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Silicon-Containing Macrocycles and Polymers via Metathesis: X-ray Crystal Structures of *cis,cis*- and *trans,trans*-1,1,6,6-Tetraphenyl-1,6-disilacyclodeca-3,8-diene

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$Mo[N\text{-}2,6\text{-}{}^iPr_2C_6H_3][CHCMe_2Ph][OCMe(CF_3)_2]_2$ (Mo-I) catalyzes the cyclodimerization of 1,1-disubstituted silacyclopent-3-enes, $RR'SiC_6H_4$ ($R = R' = Ph$ (**1**); $R = Me$, $R' = Ph$ (**2**); $R = R' = Me$ (**3**)), in aromatic solvent to mixtures of *cis,cis*-, *cis,trans*-, and *trans,trans*-disilacyclodeca-3,8-dienes. Acyclic metal alkylidene end-capped oligomers are also evident (by NMR) in the equilibrium reaction mixtures. *cis,cis*-1,1,6,6-Tetraphenyl-1,6-disilacyclodeca-3,8-diene (**6a**) crystallizes from the reaction medium at room temperature: an X-ray structure determination (monoclinic, $I2/a$, $a = 25.058(2)$ Å, $b = 6.6731(6)$ Å, $c = 16.769(1)$ Å, $\beta = 101.961(9)°$, $V = 2743.1$ Å^3, $Z = 4$, final $R = 0.0409$, $R_w = 0.0351$ based on 2184 reflections) shows an "armchair" conformation which is also consistent with low-temperature ^1H NMR data for **6a**. In the absence of solvent, Mo-I polymerizes **1** and **2** to poly(silapentenes), containing 55% and 75% trans double bonds, respectively. By comparison, the conventional initiator WCl_6/Me_4Sn affords >90% *cis*-poly-**1** and ca. 80% *cis*-poly-**2**, respectively. The molecular weight distributions of all the polymers tend to the most probable value of 2.0, consistent with substantial secondary metathesis reactions. The polymers may also be degraded back to an equilibrium mixture of the 5- and 10-membered rings upon treatment with Mo-I in aromatic solvent. "Living" polymers degrade similarly upon dissolution in benzene or toluene. Mo-I also catalyzes the cyclization and cyclodimerization of diallylsilicon reagents (with evolution of ethylene) to similar equilibrium mixtures of 5- and 10-membered rings in aromatic solvent; polymers were obtained in the absence of solvent. Significantly, poly-**1**–**3** prepared in this manner possess a substantially higher trans content than those obtained from **1**–**3**. Degradation of high *trans*-poly-**1** by Mo-I in toluene gives *trans,trans*-1,1,6,6-tetraphenyl-1,6-disilacyclodeca-3,8-diene (**6c**), whose crystal structure has been determined (triclinic, $P\bar{1}$, $a = 7.002(1)$ Å, $b = 17.074(2)$ Å $c = 18.890(2)$ Å, $\alpha = 79.67(1)°$, $\beta = 79.68(1)°$, $\gamma = 87.65(1)°$, $V = 2185.7$ Å^3, $Z = 3$, final $R = 0.0769$, $R_w = 0.0656$ based on 4104 reflections). The mechanistic implications of these observations are discussed.

Introduction

Silicon-containing hydrocarbon polymers are of interest due to their opto-electronic properties[2] and as potential precursors to ceramics and silicon carbide fibers.[3] Anionic ring opening of 1,1-disubstituted silacyclopent-3-enes has been investigated extensively by Weber and co-workers.[4] However, there have been only brief reports of the ring-opening metathesis polymerization (ROMP) of five-membered silicon ring systems; these studies have all employed conventional catalyst formulations.[5]

In general, due to the relatively small ring strain in the monomer, the free energy change accompanying the ring opening of five-membered ring systems is only moderately negative.[6] Cyclopentene ($\Delta G° = 2.3$ kJ mol^{-1}) has been studied by Schrock and co-workers using the well-defined catalyst $W[N\text{-}2,6\text{-}{}^iPr_2C_6H_3][CHCMe_3][OCMe(CF_3)_2]_2$. At −60 °C, living polypentenamer is obtained, but at +60 °C the polymer is degraded back to a mixture of monomer and free catalyst.[7] This gives some idea of the delicate energetic balance between polymerization and depolymerization for five-membered-ring systems. In this regard, the ring-opening polymerization of heteroatom-containing cyclopentenes is of considerable academic interest in addition to its potential for generating new materials of technological relevance.

Here, we report the results of our investigations into the metathesis chemistry of silicon-containing ring systems of type **1**–**3** with the well-defined Schrock molybdenum alkylidene catalyst Mo-I;[8] the microstructures of the

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[1] (a) University of Durham. (b) University of Newcastle upon Tyne. (c) Ciba Geigy plc.

[2] Zeldin, M., Wynne, K. J., Allcock, H. R., Eds. *Inorganic and Organometallic Polymers (Macromolecules Containing Silicon, Phosphorus and Other Inorganic Elements)*; American Chemical Society: Washington, DC, 1988, and references therein.

[3] (a) Yajima, S.; Hasegawa, Y.; Hayashi, J.; Ilmura, M. T. *J. Mater. Sci.* **1978**, *13*, 2569. (b) Hasegawa, Y.; Ilmura, M. T.; Yajima, S. *J. Mater. Sci.* **1980**, *15*, 720. (c) Boury, B.; Corriu, R. J. P.; Leclercq, D.; Mutin, P. H.; Planeix, J.-M.; Vioux, A. *Organometallics* 1991, *10*, 1457.

[4] (a) Zhou, S. Q.; Park, Y. T.; Manuel, G.; Weber, W. P. *Polym. Bull.* **1990**, *23*, 491. (b) Liao, X.; Ko, Y.-H.; Manuel, G.; Weber, W. P. *Polym. Bull.* **1991**, *25*, 63. (c) Zhang, X.; Zhou, Q.; Weber, W. P.; Horvath, R. F.; Chan, T. H.; Manuel, G. *Macromolecules* 1988, *21*, 1563.

[5] (a) Lammens, H.; Sartori, G.; Siffert, J.; Sprecher, N. *J. Polym. Sci., Part B* 1971, *9*, 341. (b) Finkel'shtein, E. S.; Portnykh, E. P.; Ushakov, N. V.; Vdovin, V. M. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1981**, *3*, 641. (c) Stonich, D. A.; Weber, W. P. *Polym. Bull.* **1991**, *25*, 629.

[6] Ivin, K. J. *Olefin Metathesis*; Academic Press: New York, 1983; Chapter 11, pp 190–194, and references therein.

[7] Schrock, R. R. *Acc. Chem. Res.* **1990**, *23*, 158.

[8] Schrock, R. R.; Murdzek, J. S.; Bazan, G. C.; Robbins, J.; DiMare, M.; O'Regan, M. *J. Am. Chem. Soc.* **1990**, *112*, 3875.

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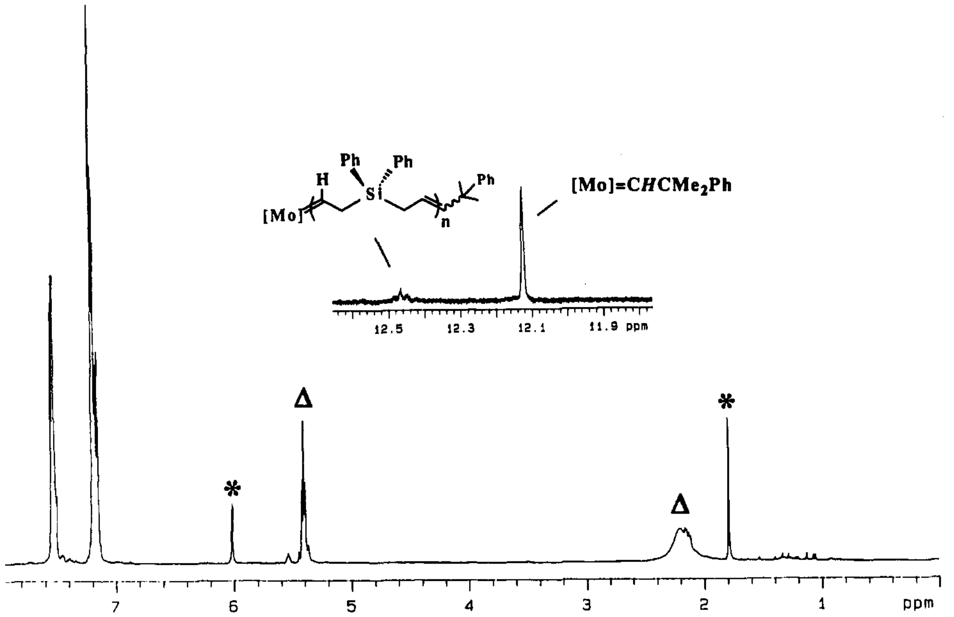
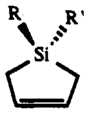
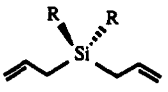


Figure 1. 400-MHz ^{1}H NMR spectrum (C_6D_6) for the reaction between 1 (25 equiv) and Mo[N-2,6-^{i}Pr$_2$C$_6$H$_3$][CHCMe$_2$Ph][OCMe(CF$_3$)$_2$]$_2$ (Mo-I): (*) resonances for 1; (Δ) resonances for 6.

