Novel Silicon-containing Hydrocarbon Rings and Polymers *via* Metathesis: X-Ray Crystal Structure of *cis,cis*-1,1,6,6-Tetraphenyl-1,6-disilacyclodeca-3,8-diene

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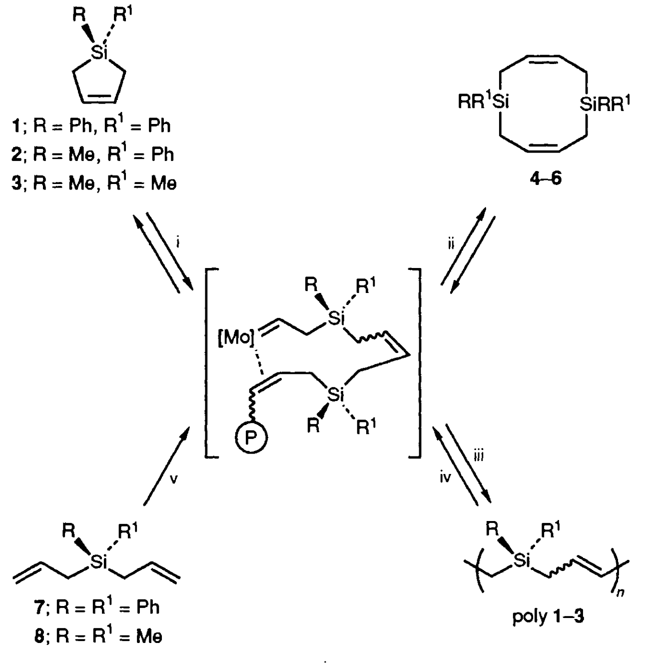
Novel disilacyclodeca-3,8-dienes and unsaturated silicon-containing polymers are accessible *via* metathesis of silacyclopent-3-enes and diallylsilicon reagents using the Schrock catalyst $[Mo(NC_6H_3Pr^i{}_2\text{-}2,6)(CHCMe_2Ph)\{OCMe(CF_3)_2\}_2]$.

Silicon-containing hydrocarbon polymers are of considerable interest due to their opto-electronic properties[1] and as potential precursors to silicon carbide.[2] While anionic polymerization of silacyclopent-3-enes has been investigated extensively by Weber and co-workers,[3] there have been only brief reports of the ring-opening metathesis polymerization (ROMP) of such silicon-containing ring systems;[4] to date, these studies have employed conventional catalyst formulations.

Here, we describe reactions of silacyclopent-3-enes and diallylsilicon reagents with the Schrock molybdenum catalyst $[Mo(NC_6H_3Pr^i{}_2\text{-}2,6)(CHCMe_2Ph)\{OCMe(CF_3)_2\}_2]$ Mo–I[5] giving rise to silicon-containing polymers and novel ten-membered ring systems depending upon the reaction conditions. The chemistry is summarised in Scheme 1. The silacyclopentenes **1–3** react with Mo–**I** in benzene to afford an equilibrium mixture of free Mo–**I**, a trace of living oligomers, monomer and ten-membered cyclo-dimers **4–6** (Scheme 1).



Scheme 1 *Reagents and conditions*: i, Mo-**I**, room temp.; ii, **1–3** in benzene, 10 min, room temp.; iii, neat **1–3**, 30 min, room temp.; iv, Mo-**I**, benzene, room temp.; v, Mo-**I**, $-C_2H_4$; benzene, 30 min, room temp. to give **4** and **6**; neat **7**, **8**, 3 h, room temp. to give poly-**1**, **3** respectively

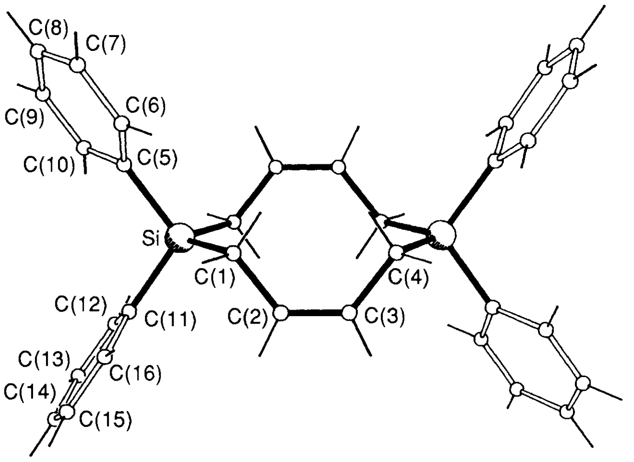


Fig. 1 Molecular structure of *cis-cis*-**4**. Key dimensions: Si-C(1) 1.872(2), Si-C(5) 1.876(2), Si-C(11) 1.874(1), Si-C(4') 1.876(2), C(1)-C(2) 1.494(2), C(2)-C(3) 1.331(2), C(3)-C(4) 1.497(2) Å; C(1)-Si-C(4') 109.8(1), C(5)-Si-C(11) 109.8(1)°.

