–C and ring N–C links are essentially the same length [1.2987(15) and 1.3014(18) Å, respectively] indicating rather compete delocalization of the electrons within the four-membered ring systems.

The synthesis of **8** was carried out by the reaction of LiNMeC(O)Et with Si_2Cl_6 or $SiCl_4$ using the stoichiometries shown in reactions (1) and (2), respectively. Reaction (1) was originally performed with the intention of making **14** in reaction (3).

$$\mathrm{4LiNMeC(O)Et + Si_2Cl_6 \rightarrow \mathit{cis}\text{-}\underset{\mathbf{8}}{Si[NMeC(O)Et]_2Cl_2} + \underset{\mathbf{13}}{[:Si[NMeC(O)Et]_2]_x} + 4LiCl} \quad (1)$$

$$\mathrm{2LiNMeC(O)Et + SiCl_4 \rightarrow \mathbf{8} + 2LiCl} \quad (2)$$

$$\mathrm{4LiNMeC(O)Et + Si_2Cl_6 \rightarrow \underset{\mathbf{14}}{Cl[NMeC(O)Et]_2SiSi[NMeC(O)Et]_2Cl}} \quad (3)$$

The formation of disproportionation product **8** (instead of **14**) suggests that silylene **13**, its silicon–silicon double bonded dimer or a cyclic oligomer had formed. Although we have been unable to isolate and characterize **13**, further efforts are underway to do so.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 172400 and 172401 for compounds **5a** and **8**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

The authors thank the NSF and the Donors of the Petroleum Research Fund administered by the American Chemical Society for grant support.

References

[1] H. Yamashita, N.P. Reddy, M. Tanaka, Organometallics 16 (1997) 5223.

[2] K. Tamao, S. Okazaki, M. Kumada, J. Organomet. Chem. 146 (1978) 87.

[3] (a) J. Yang, J.G. Verkade, J. Am. Chem. Soc. 120 (1998) 3855;
(b) J. Yang, J.G. Verkade, Organometallics 19 (2000) 893.

[4] (a) I. El-Sayed, Y. Hatanaka, C. Muguruma, S. Shimada, M. Tanaka, N. Koga, M. Mikami, J. Am. Chem. Soc. 121 (1999) 5095;
(b) I.D. Kalikhman, I.B. Bannikova, L.P. Petuchov, V.A. Pestunovich, M.G. Voronkov, Dokl. Akad. Nauk. SSSR 287 (1986) 87.

[5] (a) I.D. Kalikhman, V.A. Pestunovich, B.A. Gostevskii, O.B. Banikova, M.G. Voronkov, J. Organomet. Chem. 338 (1988) 169;
(b) A.A. Macharashvili, V.E. Shklover, Yu.T. Struchkov, B.A. Gostevskii, I.D. Kalikhman, O.B. Bannikova, M.G. Voronkov, V.A. Pestunovich, J. Organomet. Chem. 356 (1988) 23;
(c) I. El-Sayed, Y. Hatanaka, C. Muguruma, S. Shimada, M. Tanaka, N. Koga, M. Mikami, J. Am. Chem. Soc. 121 (1999) 5095.

[6] I. Kalikhman, O. Girshberg, L. Lameyer, D. Stalke, D. Kost, Organometallics 19 (2000) 1927.

[7] R.H. Blessing, Acta Crystallogr. A51 (1995) 33.

[8] All software and sources of the scattering factors are contained in the SHELXTL (version 5.1) program library (G. Sheldrick, Bruker Analytical X-Ray System, Madison WI).

[9] (a) K. Creber, T. Ho, Can. J. Chem. 60 (1982) 1054;
(b) B. Adeleka, J. Wan, J. Chem. Soc. Perkin Trans. 2 1 (1980) 225.

[10] Yu.N. Volynov, B.N. Dolgov, Zhurnal obschei Khimii 10 (1940) 550.

[11] For reviews on hypercoordinated silicon chemistry, see: (a) C. Chuit, R.J.P. Corriu, J.C. Young, Chem. Rev. 93 (1993) 1371;
(b) R.R. Holmes, Chem. Rev. 96 (1996) 927.

[12] S. Kobayashi, K. Nishio, J. Org. Chem. 59 (1994) 6620.

[13] A. Bassindale, M. Borbaruah, S. Glynn, D. Parker, P. Taylor, J. Chem. Soc. Perkin Trans. 2 110 (1999) 2099.