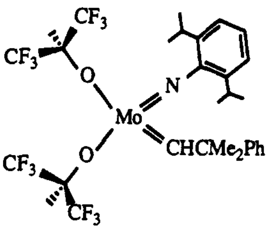
resultant polymers are compared with those obtained using a classical catalyst formulation. An unexpected outcome of these studies was the ready isolation of silicon-containing macrocycles, two of which have been structurally characterized. Diallyl substrates 4 and 5 have also been investigated and found to enter a similar manifold of reactivity with this molybdenum hexafluoro-*tert*-butoxide catalyst. A preliminary account of this work has appeared.[9] During the course of these investigations, we became aware of some related *acyclic diene metathesis* (ADMET) studies on vinyl- and allylsilicon reagents by Wagener and Smith[10] using an analogous Schrock tungsten catalyst system. The diallyldimethylsilicon substrate 5 is common to both of these studies, allowing a direct comparison to be made between the two closely related catalyst systems.



R = R' = Ph (1)
R = Me, R' = Ph (2)
R = R' = Me (3)



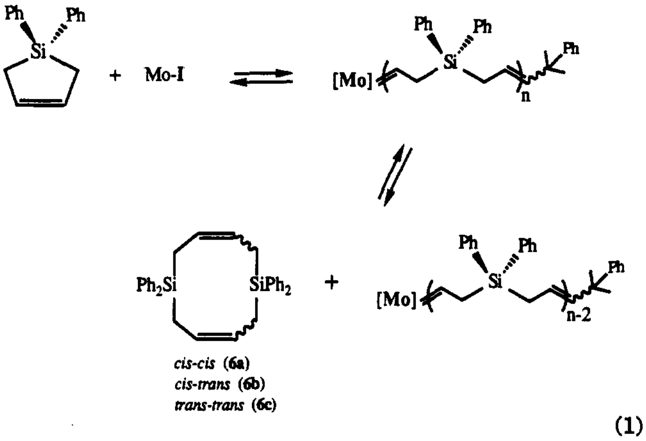
R = Ph (4)
R = Me (5)



Mo-I

Results

I. Reactions of 1–3 with Mo[N-2,6-^{i}Pr$_2$C$_6$H$_3$][CHCMe$_2$Ph][OCMe(CF$_3$)$_2$]$_2$ (Mo-I) in Benzene. The ^{1}H NMR spectrum arising from the treatment of Mo-I with 25 equiv of 1 in benzene-d_6 is shown in Figure 1. The spectrum shows that an equilibrium mix is generated in which signals attributable to free Mo-I, metal alkylidene end-capped oligomers, the monomer, and new cyclic dimer species 6 may be identified; the monomer–dimer ratio is about 40:60. The overall reaction is best viewed as shown in eq 1. In the low-field region of the spectrum, the resonance at δ 12.12 ppm is attributable to the alkylidene hydrogen of free Mo-I, while the nearby low-intensity triplet resonance at δ 12.46 ppm can be attributed to acyclic living oligomers, the triplet pattern arising from coupling of the alkylidene hydrogen to the β methylene protons. Monomer is also clearly evident (asterisked resonances). The triplet resonance at δ 5.40 ppm and the minor signal at δ 5.48 ppm, plus the unresolved broadened signal at δ 2.20 ppm, are due to a mixture of cis,cis (**6a**), cis,trans (**6b**), and trans,trans (**6c**) cyclodimer products. Most of this mixture (84%) consists of the cis,cis isomer (**6a**) which crystallizes selectively from the reaction mixture upon standing at room temperature. The structure of this compound has been determined by X-ray crystallography (see below).



cis-cis (**6a**)
cis-trans (**6b**)
trans-trans (**6c**)

(1)

Reactions of 2 and 3 with Mo-I in benzene give analogous equilibrium mixtures, including the new cyclodimer products 7 and 8, which, unlike 6, do not crystallize from the

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(9) Anhaus, J. T.; Clegg, W.; Collingwood, S. P.; Gibson, V. C. *J. Chem. Soc., Chem. Commun.* **1991**, 1720.

(10) Wagener, K. B.; Smith, D. W., Jr. *Macromolecules* **1991**, *24*, 6073. Wagener, K. B.; Smith, D. W., Jr. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* 1991, 373.

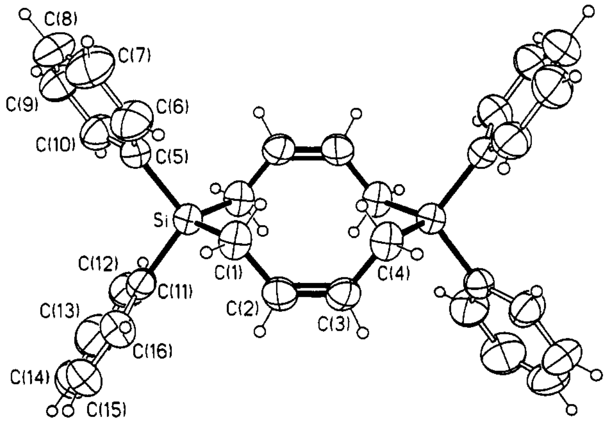

Figure 2. Molecular structure of *cis,cis*-[$Ph_2Si(C_4H_6)]_2$ (**6a**) showing the atom labeling and "armchair" conformation. Thermal ellipsoids are at the 50% probability level for non-H atoms.

Table I. Crystal Data for 6a and 6c

	6a	6c
molecular formula	$C_{32}H_{32}Si_2$	$C_{32}H_{32}Si_2\cdot{}^1/_3C_7H_8$
M_r	472.8	503.5
cryst syst	monoclinic	triclinic
cryst size (mm)	0.20 × 0.45 × 0.60	0.08 × 0.16 × 0.52
space group	*I*2/*a* (nonstd setting of *C*2/*c*)	$P\bar{1}$
a (Å)	25.058(2)	7.002(1)
b (Å)	6.6731(6)	17.074(2)
c (Å)	16.769(1)	18.890(2)
α (deg)		79.67(1)
β (deg)	101.961(9)	79.68(1)
γ (deg)		87.65(1)
V (Å^3)	2743.1	2185.7
Z	4	3
D_c (g cm^{-3})	1.145	1.147
F(000)	1008	805
μ (mm^{-1})	1.28	1.24
2θ range (deg)	3–130	3–110
max indices *hkl*	29,7,19	7,18,20
no. of rflns measd	5882	10 961
no. of unique rflns	2290	5437
no. of obsd rflns	2184	4101
R_{int}	0.040	0.083
transmission factors	0.473–0.589	0.605–0.848
weighting params	6, 22, 18, –10, 5, –37	5, 49, –32, –6, 5, –95
extinction param *x*	[5.6(6)] × 10^{-6}	0
no. of params refined	155	471
max shift/esd	0.003	0.091
max final electron density diff (e Å^{-3})	0.33	0.59
final *R*	0.0409	0.0769
final R_w	0.0351	0.0656
goodness of fit	1.13	1.12

Table II. Selected Bond Lengths (Å) and Angles (deg) Involving the Non-Hydrogen Atoms of 6a

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)	C(5)–C(6)	1.387(3)
C(5)–C(10)	1.395(3)	C(6)–C(7)	1.391(4)
C(7)–C(8)	1.374(5)	C(8)–C(9)	1.373(5)
C(9)–C(10)	1.379(3)	C(11)–C(12)	1.399(3)
C(11)–C(16)	1.395(3)	C(12)–C(13)	1.401(3)
C(13)–C(14)	1.372(6)	C(14)–C(15)	1.347(6)
C(15)–C(16)	1.397(3)		
C(1)–Si–C(5)	109.9(1)	C(1)–Si–C(11)	109.8(1)
C(5)–Si–C(11)	109.8(1)	C(1)–Si–C(4′)	109.8(1)
C(5)–Si–C(4′)	108.4(1)	C(11)–Si–C(4′)	109.1(1)
Si–C(1)–C(2)	112.9(1)	C(1)–C(2)–C(3)	127.8(1)
C(2)–C(3)–C(4)	127.3(1)	C(3)–C(4)–Si′	111.4(1)
Si–C(5)–C(6)	122.1(1)	Si–C(5)–C(10)	120.0(1)
C(6)–C(5)–C(10)	117.9(2)	C(5)–C(6)–C(7)	120.0(2)
C(6)–C(7)–C(8)	121.1(3)	C(7)–C(8)–C(9)	119.5(2)
C(8)–C(9)–C(10)	119.9(3)	C(5)–C(10)–C(9)	121.6(2)
Si–C(11)–C(12)	121.3(1)	Si–C(11)–C(16)	121.4(1)
C(12)–C(11)–C(16)	117.3(2)	C(11)–C(12)–C(13)	120.0(3)
C(12)–C(13)–C(14)	121.3(3)	C(13)–C(14)–C(15)	119.1(2)
C(14)–C(15)–C(16)	121.3(3)	C(11)–C(16)–C(15)	121.0(3)

Table III. Fractional Non-Hydrogen Atomic Coordinates (×10^4) for 6a

atom	*x*	*y*	*z*
Si	3438(1)	6525(1)	7100(1)
C(1)	2974(1)	4788(2)	7512(1)
C(2)	2885(1)	5407(2)	8332(1)
C(3)	2416(1)	5863(2)	8541(1)
C(4)	1859(1)	5884(2)	8000(1)
C(5)	3514(1)	5659(2)	6065(1)
C(6)	3247(1)	3974(4)	5694(1)
C(7)	3311(1)	3410(6)	4921(2)
C(8)	3640(1)	4479(6)	4516(1)
C(9)	3910(1)	6141(5)	4878(1)
C(10)	3849(1)	6719(3)	5644(1)
C(11)	4122(1)	6599(3)	7809(1)
C(12)	4450(1)	8311(4)	7878(1)
C(13)	4961(1)	8320(7)	8411(2)
C(14)	5147(1)	6683(8)	8882(2)
C(15)	4833(1)	5029(6)	8823(1)
C(16)	4324(1)	4952(4)	8290(1)

reaction mixtures. We have, however, been able to isolate the dimethyl cyclodimer **8** via sublimation from the crude product mixture.

