

Silenes as novel synthetic reagents: identification of a practical method for silene generation and trapping

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The elucidation of a robust and reliable sequence for the generation of highly reactive transient silenes from simple aldehydes is described. The key step involves a silyl-modified Peterson olefination which critically depends on the presence of a sub-stoichiometric amount of soluble lithium salts (LiBr).

Introduction

Owing to their high reactivity, and in most cases, transient existence silenes – compounds containing a silicon–carbon double bond – have been the object of considerable interest.^{1–6} Much of this effort has been focused on structural and bonding aspects with a particular emphasis on the preparation of stable isolable silenes. In many cases, evidence for the formation of silenes is obtained from the isolation of adducts from reaction with a large variety of functionality including alcohols, alkenes and carbonyl compounds, Fig. 1.

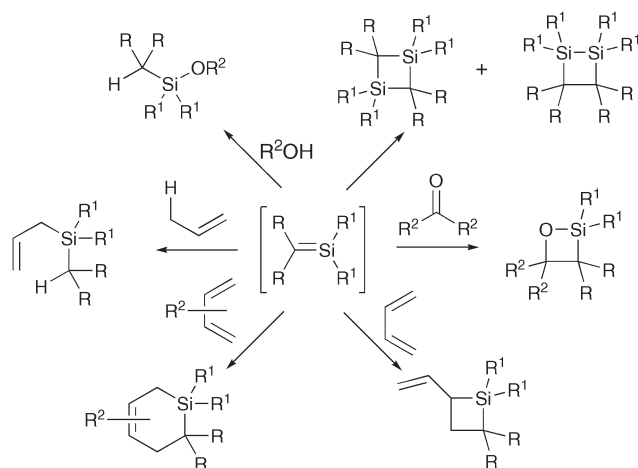
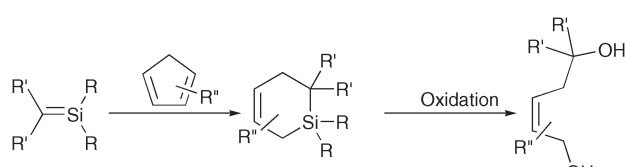


Fig. 1 Typical reactions of silenes.

However, despite this broad repertoire of chemistry there has been little effort to exploit the unique reactivity of these species in organic synthesis. With this objective in mind, we have initiated a programme to explore this aspect of silene chemistry with a particular emphasis on cycloaddition chemistry coupled with recently developed silicon oxidation methods to provide a novel strategy for the functionalisation of dienes, Scheme 1.

Synthetic approaches to silenes date to 1912 when Schlenk and Renning first claimed an approach through the dehydration of

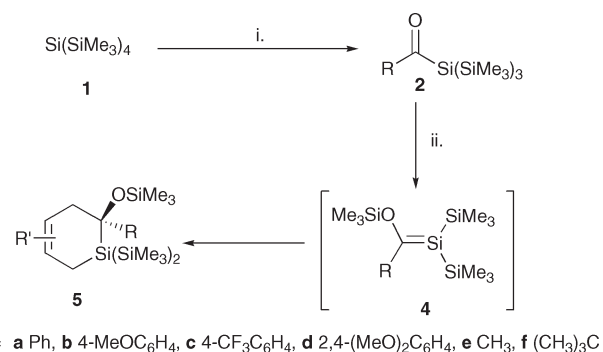


Scheme 1

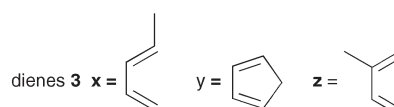
diphenylsilylmethanol.⁷ This report was subsequently shown to be erroneous⁸ and the first synthesis was not realised until 1967, when Gusel'nikov and Flowers unambiguously demonstrated the transient existence of silenes in the pyrolysis of dimethylsilacyclobutane.⁹ Since then, reflecting the growing interest in their chemistry, a large number of methods have been developed for the generation of silenes. However, many of these are not suitable for general preparative purposes as they require reagents or conditions that are incompatible with many functional groups. In this paper we describe our attempts to develop robust and versatile methods for the selective generation of silenes. In particular we report our mechanistic findings on the modified Peterson olefination strategy to provide a convenient method for low temperature silene generation.¹⁰ In the accompanying paper (see ref. 38) we describe how this approach can be employed to provide a novel method for the functionalisation of simple butadienes.

Results and discussion

Our initial approach to the application of silenes as new synthetic reagents was based on the thermolysis of acylpolysilanes first reported by Brook *et al.*¹¹ The requisite acylsilanes **2** were prepared by condensation of the Gilman reagent, $(\text{Me}_3\text{Si})_3\text{SiLi}\cdot 3\text{THF}$,^{12,13} generated *in situ* from $(\text{Me}_3\text{Si})_4\text{Si}$ **1** and MeLi, with the appropriate acid chloride, Scheme 2.^{14,15} Subsequently, heating a degassed toluene solution of the acylpolysilane and a two-fold excess of the diene **3** in a sealed glass tube at 180 °C for 4 h afforded the [4 + 2] silacycloaducts **5** in good yields, Table 1, and moderate selectivities favouring the *endo* silene R substituent.^{10a}



R = a Ph, b 4-MeOC₆H₄, c 4-CF₃C₆H₄, d 2,4-(MeO)₂C₆H₄, e CH₃, f (CH₃)₃C



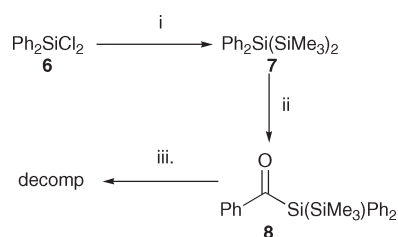
Scheme 2 Reagents and conditions: i. MeLi, THF, 18 h, rt then RCOCl (52–94%); ii. diene **3**, PhMe, 180 °C (20–91%).

Table 1 Yields of trisilanes **5** obtained through thermolysis of acylpolysilanes **2** in the presence of dienes **3**

Diene	Silene					
	4a	4b	4c	4d	4e	4f
3x	64% (2:1)	80% (3:2)	46% (4:1)	(80%) ^a (2:1)	46% (4:1)	— ^b
3y	91% (3:1)	68% (2.5:1)	85% (4:1)	n.a.	n.a.	70% (6:1)
3z	61% ^c	n.a.	n.a.	n.a.	n.a.	n.a.

^a Decomposed upon purification – GC yield. ^b Inseparable mixture with competing ene product. ^c Ca. 1:1 mixture of regioisomers.

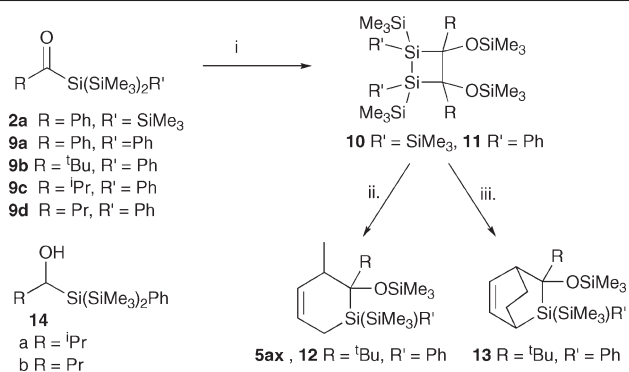
However, despite several literature precedents,^{16–18} we were unable to achieve the desired oxidative fragmentation of the trisilanes **5**. Based on the work of Fleming *et al.*, we recognised that incorporation of a silyl aryl group into the silene precursor would facilitate the oxidative fragmentation.¹⁹ Consequently we prepared the corresponding bis-phenylacyldisilane **8** as outlined in Scheme 3. Disappointingly, all attempts to carry out the thermolysis with this substrate failed affording only a polymeric residue.²⁰ At this point, although providing an efficient means for silene generation we recognised that this thermal approach had a number of other limitations, namely the use of sealed tube technologies and the moderate diastereoselectivities.



Scheme 3 Reagents and conditions: i. Mg, TMSCl, HMPA, THF (53%); ii. MeLi, THF, 18 h, rt then RCOCl (54%); iii. diene, PhMe, 180 °C.

Attempts to enhance the selectivity through the use of various silyl Lewis acids did not provide a viable solution,²¹ so we turned to alternative strategies which avoided the high temperatures required in the simple thermolysis. In his early work towards stable silenes, Brook and co-workers demonstrated that silenes can exist in equilibrium with their corresponding head-to-head dimers.¹⁴ Based on this we speculated that these dimers might provide a convenient lower temperature source of silenes for our studies. Interestingly, to the best of our knowledge, no examples have been reported of the reaction of such silene dimers with dienes. Preliminary studies using acylpolysilane **2a** involved generation of the silene dimer **10a** through photolytic activation using a 1 kW mercury arc lamp in 45% yield, Scheme 4. Dissolution of **10a** in THF in the presence of *E*-1,3-pentadiene and heating at reflux for 2 h afforded a mixture of the desired cycloadduct **5ax** and unreacted dimer. Importantly, the diastereoselectivity was slightly enhanced (3:1) as compared to the original sealed tube thermolysis protocol. Encouraged by this we then prepared the Si-phenyl-substituted acylpolysilanes **9a–d**. The phenyl **9a** and *tert*-butyl **9b** derivatives could be generated by a method analogous to that described above whilst the alkyl analogues **9c** and **9d** required a two-step procedure proceeding *via* the silyl alcohols **14** (*vide infra*) to circumvent problems of enolisation of the initially formed acylsilanes.

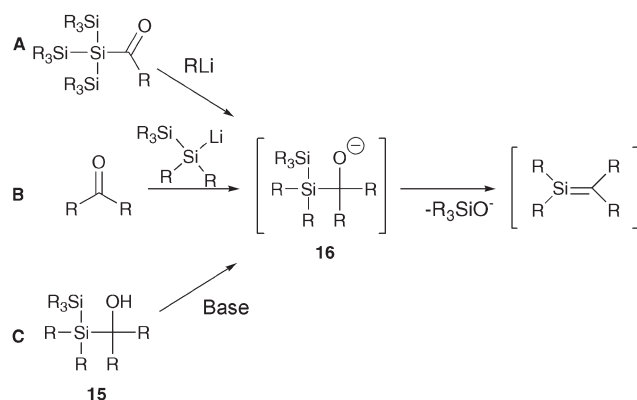
Photolysis of acylsilane **9b** using a 125 W medium pressure mercury lamp in a cooled jacketed reactor afforded the desired head-to-head dimer **11b** in excellent yield. Interestingly, it proved necessary to use a dilute (0.5 M) solution of CuSO₄ as the coolant to obtain efficient yields. We speculate that this acts as a crude filter of higher energy wavelengths which promote decomposition of the dimer or intermediate silene. Simply stirring this dimer in THF in the presence of cyclohexadiene and pentadiene afford the desired [4 + 2]



Scheme 4 Reagents and conditions: i. *hν*, cyclohexane **10** 45%, **11a** 5%, **11b** 100%; ii. 1,3-pentadiene, THF, 70 °C, **5ax** or 1,3-pentadiene, THF, rt, **12b** 70%; iii. cyclohexadiene, THF, rt, **13b** 69%.

adducts **12** and **13** in good yields, albeit as inseparable 1:1 mixtures of diastereoisomers. Having established that these dimers can represent a convenient source of silenes we then attempted to extend the scope of this approach. However, photolysis of the corresponding phenyl analogue **9a** afforded the desired dimer in only 5% yield whilst the alkyl-substituted acylsilanes **9c** and **9d** underwent complete decomposition. Whilst these problems could potentially be circumvented by more precise control of the photolysis conditions the low diastereoselectivity and difficulties in carrying out Fleming–Tamao oxidations of the cycloadducts caused us to abandon this approach and explore alternative silene generation strategies.

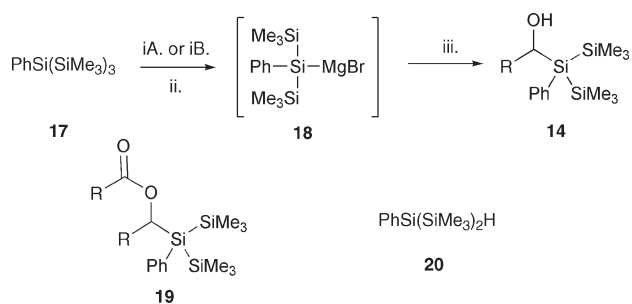
Attracted by the pioneering studies by Oehme and his co-workers, we turned to the silyl-modified Peterson reaction in which elimination of R₃SiO[−] from a disilanyl alkoxide **16** drives the generation of the transient silene.^{22–28} This key intermediate can be generated in a number of ways, Scheme 5, and we opted to use the two-stage process *via* the hydroxypolysilane **15** (path C) since this would avoid potential problems of competing enolisation and electron transfer reactions that have been reported with the alternative pathways.^{29,30}



Scheme 5

Consequently, silicon–metal exchange of phenyltrimethylsilylsilane **17** with MeLi in THF for 18 h at room temperature afforded the corresponding silyllithium reagent. Following solvent exchange to Et₂O, transmetalation with MgBr₂ afforded the desired silyl Grignard reagent **18**. More conveniently, using the elegant chemistry developed by Marschner, we found that we could generate **18** by treatment of the silane with KO^tBu at room temperature for 2 h prior to transmetalation with MgBr₂ in diethyl ether.³¹ Subsequent addition of the aldehyde at −78 °C then afforded the desired alcohol **14** albeit with only moderate levels of conversion (*ca.* 50%), Scheme 6.

A major by-product in this process was the ester **19** which we propose was formed by a Tischenko-type process triggered by addition of the initially formed alkoxide to unreacted aldehyde, Scheme 7.³² Evidence to support this came from a simple crossover experiment in which the isopropyl-substituted alkoxide **21** was generated by



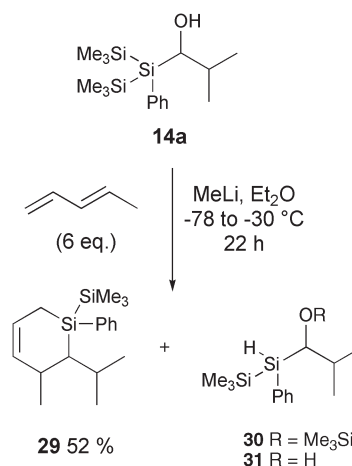
Scheme 6 Reagents and conditions: iA. MeLi, THF, rt 18 h; iB. KO^tBu, THF, 2 h; ii. MgBr₂, Et₂O; iii. RCHO, Et₂O, -78 °C; **a** CH(CH₃) 52%, **b** C₃H₇ 74%, **c** Me 49%, **d** CH(CH₃)C₂H₅ 58%, **e** C(CH₃)₃ 37%, **f** *c*-C₆H₁₁ 38%, **g** Ph 63%.

treatment of **14a** with MeMgBr and then combined with benzaldehyde. GCMS analysis of the reaction mixture revealed formation of both the cross ester **25** and benzyl alcohol **26** together with trace amounts of the acylsilane **24**, presumably formed by an alternative hydride transfer process **27**.

