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SYNTHESIS OF SOME [4.1.1]- AND [3.1.1]PROPELLANES WITH SILICON, PHOSPHORUS, SULFUR, TITANIUM, GERMANIUM, OR TIN IN THE LONG BRIDGE†

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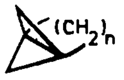
Abstract—The doubly lithiated silanes **8b** and **13b** were cyclized by several dihalides XCl_2 affording the [4.1.1]propellanes **9a–g** and, respectively, the [3.1.1]propellanes **14a–d**. On irradiation of the titanacycle **9f**, "titanocene" was eliminated forming the [3.1.1]propellane **11**. Silane **15a** was brominated in pyridine to give the dibromide **15b**, which served as starting material for the synthesis of propellanes **14e** and **16**.

The rapid development of the synthesis of small-ring [*k.l.m*]propellanes ($l, m = 1, 2; k+1+m \leqslant 8$) in recent years has made nearly all parent systems of this class of compounds accessible or at least has provided evidence for their existence as fleeting intermediates.[1,2] In most cases of the successful syntheses of [*k*.1.1]propellanes, which contain the bicyclo[1.1.0]butane framework as a structural subunit, a strategy was followed in which the central propellane C—C bond was formed in the last reaction step. Propellanes **1a–c** were obtained in this way by reduction of halides **2a–c**,[3–5] whereas the synthesis of **1d**[6] and of some derivatives of **1c**[7,8] was achieved by intramolecular cyclization of an allylic carbene of type **3**.



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1,2	a	b	c	d
n	1	2	3	4

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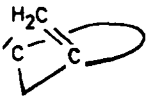

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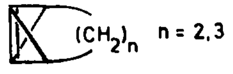

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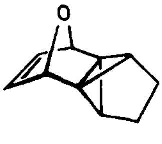

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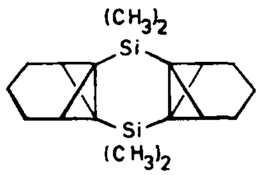

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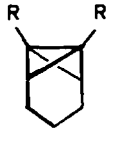
Some years ago we were able to prepare several [4.1.1]- and [3.1.1]propellanes by the Diels–Alder reaction of some short-lived bicyclo[1.1.0]but-1(3)-ene derivatives **4** with cyclic 1,3-dienes, like anthracene, furan and isoindole,[9] leading to **5** and related adducts. In these cases, the third bridge of the propellane **5** is connected to C-1 and C-3 of **4** in a single reaction step.

In this paper we present our results on another strategy of [*k*.1.1]propellane synthesis: starting from a bicyclo[1.1.0]butane, the acidity of the bridgehead positions is used to introduce the third bridge in two separate reaction steps. We have previously applied this method for the synthesis of [4.1.1]propellane **6**.[10]

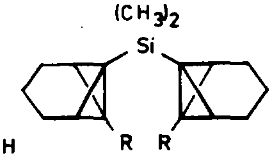
[4.1.1]*Propellanes*

The facile preparation of tricyclo[4.1.0.$0^{2,7}$]heptane (**7a**)[11,12] made this compound a suitable starting material for further investigation. Recently it was shown that **7a** could be converted to the dilithio derivative **7b** by complexing n-butyllithium (BuLi) and 1,2-bis(dimethylamino)ethane (TMEDA) in hexane.[13] The obvious idea of synthesizing [*k*.1.1]propellanes by treating **7b** with bifunctional electrophiles, however, has not been successful so far. The low solubility of **7b** in hydrocarbon and ether solvents combined with its oligomeric structure[13] might account for this failure.



a: R = H
b: R = Li

7



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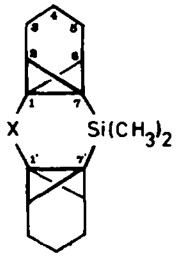

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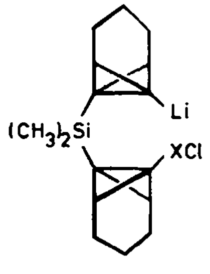

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Dilitho **8b**, prepared from silane **8a** by metalation with the BuLi/TMEDA complex in hexane or with BuLi in ether, was known to cyclize with dichlorodimethylsilane affording **6**.[10] Addition of several other dichlorides XCl_2 to a solution of **8b** led to the formation

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† Dedicated to Professor Rudolf Gompper on his 60th birthday.