Crystals of **6a** suitable for X-ray diffraction were grown from a saturated benzene solution. The crystal data are summarized in Table I. The molecular structure is illustrated in Figure 2, and selected bond distances and angles are given in Table II. Non-hydrogen atom coordinates are reported in Table III. The molecule lies on a crystallographic inversion center adopting an "armchair" conformation with C_{2h} molecular symmetry in which a mirror plane bisects the C=C double bonds. The Si—C, C—C, and C=C bond lengths, at 1.874(2) Å (av), 1.496(2) Å (av), and 1.331(2) Å, are unexceptional and comparable with the only other structurally characterized *cis,cis*-1,6-disilacyclodeca-3,8-diene ring system.[11] To our knowledge, this is the first crystal structure of a cyclooligomer obtained by metathesis equilibration of a cyclic olefin.

II. NMR Studies on the Disilacyclodecadienes 6a and 8. The room temperature ^1H NMR spectrum (toluene-d_8) of **6a** is shown at the top of Figure 3. The sharp triplet resonance at δ 5.40 ppm, attributable to the olefinic hydrogens, is consistent with a centrosymmetric cyclodimer species rather than an acyclic product of ring opening; the broadening observed for the methylene resonance at δ 2.20 ppm is due to low-energy conformational changes within the ring. When the temperature is lowered, this signal collapses into the base line (ca. 0 °C) and reemerges (−10 °C) as two broadened resonances centered at δ 2.51 and 1.77 ppm. These sharpen to an apparent triplet and doublet, respectively, at −60 °C. The olefinic hydrogen signal also now appears as a doublet. There is negligible change in the shapes of these signals upon further cooling. Irradiation of the olefinic signal at −60 °C causes the collapse of the triplet resonance to a doublet while having no effect on the doublet resonance at δ 1.79 ppm. The low-field triplet resonance is thus assigned to H_a, which forms a torsion angle of approxi-

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[11] Park, Y. T.; Zhou, S. Q.; Manuel, G.; Bau, R.; Weber, W. P. *Organometallics* **1990**, *9*, 2811.

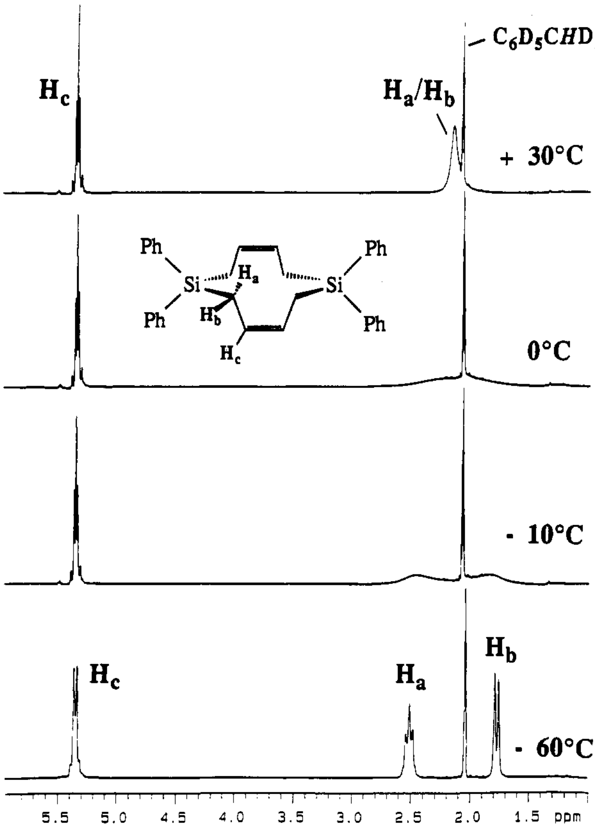


Figure 3. Variable-temperature 400-MHz ^1H NMR spectra (C_7D_8) for **6a**.

Table IV. ^{13}C and ^{29}Si NMR ($CDCl_3$) Shifts for Cis,cis, Cis,trans, and Trans,trans Isomers of 6 and 8

compd	group	chem shift (ppm)		
		cis,cis	cis,trans	trans,trans
6	$-CH_2-$	12.6	13.9[a] 19.6[b]	20.0
	$-CH=$	123.0	122.7 123.5	125.7
	Si	−11.1	−16.8	−23.5
8	$-CH_2-$	15.7	16.3[a] 22.6[b]	22.9
	$-CH=$	122.8	122.5 123.0	125.0
	Si	−0.6	−5.5	−11.9

[a] Adjacent to cis double bond. [b] Adjacent to trans double bond.

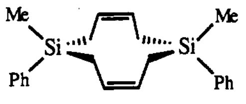
mately 180° with H_c; the absence of detectable coupling between H_b and H_c is consistent with the torsion angle of approximately 60° between these substituents, which according to a Karplus analysis[12] is expected to be small. Thus, the couplings observed at the low-temperature limit in solution are consistent with the ground-state "armchair" conformation established by the X-ray structure determination.

Cis,trans and trans,trans cyclodimer products can also be detected in the ^{13}C and ^{29}Si NMR spectra of the crude equilibrium mixture; these account for 14% and 2%, respectively, of the total dimer content. The ^{13}C and ^{29}Si NMR shifts are collected in Table IV for comparative purposes. Both ^{13}C and ^{29}Si shifts are useful for distinguishing between the isomers, particularly the ^{29}Si resonances, which are separated by 5–7 ppm. Since the catalyst Mo-I is still present in the reaction mixture, the ratio of the cc, ct, and tt species must reflect the relative thermodynamic stabilities of these ring systems. Consistent with this, treatment of pure *cis,cis*-**6a** with Mo-I in benzene reestablishes the same equilibrium mixture of all three isomers.

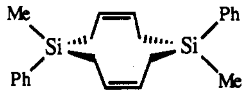
Table V. GPC Data for poly-1 and poly-2

initiator	monomer/amt (equiv)	M_w	M_n	PDI
Mo-I	$Ph_2SiC_4H_6$ (**1**)/60	96 800	45 310	2.14
Mo-I	**1**/100	72 570	35 030	2.07
Mo-I	**1**/200	81 770	47 000	1.74
Mo-I	**1**/543	72 270	40 260	1.80
Mo-I	**1**/1057	107 800	61 100	1.76
WCl_6/Me_4Sn	**1**/500	65 400	28 240	2.32
Mo-I	$PhMeSiC_4H_6$ (**2**)/98	76 650	38 330	2.00
Mo-I	**2**/720	45 520	21 300	2.14

Reactions of 10 equiv of **2** or **3** with Mo-I afford analogous equilibrium mixtures of monomer, metal alkylidene end-capped oligomers, and 10-membered-ring systems. In the case of **2**, the predominant cis,cis dimer gives a complex multiplet attributable to the vinyl hydrogens at δ 5.38 ppm, two unresolved broadened resonances at δ 1.85 and 1.75 ppm due to the methylene hydrogens, and two singlets of equal intensity at δ 0.22 and 0.25 ppm due to methyls attached to silicon. Inequivalent methyl environments are consistent with a mixture of isomers **7a** and **7b**,



7a



7b

assuming that a ground-state cis,cis "armchair" conformation predominates as established for **6a**. Consistently, two equal-intensity signals are observed at δ −3.29 and −3.50 ppm in the ^{29}Si NMR spectrum (C_6D_6). An additional pair of weak-intensity resonances at δ −8.54 and −8.68 ppm is most probably due to the trans,trans cyclodimer, and a cluster of four very weak intensity signals in the range δ −4.72 to −5.52 ppm is likely attributable to the cis,trans isomers. There could be a total of eight energetically accessible isomers giving up to ten ^{29}Si resonances. A good number of these, but not all, are resolved.

