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Synthesis and Reactions of a 2,5-Dithia-3,4-disilatitanacyclopentane

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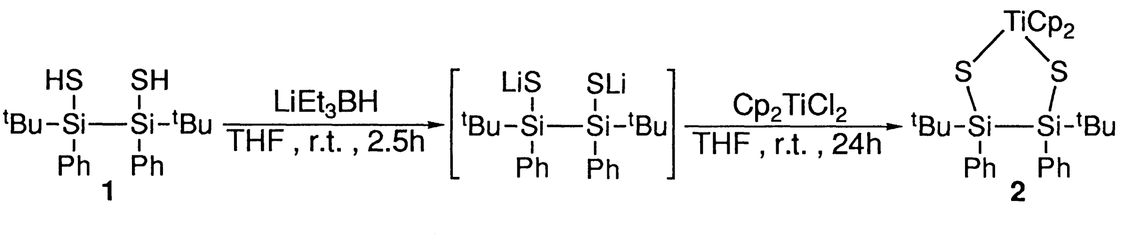
Lithium 1,2-di-*tert*-butyl-1,2-diphenyldisilane-1,2-dithiolate reacted with titanocene dichloride to afford *cis*-3,4-di-*tert*-butyl-3,4-diphenyl-2,5-dithia-3,4-disila-1-bis(cyclopentadienyl)titanacyclopentane (**2**), whose structure was determined by X-ray analysis. The titanacycle **2** is reacted with electrophilic reagents (SCl_2, S_2Cl_2, $PhPCl_2$, Ph_2GeCl_2) to afford the corresponding heterocycles in good yields.

Recently, heterocycles containing silicon (*e.g.* cyclosilazane,1a) cyclosilaphosphane,1b) cyclosilathiane1c)) have received increasing attention in the field of material science. On the other hand, the chemistry of metallacycles with incorporated titanocene units2) has attracted much interest, and these compounds have found widespread applications in organic synthesis.3) Nevertheless, the utility of these promising building blocks as a precursor of heterocyclic compounds containing silicon has not been fully realized.4) Herein we report the synthesis as well as structural features of a novel *cis*-3,4-di-*tert*-butyl-3,4-diphenyl-2,5-dithia-3,4-disila-1-bis(cyclopentadienyl)titanacyclopentane (**2**) and furthermore we demonstrate its suitability as a precursor for a variety of heterocycles containing a 1,4-dithia-2,3-disila fragment (eq.1).



(1)

To 819 mg (2.10 mmol) of *meso*-disilane-1,2-dithiol **1**5) dissolved in 20 mL of THF were added at room temperature 2.20 mL (2.20 mmol) of a 1.0 M solution of $LiBEt_3H$ in THF. After 3 h a solution of 522 mg (2.10 mmol) of Cp_2TiCl_2 in 10 mL of THF was introduced and the resulting mixture was stirred for 12 h. The crude product, obtained after filtration and evaporation of the solvent, was purified by preparative GPC (eluent: toluene) to yield 952 mg (80%) of *cis*-3,4-di-*tert*-butyl-3,4-diphenyl-2,5-dithia-3,4-disila-1-bis(cyclopentadienyl)titanacyclopentane (**2**)6) in diastereomerically pure form. The structure of **2** was determined by single crystal X-ray diffraction analysis.7) The titanacycle of **2** exhibits a half-chair conformation as depicted in Fig. 1.

The Ti-S bond lengths (2.39 Å resp. 2.47 Å) are within the normal range (2.42-2.45 Å3c)), the Si-S bonds (2.13 Å) are slightly shortened (usually 2.16-2.17 Å).3c) Interestingly, the Ti-S-Si bond angles (109.7° resp. 113.2°) are larger than those of other five-membered dithiatitanacycles (*e.g.* o-$C_6H_4S_2TiCp_2$: 95.7-

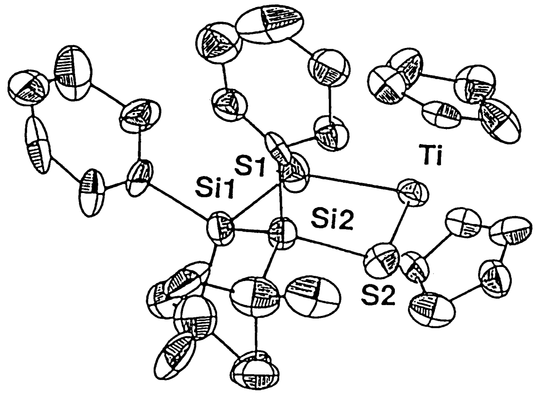


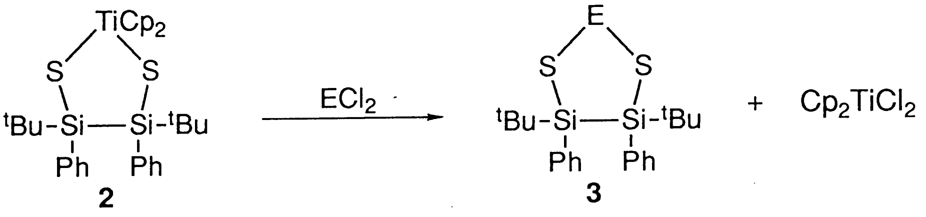
Fig. 1. ORTEP Drawing of **2**.