Table 1. Specification of X, isolated yields and selected ^{1}H and ^{13}C chemical shifts of the [4.1.1]propellanes **9a–h** and **6** (δ values in $CDCl_3$)

9	**a**	**b**	**c**	**d**	**e**	**f**	**g**	**h**	**6**
X	$GeMe_2$	$SnMe_2$	PPh	S	CO	$TiCp_2$[a]	CHOH	SO_2	$SiMe_2$
% Yield	5.8	9.6	9.4	12	9	7	4.8	78	23
NMR									
δ 2-H	1.83	2.14	2.03	2.03	3.03	3.28	2.22	3.00	1.92
δ 6-H	1.83	2.14	2.29[b]	2.03	3.03	3.28	2.41[c]	3.00	1.92
δ C-1	7.6	5.5	23.1	33.1	33.9	71.5	31.8	38.6	12.5
δ C-2	46.4	46.9	50.8	54.9	51.1	59.9	46.6	51.0	46.3
δ C-6	46.4	46.9	52.7[b]	54.9	51.1	59.9	49.8[c]	51.0	46.3
δ C-7	15.7	12.7	12.7	1.5	32.2	—[d]	11.3	27.6	12.5

[a] Cp, cyclopentadienyl; **9f** was obtained as a 1 : 2 mixture with **8a**, the yield was determined by quant. ^{1}H-NMR; chemical shifts in C_6D_6.

[b] *Cis* to Ph at P.

[c] *Cis* to OH.

[d] The signal of C-7 was not detected.

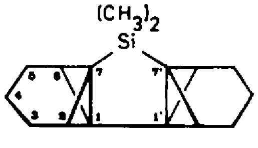
of [4.1.1]propellanes **9a–g**. As the dilution principle for optimum cyclization of the intermediate **10** was only moderately applied, polymeric material was obtained as the main product, which made isolation of **9a–g** difficult and kept the yields low. The nature of the dichloride, the isolated yields of **9a–g** and the ^{1}H- and ^{13}C-NMR chemical shifts of the bicyclo[1.1.0]butane unit of **9** are given in Table 1. Compound **9g** was synthesized from **8b** and methyl formate. Sulfone **9h** was prepared in 78% yield by hydrogen peroxide oxidation of **9d**. The data for this propellane are also included in Table 1. For comparison, the last column shows the corresponding data for **6**, the X-ray structure of which has been previously determined.[10] The chemical shifts of **9a–h** are in accord with the [4.1.1]propellane structure, as are the analytical data and the mass spectra.

[3.1.1]*Propellanes*

In this section we report the results directed towards the syntheses of [3.1.1]propellanes, which were only in part successful. For the synthesis of small-ring propellanes, ring-contraction reactions have been masterly applied by Eaton and Temme[14] and by Paquette and Houser.[15] Our propellanes **9e**, **f** and **h** offered the possibility of ring contraction by elimination of group X and formation of a new C—C bond, affording [3.1.1]propellane **11**. The thermal extrusion of sulfur dioxide from cyclic sulfones by ring contraction is well established.[16] However, when sulfone **9h** was distilled at 0.001 Torr through a quartz tube at 370°, it was recovered unchanged. Repeating this experiment at 470° led to completely unspecific decomposition of **9h** without any **11** in the small fraction of volatile product. Attempts to eliminate carbon monoxide by irradiating solutions of ketone **9e** were, likewise, unsuccessful.[17]