Examination of the ^{13}C NMR spectrum of the crude product mixture arising from treatment of **3** with Mo-I shows a ratio of 73:21:6 for the cc, ct, and tt cyclodimers of **8**; the same ratio persists in a sublimed sample. The low-temperature ^1H NMR data for the major cis,cis isomer are directly comparable with those of **6a**, indicating an analogous structure in solution. The methylene resonance, however, at δ 1.43 ppm is a clearly resolved doublet at room temperature. This signal broadens as the temperature is lowered and resolves in the temperature range −40 to −50 °C into two new resonances at δ 1.02 and 1.83 ppm; this is at a much lower temperature than observed for the methylene hydrogens of **6a**, which coalesce in the range 0 to −10 °C (Figure 3). The energy barrier to conformer interconversion is, therefore, substantially reduced when methyl rather than phenyl substituents are attached to the silicons of the cyclodimers.

III. Polymerizations of 1–3. When added neat to Mo-I, **1** and **2** are readily polymerized; however, for **3** only very low molecular weight oligomeric material was ob-

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[12] (a) Karplus, M. *J. Chem. Phys.* **1959**, *30*, 11. (b) Karplus, M. *J. Chem. Phys.* **1960**, *33*, 1842. (c) Karplus, M. *J. Am. Chem. Soc.* **1963**, *85*, 2870.

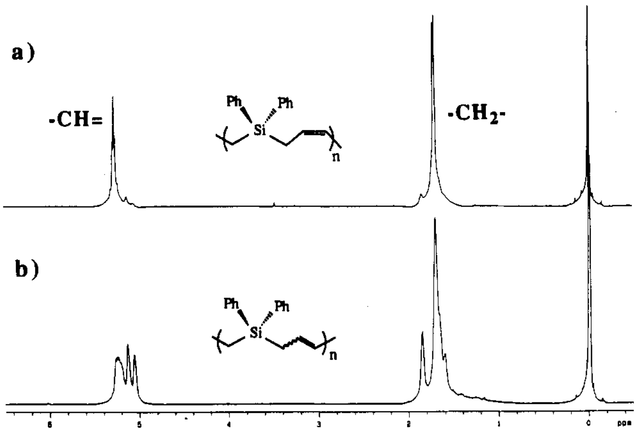


Figure 4. 400-MHz ^{1}H NMR spectra (C_6D_6) for poly-1 obtained using (a) $WCl_6/SnMe_4$ and (b) Mo[NAr][$CHCMe_2Ph$][$OCMe(CF_3)_2$]$_2$ (Mo-I).

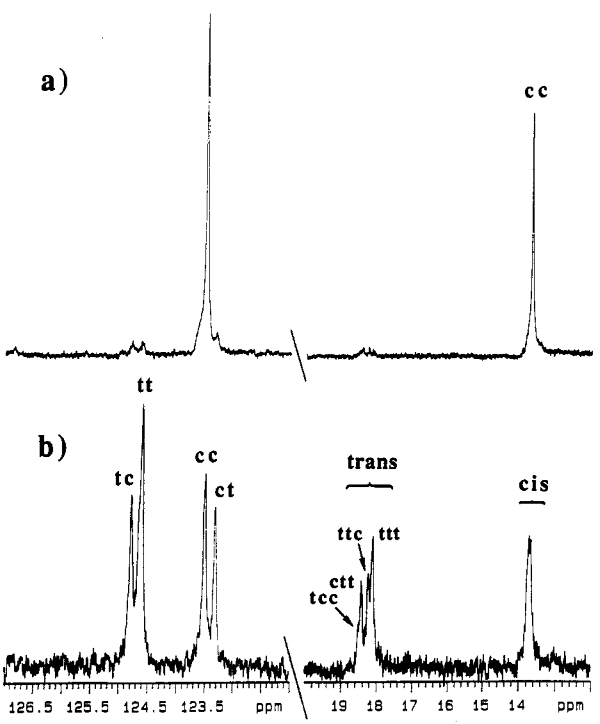
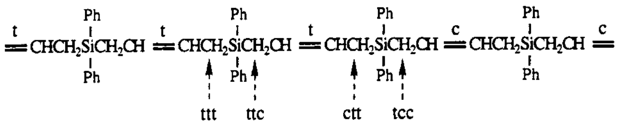


Figure 5. ^{13}C NMR spectra of the vinylene (123–125 ppm) and methylene (13–19 ppm) regions for poly-1 obtained using (a) $WCl_6/SnMe_4$ and (b) Mo[NAr][$CHCMe_2Ph$][$OCMe(CF_3)_2$]$_2$ (Mo-I).

tained. GPC data for poly-1 and poly-2 are given in Table V. The ^{1}H NMR spectrum of poly-1 is shown in Figure 4b together with a spectrum of a high-cis polymer prepared using WCl_6/Me_4Sn (1:1) in chlorobenzene (Figure 4a) for comparative purposes. It can be seen that the high-cis polymer gives a relatively clean spectrum exhibiting an apparent triplet at δ 5.46 ppm and a doublet resonance at δ 1.90 ppm, whereas several additional signals are evident in the spectrum of poly-1 prepared using Mo-I. These are due to the presence of the trans double bonds within the polymer. The ^{13}C NMR spectra (Figure 5) provide useful further information, since the chemical shifts of the methylene and vinylene carbons are sensitive to the cis,-trans configuration of the nearby double bonds. Resonances attributable to methylene carbons adjacent to cis double bonds occur at ca. δ 14 ppm (cc and ct unresolved[13]), while those adjacent to trans double bonds are found approximately 5 ppm to lower field (ca. δ 18–19 ppm). The splitting observed in this region is due to the double-bond triads tcc, ctt, ttc, and ttt:



The central letter in each triad refers to the nearest double bond, the first letter to the second nearest, and the third letter to the third nearest double bond. ctt and ttc represent two carbons on either side of the Ph_2Si fragment and, therefore, must be of equal intensity; these are assigned to the two central peaks. Of the other two resonances, the stronger is assigned to ttt and the weaker (shoulder) to tcc consistent with the tt:tc ratio of ~1.5 observed in the olefinic region. Here, the tt and tc pairs occur at δ 124.58 and 124.77 ppm and the cc and ct pairs at δ 123.31 and 123.49 ppm, respectively. Thus, while poly-1 prepared using the classical initiator gives a single major resonance (Figure 5a) for the methylene and vinylene carbons respectively attributable to a >90% cis polymer, poly-1 (55% trans) prepared using Mo-I shows numerous splittings due to the cis,trans double-bond placements (Figure 5b). From the vinylene carbon region for the latter, the fraction of cis double bonds σ_c is calculated to be approximately 0.45 and $r_tr_c \approx 1.3$ (where r_t = tt/tc and r_c = cc/ct); the latter is indicative of a slightly blocky distribution of cis and trans double bonds. In the high-cis polymer, it can be seen that the residual tc and tt signals are of equal intensity, implying that the trans double bonds occur in pairs. This effect is also seen in polymers of norbornene[14,15] and cyclopentene[16] and has been analyzed in detail and interpreted mechanistically by Ivin and coworkers.[15] The ^{29}Si NMR spectrum gives a single resonance at δ −10.54 ppm for the predominantly cis polymer and additional resonances at δ −10.92, −11.25, and −11.34 ppm for poly-1 prepared using Mo-I. Although these signals are likely attributable to cis,trans splittings, an unambiguous assignment of these resonances was not possible.

Polymerization of **2** with WCl_6/Me_4Sn (1:1) in chlorobenzene affords a polymer with a cis content of approximately 80%. Analysis of the vinylene carbon region of the ^{13}C NMR spectrum gives $r_tr_c \approx 5.5$, indicating that this polymer is blocky. The ^{29}Si NMR spectrum gives three signals at δ −4.31, −4.74, and −5.18 ppm ($CDCl_3$) in the ratio 72:20:8, implying assignments as cc, ct, and tt respectively. Poly-2 formed using Mo-I as initiator gave a cis content of 25% with $r_tr_c \approx 0.80$, indicating that there is a tendency toward alternating cis–trans double bonds in this polymer.

IV. Reactions of the Diallylsilanes 4 and 5 with Mo-I. Treatment of **4** or **5** with Mo-I in benzene solution results in the liberation of ethylene and generation of the same equilibrium mixture of 5- and 10-membered silicon rings as found for the treatment of the silacyclopentenes

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[13] cc and ct refer to methylene carbons adjacent to cis double bonds with a cis and trans next-nearest neighbor, respectively.

[14] Ivin, K. J.; Laverty, D. T.; O'Donnell, J. H.; Rooney, J. J.; Stewart, C. D.; *Makromol. Chem.* **1979**, *180*, 1989.

[15] Greene, R. M. E.; Hamilton, J. G.; Ivin, K. J.; Rooney, J. J. *Makromol. Chem.* **1986**, *187*, 619.

[16] Ceausescu, E.; Cornilescu, A.; Nicolescu, E.; Popescu, M.; Coca, S.; Cuzmici, M.; Oprescu, C.; Dimonie, M.; Hubca, G.; Teodorescu, M.; Grosescu, R.; Vasilescu, A.; Dragutan, V. *J. Mol. Catal.* **1986**, *36*, 163.