Table 1 GPC Data for poly-**1** and -**2** (relative to polystyrene standards in THF)[a]

Monomer equiv.	M_w	M_n	PDI $(M_w/M_n)^b$
$Ph_2SiC_4H_6$ **1**, 100	72 570	35 030	2.07
1, 200	81 770	47 000	1.74
1, 543	72 270	40 260	1.80
1, 1057	107 800	61 100	1.76
$PhMeSiC_4H_6$ **2**, 98	76 650	38 330	2.00
2, 720	45 520	21 300	2.14

[a] Using Mo-**I** as initiator. [b] PDI = polydispersity index.

The *cis,cis, cis,trans* and *trans,trans* alkenic isomers of **4–6** are evident in the crude mixtures by NMR,† but only the *cis,cis* isomers of **4** and **6** have been isolated in pure form. The crystal structure of *cis-cis*- **4**‡ has been determined and is shown in Fig. 1. The molecule adopts an 'arm-chair' conformation which is also consistent with its low temperature solution ^1H NMR data.† To our knowledge, there is only one other structurally characterised example of such a ten-membered disilicon ring system,[6] and we have found no evidence for these macrocycles when using conventional metathesis catalysts.[7] The dienes arise by secondary metathesis or 'back-biting' reactions in which the living alkylidene metathesises a double bond in the growing polymer chain (Scheme 1). This is consistent with the highly reactive nature of the hexafluoro-*tert*-butoxide catalyst which has been shown to be capable of metathesising ordinary alkenes.[5]

In the absence of solvent, **1** and **2** are readily polymerised by Mo-**I**; **3** gives low molecular weight oligomeric material. Selected gel-permeation chromatography (GPC) data for poly-**1** and poly-**2** are shown in Table 1. The polymers are found to contain a mixture of *cis* and *trans* double bonds by ^{13}C NMR.§ (55% *trans* for poly-**1**; 75% *trans* for poly-**2**: by contrast, conventional initiators tend to give high *cis* polymers

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† *Selected NMR data* for *cis-cis*-**4**: ^1H NMR (C_7D_8, 400 MHz, 298 K): δ 2.20 (br m, 8 H, CH_2), 5.40 (apparent t, $^3J_{HH}$ 5.6 Hz, 4 H, CH), 7.1–7.6 (aromatic C–H); (C_7D_8, 400 MHz, 213 K): δ 1.77 (d, $^3J_{HH}$ 12.8 Hz, 4 H, CH_2), 2.51 (dd, $^3J_{HH}$ 10.8 and 12.8 Hz, 4 H, CH_2), 5.39 (d, $^3J_{HH}$ 10.8 Hz, 4 H, CH). ^{13}C NMR ($CDCl_3$, 100.6 MHz, 298 K): δ 12.6 (s, CH_2), 123.0 (s, CH), 127.9, 129.4, 134.6, 135.6 (aromatic C). ^{29}Si NMR ($CDCl_3$, 79.5 MHz, 298 K): δ −11.10 (s). For *cis-trans*-**4**: ^{13}C NMR ($CDCl_3$, 100.6 MHz, 298 K): δ 13.9 (s, CH_2), 19.6 (s, CH_2), 122.7 (s, CH), 123.5 (s, CH). ^{29}Si NMR ($CDCl_3$, 79.5 MHz, 298 K): δ −16.8 (s). For *trans-trans*-**4**: ^{13}C NMR ($CDCl_3$, 100.6 MHz, 298 K): δ 20.0 (s, CH_2), 125.7 (s, CH). ^{29}Si NMR ($CDCl_3$, 79.5 MHz, 298 K): δ −23.5 (s). For *cis-cis*-**6**: ^1H NMR ($CDCl_3$, 400 MHz, 298 K); δ 0.09 (s,CH_3), 1.43 (d, $^3J_{HH}$ 6.4 Hz, 8 H, CH_2), 5.28 (m, 4 H, CH). ^{13}C NMR ($CDCl_3$, 100.6 MHz, 298 K): δ −3.0 (s, CH_3), 15.7 (s, CH_2), 122.8 (s, CH). ^{29}Si NMR ($CDCl_3$, 79.5 MHz, 298 K): δ −0.63 (s). For *cis-trans*-**6**: ^{13}C NMR ($CDCl_3$, 100.6 MHz, 298 K): δ 16.3 (s, CH_2), 22.6 (s, CH_2), 122.5 (s, CH), 123.0 (s, CH). ^{29}Si NMR ($CDCl_3$, 79.5 MHz, 298 K): δ −5.5 (s). For *trans-trans*-**6**: ^{13}C NMR ($CDCl_3$, 100.6 MHz, 298 K): δ 22.9 (s, CH_2), 125.0 (s, CH). ^{29}Si NMR ($CDCl_3$, 79.5 MHz, 298 K): δ −11.9 (s).