Bond Lengths (Å) and Angles (degree)

Ti-S1	2.47	Ti-S1-Si1	113.2
Ti-S2	2.39	Ti-S2-Si2	109.7
Si1-S1	2.13	S1-Ti-S2	93.9
Si2-S2	2.13	S1-Si1-Si2	99.0
Si1-Si2	2.41	S2-Si2-Si1	100.9

97.0°[8a)]; SCH=CHSTiCp$_2$: 94.2-95.0°[8b)]) and resemble those of acyclic derivatives (*e.g.* $Cp_2Ti(SPh)_2$: 113.6-115.5°[8c)]). On the other hand the S-Ti-S bond angle (93.9°) takes an intermediate value between five-membered titanacycles (*e.g.* *o*-$C_6H_4S_2TiCp_2$: 82.2°[8a)] ; SCH=CHSTiCp$_2$: 83.2°[8b)]) and acyclic ones (e. g. $Cp_2Ti(SPh)_2$ (99.3°)[8c)]).

Titanacycle **2** reacted with several electrophilic reagents under substitution of the titanocene unit to yield heterocycles in fair to good yields (eq. 2, Table 1). *E. g.* to a solution of 113 mg (0.200 mmol) of **2** in 10 mL of CS_2 was added under stirring at -78 °C a solution of 20.6 mg (0.200 mmol) of SCl_2 in 5 mL of CS_2. After 30 min the solvent was removed *in vacuo* and 10 mL of n-pentane were added. Reddish solids[9)] were filtered off, the solvent was evaporated and the residue recrystallized from n-pentane to afford 76 mg (90%) of 3,4,5-trithia-1,2-disilacyclopentane **3a**[10)] (entry 1 of Table 1), whose structure was confirmed by X-ray analysis[14)] (Fig. 2).



(2)

Table 1. Reactions of Disilatitanacycle **2** with Various Electrophilic Reagents

run		E[a)]	Solvent	Temp/°C	Time/h	Isolated Yield/%
1	**3a**[10)]	S	CS_2	-78	0.5	90
2	**3b**[11)]	SS	CS_2	-78	0.5	92
3	**3c**[12)]	PhP	Benzene	20	1	42
4	**3d**[13)]	Ph_2Ge	Toluene	110	24	55
5	**3e**	Ph_2Si	Xylene	140	72	——

a) The corresponding dichlorides ECl_2 were employed as reagents.

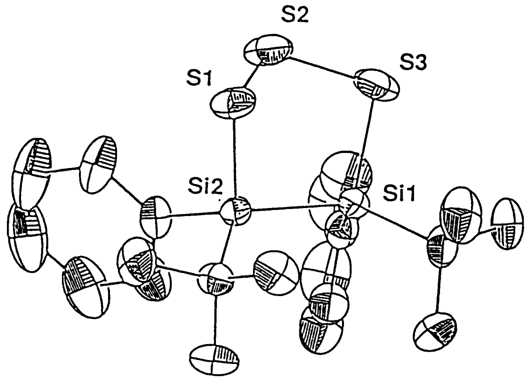


Fig. 2. ORTEP Drawing of **3a**.

Bond Length (Å) and Angles (degree)

Si1-Si2	2.41	Si1-Si2-S1	100.2
Si2-S1	2.17	Si2-Si1-S3	100.6
Si1-S3	2.18	Si2-S1-S2	92.7
S1-S2	2.06	S1-S2-S3	103.3
S2-S3	2.06	S2-S3-Si1	97.9

In the transformations of **2** with $PhPCl_2$, and especially with Ph_2GeCl_2 (Table 1, entries 3,4) more drastic conditions, *i. e.* evaluated temperature and prolonged reaction time were necessary to achieve full conversion. Nevertheless, it was not possible to convert **2** with Ph_2SiCl_2; even after 72 h in refluxing xylene only unreacted **2** was re-isolated.

Further work to elucidate the synthetic utility of dithiadisilatitanocene derivatives related to **2** is in progress.