Whilst the KO^tBu method tended to afford greater quantities of the ester it was found that this could be minimised by the use of 1.1 equivalents of the aldehyde. This optimised procedure afforded the desired alcohol in yields ranging from 37 to 63% with the major by-product being the silane **20** corresponding to protonation of the silyl metallic reagent. Enolisation of the aldehyde was ruled out as a major factor in this process as a study of the reaction with pivaldehyde revealed a similar, if unoptimised, product profile. Our current hypothesis is that there may be a ligand exchange process occurring involving the alkoxide and silyl Grignard reagent to produce the mixed organometallic species **28** which is unreactive with respect to aldehydes.³³ Attempts to enhance the conversion (yield) through a screen of various other metal counter ions (including Ce, Yb, Cu and Zn) and additives (TMEDA, DMPU, *etc.*) were not productive and further detailed studies of this transformation are in progress.

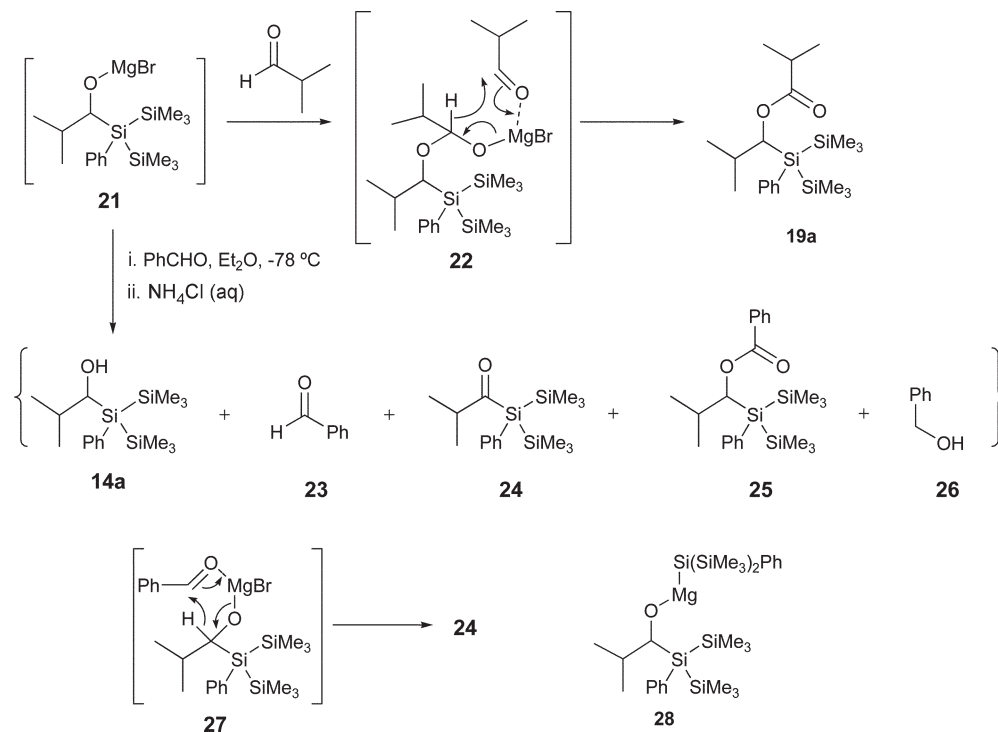
With the silyl alcohols readily available we then turned to study the key silene generation step. Oehme had reported that deprotonation with MeLi in the presence of a diene at -78 °C afforded the silene as detected by the [4 + 2] cycloadduct formed with 2,3-dimethylbutadiene.²⁶ In our hands, using alcohol **14a** as the silene precursor and *E*-1,3-pentadiene as the silenophile, no reaction occurred until the mixture was warmed to *ca.* -30 °C, when the

silacycle **29** could be isolated in 50–63% yield accompanied by a number of minor components including the silanes **30** and **31** (*vide infra*), Scheme 8. However, since attempts to reproduce and optimise this observation gave extremely inconsistent results, we undertook a detailed analysis of the process. The proposed mechanism for the generation of the silene involved generation of the alkoxide, migration of a trimethylsilyl group and then elimination of TMSOLi.²⁵ This suggested that almost any strong base would be sufficient to promote this reaction and we therefore screened a number of alternative conditions, Table 2. Entries 1–3 highlight the unreliability of MeLi for silene generation although, ironically, no other base led to generation of silacycle **29**, which implies that no other base gave silene. Entries 4–7 show that the reaction proceeds through the 1,3-*Si*-*O* TMS migration with ^tBuLi and NaH but the resulting silyl anion does not eliminate Me₃SiO⁻ to give silene, hence silanes **30**/**31** are produced on work-up. Entry 7 shows that the migration can be forced to completion by the use of higher temperatures. Entries 8–10 involve bases which are too weak to sufficiently deprotonate the silyl alcohol **14a**, which is believed to have a high p*K*_a due to electron donation by the electropositive silyl group.



Scheme 8

The use of TBAF and Me₃SiOK in entries 11 and 12 were tests of an alternative mechanistic hypothesis involving nucleophilic attack at a TMS group of silyl alcohol **14a** and elimination of hydroxide to produce the silene, Scheme 9.³⁴ However, in neither case was



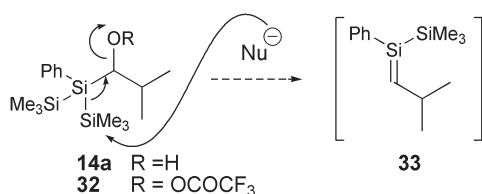
Scheme 7

Table 2

Entry	Base	Temp./°C	Time/h	Molar % by NMR ^a		
				14a	30	29
1	MeLi ^b	-78 to -30	22	0	9	91 ^c
2	MeLi ^d	-78 to -30	18	83	17	0
3	MeLi ^e	-78 to -30	20	72	8	20
4	ⁿ BuLi	-78 to -30	18	52	48	0
5	NaH	-78 to RT	39	69	31	0
6	2NaH	-78 to -30	87	18	82	0
7	2NaH	-78 to reflux	7	0	100	0
8	LiH	-78 to -30	18	95	5	0
9	2LiH	-78 to reflux	41	95	5	0
10	LiOH	-78 to -30	18	100	0	0
11	TBAF	-78 to -30	18	100	0	0
12	Me ₃ SiOK	-78 to -20	21	93	7	0

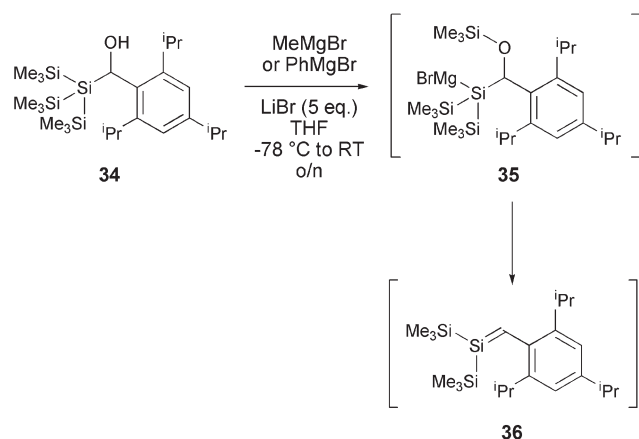
^aRatio of products detected in the crude NMR spectrum for the reaction with each base. ^bBatch X \leq 6 mol% LiBr. ^cIsolated yield 52%. ^dBatch Y. ^eBatch Z.

the silene generated. Speculating that a better leaving group than hydroxide was required, attempts were made to convert the alcohol into the tosylate and mesylate. Although these reactions failed due to the steric congestion around the silyl alcohol **14a**, the corresponding trifluoroacetate was prepared. However, reaction of this with MeLi re-generated silyl alcohol **14a**, due to nucleophilic attack at the ester, and treatment with TBAF yielded a complex mixture of products, none of which could be ascribed to silene generation.



Scheme 9

At this stage suspecting that additive(s) within the commercial samples of ethereal MeLi used were aiding the generation of the silene we looked in more detail at the MeLi solutions that had been used. Although described as 'low chloride', these are reported to contain varying amounts of LiBr (\leq 6%). In contrast, the ⁿBuLi used was a solution in hexane and free from additional lithium salts which was consistent with our inability to generate silenes with this base. A search of the literature revealed that Oehme and co-workers had found the presence of LiBr to have an effect on the rate of silene generation;³⁵ formation of silene **36**, by treatment of silyl alcohol **34** with a Grignard reagent, normally proceeded extremely slowly, but in the presence of LiBr, the reaction was complete within a few hours, Scheme 10. Unfortunately, Oehme's group did not offer an explanation for this observation.



Scheme 10

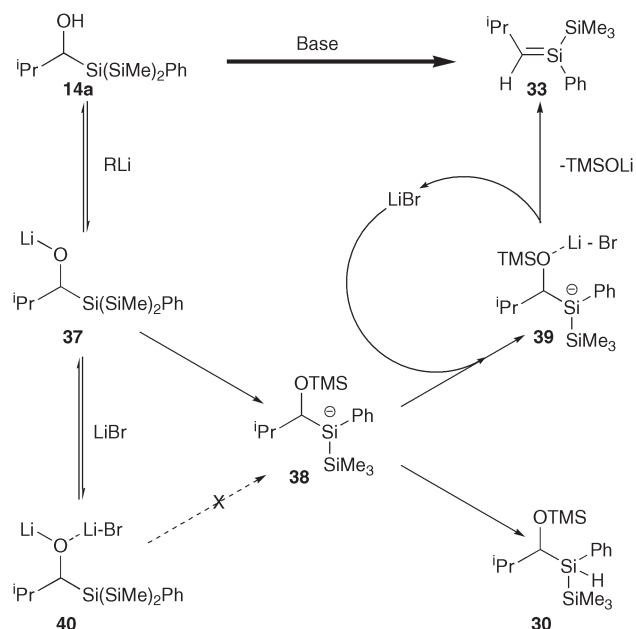
Table 3

Entry	Base	Additive (mol%)	Method	Molar % by NMR ^a		
				14a	30	33 ^b
1	ⁿ BuLi	None	—	52	48	0
2	NaH ^c	LiCl (220%)	B	12	88	0
3	ⁿ BuLi	LiCl (60%)	A	71	29	0
4	ⁿ BuLi ^d	LiBr (70%)	A	100	0	0
5	ⁿ BuLi	LiBr (100%)	A	86	14	0
6	ⁿ BuLi	LiBr (30%)	A	90	10	0
7	ⁿ BuLi	LiBr (6%)	A	60	40	0
8	ⁿ BuLi	LiBr (100%)	B	7	17	76 ^e
9	ⁿ BuLi	LiBr (10%)	B	7	21	72
10	ⁿ BuLi	LiI 100% ^c	B	6	14	80 ^f

^aAnalysis of crude reaction mixture following work-up – see Experimental section. ^bIdentified as [4 + 2] cycloadduct **29**. ^c2 equiv. ^d1.7 equiv. ^e50% isolated yield. ^f36% isolated yield.

A thorough investigation into the addition of lithium salts to the reaction mixture of silyl alcohol **14a**, 1,3-pentadiene and base was then undertaken and these results are summarised in Table 3. The salts were added either prior to the addition of base (Method A) or after complete conversion to silylmetallic **38** (Method B). Addition of LiCl even in large excesses did not lead to any products arising from a silene being detected (entries 2, 3). This suggested that elimination of Me₃SiOLi had not occurred, which could be attributed to the insolubility of LiCl. Attempts to simulate successful reactions using MeLi by the addition of LiBr prior to base were also unsuccessful (entries 4–7). Finally, it was discovered that low temperature addition of LiBr, after complete conversion of silyl alcohol **14a** to silyllithium **37** by treatment with ⁿBuLi at rt for 3 h, afforded silene (entry 8) and that the LiBr could be used in sub-stoichiometric quantities (entry 9). Similar experiments with LiI were also successful but this reagent was harder to dry, due to its lower temperature of sublimation, and ultimately produced lower overall yields (entry 10).

We rationalise these observations using the mechanistic scheme shown below, Scheme 11. Treatment of the silyl alcohol with BuLi generates the alkoxide **37**. A 1,3-Si–O silyl migration then occurs over 3 h at rt to produce the silyl anion **38** which undergoes elimination promoted by a catalytic amount of LiBr.³⁶ In the absence of soluble Li salts no elimination occurs, whilst in the presence of a high initial concentration of Li ions the initial silyl migration is hindered by coordination/aggregation resulting in low conversions.



Scheme 11

With a reliable protocol in hand we were able to extend our studies to a range of different silenes and dienes (silenophiles), Fig. 2. In all cases the reactions were carried out by treating the mixture of silyl alcohol, diene in Et₂O with BuLi at room temperature until complete migration of the trimethylsilyl group had occurred as monitored by analysis of an aliquot (GC/TLC). Cooling to -78 °C, addition of a freshly dried sample of LiBr in Et₂O and allowing the reaction to warm to -30 °C overnight afforded, after simple aqueous work-up and chromatography, the desired silacycles, accompanied by small and varying amounts of competing ene, [2 + 2] and silene dimers. However, with dienes lacking a terminal methyl group, 2,3-dimethylbutadiene and isoprene, more significant amounts of ene product were isolated (*ca.* 12%). In all cases involving non-symmetrical dienes good regioselectivity was observed, being consistent with simple FMO theory placing the largest coefficient of the silene LUMO on silicon. Moreover, good diastereoselectivity was observed suggesting that silene generation had occurred with a high degree of selectivity.³⁷ The only difference between this method and those using MeLi that were successful is that the latter affords slightly higher, albeit less reproducible, selectivities (see Experimental section). We speculate that, when successful, the use of MeLi solutions affords a slower elimination of Me₃SiOLi, limiting the transient concentration of silene present and thus minimising the possibility for the alternative pathways. Limitations appeared in that more hindered dienes, *e.g.* cyclohexadiene, do not undergo the reaction competitively with silene dimerisation, whilst attempts to carry out the reaction with 1,6-bismethoxyhexa-2,4-diene failed to proceed beyond the silyl migration stage.

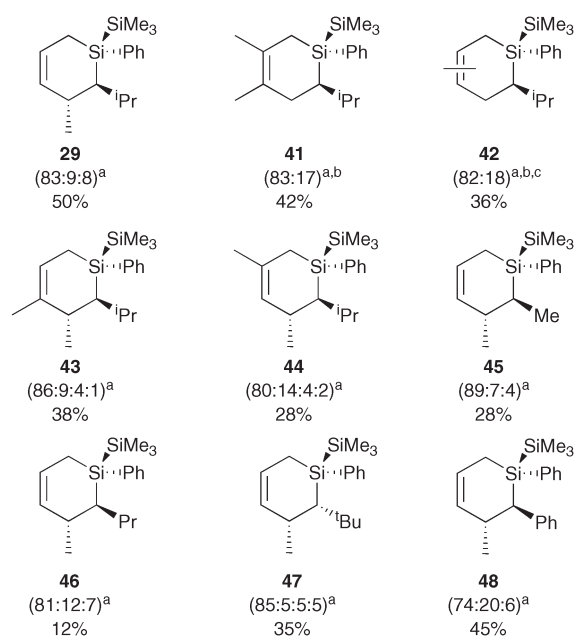


Fig. 2 [4 + 2] Silacycloadducts generated *via* the modified Peterson reaction: ^a ratio of isomeric [4 + 2] cycloadducts (major isomer only shown – see ref. 39); ^b accompanied by *ca.* 12% ene product; ^c mixture of regioisomers.