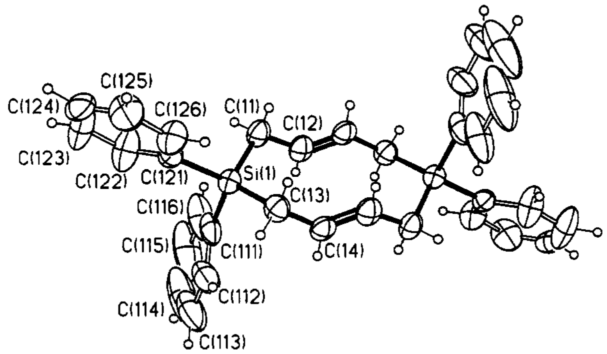


Figure 6. Molecular structure of *trans,trans*-$[Ph_2Si(C_4H_6)]_2$ (**6c**) showing the atom labeling and "crownlike" puckering. Thermal ellipsoids are at the 50% probability level for non-H atoms.

Table VI. Selected Bond Lengths and Angles Involving the Non-Hydrogen Atoms of 6c

Si(1)–C(11)	1.878(6)	Si(1)–C(13)	1.881(5)
Si(1)–C(111)	1.885(5)	Si(1)–C(121)	1.885(4)
C(11)–C(12)	1.491(7)	C(12)–C(14a)	1.299(9)
C(13)–C(14)	1.502(7)	Si(2)–C(21)	1.870(4)
Si(2)–C(23)	1.871(5)	Si(2)–C(211)	1.877(4)
Si(2)–C(221)	1.865(7)	C(21)–C(22)	1.509(7)
C(22)–C(24b)	1.313(7)	C(23)–C(24)	1.491(7)
Si(3)–C(31)	1.872(6)	Si(3)–C(33)	1.869(6)
Si(3)–C(311)	1.884(5)	Si(3)–C(321)	1.860(7)
Si(3)–C(331)	1.943(7)	C(31)–C(32)	1.488(7)
C(32)–C(34c)	1.310(10)	C(33)–C(34)	1.494(7)

C(11)–Si(1)–C(13)	111.0(3)	C(11)–Si(1)–C(111)	108.1(2)
C(13)–Si(1)–C(111)	109.7(2)	C(11)–Si(1)–C(121)	108.4(2)
C(13)–Si(1)–C(121)	110.1(2)	C(111)–Si(1)–C(121)	109.4(2)
Si(1)–C(11)–C(12)	114.4(3)	C(11)–C(12)–C(14a)	126.5(4)
Si(1)–C(13)–C(14)	112.4(3)	C(13)–C(14)–C(12a)	125.6(4)
Si(1)–C(111)–C(112)	119.4(2)	Si(1)–C(111)–C(116)	120.6(2)
Si(1)–C(121)–C(122)	119.4(1)	Si(1)–C(121)–C(126)	120.4(1)
C(21)–Si(2)–C(23)	111.3(2)	C(21)–Si(2)–C(211)	106.0(2)
C(23)–Si(2)–C(211)	110.3(2)	C(21)–Si(2)–C(221)	108.6(3)
C(23)–Si(2)–C(221)	109.9(3)	C(211)–Si(2)–C(221)	110.5(2)
Si(2)–C(21)–C(22)	114.7(3)	C(21)–C(22)–C(24b)	125.8(6)
Si(2)–C(23)–C(24)	111.7(4)	C(23)–C(24)–C(22b)	125.9(6)
Si(2)–C(211)–C(212)	120.1(1)	Si(2)–C(211)–C(216)	119.9(1)
Si(2)–C(221)–C(222)	120.7(2)	Si(2)–C(221)–C(226)	119.3(2)
C(31)–Si(3)–C(33)	111.1(3)	C(31)–Si(3)–C(311)	108.8(2)
C(33)–Si(3)–C(311)	110.4(2)	C(31)–Si(3)–C(321)	101.1(3)
C(33)–Si(3)–C(321)	119.0(2)	C(311)–Si(3)–C(321)	105.6(3)
C(31)–Si(3)–C(331)	114.8(2)	C(33)–Si(3)–C(331)	101.4(3)
C(311)–Si(3)–C(331)	110.1(3)	C(31)–C(32)–C(34c)	125.4(5)
Si(3)–C(31)–C(32)	114.4(3)	C(33)–C(34)–C(32c)	125.4(5)
Si(3)–C(33)–C(34)	113.8(4)	Si(3)–C(311)–C(316)	120.3(2)
Si(3)–C(311)–C(312)	119.7(2)	Si(3)–C(321)–C(326)	120.7(2)
Si(3)–C(321)–C(322)	119.2(2)	Si(3)–C(331)–C(336)	118.8(1)
Si(3)–C(331)–C(332)	121.1(1)		

1 and **3** with the hexafluoro-*tert*-butoxide catalyst. The cyclodimer **6a** crystallizes from this mixture at room temperature. We were also able to isolate the cyclodimer **8** from the reaction of **5** with Mo-I in benzene. Thus, it is possible for these diallyl substrates to enter the same manifold of reactivity as the silacyclopentenes.

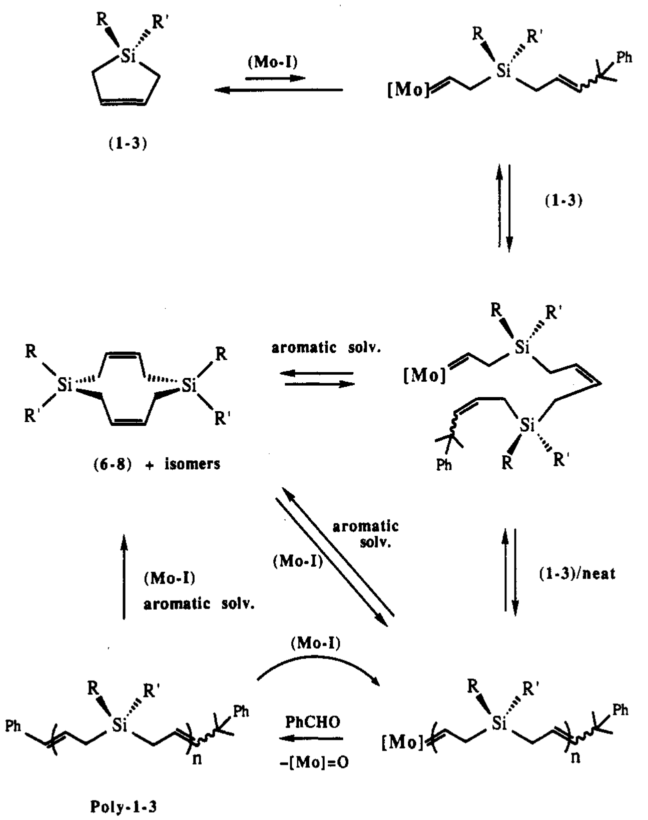
When *neat* **4** was treated with Mo-I, a good yield of high-trans polymer was obtained (ca. 90% trans by NMR); this compares with 55% trans for poly-**1** prepared via ROMP of the silacyclopentene **1** with Mo-I. A sample of poly-**3** prepared from **5** was found to contain 75% trans linkages, which compares with 81% for poly-**3** prepared using the tungsten hexafluoro-*tert*-butoxide catalyst.[10] The yield of poly-**3** was also improved over that for the ROMP procedure; however, we were still only able to isolate low-molecular-weight samples (typically in the range 1500–3000).

Table VII. Fractional Non-Hydrogen Atomic Coordinates ($\times 10^4$) for 6c

atom	*x*	*y*	*z*
Si(1)	574(1)	6000(1)	1011(1)
C(11)	−959(6)	6321(2)	288(3)
C(12)	−1966(6)	5658(2)	93(3)
C(13)	2545(6)	5288(2)	708(3)
C(14)	1749(6)	4549(2)	546(3)
C(112)	−255(7)	4947(2)	2372(3)
C(113)	−1437	4576	3009
C(114)	−3414	4760	3139
C(115)	−4210	5313	2631
C(116)	−3028	5683	1994
C(111)	−1050	5500	1865
C(122)	546(4)	7387(2)	1651(2)
C(123)	1282	8100	1747
C(124)	3144	8340	1394
C(125)	4270	7867	946
C(126)	3534	7153	850
C(121)	1672	6914	1202
Si(2)	−1468(2)	6576(1)	4594(1)
C(21)	−3051(6)	5708(2)	5047(3)
C(22)	−2142(7)	5094(3)	5569(3)
C(23)	788(7)	6255(2)	4020(3)
C(24)	1943(6)	5669(3)	4461(3)
C(212)	−3372(6)	7047(2)	3373(2)
C(213)	−4566	7535	2960
C(214)	−5348	8234	3182
C(215)	−4936	8446	3818
C(216)	−3743	7958	4232
C(211)	−2961	7259	4009
C(222)	−2136(10)	7121(3)	5956(3)
C(223)	−1633	7508	6486
C(224)	190	7855	6375
C(225)	1510	7815	5735
C(226)	1007	7428	5205
C(221)	−816	7080	5315
Si(3)	1237(1)	−1021(1)	−1051(1)
C(31)	−761(8)	−1304(3)	−252(4)
C(32)	−1922(7)	−620(3)	−10(4)
C(33)	2990(7)	−335(3)	−841(4)
C(34)	2081(7)	418(3)	−635(4)
C(312)	4210(6)	−2208(3)	−1023(3)
C(313)	5141	−2908	−1186
C(314)	4382	−3355	−1619
C(315)	2691	−3101	−1890
C(316)	1759	−2401	−1727
C(311)	2519	−1954	−1294
C(322)	550(8)	−33(3)	−2346(4)
C(323)	−451	226	−2922
C(324)	−2180	−139	−2944
C(325)	−2907	−764	−2390
C(326)	−1905	−1023	−1814
C(321)	−177	−657	−1792
C(332)	1671(7)	147(3)	−2400(4)
C(333)	1083	561	−3033
C(334)	−764	441	−3171
C(335)	−2023	−93	−2678
C(336)	−1435	−508	−2046
C(331)	412	−388	−1907
C(41)	3342	360	4768
C(42)	3180	−159	5435
C(43)	4839	−519	5668
C(44)	1559	747	4518
C(45)	1224	−331	5903
C(46)	4666	−1078	6385