‡ *Crystal data* for $C_{32}H_{32}Si_2$: $M = 472.8$, monoclinic, $I2/a$ (non-standard setting of $C2/c$), $a = 25.058(2)$, $b = 6.6731(6)$, $c = 16.769(1)$ Å, $\beta = 101.961(9)°$, $U = 2743.1$ Å³, $Z = 4$, $D_c = 1.145$ g cm^{-3}, λ(Cu-Kα) = 1.54184 Å, $\mu = 1.28$ mm^{-1}, $F(000) = 1008$, $T = 295$ K. 2184 reflections with $F > 4\sigma_c(F)$ were used in the analysis (σ_c from counting statistics only). The structure was determined by direct methods and difference syntheses, with blocked-cascade least-squares refinement on F. Intensities were measured by an on-line profile fitting method.[9] SHELXTL[10] and locally written computer programs were employed, and atomic scattering factors were taken from ref. 11. The weighting scheme was $w^{-1} = \sigma^2(F_o) = \sigma_c^2(F_o) + A_1 + A_2G + A_3G^2 + A_4H + A_5H^2 + A_6GH$, where $G = F_o/F_{max}$ and $H = \sin\theta/\sin\theta_{max}$; the coefficients A were derived from analysis of the data.[12] The final $R = 0.0409$, $R_w = (\Sigma w\Delta^2/\Sigma wF_o^2)^{1/2} = 0.0351$ for 155 parameters. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

§ *Selected spectroscopic data* (*c* = *cis; t* = *trans*; *cc* and *ct* refer to carbons adjacent to *cis* double bonds with a *cis* and *trans* next neighbour, respectively) for poly-**1** (55% *trans*): ^1H NMR ($CDCl_3$, 400 MHz, 298 K): δ 1.61, 1.66, 1.71, 1.85 (br m, CH_2), 5.06, 5.13, 5.20, 5.24, 5.27 (br m, CH), 7.10–7.66 (aromatic C–H). ^{13}C NMR ($CDCl_3$, 100.6 MHz, 298 K): δ 13.67 (*cc*, CH_2), 18.10, 18.24, 18.43 (*tt*/*tc*, CH_2), 123.34 (*ct*, CH), 123.49 (*cc*, CH), 124.58 (*tt*, CH), 124.77 (*tc*, CH), 127–136 (aromatic C). ^{29}Si NMR ($CDCl_3$, 79.5 MHz, 298 K): δ −10.54 (s), −10.92 (s), −11.25 (s), −11.34 (s). For poly-**2** (75% *trans*): ^1H NMR ($CDCl_3$, 400 MHz, 298 K): δ 0.09, 0.16, 0.21 (s, Me), 1.56, 1.63 (d, *J* 4.8 Hz, CH_2), 5.14, 5.27 (t, *J* 4.8 Hz, CH), 7.27–7.50 (m, aromatic C–Hs). ^{13}C NMR ($CDCl_3$, 100.6 MHz, 298 K): δ −5.45 (CH_3), 15.30 (*cc*, *ct*, CH_2), 19.78 (*tt*, CH_2), 19.91 (*tc*, CH_2), 123.10 (*ct*, CH), 123.24 (*cc*, CH), 124.37 (*tt*, CH), 124.47 (*tc*, CH), 127.7, 129.0, 133.9, 137.8 (aromatic C). ^{29}Si NMR ($CDCl_3$, 79.5 MHz, 298 K): δ −4.31, −4.74, −5.18.

with **1** and **2**[4,7]). The molecular weight distributions of all these polymers also tend to the most probable value of 2 consistent with secondary metathesis reactions.[8] Advantage can be taken of such reactivity to degrade living poly-**1** and poly-**2** back to a mixture of the silacyclopent-3-enes and disilacyclodeca-3,8-dienes simply by addition of benzene. Capped (or 'dead') polymers can be degraded similarly by treatment with catalytic quantities of Mo–**I** in aromatic hydrocarbon solvent.

The ability of Mo–**I** to metathesise ordinary alkenes led us to investigate whether diallylsilicon monomers could be utilised (with elimination of ethylene) in a similar dimerization/polymerization manifold of reactivity. This is indeed the case: in aromatic solvent, Mo–**I** catalyses the conversion of $R_2Si(C_3H_5)_2$ (**7**, R = Ph; **8**, R = Me) to an equilibrium mixture of the silacyclopentenes **1** and **3**, and the ten-membered disilicon rings **4** and **6**. When added neat, **7** and **8** readily polymerize to poly-**1** and poly-**3** with elimination of C_2H_4. These polymers contain a higher *trans* content (90 and 75%, respectively) than observed in the polymers arising from silacyclopent-3-enes, most probably due to the predominance of a metathesis polycondensation mechanism.[13]

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