In conclusion, we have developed a reliable method for the generation of simple alkyl- and aryl-silenes from aldehydes. These can be trapped *in situ* by alkylbutadienes to afford silacycles in moderate yields and good selectivities. These represent useful building blocks for the generation of diols and lactones and this is described in detail in the following paper.³⁸

Experimental

All air- and/or moisture-sensitive reactions were carried out under an argon atmosphere. Solvents were purified following established protocols. Petrol refers to petroleum spirit, boiling point in the 40–60 °C range. Ether refers to diethyl ether. Commercially available reagents were used as received unless otherwise stated. Flash column chromatography was performed according to the method of

Still *et al.* (W. C. Still, M. Kahn and A. Mitra, *J. Org. Chem.*, 1978, **43**, 2923) using 200–400 mesh silica gel. Yields refer to isolated yields of products of greater than 95% purity as determined by ¹H and ¹³C NMR spectroscopy or elemental analysis (Durham University Microanalytical Laboratory).

Melting points were determined using Gallenkamp melting point apparatus and are uncorrected. Infrared spectra were recorded as thin films between KBr plates (liquids) or as compression-formed discs made using KBr (solids) on a Perkin-Elmer FT-IR 1600 spectrometer. Unless otherwise stated ¹H NMR spectra were recorded in CDCl₃ on Varian Mercury 200, Bruker AM-250, Varian Unity-300, Varian VXR-400 or Varian Inova-500 spectrometers and are reported as follows: chemical shift δ (ppm) [number of protons, multiplicity, coupling constant *J* (Hz), assignment]. Residual protic solvent CHCl₃ ($\delta_{\text{H}} = 7.26$ ppm) was used as the internal reference. ¹³C NMR spectra were recorded at 63 MHz, 101 MHz or 126 MHz on Bruker AM-250, Varian VXR-400 or Varian Inova-500 instruments, respectively, using the central resonance of CDCl₃ ($\delta_{\text{C}} = 77.0$ ppm) as the internal reference. ²⁹Si NMR spectra were recorded at 99 MHz on a Varian Inova-500 spectrometer. ¹⁹F NMR spectra were recorded at 376 MHz or 282 MHz on Varian VXR-400 or Varian Unity-300 spectrometers, respectively. All chemical shifts are quoted in parts per million relative to tetramethylsilane ($\delta_{\text{H}} = 0.00$ ppm) and coupling constants are given in Hertz to the nearest 0.3 Hz. All ¹³C spectra were proton decoupled. Assignment of spectra was carried out using DEPT, COSY, HSQC and NOESY experiments. Low-resolution mass spectra (EI or CI) were obtained on a Micromass Autospec Mass Spectrometer. Gas chromatography–mass spectra (GCMS, EI or CI) were taken using a Hewlett Packard 5890 Series II gas chromatograph, equipped with a 25 m 5% diphenyl-/95% dimethyl-polysiloxane column and flame ionisation detection, connected to a VG Trio-1000 mass spectrometer. Electrospray mass spectra (ES) were obtained on a Micromass LCT Mass Spectrometer. High-resolution mass spectra were performed by the EPSRC service at the University of Swansea or on a Micromass Autospec Mass Spectrometer in Durham.

General procedure for the formation of acyltris(trimethylsilyl)silanes (ref. 11)

Methylolithium (1.6 M solution in ether) was added to a solution of tetrakis(trimethylsilyl)silane (0.23 M, 1 equiv.) in THF. After approximately 18 h, ¹H NMR showed the complete disappearance of the signal for tetrakis(trimethylsilyl)silane and the appearance at 0.32 ppm of the signal for tris(trimethylsilyl)silyllithium. The yellow solution was then cooled to -78 °C and added dropwise *via* cannula to a cooled (-78 °C) solution of acyl chloride (0.46 M, 2 equiv.) in THF over a 2 h period. After stirring for 4 h at -78 °C, dilute HCl (3 M, 100 ml) was added. The organic layer was separated, and the aqueous layer extracted with diethyl ether. The combined organic layers were dried over MgSO₄. The mixture was then filtered, and the solvents removed *via* rotary evaporation. Flash column chromatography yielded the pure acyltris(trimethylsilyl)silane.

Benzoyltris(trimethylsilyl)silane 2a.¹¹ (77% yield) ν_{max} (thin film) 3062, 2949, 2893, 2360, 2341, 1737, 1607, 1593, 1575, 1445, 1399, 1308, 1245, 1200, 1167 cm⁻¹; δ_{H} (200 MHz) 7.7–7.3 (5H, m, Ar-H), 0.25 (27H, s, Si(CH₃)₃); δ_{C} (126 MHz) 234.26, 144.09, 133.35, 128.48, 127.52, 1.26; MS (EI) *m/z* 352 (M⁺, 1%), 279 [M⁺ – Si(CH₃)₃, 5%], 135 (14), 73 (100).

4-Methoxybenzoyltris(trimethylsilyl)silane 2b.³⁹ (62%). ν_{max} (thin film) 3004, 2953, 2895, 2839, 2360, 2341, 1691, 1608, 1586, 1569, 1505, 1463, 1552, 1399, 1307, 1259, 1209, 1159 cm⁻¹; δ_{H} (400 MHz) 7.73 (2H, d, *J* = 8.7 Hz, Ar-H), 6.92 (2H, d, *J* = 8.7 Hz, Ar-H), 3.67 (3H, s, OCH₃), 0.25 (27H, Si(CH₃)₃); δ_{C} (126 MHz) 232.98, 163.16, 137.61, 129.97, 113.28, 55.42, 1.528; MS (EI) *m/z* 383 (MH⁺, 4%), 367 (M⁺ – CH₃, 15%), 311 (MH⁺ – SiMe₃, 17%), 279 (40), 221 (12), 209 (41) 152 (100), 147 (61), 135 (100), 92 (40), 73 (100); MS (CI) *m/z* 383 (MH⁺, 6%), 209 (19), 170 (17), 152 (27), 137 (32), 90 (42).

4-Trifluoromethylbenzoyltris(trimethylsilyl)silane 2c. (94%) ν_{\max} (thin film) 3063, 2956, 2896, 1933, 1800, 1730, 1619, 1605, 1580, 1505, 1405, 1327, 1249 cm^{-1} ; δ_{H} (200 MHz) 7.80 (2H, d, $J = 8.4$ Hz)–7.72 (2H, d, $J = 8.4$ Hz), 0.23 (27H, s, $3 \times \text{Si}(\text{CH}_3)_3$); δ_{C} (126 MHz) 236.50, 145.88, 133.28 (q, ${}^2J_{\text{C-F}} = 32.7$ Hz, C–CF₃), 127.02, 125.11 (q, ${}^3J_{\text{C-F}} = 3.8$ Hz, C–CF₃), 123.34 (q, ${}^1J_{\text{C-F}} = 272.9$ Hz, CF₃), 1.20; δ_{F} (235 MHz) –63.28; MS (EI) m/z 405 ($\text{M}^+ - \text{CH}_3$), 281 (60), 207 (36), 190 (35), 173 (62), 147 (66), 73 (100).

2,4-(Dimethoxy)benzoyltris(trimethylsilyl)silane 2d. (35%) ν_{\max} (thin film) 2955, 2893, 2837, 2361, 2340, 1606, 1497, 1464, 1439, 1412, 1307, 1284, 1258, 1245, 1159 cm^{-1} ; δ_{H} (250 MHz) 7.20–7.10 (1H, m, *Ar*), 6.5–6.3 (2H, m, *Ar*), 3.83 (3H, s, –OCH₃), 3.78 (3H, s, –OCH₃), 0.19 (27H, s, –Si(CH₃)₃); δ_{C} (63 MHz) 237.81, 162.43, 157.35, 131.38, 129.92, 103.59, 98.56, 56.51, 1.27; MS (EI) m/z 413 (MH^+ , 15%), 398 ($\text{MH}^+ - \text{CH}_3$, 15%), 339 [$\text{M}^+ - \text{Si}(\text{CH}_3)_3$, 11%], 309 (31), 281 (24), 239 (36), 191 (60), 165 (100), 149 (63), 131 (58), 73 (100).

Acetyltris(trimethylsilyl)silane 2e.¹¹ (76%) ν_{\max} (CHCl₃) 3019, 2959, 2867, 2360, 2340, 1740, 1626, 1251, 1225 cm^{-1} ; δ_{H} (200 MHz) 2.29 (3H, s, –CH₃), 0.24 (27H, s, –SiCH₃); δ_{C} (50 MHz) 244.03, 42.11, 1.00.

Trimethylacetyltris(trimethylsilyl)silane 2f.¹¹ (52%). Mp 181–182 °C decomp. ν_{\max} (CHCl₃) 3020, 2963, 2896, 1709, 1619, 1522, 1247, 1225 cm^{-1} ; δ_{H} (250 MHz) 1.02 [s, 9H, C(O)C(CH₃)₃], 0.23 [s, 27H, $3 \times \text{Si}(\text{CH}_3)_3$]; δ_{C} (63 MHz) 248.5, 49.5, 24.7, 1.61; MS (EI) m/z 317 ($\text{M}^+ - \text{CH}_3$, 16%), 275 [$\text{M}^+ - \text{C}(\text{CH}_3)_3$, 5%], 259 [$\text{M}^+ - \text{Si}(\text{CH}_3)_3$, 22%], 205 (11), 191 (10), 173 (100), 159 (19), 147 (55), 131 (31), 117 (21), 73 (100); (CI) m/z 317 ($\text{M}^+ - \text{CH}_3$, 13%), 191 (9), 90 (13).

Benzoyldiphenyltrimethylsilylsilane 8. Prepared in an identical fashion starting from diphenylbis(trimethylsilyl)silane (3.02 g, 9.21 mmol) to give the title compound as a colourless oil (1.79 g, 54%). ν_{\max} (thin film) 3067, 3050, 2955, 2894, 1608, 1574, 1428, 1246, 1207, 839 cm^{-1} ; δ_{H} (300 MHz) 7.80–7.30 (15H, m, *Ar-H*), 0.22 [9H, s, Si(CH₃)₃]; δ_{C} (50 MHz) 232.76, 142.22, 135.81, 134.11, 129.40, 128.33, 128.19, 128.10, 127.74, –1.21; m/z (EI) 360 (M^+ , 5%), 345 ($\text{M}^+ - \text{Me}$, 22%), 287 ($\text{M}^+ - \text{SiMe}_3$, 25%), 105 (67), 73 (100).

Benzoylbis(trimethylsilyl)phenylsilane 9a. Prepared in an identical fashion starting from phenyltris(trimethylsilyl)silane (5.16 g, 15.94 mmol) to give the title compound as a yellow oil (2.75 g, 50%). ν_{\max} (thin film) 3066, 2953, 2893 1739, 1720, 1700, 1605, 1573, 1400, 1314, 1247, 1202, 1171, 1110, 1065, 838 cm^{-1} ; δ_{H} (300 MHz) 7.75–7.30 (10H, m, *Ar-H*), 0.23 [18H, s, Si(CH₃)₃]; δ_{C} (100 MHz) 235.39, 142.65, 135.77, 134.91, 132.60, 128.52, 128.37, 128.26, 128.17, 0.42; m/z (ES+) 357 ($\text{M} + 1$, 20%), 279 ($\text{M} - \text{Ph}$, 100%).

Trimethylacetylbis(trimethylsilyl)phenylsilane 9b.¹⁴ Prepared in an identical fashion using phenyltris(trimethylsilyl)silane (14.85 g, 45.83 mmol) and trimethylacetyl chloride to give the title compound as a colourless oil (12.57 g, 82%). ν_{\max} (thin film) 3069, 2957, 2897, 2868, 1729, 1703, 1619, 1475, 1428, 1361, 1246, 1063, 943, 837 cm^{-1} ; δ_{H} (200 MHz) 7.64–7.30 (5H, m, *Ar-H*), 0.95 [9H, s, –C(CH₃)₃], 0.25 [18H, s, Si(CH₃)₃]; δ_{C} (125 MHz) 249.55, 136.87, 135.38, 128.76, 128.10, 50.27, 25.01, 0.33; m/z (EI) 279 [$\text{M}^+ - \text{C}(\text{CH}_3)_3$, 25%], 265 [$\text{M}^+ - \text{Si}(\text{CH}_3)_3$, 3%], 251 [$\text{M}^+ - \text{C}(\text{O})\text{Bu}$, 100%], 209 (26), 193 (32), 177 (22), 73 (67).

General procedure for the thermolysis of acyltris(trimethylsilyl)silanes in the presence of dienes.

A solution of the acylpolysilane (0.28 M) and diene (2 equiv.) in benzene or toluene was placed in a Carius tube, and thoroughly degassed using the freeze–pump–thaw technique (minimum 3 cycles). The tube was then sealed, and heated at 180 °C for 4 h. Removal of the solvent by rotary evaporation, followed by flash

column chromatography, gave the Diels–Alder adduct as a mixture of regio- and/or diastereo-isomers.

1,1-Bistrimethylsilyl-2-phenyl-2-(trimethylsilyloxy)-4-methylsilacyclohex-4-ene 5aA; and 1,1-bistrimethylsilyl-2-phenyl-2-(trimethylsilyloxy)-5-methylsilacyclohex-4-ene 5aB.

Reaction of benzoyltris(trimethylsilyl)silane with isoprene gave the title compounds as a mixture of regioisomers (1 : 1) (61%). Mp 113–114 °C. ν_{\max} (CHCl₃) 3019, 2955, 2894, 1597, 1488, 1443, 1400, 1248 cm^{-1} ; δ_{H} 7.45–6.90 (5H, m, *Ar-H*), 6.75–5.65 [0.5H, m, 4-*H*, (B)], 5.45–5.35 [0.5H, m, 5-*H*, (A)], 2.95–2.50 (2H, m, 3-*H*), 1.79 [1.5H, s, 5-(CH₃) (B)], 1.70 [1.5H, s, 4-(CH₃) (A)], 1.65–1.15 (2H, m, 6-*H*), 0.11 [4.5H, s, Si(CH₃)₃], 0.02 [4.5H, s, Si(CH₃)₃], 0.01 [4.5H, s, Si(CH₃)₃], –0.08 [4.5H, s, Si(CH₃)₃], –0.18 [4.5H, s, Si(CH₃)₃], –0.25 [4.5H, s, Si(CH₃)₃]; δ_{C} (63 MHz) 149.89, 135.41, 134.25, 127.79, 125.32, 125.07, 124.59, 121.60, 46.27, 40.50, 30.87, 27.60, 25.30, 13.80, 7.90, 2.89, 0.07, –0.49; m/z (CI) 421 (MH^+ , 2%), 348 (18), 331 (67), 90 (64), 73 (100); HRMS (CI): Found MH^+ , 421.2235; C₂₁H₄₀Si₄O requires M, 421.2234.

1,1-Bistrimethylsilyl-2-phenyl-2-(trimethylsilyloxy)-3-methyl-silacyclohex-4-ene 5ax.