An unexpected result of degrading a sample of high-trans poly-**1** in toluene solvent with Mo-I was the isolation of the trans,trans cyclodimer **6c**, whose structure has been determined. The crystal data are collected in Table I and selected bond distances and angles in Table VI, and non-hydrogen atom coordinates are given in Table VII. The molecular structure is illustrated in Figure 6 and reveals "crownlike" puckering of the 10-membered ring. All three independent molecules of **6c** lie on crystallographic inversion centers and, as for **6a**, possess C_{2h} molecular

Scheme I



symmetry, in this case with a mirror plane orthogonal to the macrocyclic ring plane and bisecting the two silicon atoms. The Si—C and C—C distances, at 1.874(6) Å (av) and 1.497(7) Å (av), respectively, are comparable with those of **6a**, while the C=C bond length is slightly shortened at 1.299(9) Å. The angles subtended at the silicon (111.0(3)°) and methylene carbon (113.4(3)°) atoms are close to those observed for **6a** (109.8(1) and 112.9(1)°, respectively), and so the small difference in the thermodynamic stabilities of **6a** and **6c**, most reasonably attributed to differences in ring strain, is not clearly evident from these structural parameters. In contrast to **6a**, variable-temperature ^{1}H NMR experiments on **6c** do not reveal any dramatic conformational changes. The room-temperature spectrum consists of a sharp triplet resonance at δ 5.30 ppm (^3J(HH) = 5 Hz) due to the olefinic hydrogens coupled to the ring methylene protons, which resonate as a sharp doublet at δ 2.22 ppm. As the sample is cooled to −80 °C (CD_2Cl_2), these resonances undergo slight broadening and the coupling becomes unresolved. Over the same temperature range, the resonances in the phenyl region (δ 7–8 ppm) show more dramatic changes consistent with "freezing" of rotation about the Si–ipso phenyl carbon bond. The high-temperature spectrum (50 °C, $CDCl_3$) shows only slight broadening and loss of resolution of the olefinic and methylene resonances.

Discussion

Scheme I summarizes the metathesis chemistry arising from reactions of **1**–**3** with Mo-I in benzene solution and in the absence of any solvent. The attainment of an equilibrium mixture of 5- and 10-membered rings is dependent upon the effectiveness of the metal alkylidenes for *secondary metathesis* or "back-biting" reactions; the ancillary hexafluoro-*tert*-butoxide ligands of Mo-I ensure that the metal alkylidene is sufficiently active to metathesize ordinary (acyclic) C=C double bonds and, in combination with the sterically demanding imido ligand, lend steric protection to the active site.

Depolymerization is favored on dilution of the solution. This does not lead only to the ring-strained monomer but also to the less strained cyclodimers and perhaps small amounts of higher oligomers, which are not present in sufficient concentration to be detected. By this compromise, the system achieves a minimum of free energy. The necessary intermediates of the equilibrium, present in very small steady-state concentrations, are the acyclic metal alkylidene end-capped oligomers. No evidence was found for the formation of cyclodimers from reactions of **1**–**3** with the conventional initiator WCl_6/Me_4Sn, implying that the alkylidene sites are not sufficiently long-lived.

In the absence of solvent, **1** and **2** are readily polymerized. The polymers are initially favored due to the very high concentration of monomer and possibly the inflexibility of the growing polymer chains in the monomer medium inhibiting effective back-biting reactions. This would, undoubtedly, also have an influence on the final molecular weight attained and may provide a rationale for the difficulties experienced in polymerizing **3**, since this polymer tends to be soluble in the monomer and back-biting may be more effective. A greater degree of success was encountered in polymerizing **3** with the less active *tert*-butoxide catalyst $Mo[N\text{-}2,6\text{-}{}^iPr_2\text{-}C_6H_3][CHCMe_2Ph][(OCMe_3]_2$, which does not readily react with acyclic olefins. The cis content of the resulting polymer was, however, the same as for the oligomers obtained using Mo-I. This was also the case for poly-**2** generated using the *tert*-butoxide initiator.

Polymers of **1** and **2** can be capped with benzaldehyde and precipitated, dried, and isolated in the usual manner. However, the "dead" polymers may also be degraded back to a mixture of 5- and 10-membered rings if stirred with Mo-I in aromatic hydrocarbons. The high cis content of the polymers prepared using WCl_6/Me_4Sn in chlorobenzene solvent and the absence of cyclooligomers is likely to be a consequence of the relatively short-lived nature of the active alkylidenes in these catalyst systems. On the other hand, the relatively high trans content of the polymers prepared using Mo-I is a good indication that substantial secondary metathesis has occurred; this has been noted to be a general phenomenon for all ring-opened polymers of cycloalkenes and is accompanied by an adjustment of the molecular weight distribution to the most probable value of 2.0.[6]

For the diallylsilicon reagents **4** and **5** (Scheme II), the generation of the silacyclopent-3-enes and 10-membered rings in solution, with evolution of C_2H_4, implies that these substrates can enter the same manifold of reactivity as **1** and **3**. When the reaction of **4** or **5** with Mo-I is carried out in the absence of solvent, ethylene is liberated and the substrates condense under reduced pressure to polymers with a much higher trans content than found when **1** and **3** are used as monomers; this is consistent with a *metathesis polycondensation* mechanism (acyclic diene metathesis polymerization or ADMET[17]) operating under solvent-free conditions. The trans content of poly-**3** does not vary

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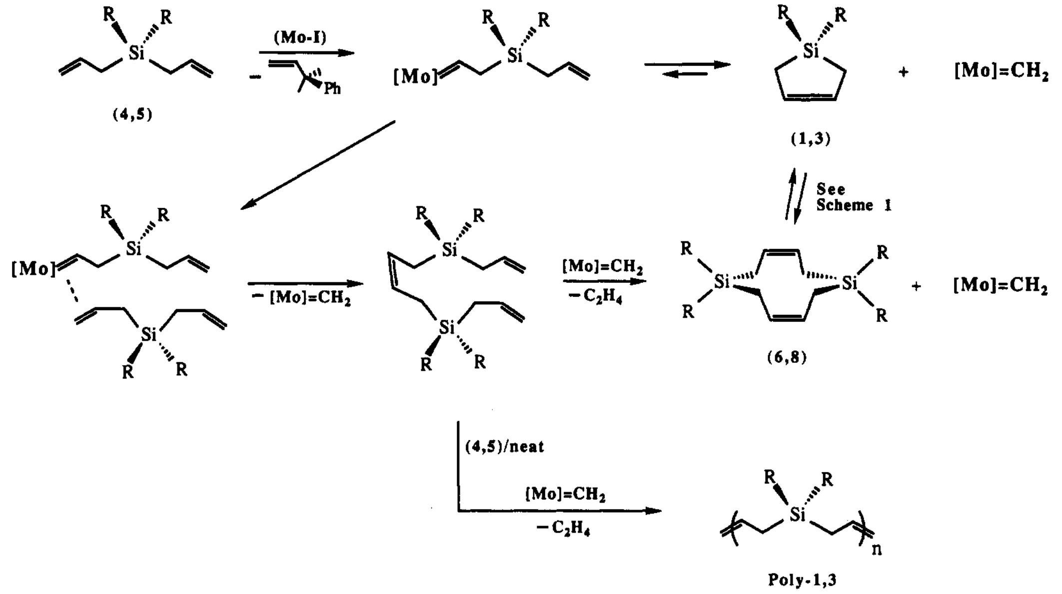
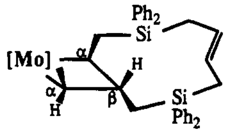
[17] Wagener, K. B.; Boncella, J. M.; Nel, J. G. *Macromolecules* **1991**, *24*, 2649 and references therein.