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5) 1,2-Di-*tert*-butyl-1,2-diphenyldisilane-1,2-dithiol was prepared by reaction of 1,2-di-*tert*-butyl-1,2-diphenyldisilane-1,2-bis(triflate) with H_2S in the presence of triethylamine in 67% yield. Recrystallization from hexane gave diastereomerically pure **1**; mp 138-139 °C; ^1H NMR (400 MHz, C_6D_6) δ 0.23 (s, 2H), 0.95 (s, 18H), 7.16-7.18 (m, 6H), 7.99-8.01 (m, 4H); ^{13}C NMR (100 MHz, C_6D_6) δ 22.3 (s), 28.0 (q), 128.7 (d), 129.9 (d), 135.1 (s), 135.9 (d); ^{29}Si NMR (80 MHz, C_6D_6) δ 1.10; Anal. Found: C, 61.31; H, 7.61; S, 16.42%. Calcd for $C_{20}H_{30}S_2Si_2$: C, 61.48; H, 7.74; S, 16.41%.

6) **2**: mp 113 °C; ^1H NMR (400 MHz, C_6D_6) δ 1.39 (s, 18H), 5.77 (s, 5H), 6.21 (s, 5H), 7.18-7.25, 8.03-8.05 (m, 10H); ^{13}C NMR (100 MHz, C_6D_6) δ 24.77 (s), 28.63 (q), 118.27 (d), 118.45 (d), 127.55 (d), 129.0 (d), 136.36 (s), 141.36 (d); ^{29}Si NMR (80 MHz, C_6D_6) δ 40.99; MS, m/z 566 (M^+), 509 (M^+-^tBu).

7) Crystal Data for **2**: $C_{30}H_{38}S_2Si_2Ti$, M=566.84 are tetragonal with a=16.954(1) Å, c=41.679(3) Å, V=11980.3 Å^3, space group I-4, Z=16, μ(Mo Kα)= 5.1 cm^{-1}, r_{calcd}=1.26 g/cm^3. The 3212 independent reflections [$|Fo|>3\sigma|Fo|$, $\theta<50°$] were measured on an Enraf-Nonius CAD4 diffractometer using Mo-Kα irradiation and ω–2θ scan. The structure was solved by the direct method and all nonhydrogen atoms refined anisotropically by full-matrix least-squares to R=0.055 and Rw= 0.063.

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9) Reddish solids were identified as Cp_2TiCl_2 by ^{1}H NMR and mass spectroscopy.

10) **3a**: mp 119 °C; ^{1}H NMR (400 MHz, C_6D_6) δ 0.95 (s, 18H), 6.63-6.73 (m, 5H), 6.80-6.91 (m, 5H); ^{13}C NMR (100 MHz, C_6D_6) δ 22.5 (s), 29.5 (q), 127.8 (d), 127.9 (d), 129.4 (d), 135.6 (s); ^{29}Si NMR (80 MHz, C_6D_6) δ 28.4; MS, m/z 420 (M^+), 363 (M^+-^{t}Bu).

11) **3b**: mp 131 °C; ^{1}H NMR (400 MHz, C_6D_6) δ 1.25 (s, 18H), 7.03-7.16 (m, 5H), 7.50-7.61 (m, 5H); ^{29}Si NMR (80 MHz, C_6D_6) δ -7.79; MS, m/z 452 (M^+), 420 (M^+-S), 395 (M^+-^{t}Bu).

12) **3c**: ^{1}H NMR (90 MHz, C_6D_6) δ 0.99 (s, 18H), 7.18-7.20, 7.99-8.10 (m, 10H); ^{29}Si NMR (18 MHz, C_6D_6) δ -1.67; MS, m/z 469 (M^+), 439 (M^+-^{t}Bu).

13) **3d**: ^{1}H NMR (400 MHz, C_6D_6) δ 1.26 (s, 18H), 6.92-7.22, 7.41-7.52, 7.60,7.70, 7.88-8.01, 8.11-8.22 (m, 20H); ^{29}Si NMR (80 MHz, C_6D_6) δ 17.4; MS, m/z 616 (M^+), 559 (M^+-^{t}Bu).

14) Crystal Data of **3a**: $C_{20}H_{28}S_3Si_2$, M= 420.81 are triclinic with a=8.013(1) Å, b=9.860(1) Å, c=16.423(2) Å, α=86.60(1)°, β=82.50(1)°, γ=64.56(26)°, V=1161.8 Å^3, space group P-1, Z=2, μ(Mo Kα)=4.1cm^{-1}, r_{calcd}=1.20 g/cm^3. The 3367 independent reflections [$|Fo|>3\sigma|Fo|$, $\theta<50°$] were measured on an Enraf-Nonius CAD4 diffractometer using Mo-Kα irradiation and ω–2θ scan. The structure was solved by the direct method and all nonhydrogen atoms refined anisotropically by full-matrix least-squares to R=0.061 and Rw= 0.087.

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