Reaction of benzoyltris(trimethylsilyl)silane with *E*-1,3-pentadiene gave the title compound as a mixture of diastereoisomers [64%, 2 : 1 *endo*(Ph):*exo*(Ph)]. Mp 173–174 °C; ν_{\max} (CHCl₃) 3155, 2998, 2953, 2895, 1793, 1639, 1599, 1471, 1389, 1251 cm^{-1} ; δ_{H} (250 MHz) 7.32–7.03 (5H, m, *Ar-H*), 5.93–5.85 (1H, m, 4-*H*), 5.56–5.43 (1H, m, 5-*H*), 3.20–3.10 (0.33H, m, 3-*H* *exo*), 3.10–2.95 (0.67H, 3-*H* *endo*) 1.80–1.23 (2H, m, 6-*H*), 1.04 (1H, d, $J = 7.4$ Hz, CH₃ *exo*), 0.95 (2H, d, $J = 7.2$ Hz, CH₃ *endo*), 0.18 [6H, s, OSi(CH₃)₃ *endo*], 0.17 [6H, s, Si(CH₃)₃ *endo*], 0.07 [3H, s, OSi(CH₃)₃ *exo*], 0.03 [3H, s, Si(CH₃)₃ *exo*], –0.02 [6H, s, Si(CH₃)₃ *endo*], –0.32 [3H, s, –Si(CH₃)₃ *exo*]; δ_{C} (50 MHz) 148.10, 146.00, 136.98, 134.44, 127.95, 127.65, 126.61, 125.89, 125.37, 125.00, 80.98, 79.11, 43.17, 40.19, 16.57, 16.19, 9.21, 8.44, 3.76, 3.50, 0.71, 0.24, –0.97; m/z (EI) 420 (M^+ , 3%), 405 ($\text{M}^+ - \text{CH}_3$, 1%), 347 ($\text{M}^+ - \text{SiMe}_3$, 37%), 205 (41), 199 (61), 73 (100).

1,1-Bistrimethylsilyl-2-(4-methoxyphenyl)-2-(trimethylsilyloxy)-3-methyl-silacyclohex-4-ene 5bx.

Reaction of 4-methoxybenzoyltris(trimethylsilyl)silane with *E*-1,3-pentadiene gave the title compound as a mixture of diastereoisomers [80%, 3 : 2 *endo*(Ar):*exo*(Ar)]. ν_{\max} (thin film) 2997, 2951, 2894, 2833, 1608, 1508, 1463, 1441, 1391, 1291, 1250, 1179, 1068, 836 cm^{-1} ; δ_{H} (400 MHz) 7.30–7.18 (2H, m, *Ar-H*), 6.90–6.75 (2H, m, *Ar-H*), 6.0–5.85 (1H, m, 4-*H*), 5.6–5.4 (1H, m, 5-*H*), 3.81 (1.2H, s, –OMe, *exo*), 3.80 (1.8H, s, –OMe, *endo*), 3.20–3.10, (0.4H, m, 3-*H* *exo*), 3.10–3.00 (0.6H, m, 3-*H* *endo*), 1.85–1.2 (2H, m, 6-*H*), 1.08 (1.2H, d, $J = 7.2$ Hz, 3-CH₃ *exo*), 0.97 (1.8H, d, $J = 7.2$ Hz, 3-CH₃ *endo*), 0.20 [5.4H, s, OSi(CH₃)₃ *endo*], 0.18 [5.4H, s, Si(CH₃)₃ *endo*], 0.08 [3.6H, s, OSi(CH₃)₃ *exo*], 0.04 [3.6H, s, Si(CH₃)₃ *exo*], –0.07 [3.6H, Si(CH₃)₃ *exo*], –0.25 [5.4H, Si(CH₃)₃ *endo*]; δ_{C} (63 MHz) 157.20, 157.17, 140.46, 138.39, 136.91, 134.46, 126.79, 126.63, 126.53, 125.88, 113.23, 113.00, 80.44, 78.82, 55.25, 55.22, 43.18, 40.31, 16.53, 16.13, 9.15, 8.50, 3.63, 3.40, 0.61, 0.23, 0.15, –0.03, –0.88; m/z (EI) 450 (M^+ , 7%), 435 ($\text{M}^+ - \text{CH}_3$, 9%), 377 [$\text{M}^+ - \text{Si}(\text{CH}_3)_3$, 12%], 275 (100), 147 (24), 73 (84).

1,1-Bistrimethylsilyl-2-(2,4-bis(methoxy)phenyl)-2-(trimethylsilyloxy)-3-methyl-silacyclohex-4-ene 5dx. Reaction of 2,4-bis(methoxy)benzoyltris(trimethylsilyl)silane **2d** with *E*-1,3-pentadiene gave the title [4 + 2] adduct as a mixture of diastereoisomers (*ca.* 80%, *ca.* 1 : 1 *endo* : *exo*) (¹H NMR) along with several inseparable components; m/z (CI) 481 (MH^+ , 100%), 408 [$\text{MH}^+ - \text{Si}(\text{CH}_3)_3$, 4%], 392 [$\text{MH}^+ - \text{OSi}(\text{CH}_3)_3$, 31%].

1-Bistrimethylsilyl-2-(4-trifluoromethyl)phenyl-2-trimethylsilyloxy-3-methylsilacyclohex-4-ene 5cx. Reaction of 4-trifluoromethylbenzoyltris(trimethylsilyl)silane **2c** with *E*-1,3-pentadiene gave the title compound as a mixture of diastereoisomers (46%,

4:1 *endo:exo*). Mp 98–100 °C; ν_{\max} (KBr disc) 2998, 2955, 2895, 1614, 1408, 1329, 1243, 1161, 1119, 1079, 1069, 835 cm^{-1} ; δ_{H} (250 MHz) 7.60–7.20 (4H, m, Ar-H), 6.00–5.80 (1H, m, 4-H), 5.50–5.20 (1H, m, 5-H), 3.20–3.10 (0.2H, m, 3-H *exo*), 3.10–3.00 (0.8H, m, 3-H *endo*), 1.80–1.30 (2H, s, 6-H₂), 1.03 (0.6H, d, $J = 7.4$ Hz, 3-CH₃ *exo*), 0.97 (2.4H, d, $J = 7.2$ Hz, 3-CH₃ *endo*), 0.22 [7.2H, s, OSi(CH₃)₃ *endo*], 0.20 [7.2H, s, Si(CH₃)₃ *endo*], 0.12 [1.8H, s, Si(CH₃)₃ *exo*], 0.08 [1.8H, s, OSi(CH₃)₃ *exo*], -0.30 [7.2H, s, Si(CH₃)₃ *endo*], -0.01 [1.2H, s, Si(CH₃)₃ *exo*]; $\delta^{19}\text{F}$ (235 MHz) -62.52; m/z (EI) 487 (M⁺ - H, 2%), 415 [M⁺ - Si(SiMe₃)₃, 17%], 312 (30), 262 (37), 147 (28), 73 (100). Repeated flash column chromatography (eluting petrol) gave the *endo* diastereoisomer as a single isomer. δ_{H} (300 MHz) 7.51 (2H, d, $J = 8.4$ Hz, Ar-H), 7.46 (2H, d, $J = 8.4$ Hz, Ar-H), 5.95 (1H, m, 4-H), 5.58 (1H, m, 5-H), 3.10 (1H, m, 3-H), 1.40 (2H, m, 6-H₂), 0.98 (3H, d, $J = 7.4$ Hz, 3-CH₃), 0.22 [9H, s, OSi(CH₃)₃], 0.20 [9H, s, Si(CH₃)₃], -0.30 [9H, s, Si(CH₃)₃]; δ_{C} (75 MHz) 150.59, 136.82, 127.06 (q, $^2J_{\text{C-F}} = 31.95$ Hz F₃C-C), 126.02, 125.32, 124.60 (q, $^3J_{\text{C-F}} = 3.75$ Hz, F₃C-C-CH), 124.49 (q, $^1J_{\text{C-F}} = 269.93$ Hz, CF₃), 122.69, 119.10, 79.09, 42.97, 16.52, 8.26, 3.45, 0.66, -1.10.

2-Methyl-1-bis(trimethylsilyl)-2-trimethylsilyloxy-3-methylsilacyclohex-4-ene 5ex. Reaction of acetyltris(trimethylsilyl)silane **4e** with *E*-1,3-pentadiene gave the title compound as a mixture of diastereoisomers (*ca.* 21%, 2:1 *endo:exo*), along with other inseparable components. δ_{H} (200 MHz) 5.80–5.20 (2H, m, =CH), 2.60–2.50 (0.33H, m, 3-H *exo*), 2.26–2.20 (0.67H, m, 3-H *endo*), 1.70–1.10 (2H, m, 6-H₂), 1.53 (1H, s, 2-CH₃ *exo*), 1.34 (2H, s, 2-CH₃ *endo*), 1.09 (1H, d, $J = 6.8$ Hz, 3-CH₃ *exo*), 1.00 (2H, d, $J = 7.2$ Hz, 3-CH₃ *endo*), 0.16–0.13 [$5 \times 9\text{H}$, s, Si(CH₃)₃]; δ_{C} (100 MHz) 135.00, 125.78, 45.62, 43.48, 30.70, 23.34, 16.48, 14.92, 8.86, 7.98, 3.54, 0.38, 0.23; m/z (EI) 285 [M⁺ - Si(CH₃)₃, 7%], 207 (61), 183 (29), 147 (72), 133 (58), 73 (100).

2,2-Bis(trimethylsilyl)-3-phenyl-3-trimethylsilyloxy-2-silabicyclo[2.2.1]hept-5-ene 5ay. Reaction of benzoyltris(trimethylsilyl)silane **2a** with cyclopentadiene gave the title compound as a mixture of diastereoisomers (0.433 g, 68%, 3:1 *endo:exo*). Mp 88–89 °C; ν_{\max} (CHCl₃) 3050, 2948, 2878, 1599, 1500, 1250, 1169, 1041, 1021, 838 cm^{-1} ; δ_{H} (400 MHz) 7.40–7.05 (5H, m, Ar-H), 6.32 (0.25H, dd, $J = 5.4$, 3.3 Hz, 5-H *exo*), 6.11 (0.75H, dd, $J = 5.4$, 3.3 Hz, 5-H *endo*), 5.86 (0.25H, dd, $J = 5.4$, 3.3 Hz, 6-H *exo*), 5.77 (0.75H, dd, $J = 5.4$, 3.3 Hz, 6-H *endo*), 3.40 (0.25H, m, 4-H, *exo*), 3.30 (0.75H, m, 4-H, *endo*), 2.45 (0.25H, m, 7-HH *exo*), 2.35 (1.75H, m, 7-H₂ *endo* and 7-HH *exo*), 2.02 (0.75H, m, 1-H *endo*), 1.95 (0.25H, m, 1-H *exo*), 0.28 [6.75H, s, OSi(CH₃)₃ *endo*], 0.21 [2.25H, s, OSi(CH₃)₃ *exo*], -0.16 [2.25H, s, Si(CH₃)₃ *exo*], -0.18 [6.75H, s, Si(CH₃)₃ *endo*], -0.28 [6.75H, s, Si(CH₃)₃ *endo*], -0.29 [2.25H, s, Si(CH₃)₃ *exo*]; δ_{C} (100 MHz) 148.11, 146.46, 140.37, 139.07, 129.89, 129.51, 127.84, 127.75, 126.10, 125.66, 87.07, 84.45, 51.54, 50.66, 45.44, 44.56, 34.15, 30.86, 2.44, 0.89, 0.06, -0.33, -0.59; m/z (EI) 418 (M⁺, 2%), 403 (M⁺ - CH₃, 1%), 345 (M⁺ - SiMe₃, 16%), 337 (50), 147 (42), 135 (21), 117 (21), 73 (100).

2,2-Bis(trimethylsilyl)-3-[4'-methoxyphenyl]-3-trimethylsilyloxy-2-silabicyclo[2.2.1]hept-5-ene 5by. Reaction of 4-methoxybenzoyltris(trimethylsilyl)silane **2b** with cyclopentadiene gave the title compound as a mixture of diastereoisomers (68%, 5:2 *endo:exo*). ν_{\max} (thin film) 3048, 2953, 2894, 1608, 1509, 1249, 1177, 1042, 1021, 838 cm^{-1} ; δ_{H} (200 MHz) 7.21 (0.56H, d, $J = 7.6$ Hz, Ar-H *exo*), 7.17 (1.44H, d, $J = 7.6$ Hz, Ar-H *endo*), 6.81 (0.56H, d, $J = 7.6$ Hz, Ar-H *exo*), 6.75 (1.44H, d, $J = 7.6$ Hz, Ar-H *endo*) 6.40–6.30 (0.28H, dd, $J = 5.4$, 3.0 Hz, 5-H *exo*), 6.20–6.10 (0.72H, dd, $J = 5.4$, 3.0 Hz, 5-H *endo*), 5.95–5.85 (0.28H, dd, $J = 5.4$, 3.0 Hz, 6-H *exo*), 5.85–5.75 (0.72H, dd, $J = 5.4$, 3.0 Hz, 6-H *endo*), 3.87 (0.84H, s, -OCH₃ *exo*), 3.85 (2.16H, s, -OCH₃ *endo*), 3.37 (0.28H, m, 4-H *exo*), 3.25 (0.72H, m, 4-H *endo*), 2.40 (0.28H, m, 7-HH *exo*), 2.35 (1.72H, m, 7-H₂ *endo* and 7-HH *exo*), 1.98 (0.72H, m, 1-H *endo*), 1.90 (0.28H, m, 1-H *exo*), 0.26 [6.48H, s, -OSi(CH₃)₃ *endo*], 0.16 [2.52H, s, OSi(CH₃)₃ *exo*], -0.14 [2.52H,

s, Si(CH₃)₃ *exo*], -0.16 [6.48H, Si(CH₃)₃ *endo*], -0.26 [6.48H, s, Si(CH₃)₃ *endo*], -0.27 [2.52H, s, Si(CH₃)₃ *exo*]; δ_{C} (50 MHz) 157.86, 140.18, 138.86, 133.52, 132.21, 131.34, 130.97, 129.73, 129.50, 113.16, 112.98, 87.50, 86.45, 55.31, 55.25, 51.85, 50.89, 45.30, 44.58, 34.22, 33.4, 30.96, 2.55, 2.46, 0.94, 0.14, -0.13, -0.37; m/z (EI) 448 (M⁺, 1%), 209 (20), 73 (100); HRMS (EI): Found M⁺, 448.2113; C₂₂H₄₀O₂Si₄ requires M, 448.2105.

2,2-Bis(trimethylsilyl)-3-[4'-(trifluoromethyl)phenyl]-3-trimethylsilyloxy-2-silabicyclo[2.2.1]hept-5-ene 5cy. Reaction of 4-trifluoromethylbenzoyltris(trimethylsilyl)silane **2c** with cyclopentadiene gave the title compound as a mixture of diastereoisomers (85%, 4:1 *endo:exo*). ν_{\max} 3062, 2955, 2896, 1926, 1794, 1614, 1445, 1406, 1326, 1250, 1168 cm^{-1} ; δ_{H} (250 MHz) 7.51 (1.6H, d, $J = 8.2$ Hz, Ar-H *endo*), 7.40 (1.6H, d, $J = 8.2$ Hz, Ar-H *endo*), 7.35 (0.4H, d, $J = 8.2$ Hz, Ar-H *exo*), 7.27 (0.4H, d, $J = 8.2$ Hz, Ar-H *exo*), 6.30 (0.2H, dd, $J = 8.3$, 3.6 Hz, 5-H *exo*), 6.15 (0.8H, dd, $J = 8.3$, 3.6 Hz, 5-H *endo*), 5.94 (0.2H, dd, $J = 8.3$, 3.2 Hz, 6-H *exo*), 5.79 (0.8H, dd, $J = 8.3$, 3.2 Hz, 6-H *endo*), 3.31 (0.2H, m, 4-H *exo*), 3.05 (0.8H, m, 4-H *endo*), 2.35 (2H, m, 7-H₂), 2.05 (0.8H, m, 6-H *endo*), 2.01 (0.2H, m, 1-H *exo*), 0.32 [7.2H, s, -OSi(CH₃)₃ *endo*], 0.14 [1.8H, s, OSi(CH₃)₃ *exo*], -0.07 [1.8H, s, Si(CH₃)₃ *exo*], -0.16 [7.2H, s, Si(CH₃)₃ *endo*], -0.30 [9H, s, Si(CH₃)₃]; δ_{C} (63 MHz) 152.85, 151.14, 141.03, 139.39, 129.54 (q, $J = 32.4$ Hz, C-CF₃ *exo*), 128.20 (q, $J = 32.4$ Hz, C-CF₃ *endo*), 125.80 (q, $J = 3.6$ Hz, C-C-CF₃ *exo*) 124.72 (q, $J = 3.7$ Hz, C-C-CF₃ *endo*), 124.24 (q, $J = 272.3$ Hz, CF₃ *endo*) 123.80 (q, $J = 272.4$ Hz, CF₃ *exo*), 86.82, 84.51, 51.53, 50.93, 45.62, 44.79, 34.21, 30.95, 2.5, 2.14, 0.86, 0.03, -0.36, -0.61; $\delta^{19}\text{F}$ (235 MHz) -62.69; m/z (CI, NH₃) 487 (MH⁺, 2%), 466 (MH⁺ - F, 3%), 405 (24), 397 (30), 203 (57), 147 (20), 90 (58), 73 (100).