Scheme II



greatly between the Mo and W initiators (75% vs 81%, respectively).[10]

An unexpected outcome of the metathesis degradation of high-trans poly-1 was the isolation of the trans,trans macrocycle **6c**. Our previous observations had shown that this is the least thermodynamically stable of the three isomers, normally constituting ca. 2% of an equilibrium mixture of **6a–c**; further confirmation was provided by treating a pure sample of **6c** with Mo-I in benzene, upon which the equilibrium mixture was readily reestablished. Kinetic conditions must then prevail in this degradation process. These observations have two implications. First, metathesis degradation of *trans*-poly-1 must initially favor formation of the trans,trans macrocycle over the cis,trans and ultimately the cis,cis forms: this is likely to arise from an energetic preference in the transition state leading to the α,α-*cis*/β-*trans*-molybdacyclobutane



Second, the catalyst must be relatively short-lived in order to avoid subsequent conversion of **6c** to the thermodynamically favored **6b** and **6a**. An explanation for the latter may lie in a key difference between ADMET polymerization and ring-opening metathesis polymerization, since the former polycondensation process requires the formation of metal methylidene species for productive metathesis (Scheme II), the lifetime of such species is expected to be much shorter than that of metal alkylidenes bearing an α-alkyl substituent which arise in ring-opening metathesis reactions.

In summary, these studies have shown that novel silicon-containing macrocycles and polymers can be synthesized selectively via ring-opening or condensation metathesis processes exploiting relatively stable, long-lived metal–alkylidene catalysts and indicate the potential for accessing other heteroatom-containing rings and polymers via these methodologies.

Experimental Section

All manipulations of air- and/or moisture-sensitive materials were performed on a conventional vacuum/inert-atmosphere nitrogen line using standard Schlenk and cannula techniques or in an inert-atmosphere- (nitrogen-) filled drybox.

The following solvents were dried by prolonged reflux over a suitable drying agent and were freshly distilled and deoxygenated prior to use (drying agent in parentheses): toluene (sodium metal), pentane (lithium aluminum hydride), and tetrahydrofuran (sodium benzophenone ketyl). Benzene-d_6 and toluene-d_8 were dried by vacuum distillation from phosphorus(V) oxide; chloroform-d and dichloromethane-d_2 were dried by distillation from calcium hydride.

Elemental analyses were performed by the microanalytical services at Durham. GPC analyses of the polymer molecular weight distribution were performed on a Viscotek differential refractometer/viscometer (Model 200). HPLC-grade THF was used as elution solvent. Retention times were calibrated against the following polystyrene standards: M_p (M_w/M_n) 1320 (1.09), 5050 (1.05), 28 500 (1.03), 156 000 (1.03), 1 030 000 (1.05). Infrared spectra were recorded on Perkin-Elmer 577 and 377 grating spectrophotometers using either KBr or CsI windows. Absorptions are abbreviated as follows: s (strong), m (medium), w (weak), br (broad), sp (sharp), sh (shoulder). Mass spectra were recorded on a VG 7070E mass spectrometer. NMR spectra were recorded on the following instruments: Varian VXR 400, Varian Gemini 200, and Bruker AC 250. The following abbreviations have been used for signal multiplicities: s (singlet), d (doublet), t (triplet), q (quartet), qnt (quintet), m (multiplet), app (apparent). ^{1}H and ^{13}C NMR spectra were internally referenced to benzene or chloroform. ^{29}Si NMR spectra were externally referenced to $SiMe_4$ in $CDCl_3$.

$Mo[NAr][CHCMe_2Ph][OCMe(CF_3)_2]_2$ and $Mo[NAr][CHCMe_2Ph][OCMe_3]_2$ were prepared by a modification of the procedure described by Schrock et al.,[8] employing the Grignard reagent $PhMe_2CCH_2MgCl$ instead of Me_3CCH_2MgCl. $Ph_2Si(C_4H_6)$ and $Me_2Si(C_4H_6)$ were prepared according to a literature procedure.[18] The following chemicals were obtained commercially (Aldrich) and used as received unless stated otherwise: WCl_6, $SnMe_4$ (distilled prior to use), and $Ph_2Si(C_3H_5)_2$ and $Me_2Si(C_3H_5)_2$ (both distilled prior to use).

***cis,cis*-1,1,6,6-Tetraphenyl-1,6-disilacyclodeca-3,8-diene (6a).** A solution of Mo-I (0.04 g, 0.052 mmol) in benzene (1 mL) was added to a stirred solution of 1,1-diphenylsilacyclopent-3-ene (3.1 g, 13.05 mmol) in benzene (30 mL). The mixture was stirred at room temperature for 24 h to give a white crystalline precipitate, which was isolated by filtration and dried in vacuo. The filtrate was treated with pentane (40 mL) to give a further

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[18] Dunogues, J.; Calas, R.; Dedier, J.; Pisciotti, F. *J. Organomet. Chem.* **1970**, *25*, 51.

crop of white product. The solids were then combined and recrystallized from a 1:1 (by volume) mixture of toluene and pentane at −20 °C to give *cis,cis*-1,1,6,6-tetraphenyl-1,6-disilacyclodeca-3,8-diene (**6a**): yield 0.62 g, 40%. Anal. Calcd for $C_{32}H_{32}Si_2$: C, 81.33; H, 6.78. Found: C, 81.05; H, 6.56. Mp: 248 °C. ^{1}H NMR (room temperature, $CDCl_3$): δ 2.14 (br m, 8H, CH_2), 5.28 (m, 4H, CH), 7.1–7.6 (complex multiplets, 20H, aromatic C–H). NMR (room temperature (C_7D_8): δ 2.20 (br m, 8H, CH_2), 5.40 (m, 4H, CH), 7.1–7.6 (aromatic C–H). ^{1}H NMR (−60 °C, C_7D_8): δ 1.77 (d, ^3J(HH) = 12.8 Hz, 4H, CH_2), 2.51 (app t, 4H, CH_2), 5.39 (d, ^3J(HH) = 10.8 Hz, 4H, CH). ^{13}C NMR ($CDCl_3$): δ 12.6 (s, CH_2), 123.0 (s, CH), 127.9, 129.4, 134.6, 135.6 (aromatic carbons). ^{29}Si NMR ($CDCl_3$): δ −11.10 (s). ^{29}Si NMR (C_7D_8): δ −8.11. Mass spectrum: *m/z* 472 $[M]^+$, 236 $[M/2]^+$. IR (KBr): 1150 (s), 1112 (s), 1035 (m), 935 (m), 820 (s), 725 (s), 700 (s), 690 (s), 685 (s), 535 (s), 470 (s) cm^{-1}.

1,1,6,6-Tetramethyl-1,6-disilacyclodeca-3,8-diene (8). A solution of Mo-I (0.02 g, 0.026 mmol) in benzene (1 mL) was added to a stirred solution of 1,1-dimethyl-1-silacyclopent-3-ene (0.147 g, 1.31 mmol) in benzene (5 mL). The mixture was stirred at room temperature for 24 h and then concentrated to a viscous oil, which was shown by NMR to be a mixture of *cc*-, *ct*-, and *tt*-1,1,6,6-tetramethyl-1,6-disilacyclodeca-3,8-diene (8). Room-temperature sublimation (5 × 10^{-2} Torr) using an air-cooled condenser gave a crystalline sample consisting of the three isomers in the same ratio as found in the crude product: yield 0.037 g, 25%. Anal. Calcd for $C_{12}H_{24}Si_2$: C, 64.26; H, 10.70. Found: C, 63.90; H, 10.79. Mp: 88 °C (for a 73:21:6 mixture of cc, ct, and tt isomers). Characterization data for *cis,cis*-**8**: ^{1}H NMR (room temperature, $CDCl_3$) δ 0.09 (s, 12H, CH_3), 1.43 (app d, 8H CH_2), 5.28 (m, 4H, CH); ^{13}C NMR ($CDCl_3$) δ −3.0 (s, CH_3), 15.7 (s, CH_2), 122.8 (s, CH); ^{29}Si NMR ($CDCl_3$) δ −0.63 (s); mass spectrum *m/z* 224 $[M]^+$, 112 $[M/2]^+$; IR (KBr) 1640 (w), 1409 (w), 1259 (sh), 1251 (s), 1159 (s), 1030 (m), 943 (m), 849 (s), 791 (m), 737 (s), 689 (w), 670 (w), 640 (m), 501 (w) cm^{-1}.

Polymerization of 1,1-Diphenyl-1-silacyclopent-3-ene (1). (a) By $WCl_6/SnMe_4$. Freshly distilled $SnMe_4$ in chlorobenzene (1.8 mL) was added to WCl_6 (0.079 g, 0.2 mmol) in chlorobenzene (3 mL) at −20 °C. The mixture was warmed to room temperature with stirring to give a red-brown solution, which was stirred for a further 2 h. This solution (0.6 mL) was then added via pipet to the neat monomer. The sample was shaken for several minutes and allowed to stand. After 1 h, the mixture had changed from red-brown to green. The polymeric product was extracted with a minimum volume of THF (5 mL) and precipitated from methanol. The resulting white precipitate was collected and dried in vacuo at 40 °C. Characterization data for 90% *cis*-poly-1: ^{1}H NMR ($CDCl_3$) δ 1.75 (d, *J* = 5.6 Hz, CH_2), 5.30 (t, *J* = 5.6 Hz, CH), 7.38–7.68 (aromatic C–H); ^{13}C NMR ($CDCl_3$) δ 13.67 (CH_2), 123.5 (CH), 127.6, 129.2, 134.9, 135.5 (aromatic carbons); ^{29}Si NMR ($CDCl_3$) δ −10.54 (s). See Table V for GPC data.