2,2-Bis(trimethylsilyl)-3-tert-butyl-3-trimethylsilyloxy-2-silabicyclo[2.2.1]hept-5-ene 5fy. Reaction of trimethylacetyltris(trimethylsilyl)silane **2f** with cyclopentadiene gave the title compound as a mixture of diastereoisomers (70%, 6:1 *endo:exo*).

ν_{\max} (thin film) 3051, 2945, 2887, 1621, 1500, 1212, 1153, 1042, 1021, 822 cm^{-1} ; δ_{H} (250 MHz) 6.31 (0.14H, dd, $J = 5.3$, 3.2 Hz, 5-H), 6.09 (0.86H, dd, $J = 5.4$, 3.2 Hz, 5-H), 5.90 (0.14H, dd, $J = 5.3$, 3.2 Hz, 6-H), 5.65 (0.86H, dd, $J = 5.4$, 3.2 Hz, 6-H), 2.89 (0.14H, m, 4-H), 2.77 (0.86H, m, 4-H), 2.35–2.18 (2H, m, 7-Hd₂), 2.90–2.80 (1H, m, 3-H), 1.06 [1.26H, s, C(CH₃)₃], 0.99 [7.74H, s, C(CH₃)₃], 0.22 [7.74H, Si(CH₃)₃], 0.21 [1.26H, Si(CH₃)₃], 0.19 [1.26H, Si(CH₃)₃], 0.17 [7.74H, Si(CH₃)₃], 0.15 [7.74H, Si(CH₃)₃], 0.14 [1.26H, Si(CH₃)₃]; δ_{C} (100 MHz) 138.77, 129.36, 100.14, 52.12, 47.69, 38.43, 31.24, 30.42, 4.68, 2.08, 1.53; m/z (EI) 400 (M⁺, 1%), 385 (M⁺ - CH₃, 1%), 73 (100).

2,2-Diphenyl-1,1,1,3,3,3-hexamethyltrisilane 7.⁴⁰ A mixture of chlorotrimethylsilane (14.96 g, 137.2 mmol) and dichlorodiphenylsilane (17.36 g, 68.62 mmol) was added to a stirred suspension of magnesium turnings in THF/HMPA (1:1, 100 ml), so as to maintain a gentle reflux. The mixture was then heated to reflux for a further 12 h. Saturated NH₄Cl solution (100 ml) was then carefully added. The organic layer was separated, and the aqueous layer extracted with ether (3 × 40 ml). The combined organic extracts were dried over MgSO₄, filtered and concentrated. Distillation gave the title compound as a colourless oil (11.90 g, 53%). Bp 140 °C/1 mbar (lit.⁴⁰ 147–148 °C/2 mbar). ν_{\max} (thin film) 3021, 2948, 2885, 1420, 1216, 1201, 1196, 914, 842 cm^{-1} ; δ_{H} (300 MHz) 7.55–7.28 (10H, m, Ar-H), 0.19 [18H, s, Si(CH₃)₃]; δ_{C} (75 MHz) 135.93, 133.97, 128.12, 127.81, -0.50; m/z (EI) 328 (M⁺, 33%), 313 (M - CH₃, 10%), 255 [M - Si(CH₃)₃, 100%].

3,4-Diphenyl-3,4-bis(trimethylsilyloxy)-1,1,2,2-tetrakis(trimethylsilyl)-1,2-disilacyclobutane 10a.¹¹ A solution of benzoyltris(trimethylsilyl)silane (0.49 g, 1.38 mmol) in cyclohexane (50 ml) was irradiated for approx. 2 h using a 1 kW mercury lamp. Concentration gave the crude product. Flash column chromatography (eluting petrol) gave the title compound as a white crystalline solid (0.21 g, 43%); mp 148 °C (lit.¹¹ 149–150 °C). ν_{\max} (KBr disc) 3050, 2956, 2893, 1597, 1489, 1442, 1402, 1250 cm^{-1} ; δ_{H} (200 MHz)

7.70–7.58 (5H, m, Ar–H), 7.40–7.20 (5H, m, Ar–H), 0.41 [18H, s, OSi(CH₃)₃], 0.07 [18H, s, Si(CH₃)₃], –0.26 [18H, s, Si(CH₃)₃]; δ_C (63 MHz) 158.28, 144.92, 132.74, 127.08, 98.69, 3.53, 3.07, 2.89; m/z (CI, NH₃) 592 (12%), 356 (12), 353 (monomer MH⁺, 11), 221 (44), 148 (65), 90 (90), 73 (100).

General procedure for oxidation of silyl alcohols to acylsilanes as applied to:

2-Methylpropanoylbis(trimethylsilyl)phenylsilane 9c. Dimethyl sulfoxide (1.20 g, 15.33 mmol) was added to a stirred solution of oxalyl chloride (1.17 g, 9.20 mmol) in DCM at –78 °C, and the resultant solution stirred at this temperature for 10 min. The solution of silyl alcohol **14a** (1.99 g, 6.14 mmol) in dichloromethane was added dropwise, and the reaction was stirred at –78 °C for a further 20 min. Triethylamine (4.26 ml, 30.7 mmol) was then added, and the reaction was allowed to attain ambient temperature. The reaction mixture was then diluted with ether (50 ml) and washed with dilute hydrochloric acid (2 × 15 ml) and saturated NaHCO₃ solution (15 ml). After back extraction of the aqueous washings with ether (20 ml), the combined organic layers were dried over MgSO₄, filtered and concentrated. Flash column chromatography (eluting: 5% ether:petrol) gave the title compound as a colourless oil (1.98 g, 93%). ν_{\max} (thin film) 3067, 2962, 2894, 2870, 1728, 1627, 1465, 1427, 1400, 1377, 1245, 1095, 971, 836 cm⁻¹; δ_H (200 MHz) 7.60–7.30 (5H, m, Ar–H), 2.95 (1H, septet, $J = 6.8$ Hz, 2-H), 0.89 (6H, d, $J = 6.8$ Hz, CH₃), 0.24 [18H, s, Si(CH₃)₃]; δ_C (50 MHz) 249.94, 136.16, 135.61, 128.69, 128.17, 46.77, 16.51, 0.13; m/z (CI, NH₃) 323 (MH⁺, 23%), 307 (M – CH₃, 8%), 249 (M – SiMe₃, 22%), 209 (37), 193 (63), 135 (100).

Butanoylbis(trimethylsilyl)phenylsilane 9d. Obtained from silyl alcohol **14b** following the procedure described for **9c** as a colourless oil (0.50 g, 95%). Found: C, 59.30; H, 9.36; Calc. for C₁₆H₃₀O₂Si₃ C, 59.56; H, 9.37%; ν_{\max} (thin film) 3068, 3051, 2958, 2894, 1631, 1427, 1399, 1246, 1095, 837 cm⁻¹; δ_H (400 MHz) 7.60–7.30 (5H, m, Ar–H), 2.58 (2H, t, $J = 7.2$ Hz, 2-H₂), 1.51 (2H, tq, 3-H₂), 0.83 (3H, t, $J = 7.2$ Hz, 4-H₃), 0.24 [18H, s, Si(CH₃)₃]; δ_C (100 MHz) 246.67, 136.04, 133.46, 128.64, 128.13, 54.22, 15.78, 13.84, 0.24; m/z (CI, NH₃) 323 (MH⁺, 11%).

3,4-Diphenyl-3,4-bis(trimethylsilyloxy)-1,2-bis(trimethylsilyl)-1,2-diphenyl-1,2-disilacyclobutane 11a. A solution of benzoylphenylbis(trimethylsilyl)silane **9a** (1.00 g, 2.80 mmol) was dissolved in cyclohexane (150 ml). This solution was then degassed by the passage of a steady flow of nitrogen for 30 min. The mixture was then irradiated for 45 min in a cooled jacketed reactor (Photochemical Reactors Ltd) using a 125 W medium pressure mercury lamp and a solution of CuSO₄ as the coolant solution. Flash column chromatography (eluting: hexane) gave the title compound as a white solid. (0.04 g, 5%); mp 165–166 °C decomp. Found: C, 62.75; H, 7.73; C₃₈H₅₆O₂Si₆ requires C, 63.98; H, 7.91%; ν_{\max} (KBr disc) 3052, 2957, 2894, 1596, 1488, 1442, 1427, 1249, 1042 cm⁻¹; δ_H (300 MHz) 7.80–7.20 (20H, m, Ar–H), –0.01 [18H, s, OSi(CH₃)₃], –0.54 [18H, s, SiSi(CH₃)₃]; δ_C (75 MHz) 144.51, 137.33, 136.51, 131.24, 128.19, 127.41, 127.15, 126.72, 95.68, 3.22, 0.39; m/z (EI) 712 (M⁺, 1%), 639 (M⁺ – TMS, 2%), 356 (monomer M⁺, 100%).

3,4-Bis(tert-butyl)-3,4-bis(trimethylsilyloxy)-1,2-bis(trimethylsilyl)-1,2-diphenyl-1,2-disilacyclobutane 11b.¹⁴ Prepared from trimethylacetylphenylbis(trimethylsilyl)silane **9b** (9.31 g, 27.7 mmol) following an identical procedure as described for **11a**. (9.15 g, 98%), mp 98–100 °C decomp. ν_{\max} (CHCl₃) 3017, 2957, 2897, 1703, 1614, 1479, 1427, 1362, 1253, 1206, 1060, 931, 841 cm⁻¹; δ_H (300 MHz) 7.70–7.25 (10H, m, Ar–H), 1.20 [18H, bs, C(CH₃)₃], 10.28 [18H, s, OSi(CH₃)₃], 0.13 [18H, s, SiSi(CH₃)₃]; δ_C (63 MHz) 137.72, 137.05, 127.74, 126.94, 108.82, 38.90, 26.93, 5.96, 0.70.

2-(tert-Butyl)-3-methyl-1-phenyl-1-trimethylsilyl-2-(trimethylsilyloxy)silacyclohex-4-ene 12b. Silene dimer **11b** (2.07 g, 3.08 mmol) and *E*-1,3-pentadiene (0.82 g, 12.40 mmol) were dissolved in THF (10 ml). The solution was stirred for 18 h. Concen-

tration followed by flash column chromatography (eluting: petrol) gave the title compound (a 1 : 1 mixture of diastereoisomers) as a colourless oil (1.74 g, 70%). ν_{\max} (thin film) 3066, 2953, 1478, 1427, 1359, 1258, 1247, 1127, 1104, 967, 887 836 cm⁻¹; δ_H (300 MHz) 7.65–7.30 (5H, m, Ar–H), 6.90–5.30 (2H, m, 4-H, 5-H), 3.3–3.0 (1H, m, 3-H), 1.70 (3H, bd $J = 6.7$ Hz, 3-CH₃), 1.55–1.22 (2H, m, 6-H₂), 1.04, [4.5H, s, C(CH₃)₃], 0.98 [4.5H, s, C(CH₃)₃], 0.11 [4.5H, s, OSi(CH₃)₃], 0.06 [4.5H, s, OSi(CH₃)₃], –0.24 [4.5H, s, SiSi(CH₃)₃], –0.30 [4.5H, s, SiSi(CH₃)₃]; δ_C (100 MHz) 138.95, 135.08, 134.574, 134.07, 128.41, 128.13, 127.58, 127.48, 124.32, 122.90, 96.17, 92.50, 53.72, 45.16, 38.00, 37.30, 28.20, 28.00 (broad), 18.03, 17.56, 11.53, 10.71, 2.80, 2.31, –0.95, –1.50; m/z (EI) 404 (M⁺, 1%), 389 (M – CH₃, 1%), 347 (M – tBu, 5%), 331 (M – SiMe₃, 5%), 263 (58), 209 (89), 193 (100); HRMS (EI): Found M⁺, 404.2397; C₂₂H₄₀O₂Si₃ requires *M*, 404.2387.

3-(tert-Butyl)-2-phenyl-2-trimethylsilyl-3-trimethylsilyloxy-2-silabicyclo[2.2.2]oct-5-ene 13b. Silene dimer **11b** (5.08 g, 7.56 mmol) and cyclohexa-1,3-diene (2.42 g, 30.26 mmol) were dissolved in THF (40 ml). The solution was stirred for 18 h. Concentration followed by flash column chromatography (eluting: petrol) gave the title compound (a 1 : 1 mixture of diastereoisomers) as a colourless solid (4.37 g, 69%), mp 114–115 °C. Found: C, 65.92; H, 9.67; required for C₂₃H₄₀O₂Si₃ C, 66.28; H, 9.67%; ν_{\max} (KBr disc) 3069, 3045, 2982, 2950, 2861, 1476, 1426, 1390, 1261, 1247, 1103, 965, 836 cm⁻¹; δ_H (500 MHz) 7.60–7.30 (5H, m, Ar–H), 6.20–6.18 (0.5H, m, 5-H), 6.16–6.14 (0.5H, m, 5-H), 6.10–6.02 (0.5H, m, 6-H), 3.25 (0.5H, m, 4-H), 2.85 (0.5H, m, 4-H) 2.42 (0.5H, m, 1-H), 2.40 (0.5H, m, 1-H), 2.02 (1H, m, 7-HH and 8-HH), 1.90 (1H, m, 7-HH and 8-HH), 1.75 (1H, m, 7-HH and 8-HH), 1.65 (1H, m, 7-HH and 8-HH), 1.08 [4.5H, s, C(CH₃)₃], 1.06 [4.5H, s, C(CH₃)₃], –0.02 [4.5H, s, OSi(CH₃)₃], 0.11 [4.5H, s, OSi(CH₃)₃], –0.18 [4.5H, s, SiSi(CH₃)₃], –0.19 [4.5H, s, SiSi(CH₃)₃]; δ_C (125 MHz) 138.20, 136.10, 132.42, 129.21, 128.03, 122.00, 121.63, 96.80, 90.22, 44.00, 42.10, 39.21, 30.11, 26.95, 21.00, 19.80, 9.80, 3.11, –0.08, –0.20; m/z (EI) 416 (M⁺, 2%), 401 (M – CH₃, 5%), 343 (M – SiMe₃, 15%), 327 (M – OSiMe₃, 10%), 73 (100).

General procedures for the preparation of silyl alcohols as applied to:

1,1,1,3,3,3-Hexamethyl-2-phenyl-2-(1'-hydroxy-2'-methylpropyl)trisilane 14a.