(b) By Mo-I. The following procedure was used for several experiments with differing amounts of monomer. To a sample of Mo-I (0.08 g, 0.105 mmol) was added neat 1,1-diphenyl-1-silacyclopent-3-ene (**1**; 4.94 g, 20.9 mmol) dropwise with stirring over a period of 20 min. During this time the mixture became viscous and solidified. The resulting solid mixture was treated with excess benzaldehyde in THF (20 mL). After filtration, the solution was concentrated under reduced pressure to ca. 5 mL and added dropwise to methanol (1 L) with stirring. The resulting white precipitate of poly-1 was collected and dried in vacuo at 40 °C: yield 2.96 g, 60%. Characterization data for 55% *trans*-poly-1 (see Figures 4 and 5 for NMR traces): ^{1}H NMR ($CDCl_3$) 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 ($CDCl_3$) 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 carbons); ^{29}Si NMR ($CDCl_3$) δ −10.54 (s), −10.92 (s), −11.25 (s), −11.34 (s). Anal. Calcd for $[C_{16}H_{16}Si]_n$: C, 81.33; H, 6.78. Found: C, 81.42; H, 6.97. See Table V for GPC data.

Polymerization of 1-Methyl-1-phenyl-1-silacyclopent-3-ene (2). (a) By $WCl_6/SnMe_4$. A procedure analogous to that described for the polymerization of 1 (procedure a) was used for the polymerization of **2**. A 0.349-g sample of **2** was polymerized to 0.227 g (65%) of poly-**2**, containing 80% cis olefinic bonds. Characterization data for *cis*-poly-**2**: ^{1}H NMR ($CDCl_3$) δ 0.23 (s, CH_3), 1.61 (app d, CH_2), 5.30 (app t, CH), 7.27–7.50 (m, aromatic C–H's); ^{13}C NMR ($CDCl_3$) δ −5.5 (CH_3), 15.3 (CH_2), 123.3 (CH), 127.7, 129.0, 133.9, 137.8 (aromatic carbons); ^{29}Si NMR ($CDCl_3$) δ −4.31.

(b) By Mo-I. A procedure analogous to that described for the polymerization of 1 (procedure b) was used. Quantities: Mo-I (0.02 g, 0.026 mmol), **2** (3.28 g, 18.8 mmol). Yield of poly-**2**: 1.44 g, 44% (75% trans). Characterization data (peaks due to cis polymer marked with an asterisk): ^{1}H NMR ($CDCl_3$) δ 0.09, 0.16, 0.21* (s, CH_3), 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–H's); ^{13}C NMR ($CDCl_3$) 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 carbons); ^{29}Si NMR ($CDCl_3$) δ −4.31, −4.74, −5.18. Anal. Calcd for $[C_{11}H_{14}Si]_n$: C, 74.23; H, 8.59. Found: C, 73.94; H, 8.72. See Table V for GPC data.

Polycondensation of Diallyldiphenylsilane (4). Freshly distilled diallyldiphenylsilane (**4**; 7 g, 26.5 mmol) was added to Mo-I (0.04 g, 0.052 mmol) in a 250-mL round-bottomed flask under a nitrogen atmosphere. The reaction commenced with evolution of ethylene, which was removed under reduced pressure. The mixture was stirred under dynamic vacuum for 3 h, during which time the viscosity of the mixture increased substantially; this mixture was allowed to stand for a further 24 h under dynamic vacuum. Excess benzaldehyde in THF was then added. The resultant solution was filtered and concentrated to ca. 5 mL and then added dropwise to methanol (1 L) to precipitate the polymer. ^{1}H and ^{13}C NMR spectra gave signals consistent with 90% *trans*-poly-1: yield 5.63 g, 90%. See Polymerization of 1,1-Diphenyl-1-silacyclopent-3-ene (1) for characterization data.

Polycondensation of Diallyldimethylsilane (5). Freshly distilled diallyldimethylsilane (**5**; 3.71 g, 26.4 mmol) was added to Mo-I (0.04 g, 0.052 mmol) in a 250-mL round-bottomed flask under a nitrogen atmosphere. The reaction commenced immediately with evolution of ethylene. For the first 1 h of the reaction, the mixture was maintained at ambient pressure and the gas vented via an oil bubbler. During this time, the mixture became viscous and was then periodically exposed to dynamic vacuum to remove additional ethylene. The resulting viscous residue was allowed to stand for 24 h under dynamic vacuum: yield 1.04 g, 35%. ^{1}H and ^{13}C NMR spectra gave signals consistent with 75% *trans*-poly-3 (peaks due to cis polymer marked with an asterisk). ^{1}H NMR ($CDCl_3$): δ −0.01, −0.02* (s, CH_3), 1.43 (m, CH_2), 5.22, 5.31* (m, CH). ^{13}C NMR ($CDCl_3$): δ −3.9, −3.7* (CH_3), 16.24 (ct, CH_2), 16.36* (cc, CH_2), 20.96 (tt), 21.23 (tc) (CH_2); δ 123.02* (cis-CH), 124.29 (trans-CH). ^{29}Si NMR ($CDCl_3$): δ 0.93 (tt), 1.71 (ct), 2.46* (cc). M_w = 3830, M_n = 1230.

***trans,trans*-1,1,6,6-Tetraphenyl-1,6-disilacyclodeca-3,8-diene (6c).** A sample of *trans*-poly-1 was generated according to the procedure outlined above for the polycondensation of diallyldiphenylsilane (4). Instead of benzaldehyde to kill the catalyst, toluene (30 mL) was added and the mixture was stirred for 24 h to give a white precipitate. After addition of pentane (30 mL), the precipitate was separated by filtration, collected and dried in vacuo, and then recrystallized from a 1:1 (by volume) mixture of toluene and pentane at −20 °C: yield 1.88 g, 30%. Anal. Calcd for $C_{32}H_{32}Si_2$: C, 81.33; H, 6.78. Found: C, 81.19; H, 7.10. Mp: 201–202 °C. ^{1}H NMR (room temperature, $CDCl_3$): δ 2.22 (d, ^3J(HH) = 5 Hz, 8H, CH_2), 5.50 (t, ^3J(HH) = 5 Hz, 4H, CH), 7.38–7.53 (complex multiplets, 20H, aromatic C–H). ^{13}C NMR ($CDCl_3$): δ 20.0 (s, CH_2), 125.7 (s, CH), 128.0, 129.4, 134.5, 136.1 (aromatic carbons). ^{29}Si NMR ($CDCl_3$): δ −23.50 (s). Mass spectrum: *m/z* 472 $[M]^+$, 236 $[M/2]^+$. IR (KBr): 1160 (s), 1115 (s), 1105 (s), 1058 (m), 987 (m), 949 (m), 836 (m), 782 (s), 770 (s), 735 (s), 700 (s), 504 (s), 440 (m) cm^{-1}.

Metathesis Degradation Reactions of poly-1–3. These reactions were performed on an NMR scale. Samples of poly-1–3 were weighed into NMR tubes along with Mo-I (0.01 g, 0.013

mmol) and C_6D_6 (0.5 mL). The samples were then flame-sealed, and the progress of the reaction was monitored by ^1H NMR spectroscopy.

X-ray Crystallography. Crystal data for **6a** and **6c** are summarized in Table I. Measurements were made with a Stoe-Siemens four-circle diffractometer and graphite-monochromated CuKα radiation (λ = 1.541 84 Å) at 295 K. Unit cell parameters were refined from 2θ values (40–50°) of 32 reflections measured at $\pm\omega$ to minimize systematic errors. Intensities were measured by an on-line profile-fitting method,[19] and scan parameters for each reflection were automatically selected. There was no significant variation in the intensities of three standard reflections. Semiempirical absorption corrections were applied.

The structures were determined by direct methods and difference syntheses, with blocked-cascade least-squares refinement on F. SHELXTL[20] and locally written computer programs were employed, and atomic scattering factors were taken from ref 21. 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 $G = F_0/F_{\max}$ and $H = \sin\theta/\sin\theta_{\max}$; the parameters A were derived from analysis of the data.[22] The isotropic extinction parameter x is defined by $F_c' = F_c/(1 + xF_c^2/\sin 2\theta)^{1/4}$. The weighted R factor $R_w = (\sum w\Delta^2/\sum wF_o^2)^{1/2}$.

In the refinement of the structure of **6c**, 2-fold disorder was resolved for one phenyl group, with occupancy factors 0.512:0.488(4). All phenyl groups were treated as ideal rigid hexagons with C–C = 1.395 Å. The structure contains three independent molecules, each located on an inversion center, together with one toluene molecule, on an inversion center such that the methyl group is disordered over all six substituent positions. There were no disorder problems for **6a**, and constraints were not applied to its phenyl groups. Isotropic hydrogen atoms were included in both structures, constrained to give normal geometry with C–H = 0.96 Å and $U(H) = 1.2U_{eq}(C)$, but were omitted from the disordered toluene.

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Supplementary Material Available: Tables listing the anisotropic thermal parameters for non-hydrogen atoms and hydrogen atom coordinates and isotropic thermal parameters for **6a,c** (7 pages). Ordering information is given on any current masthead page.

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