Method A. Methylolithium (1.6 M solution in ether, 21 ml, 33 mmol) was added to a stirred solution of phenyltris(trimethylsilyl)silane **17** (10.15 g, 31.3 mmol) in THF (56 ml) at 0 °C. This was allowed to warm to RT and stirred for 17 h to produce a dark red solution of the silyl anion. The THF was evaporated directly using a vacuum manifold and ether (50 + 6 ml) was added. The resulting solution was added *via* cannula to a suspension of magnesium bromide diethyl etherate (11.33 g, 43.9 mmol) in ether (56 ml). After becoming a homogeneous solution, the reaction mixture was stirred for 1 h and was then cooled to –78 °C. Freshly distilled isobutyraldehyde (4.3 ml, 47 mmol) was added dropwise. The reaction was then stirred for 19 h. Saturated ammonium chloride solution (100 ml) was added and the mixture allowed to reach RT. The aqueous layer was separated and extracted with ether (3 × 100 ml). The combined organic layers were dried over MgSO₄, filtered, concentrated and dried *in vacuo*. Flash column chromatography, gradient elution (petroleum ether; petroleum ether/ether [29 : 1]; [19 : 1]; [12 : 1]; ether) gave a mixture of the starting material phenyltris(trimethylsilyl)silane [PhSi(SiMe₃)₃] **17** and bis(trimethylsilyl)phenylsilane [PhSi(H)(SiMe₃)₂] **20** (0.79 g, 10 and 8%, respectively, calculated from NMR); *R_f* (petroleum ether/ether [9 : 1]) 0.89; δ_H for **20** (300 MHz) 7.46–7.40 (2H, m, Ar–H), 7.28–7.23 (3H, m, Ar–H), 3.74 (1H, s, Si–H), 0.22 [18H, s, Si(Si(CH₃)₃)₂] followed by the title compound **14a** as a colourless oil (6.76 g, 67%).

Method B. Dry phenyltris(trimethylsilyl)silane **17** (4.82 g, 14.88 mmol) and potassium *tert*-butoxide (1.72 g, 15.33 mmol) were combined under Ar. THF (27 ml) was added and the resulting

solution stirred for 2 h after which time it had become bright red. The THF was evaporated directly using a vacuum manifold and ether (20 + 7 ml) was added. The resulting solution was added *via* cannula to a suspension of magnesium bromide diethyl etherate (5.00 g, 19.3 mmol) in ether (27 ml). The reaction mixture was stirred for 1 h and was then cooled to -78°C . Freshly distilled isobutyraldehyde (1.49 ml, 16.37 mmol) was added and the mixture stirred for 17 h. Saturated ammonium chloride solution (50 ml) was added and the mixture allowed to reach RT. The aqueous layer was separated and extracted with ether (3 \times 50 ml). The combined organic layers were dried over MgSO_4 , filtered, concentrated and dried *in vacuo*. Flash column chromatography, gradient elution (petroleum ether; petroleum ether/ether [39 : 1]; [29 : 1]) gave a mixture of the starting material phenyltris(trimethylsilyl)silane [$\text{PhSi}(\text{SiMe}_3)_3$] **17** and bis(trimethylsilyl)phenylsilane [$\text{PhSi}(\text{H})(\text{SiMe}_3)_2$] **20** (1.09 g, 2 and 26%, respectively, NMR) followed by the title compound **14a** as a colourless oil (2.50 g, 52%); R_f (petroleum ether/ether [9 : 1]) 0.57; ν_{max} (thin film) 3590 and 3480 (broad, O–H), 3070, 3054, 2955, 2900, 2820, 1468, 1430, 1245 (Si–C), 1100, 988, 835 cm^{-1} ; δ_{H} (300 MHz) 7.54–7.45 (2H, m, Ar–H), 7.30–7.28 (3H, m, Ar–H), 3.79 (1H, d, $J = 6.9$ Hz, CHOH), 1.96 [1H, octet, $J = 6.9$ Hz, $\text{CH}(\text{Me})_2$], 0.99 and 0.88 [3H, d, $J = 6.9$ Hz, $\text{CH}(\text{CH}_3)_2$], 0.24 and 0.20 [9H, s, $\text{Si}(\text{CH}_3)_3$]; δ_{C} (63 MHz) 136.44 (Ar), 135.60 (Ar), 128.04 (Ar), 127.83 (Ar), 72.39 (Si–CH), 34.63 [$\text{CH}(\text{Me})_2$], 21.18 and 19.88 [$\text{CH}(\text{CH}_3)_2$], 0.50 [$\text{Si}(\text{CH}_3)_3$], 0.32 [$\text{Si}(\text{CH}_3)_3$]; m/z (CI) 342 ($\text{M} + \text{NH}_4^+$, 100%), 324 (M^+ , 90%), 307 ($\text{M}^+ - \text{OH}$, 68%).

1-(1',1',1',3',3',3'-Hexamethyl-2'-phenyl-trisilan-2'-yl)-2-methylpropyl-2''-methylpropanoate 19. Ester **19a** was sometimes obtained as a by-product of the above reaction and could be isolated as a pure sample by repeated chromatography. R_f (petroleum ether/ether [9 : 1]) 0.61; ν_{max} (thin film) 3070, 3050, 2963, 2894, 1730 (C=O), 1469, 1427, 1385, 1246, 1187, 1153, 1095, 837 cm^{-1} ; δ_{H} (300 MHz) 7.50–7.46 (2H, m, Ar–H), 7.30–7.25 (3H, m, Ar–H), 5.38 (1H, d, $J = 7.0$ Hz, 1-H), 2.49 (1H, septet, $J = 6.9$ Hz, $\text{Me}_2\text{CH}-\text{C}=\text{O}$), 2.05 (1H, octet, $J = 7.0$ Hz, 2-H), 1.15 [3H, d, $J = 6.9$ Hz, C=O– $\text{CH}(\text{CH}_3)_2$], 1.07 [3H, d, $J = 6.9$ Hz, C=O– $\text{CH}(\text{CH}_3)_2$], 0.87 (3H, d, $J = 7.0$ Hz, 3-H₃), 0.84 (3H, $J = 7.0$ Hz, 3-H₃), 0.22 [18H, s, $\text{Si}(\text{CH}_3)_3$]; δ_{C} (63 MHz) 176.74 (C=O), 135.71 (Ar), 135.55 (Ar), 128.07 (Ar), 127.72 (Ar), 72.49 (Si–CH), 34.45 [$\text{CH}(\text{Me})_2$], 33.51 [$\text{CH}(\text{Me})_2$], 21.19, 20.09, 19.62 [$\text{CH}(\text{CH}_3)_2$], 18.69 [$\text{CH}(\text{CH}_3)_2$], 0.28 [9H, s, $\text{Si}(\text{CH}_3)_3$], 0.10 [9H, s, $\text{Si}(\text{CH}_3)_3$]; m/z (CI) 379 ($\text{M}^+ - \text{Me}$, 8%), 321 ($\text{M}^+ - \text{SiMe}_3$, 30%), 265 ($\text{M}^+ - \text{Me} - \text{PrCO} - \text{Pr}$, 100%), 251 ([$\text{PhSi}(\text{SiMe}_3)_2$] $^+$, 32%); HRMS (CI) Found MNH_4^+ , 412.2525; $\text{C}_{20}\text{H}_{42}\text{NO}_2\text{Si}_3$ requires MNH_4 , 412.2523.

1,1,1,3,3,3-Hexamethyl-2-phenyl-2-(1'-hydroxybutyl)-trisilane 14b. Obtained from butanal in 74% yield following method A or 36% yield following method B; R_f (petroleum ether/ether [9 : 1]) 0.41. Found: C, 59.24; H, 10.00; required for $\text{C}_{16}\text{H}_{32}\text{OSi}_3$: C, 59.19; H, 9.93%. ν_{max} (thin film) 3582 and 3463 (broad, O–H), 3066, 3050, 2955, 2894, 1427, 1245, 1095, 835, 699 cm^{-1} ; δ_{H} (400 MHz) 7.53–7.50 (2H, m, Ar–H), 7.34–7.31 (3H, m, Ar–H), 4.09 (1H, dd, $J = 11.0$ Hz, 2.5, Si–C–H), 1.82–1.57 (3H, m, 3'-HH and 2'-H₂), 1.37 (1H, m, 3'-HH), 0.94 (3H, t, $J = 7.0$ Hz, 4'-H₃), 0.23 [9H, s, $\text{Si}(\text{CH}_3)_3$], 0.22 [9H, s, $\text{Si}(\text{CH}_3)_3$]; δ_{C} (100 MHz) 135.65 (*meta*-Ar), 135.37 (*ipso*-Ar), 128.18 (*para*-Ar), 127.95 (*ortho*-Ar), 65.39 (1'-C), 38.80 (2'-C), 20.44 (3'-C), 13.78 (4'-C), 0.28 [$\text{Si}(\text{CH}_3)_3$], 0.14 [$\text{Si}(\text{CH}_3)_3$]; m/z (CI) 342 ($\text{M} + \text{NH}_4^+$, 100%), 325 ($\text{M} + \text{H}^+$, 91%), 308 ($\text{M} + \text{H}^+ - \text{OH}$, 72%), 247 (34), 237 (45), 209 (16), 194 (16), 152 (28), 135 (20); HRMS (CI): Found MNH_4^+ , 342.2099; $\text{C}_{16}\text{H}_{36}\text{NOSi}_3$ requires MNH_4 , 342.2103.

1,1,1,3,3,3-Hexamethyl-2-phenyl-2-(1'-hydroxyethyl)-trisilane 14c. Reaction with acetaldehyde following method A afforded the title compound (49%); R_f (petroleum ether/ether [9 : 1]) 0.19; ν_{max} (thin film) 3441 (broad, O–H), 3067, 2950, 2893, 1427, 1245, 1049, 1068, 1029, 835 cm^{-1} ; δ_{H} (500 MHz) 7.54–7.52 (2H, m, Ar–H), 7.33–7.32 (3H, m, Ar–H), 4.24 (1H, q, $J = 7.5$ Hz, CHOH), 1.49 (3H, d, $J = 7.5$ Hz, CH_3 –COH), 0.25 [9H, s, $\text{Si}(\text{CH}_3)_3$], 0.21 [9H, s, $\text{Si}(\text{CH}_3)_3$]; δ_{C} (126 MHz) 135.64 (Ar), 135.18 (*ipso*-Ar),

128.23 (Ar), 127.99 (Ar), 61.52 (Si–CH), 22.79 (CH_3 –COH), 0.31 [$\text{Si}(\text{CH}_3)_3$], 0.01 [$\text{Si}(\text{CH}_3)_3$]; m/z (ES^+) 319 ($\text{M} + \text{Na}^+$, 100%); HRMS (ES^+): Found MNH_4^+ , 314.1786; $\text{C}_{14}\text{H}_{32}\text{NOSi}_3$ requires MNH_4 , 314.1792.

1,1,1,3,3,3-Hexamethyl-2-phenyl-2-(1'-hydroxy-2'-methylbutyl)trisilane 14d. Reaction with 2-methylbutyraldehyde following method B afforded the title compound as a mixture of diastereoisomers (5 : 2, 58%); R_f (petroleum ether/ether [9 : 1]) 0.61; ν_{max} (thin film) 3594 and 3472 (broad, O–H), 3067, 2959, 2893, 2875, 1461, 1427, 1245, 1093, 835 cm^{-1} ; δ_{H} (300 MHz) (* signals for minor diastereoisomer) 7.56–7.51 (2H, m, Ar–H), 7.32–7.29 (3H, m, Ar–H), 4.01 (0.86H, d, $J = 5.0$ Hz, 1'-H), 3.89 (0.4H, d, $J = 5.0$ Hz, 1'-H*), 1.79–1.63 (1.14H, m, 2-H, 2-H* and 3-HH*), 1.43 (0.86H, m, 3-HH), 1.30–1.11 (1H, m, 3-HH and 3-HH*), 0.95 (2.58H, d, $J = 7.0$ Hz, 2'- CH_3), 0.88 (2.58H, t, $J = 7.5$ Hz, 4'-H₃), 0.86 (0.42H, t, $J = 7.0$ Hz, 4'-H₃*), 0.86 (0.42H, d, $J = 7.0$ Hz, 2'- CH_3^*), 0.24 [1.26H, s, $\text{Si}(\text{CH}_3)_3^*$], 0.23 [7.74H, s, $\text{Si}(\text{CH}_3)_3$], 0.22 [7.74H, s, $\text{Si}(\text{CH}_3)_3$], 0.21 [1.26H, s, $\text{Si}(\text{CH}_3)_3^*$]; δ_{C} (100 MHz) 136.56 (*ipso*-Ar*), 136.40 (*ipso*-Ar), 135.75 (Ar), 135.60 (Ar*), 128.07 (Ar and Ar*), 127.87 (Ar*), 127.84 (Ar), 71.44 (Si–CH*), 70.10 (Si–CH), 41.00 (2-C and 2-C*), 27.42 (3-C), 25.94 (3-C*), 17.17 (5-C*), 16.49 (5-C), 11.97 (4-C), 11.16 (4-C*), 0.50 [$\text{Si}(\text{CH}_3)_3^*$], 0.36 [$\text{Si}(\text{CH}_3)_3$], 0.27 [$\text{Si}(\text{CH}_3)_3$], 0.23 [$\text{Si}(\text{CH}_3)_3^*$]; m/z (CI) 356 ($\text{M} + \text{NH}_4^+$, 50%), 338 ($\text{M} + \text{NH}_4^+ - \text{OH}_2$, 90%), 268 (42); HRMS (CI): Found MNH_4^+ , 356.2266; $\text{C}_{17}\text{H}_{38}\text{NOSi}_3$ requires MNH_4 , 356.2261.

1,1,1,3,3,3-Hexamethyl-2-phenyl-2-(1'-hydroxy-2',2'-dimethylpropyl)trisilane 14e. Reaction with trimethylacetaldehyde following method B afforded the title compound (37%); R_f (petroleum ether/ether [9 : 1]) 0.66; ν_{max} (thin film) 3477 (broad, O–H), 3067, 3050, 2951, 2896, 2867, 2813, 1476, 1463, 1427, 1393, 1363, 1245, 1093, 975, 835, 699, 689 cm^{-1} ; δ_{H} (300 MHz) 7.55–7.52 (2H, m, Ar–H), 7.30–7.27 (3H, m, Ar–H), 3.83 (1H, d, $J = 6.0$ Hz, CHOH), 1.30 (1H, d, $J = 6.0$ Hz, O–H), 0.92 [9H, s, $\text{C}(\text{CH}_3)_3$], 0.30 [9H, s, $\text{Si}(\text{CH}_3)_3$], 0.21 [9H, s, $\text{Si}(\text{CH}_3)_3$]; δ_{C} (101 MHz) 137.03 (*ipso*-Ar), 136.06 (*meta*-Ar), 128.14 (*para*-Ar), 127.85 (*ortho*-Ar), 77.19 (CHOH), 36.64 [$\text{C}(\text{CH}_3)_3$], 28.05 [$\text{C}(\text{CH}_3)_3$], 1.02 [$\text{Si}(\text{CH}_3)_3$], 0.43 [$\text{Si}(\text{CH}_3)_3$]; m/z (CI) 356 ($\text{M} + \text{NH}_4^+$, 15%), 338 (M^+ , 7%), 321 ($\text{M}^+ - \text{OH}$, 100%), 268 (12), 250 (14), 233 (20), 208 (30), 191 (44).

1,1,1,3,3,3-Hexamethyl-2-phenyl-2-(1'-hydroxy-1'-cyclohexylmethyl)trisilane 14f. Reaction with cyclohexanecarboxaldehyde following method A afforded the title compound (38%); R_f (petroleum ether/ether [9 : 1]) 0.56; ν_{max} (thin film) 3591 and 3473 (broad, O–H), 3066, 3049, 2925, 2896, 2851, 1448, 1427, 1245, 835 cm^{-1} ; δ_{H} (400 MHz) 7.53–7.50 (2H, m, Ar–H), 7.30–7.29 (3H, m, Ar–H), 3.86 (1H, d, $J = 7.2$ Hz, Si–C–H), 1.99–0.98 [11H, m, $(\text{CH}_2)_5\text{CH}$], 0.24 [9H, s, $\text{Si}(\text{CH}_3)_3$], 0.21 [9H, s, $\text{Si}(\text{CH}_3)_3$]; δ_{C} (100 MHz) 136.57 (*ipso*-Ar), 135.52 (Ar), 128.00 (Ar), 127.84 (Ar), 71.63 (Si–CH), 44.64 (2-C), 31.35 [– $(\text{CH}_2)_5$ –], 30.44 [– $(\text{CH}_2)_5$ –], 26.42 [– $(\text{CH}_2)_5$ –], 26.30 [– $(\text{CH}_2)_5$ –], 26.17 [– $(\text{CH}_2)_5$ –], 0.43 [$\text{Si}(\text{CH}_3)_3$], 0.18 [$\text{Si}(\text{CH}_3)_3$]; m/z (CI) 365 ($\text{M} + \text{H}^+$, 2%), 349 ($\text{M}^+ - \text{Me}$, 60%), 291 ($\text{M}^+ - \text{SiMe}_3$, 41%), 274 (29), 259 (71), 251 [$\text{PhSi}(\text{SiMe}_3)_2^+$, 54%], 215 (34), 200 (35), 195 (53), 190 (46), 177 (35), 135 (71); HRMS (ES^+): Found MNa^+ , 387.1982; $\text{C}_{19}\text{H}_{36}\text{NaOSi}_3$ requires MNa , 387.1972.

1,1,1,3,3,3-Hexamethyl-2-phenyl-2-(1'-hydroxy-1'-phenylmethyl)trisilane 14g. Reaction with benzaldehyde (1.15 ml, 11.29 mmol) following method B afforded the title compound as a yellow crystalline solid (2.41 g, 63%); R_f (petroleum ether/ether [9 : 1]) 0.56; mp 61–62 $^{\circ}\text{C}$; ν_{max} (KBr disc) 3538, 3428 (broad, O–H), 3066, 3050, 3024, 2946, 2890, 1594, 1488, 1447, 1426, 1398, 1243, 1189, 1093, 1004, 840, 763, 734, 699 cm^{-1} ; δ_{H} (300 MHz) 7.47 (2H, m, Ar–H), 7.27 (2H, m, Ar–H), 7.16 (3H, m, Ar–H), 7.07 (3H, m, Ar–H), 5.11 (1H, s, CHOH), 0.06 [9H, s, $\text{Si}(\text{CH}_3)_3$], 0.02 [9H, s, $\text{Si}(\text{CH}_3)_3$]; δ_{C} (126 MHz) 145.50 (*ipso*-C–Ar), 136.21 (*meta*-Si–Ar), 135.15 (*ipso*-Si–Ar), 128.49 (*para*-Si–Ar), 128.23 (*ortho*- or *meta*-C–Ar), 127.93 (*ortho*-Si–Ar), 125.98 (*para*-C–Ar), 125.08 (*ortho*-

or *meta*-C-Ar), 69.70 (CHOH), 0.15 [Si(CH₃)₃], 0.01 [Si(CH₃)₃]; *m/z* (CI) 376 (M + NH₄⁺, 8%), 358 (M⁺, 100%), 341 (M⁺ - OH, 33%), 281 (31).

Trifluoroacetic acid 1-(1',1',1',3',3',3'-hexamethyl-2'-phenyl-trisilan-2'-yl)-2-methyl-propyl ester 32. A mixture of silyl alcohol **14a** (0.28 g, 0.85 mmol) and triethylamine (0.18 ml, 1.28 mmol) in dry DCM (16 ml) was cooled to -10 °C. Trifluoroacetic anhydride (0.14 ml, 0.98 mmol) was added dropwise. The solution was warmed to RT and stirred for 17 h. Water (15 ml) was then added. The aqueous layer was separated and extracted with DCM (3 × 15 ml). The combined organic extracts were dried over MgSO₄, filtered, concentrated and dried *in vacuo*. Filtration through a pad of silica (hexane) gave the title compound as a clear oil (0.26 g, 73%); *R_f* (hexane/ether [9:1]) 0.99; *v*_{max} (thin film) 2963, 2896, 1777 (C=O), 1428, 1369, 1248, 1216, 1154, 1095, 837, 743, 735, 699 cm⁻¹; *δ*_H (200 MHz) 7.50–7.45 (2H, m, Ar-H), 7.32–7.28 (3H, m, Ar-H), 5.49 (1H, d, *J* = 6.8 Hz, CHOCOCF₃), 2.15 [1H, octet, *J* = 6.8 Hz, CH(Me)₂], 0.90 and 0.86 (3H, d, *J* = 6.8 Hz, CH(CH₃)₂), 0.25 and 0.20 [9H, s, Si(CH₃)₃]; *δ*_C (63 MHz) 157.75 (q, *J* = 41.2 Hz, C=O), 135.56 (Ar), 134.35 (Ar), 128.61 (Ar), 128.04 (Ar), 114.86 (q, *J* = 286.7 Hz, CF₃), 79.67 (Si-CH), 33.42 [CH(Me)₂], 20.88 and 19.74 [CH(CH₃)₂], 0.16 [Si(CH₃)₃], 0.10 [Si(CH₃)₃]; *δ*_F (188 MHz) -74.85 (3 F, s, CF₃); *m/z* (CI) 438 (M + NH₄⁺, 100%), 342 (3), 324 (M + H⁺ - CF₃CO, 10%); HRMS (ES⁺): Found MNH₄⁺ 438.1927; C₁₈H₃₄F₃NO₂Si₃ requires MNH₄⁺, 438.1928.

General protocols for silene generation and trapping as applied to:

1-Phenyl-1-trimethylsilyl-2-(prop-2'-yl)-3-methylsilacyclohex-4-ene 29.

Method A. Methylolithium (1.6 M solution in ether, 13.0 ml, 20.9 mmol) was added to a stirred solution of silyl alcohol **14a** (6.76 g, 20.9 mmol) and 1,3-pentadiene (mixture of *endo*- and *trans*-isomers, 12.5 ml, 125.2 mmol) in ether (300 ml) at -78 °C. The mixture was allowed to warm to -30 °C and stirred for 22 h, then to 0 °C and stirred for 8 h. Saturated ammonium chloride solution (200 ml) was added and the mixture allowed to reach RT. The aqueous layer was separated and extracted with ether (3 × 200 ml). The combined organic layers were dried over MgSO₄, filtered, concentrated and dried *in vacuo*. Flash column chromatography (hexane) gave the title compound as a mixture of diastereoisomers as a colourless oil (3.25 g, 52%).

Method B. *n*-Butyllithium (1.6 M solution in hexane, 0.58 ml, 0.92 mmol) was added to a stirred solution of silyl alcohol **14a** (0.29 g, 0.88 mmol) and 1,3-pentadiene (mixture of *cis*- and *trans*-isomers, 0.53 ml, 5.28 mmol) in dry ether (10 ml) at RT. The mixture was stirred for 2 h after which time TLC showed complete consumption of starting material. The solution was cooled to -20 °C and an anhydrous suspension of LiBr in ether (1.75 M, 0.5 ml, 0.88 mmol) was added and seen to go into solution. The mixture was stirred at -20 °C for 19.5 h after which time saturated ammonium chloride solution (10 ml) was added and the mixture allowed to reach RT. The aqueous layer was separated and extracted with ether (3 × 10 ml). The combined organic layers were dried over MgSO₄, filtered, concentrated and dried *in vacuo*. Flash column chromatography (petroleum ether) gave the title compound as a colourless oil (0.133 g, 50%) as a mixture of diastereoisomers in a ratio of 83:9:8 (ratio of product peak integrals by GC); *R_f* (hexane) 0.71; *v*_{max} (thin film) 3067, 2997, 2958, 2872, 1461, 1396, 1246, 1108, 855, 838, 736, 702 cm⁻¹; NMR data for major isomer: *δ*_H (200 MHz) 7.51–7.48 (2H, m, Ar-H), 7.31–7.28 (3H, m, Ar-H), 5.82 (1H, dtd, *J* = 10.5, 5.2, 1.8 Hz, 5-H), 5.54 (1H, dtd, *J* = 10.5, 4.4, 1.8 Hz, 4-H), 2.36 (1H, m, 3-H), 2.10 [1H, septet d, *J* = 6.8, 3.3 Hz, CH(CH₃)₂], 1.68 (1H, dtd, *J* = 17.2, 5.2, 1.8 Hz, 6-HH), 1.47 (1H, dtd, *J* = 17.2, 5.2, 1.8 Hz, 6-HH), 1.20 (1H, dd, *J* = 6.5, 3.3 Hz, 2-H), 1.03 [3H, d, *J* = 6.8 Hz, CH(CH₃)₂], 0.93 (3H, d, *J* = 7.2 Hz, 7-H₃), 0.88 [3H, d, *J* = 6.8 Hz, CH(CH₃)₂], 0.14 [9H, s, Si(CH₃)₃]; *δ*_C (126 MHz) 139.36 (*ipso*-Ar), 137.41 (4-C), 134.48 (Ar), 128.19

(Ar), 127.66 (Ar), 123.56 (5-C), 38.21 (2-C), 32.77 (3-C), 30.02 (2'-C), 23.56 (7-C), 22.99 (1'-C), 22.45 (1'-C), 9.74 (6-C), -0.55 [CH₃]₃; *m/z* (EI) 302 (M⁺, 7%), 259 (M⁺ - ⁱPr, 4%), 229 (M⁺ - SiMe₃, 56%), 218 (27), 203 (47), 185 (11), 173 (29), 161 (100), 145 (31), 135 (82), 121 (69); HRMS (EI): Found M⁺, 302.1889; C₁₈H₃₀Si₂ requires M, 302.1886.

1-Phenyl-1-trimethylsilyl-2-(prop-2'-yl)-4,5-dimethylsilacyclohex-4-ene 41, and 1-phenyl-1-isobutyl-2,2,2-trimethyl-1-(3-methyl-2-methylene-but-3-enyl)-disilane 49. Reaction of **14a** with 2,3-dimethylbutadiene according to method A gave the title compounds as a mixture in a ratio of **41**:**49** ([83:8]:7), (45%) and according to method B in a ratio of **41**:**49** ([73:15]:12), (48%) (ratio of product peak integrals by GC); *R_f* (petroleum ether) 0.70; *v*_{max} (thin film) 3067, 3049, 2953, 2925, 2866, 1464, 1443, 1430, 1390, 1246, 1121, 1108, 853, 838, 732, 706 cm⁻¹; **41**: *δ*_H (200 MHz) 7.48–7.47 (2H, m, Ar-H), 7.30–7.29 (3H, m, Ar-H), 2.23 (1H, dd, *J* = 15.0, 5.0 Hz, 3a-H), 1.98 (1H, dd, *J* = 15.0, 11.0 Hz, 3b-H), 1.83 [1H, m, CH(CH₃)₂], 1.74 (3H, s, 8-H₃), 1.69 (3H, s, 7-H₃), 1.58 (2H, s, 6-H₂), 1.09 (1H, ddd, *J* = 11.0, 8.5, 5.0 Hz, 2-H), 0.99 [3H, d, *J* = 7.0 Hz, CH(CH₃)₂], 0.98 [3H, d, *J* = 7.0 Hz, CH(CH₃)₂], 0.11 [18H, s, Si(Si(CH₃)₃)₂]; *δ*_C (126 MHz) 139.51 (*ipso*-Ar), 134.52 (Ar), 128.68 (4 or 5-C), 128.26 (Ar), 127.66 (Ar), 125.33 (4- or 5-C), 35.33 (3-C), 34.47 (2-C), 30.30 (2'-C), 24.89 (1'-C), 22.61 (8-C), 22.20 (1'-C), 20.74 (7-C), 18.92 (6-C), -0.33 [Si(Si(CH₃)₃)₂]; *m/z* (GCMS, CI) 317 (M + H⁺, 100%), 316 (M⁺, 65%), 315 (M⁺ - H, 15%), 303 (25), 301 (M⁺ - Me, 60%), 273 (M⁺ - ⁱPr, 1%), 243 (M⁺ - SiMe₃, 79%), 245 (13), 239 (M⁺ - Ph, 23%), 187 (24), 161 (21), 135 (17); **49**: *δ*_H (200 MHz) (discernable peaks only) 5.08 (1H, s, =CH₂), 5.06 (1H, s, =CH₂), 4.98 (1H, s, =CH₂) and 4.86 (1H, s, =CH₂); *m/z* (GCMS, EI) 316 (M⁺, 13%), 259 [M⁺ - (CH₃)₂CHCH₂, 9%], 245 (10), 243 (M⁺ - SiMe₃, 9%), 235 [M⁺ - CH₂CH(CH₃)CH(CH₂)CH₂, 8%], 187 (72), 180 (55), 179 (100), 177 (22), 159 (20), 145 (29), 135 (84), 121 (40).

1-Phenyl-1-trimethylsilyl-2-(prop-2'-yl)-5-methylsilacyclohex-4-ene 42a, 1-phenyl-1-trimethylsilyl-2-(prop-2'-yl)-4-methylsilacyclohex-4-ene 42b, and 1-phenyl-1-isobutyl-2,2,2-trimethyl-1-(2-methylene-but-3-enyl)-disilane 50. Reaction of **14a** with isoprene according to method A gave the title compounds as a mixture in a ratio of **42a**:**42b**:**50** ([84:11]:5), (27%) and according to method B in a ratio of **42a**:**42b**:**50** ([72:16]:12), (41%) (ratio of product peak integrals by GC); *v*_{max} (thin film) 2954, 2927, 2893, 2869, 1462, 1445, 1427, 1244, 1101, 855, 833, 733, 719, 699 cm⁻¹. **42a**: *δ*_H (500 MHz) 7.51–7.49 (2H, m, *meta*-Ar-H), 7.32–7.31 (3H, m, *ortho*- and *para*-Ar-H), 5.48 (1H, m, 4-H), 2.34 (1H, dt, *J* = 15.5, 6.5 Hz, 3-HH), 1.96 (1H, m, 3-HH), 1.87 [1H, m, CH(CH₃)₂], 1.78 (3H, s, 7-H₃), 1.53 (2H, m, 6-H₂), 1.14 (1H, m, 2-H), 0.96 [3H, d, *J* = 6.5 Hz, CH(CH₃)₂], 0.94 [3H, d, *J* = 6.5 Hz, CH(CH₃)₂], 0.18 [9H, s, Si(CH₃)₃]; *δ*_C (126 MHz) 134.45 (*meta*-Ar), 128.34 (*para*-Ar), 127.71 (*ortho*-Ar), 123.80 (4-C), 32.34 (2-C), 30.27 (2'-C), 27.75 (3-C), 27.62 (7-C), 24.51 (1'-C), 21.90 (1'-C), 16.38 (6-C), -0.37 [Si(CH₃)₃]; *m/z* (GCMS, CI) 303 (M + H⁺, 39%), 302 (M⁺, 96%), 288 (M + H⁺ - Me, 31%), 287 (M⁺ - Me, 100%), 245 (16), 233 (10), 231 (18), 230 (M + H⁺ - SiMe₃, 29%), 229 (M⁺ - SiMe₃, 86%), 225 (35), 217 (13), 193 (14), 179 (14), 173 (23), 169 (13), 167 (11), 161 (48), 155 (24), 152 (16), 135 (49); HRMS (EI): Found M⁺, 302.1882; C₁₈H₃₀Si₂ requires M, 302.1886). **42b**: *δ*_H (500 MHz) (discernable peak) 5.61 (1H, m, 5-H); *m/z* (GCMS, CI) 303 (M + H⁺, 24%), 302 (M⁺, 93%), 288 (M + H⁺ - Me, 31%), 287 (M⁺ - Me, 100%), 245 (17), 233 (11), 231 (20), 230 (M + H⁺ - SiMe₃, 33%), 229 (M⁺ - SiMe₃, 94%), 225 (29), 217 (13), 193 (21), 179 (31), 173 (31), 169 (13), 167 (14), 161 (62), 155 (24), 152 (20), 145 (10), 135 (49). **50**: *δ*_H (500 MHz) (discernable peaks) 6.35 (1H, dd, *J* = 16.5 Hz, 10.5, 4-H), 5.11 (1H, d, *J* = 16.5 Hz, 5-H^β), 5.01 (1H, d, *J* = 10.5 Hz, 5-H^α), 4.94 (1H, s, 6-HH), 4.81 (1H, s, 6-HH); *m/z* (GCMS, CI) 302 (M⁺, 13%), 287 (M⁺ - Me, 10%), 247 (14), 246 (24), 245 (M⁺ - CH₂ⁱPr, 50%), 235 [M⁺ - CH₂C(=CH₂)CH=CH₂, 23%], 231 (31), 179 (100), 173 (13), 169 (15), 135 (26), 105 (12).

1-Phenyl-1-trimethylsilyl-2-(prop-2'-yl)-3,4-dimethylsilacyclohex-4-ene 43. Reaction of **14a** with *trans*-3-methyl-1,3-pentadiene according to method B gave the title compound as a mixture of isomers in a ratio of 86:9:4:1 (38%) (ratio of product peak integrals by GC); R_f (petroleum ether) 0.75 as a mixture of four isomers in a ratio of % (ratio of product peak integrals by GC); ν_{\max} (thin film) 2955, 2926, 2891, 2869, 1427, 1382, 1243, 1099, 1057, 1027, 854, 833, 699 cm^{-1} . NMR data for the major isomer: δ_{H} (500 MHz) 7.51–7.49 (2H, m, *meta*-Ar-H), 7.33–7.29 (3H, m, *ortho*- and *para*-Ar-H), 5.56 (1H, ddd, $J = 7.5, 4.0, 1.5$ Hz, 5-H), 2.24 (1H, qd, $J = 7.0, 2.5$ Hz, 3-H), 2.00 [1H, m, CH(CH₃)₂], 1.72 (3H, s, 8-H₃), 1.71 (1H, m, 6-HH), 1.55 (1H, dd, $J = 15.5, 7.5$ Hz, 6-HH), 1.24 (1H, dd, $J = 5.0, 2.5$ Hz, 2-H), 1.03 [3H, d, $J = 7.0$ Hz, CH(CH₃)₂], 0.93 [3H, d, $J = 7.0$ Hz, CH(CH₃)₂], 0.92 (3H, d, $J = 7.0$ Hz, 7-H₃), 0.09 [9H, s, Si(CH₃)₃]; δ_{C} (101 MHz) 142.52 (5-C or *ipso*-Ar), 140.16 (5-C or *ipso*-Ar), 134.17 (Ar), 128.06 (Ar), 127.64 (Ar), 118.76 (Ar), 39.08 (2-C), 37.66 (3-C), 31.70 (2'-C), 24.95 (8-C), 24.06 (1'-C), 22.42 (7-C), 21.88 (1'-C), 9.32 (6-C), -0.72 [Si(CH₃)₃]; m/z (GCMS, EI) 316 (M⁺, 7%), 243 (M⁺ - SiMe₃, 65%), 217 (10), 215 (12), 187 (47), 161 (100), 135 (38), 121 (40), 110 (22), 105 (PhSi⁺, 29%); HRMS (EI): Found M⁺, 316.2039; C₁₉H₃₂Si₂ requires M, 316.2037.

1-Phenyl-1-trimethylsilyl-2-(prop-2'-yl)-3,5-dimethylsilacyclohex-4-ene 44. Reaction of **14a** with 2-methyl-1,3-pentadiene according to method A gave the title compounds as a mixture of isomers in a ratio of 94:5:1 (9%) and according to method B in a ratio of 80:14:4:2 (44%) (ratio of product peak integrals by GC); R_f (petroleum ether) 0.77; ν_{\max} (thin film) 2956, 2928, 2900, 2868, 1427, 1244, 1101, 855, 833, 725, 697 cm^{-1} ; NMR data for the major isomer: δ_{H} (400 MHz) 7.51–7.49 (2H, m, Ar-H), 7.33–7.30 (3H, m, Ar-H), 5.32 (1H, m, 4-H), 2.33 (1H, m, 3-H), 2.10 [1H, m, CH(CH₃)₂], 1.82 (3H, s, 8-H₃), 1.64 (1H, d, $J = 16.8$ Hz, 6-HH), 1.43 (1H, d, $J = 16.8$ Hz, 6-HH), 1.14 (1H, ddd, $J = 6.4, 3.2, 0.8$ Hz, 2-H), 1.03 [3H, d, $J = 6.8$ Hz, CH(CH₃)₂], 0.95 (3H, d, $J = 6.8$ Hz, 7-H₃), 0.89 [3H, d, $J = 6.8$ Hz, CH(CH₃)₂], 0.16 [9H, s, Si(CH₃)₃]; δ_{C} (101 MHz) 139.71 (5-C), 135.20 (*ipso*-Ar), 134.40 (Ar), 131.17 (4-C), 128.15 (Ar), 127.62 (Ar), 38.38 (2-C), 33.05 (3-C), 29.64 (2'-C), 28.27 (8-C), 23.56 (7-C), 22.81 [1'-C (×2)], 15.05 (6-C), 0.44 [Si(CH₃)₃]; m/z (GCMS, EI) 316 (M⁺, 43%), 301 (M⁺ - Me, 4%), 273 (M⁺ - iPr, 3%), 259 (6), 245 (27), 243 (M⁺ - SiMe₃, 93%), 232 (17), 219 (56), 217 (45), 201 (86), 187 (87), 161 (100), 135 (79), 121 (81), 109 (84); HRMS (EI): Found M⁺, 316.2038; C₁₉H₃₂Si₂ requires M, 316.2043.

2,3-Dimethyl-1-phenyl-1-(trimethylsilyl)silacyclohex-4-ene 45. Reaction of **14c** with 1,3-pentadiene according to method B gave the title compound as mixture of diastereoisomers in a ratio of 89:7:4 (28%) (ratio of product peak integrals by GC); R_f (petroleum ether) 0.58; ν_{\max} (thin film) 2998, 2951, 2867, 1427, 1243, 1102, 855, 833, 698 cm^{-1} . NMR data for the major isomer: δ_{H} (500 MHz) 7.52–7.49 (2H, m, Ar-H), 7.35–7.32 (3H, m, Ar-H), 5.82 (1H, m, 5-H), 5.48 (1H, dm, $J = 10.5$ Hz, 4-H), 2.13 (1H, m, 3-H), 1.68 (1H, ddd, $J = 18.0, 5.0, 2.0$ Hz, 6-HH), 1.52 (1H, ddd, $J = 18.0, 5.5, 2.0$ Hz, 6-HH), 1.20 (3H, d, $J = 7.5$ Hz, 7-H₃), 1.08 (3H, d, $J = 7.0$ Hz, 8-H₃), 1.05 (1H, m, 2-H), 0.16 [9H, s, Si(CH₃)₃]; δ_{C} (126 MHz) 137.90 (*ipso*-Ar), 137.03 (4-C), 134.44 (*meta*-Ar), 128.53 (*para*-Ar), 127.76 (*ortho*-Ar), 124.12 (5-C), 38.00 (3-C), 23.87 (2-C), 21.35 (8-C), 15.97 (7-C), 9.70 (6-C), -0.50 [Si(CH₃)₃]; m/z (GCMS, EI) 274 (M⁺, 42%), 259 (M⁺ - Me, 30%), 245 (7), 231 (12), 218 (56), 203 (91), 200 (M⁺ - H - SiMe₃, 95%), 191 (73), 179 (48), 177 (51), 175 (57), 173 (56), 163 (46), 158 (78); HRMS (EI): Found M⁺, 274.1567; C₁₆H₂₆Si₂ requires M, 274.1568.

3-Methyl-1-phenyl-2-propyl-1-(trimethylsilyl)silacyclohex-4-ene 46. Reaction of **14b** with 1,3-pentadiene according to method B gave the title compound as a mixture of diastereoisomers in a ratio of 81:12:7 (12%) (ratio of product peak integrals by GC); R_f (petroleum ether) 0.65; ν_{\max} (thin film) 3066, 2997, 2953, 2925, 2869, 1460, 1427, 1396, 1243, 1101, 852, 833, 734, 698 cm^{-1} . NMR

data for the major isomer: δ_{H} (400 MHz) 7.51–7.49 (2H, m, Ar-H), 7.34–7.31 (3H, m, Ar-H), 5.83 (1H, ddt, $J = 10.5, 5.0, 2.0$ Hz, 5-H), 5.51 (1H, ddt, $J = 10.5, 4.0, 2.0$ Hz, 4-H), 2.25 (1H, m, 3-H), 1.65 (1H, ddt, $J = 17.5, 5.0, 2.0$ Hz, 6-HH), 1.64–1.50 (3H, m, 6-HH and 1'-H₂), 1.48–1.27 (3H, m, 2-H and 2'-H₂), 1.03 (3H, d, $J = 7.0$ Hz, 7-H₃), 0.86 (3H, t, $J = 7.5$ Hz, 3'-H₃), 0.17 [9H, s, Si(CH₃)₃]; δ_{C} (126 MHz) 136.95 (4-C), 134.50 (*ipso*-Ar), 134.43 (*meta*-Ar), 128.36 (*para*-Ar), 127.70 (*ortho*-Ar), 124.07 (5-C), 35.93 (3-C), 34.19 (6-C), 30.04 (1'-C), 23.44 (2'-C), 22.26 (7-C), 14.49 (3'-C), 9.87 (2-C), -0.57 [Si(CH₃)₃]; m/z (GCMS, EI) 302 (M⁺, 18%), 287 (M⁺ - Me, 6%), 229 (M⁺ - SiMe₃, 80%), 218 (67), 203 (88), 201 (58), 187 (68), 177 (65), 175 (54), 173 (100), 163 (37), 161 (58), 159 (71), 145 (83), 135 (98), 121 (95).

3-Methyl-2-(2'-dimethylethyl)-1-phenyl-1-(trimethylsilyl)silacyclohex-4-ene 47. Reaction of **14e** with 1,3-pentadiene according to method B gave the title compound as a mixture of diastereoisomers in a ratio of 85:5:5:5 (35%) (ratio of product peak integrals by GC); R_f (petroleum ether) 0.65; ν_{\max} (thin film) 3067, 3049, 2995, 2954, 2897, 2867, 1465, 1427, 1393, 1364, 1245, 1099, 853, 835, 737, 711, 699 cm^{-1} ; NMR data for the major isomer: δ_{H} (500 MHz) 7.53–7.52 (2H, m, Ar-H), 7.33–7.29 (3H, m, Ar-H), 5.85 (1H, m, 5-H), 5.74 (1H, dd, $J = 10.0$ Hz, 7.0, 4-H), 2.53 (1H, pent, $J = 7.0$ Hz, 3-H), 1.75 (1H, dd, $J = 16.5$ Hz, 2.0, 6-HH), 1.50 (1H, dd, $J = 16.5$ Hz, 6.0, 6-HH), 1.24 (1H, s, 2-H), 1.02 [s, C(CH₃)₃], 0.89 (3H, d, $J = 7.0$ Hz, 7-H₃), 0.14 [9H, s, Si(CH₃)₃]; δ_{C} (126 MHz) 140.40 (*ipso*-Ar), 136.88 (4-C), 134.49 (*meta*-Ar), 127.92 (*para*-Ar), 127.60 (*ortho*-Ar), 123.83 (5-C), 45.77 (2-C), 34.50 [C(CH₃)₃], 32.65 (3-C), 30.65 [C(CH₃)₃], 24.55 (7-C), 9.35 (6-C), -0.41 [Si(CH₃)₃]; m/z (GCMS, EI) 316 (M⁺, 20%), 301 (M⁺ - Me, 7%), 259 (21), 247 (26), 243 (M⁺ - SiMe₃, 83%), 218 (57), 203 (79), 175 (100).

3-Methyl-1,2-diphenyl-1-(trimethylsilyl)silacyclohex-4-ene 48. Reaction of **14g** with 1,3-pentadiene according to method B gave the title compounds as a mixture of diastereoisomers in a ratio of 74:20:6 (45%) (ratio of product peak integrals by GC); R_f (petroleum ether) 0.40; ν_{\max} (thin film) 3065, 3019, 2998, 2951, 2920, 2890, 2868, 1597, 1490, 1449, 1427, 1243, 1102, 857, 834, 783, 735, 699 cm^{-1} ; NMR data for the major isomer: δ_{H} (500 MHz) 7.33–7.27 (5H, m, Ar-H), 7.17–7.12 (3H, m, Ar-H), 6.02 (1H, dtd, $J = 10.5, 5.5, 2.5$ Hz, 5-H), 5.68 (1H, ddt, $J = 10.5, 3.0, 2.0$ Hz, 4-H), 2.88 (1H, m, 3-H), 2.46 (1H, d, $J = 9.5$ Hz, 2-H), 1.89 (1H, ddt, $J = 17.0, 5.0, 2.0$ Hz, 6-HH), 1.69 (1H, ddt, $J = 17.0, 5.5, 2.0$ Hz, 6-HH), 1.01 (3H, d, $J = 7.0$ Hz, 7-H₃), -0.02 [9H, s, Si(CH₃)₃]; δ_{C} (126 MHz) 144.53 (*ipso*-Ar), 136.62 (4-C), 134.45 (Ar), 134.00 (Ar), 128.52 (Ar), 128.34 (Ar), 128.09 (Ar), 127.59 (Ar), 124.62 (Ar), 124.58 (5-C), 40.90 (2-C), 36.22 (3-C), 22.02 (7-C), 9.57 (6-C), -1.29 [Si(CH₃)₃]; m/z (GCMS, EI) 336 (M⁺, 36%), 321 (M⁺ - Me, 10%), 268 (93), 253 (100), 235 (42), 221 (57), 207 (49), 203 (76), 197 (44), 185 (67), 183 (78), 177 (61), 175 (73), 159 (54), 145 (70), 135 (91); HRMS (EI): Found M⁺, 336.1726; C₂₁H₂₈Si₂ requires M, 336.1730.

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