Organotitanium compounds of type Cp_2TiR_2 (Cp = η^5-cyclopentadienyl) have been shown to decompose photochemically to "titanocene" and R_2, the usefulness of this reaction depending strongly on the nature of R.[18] We report that when a solution of **9f** in benzene was irradiated with a 150 W mercury high-pressure lamp at room temperature, [3.1.1]propellane **11** was generated. The yield of **11** was improved to 70% by addition of diphenylacetylene, which has been shown to react with "titanocene" forming the titanacycle **12**.[19]

Propellane **11** could only be obtained as a mixture with **8a**. The propellane was characterized by its ^{1}H- and ^{13}C-NMR spectrum. It could be distilled at 120°/10^{-5} Torr; solutions in C_6D_6 remained unchanged for 24 h at room temperature. After that time, a slow decomposition of **11** was observed. The assignment of the two singlets in the ^{13}C-NMR spectrum of the **8a**/**11** mixture at δ 46.0 and 38.7 to C-1 and C-7 of **11** should be regarded as tentative. However, these two singlets showed the expected decrease of the ^{13}C-NMR signal intensities when the spectrum of the **8a**/**11** mixture was recorded in intervals of two days. It should be noticed that the ^{13}C resonance of the central C atoms of [3.1.1]propellane **1c** is shifted downfield by 23 ppm with respect to the resonance of the corresponding C atoms of [4.1.1]propellane **1d**.[5,6]



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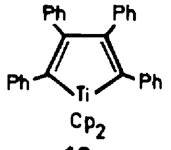

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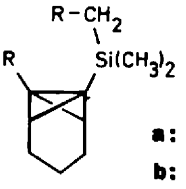

a: R = H

b: R = Li

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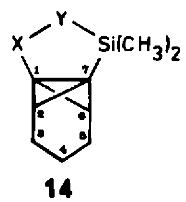

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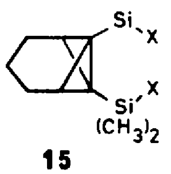


a: X = H

b: X = Br

15

Table 2. Specification of X and Y, isolated yields and selected ^1H- and ^{13}C-NMR chemical shifts of [3.1.1]propellanes **14a–f** and **11** (δ values in $CDCl_3$)

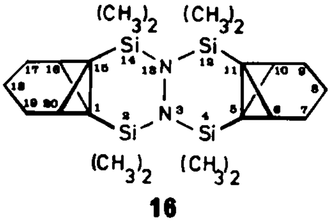
14	**a**	**b**	**c**	**d**	**e**	**f**	**11**[a]
X	$SiMe_2$	SiHMe	SiMePh	$GeMe_2$	$SiMe_2$	$SiMe_2$	—
Y	CH_2	CH_2	CH_2	CH_2	O	NH	—
% Yield	17	8	66	4.4	11	7.8	70
NMR							
δ 2-H	2.40	2.47	2.70[b]	2.45	2.65	2.56	3.46
δ 6-H	2.40	2.47	2.40	2.45	2.65	2.56	3.46
δ C-1	17.6	15.9	17.7	22.3	17.8	15.3	46.0
δ C-2	50.4	50.1	52.5	51.3	50.8	50.2	55.9
δ C-6	50.4	52.3	49.4	51.3	50.8	50.2	55.9
δ C-7	17.6	17.3	16.6	16.8	17.8	15.3	38.2

[a] Yield by quant. ^1H-NMR spectroscopy; chemical shifts in C_6D_6.
[b] *Cis* to Ph.

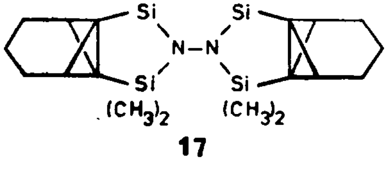
The photoelimination of "titanocene" from **9f** is not only a valuable ring-contraction reaction, at the same time it seems to be an efficient method of coupling two bicyclo[1.1.0]butane units at their bridgehead positions. Currently, this aspect is being further investigated in this laboratory.

Two additional routes to [3.1.1]propellanes have been examined. Metalation of silane **13a** by the BuLi/TMEDA complex or by a mixture of BuLi/t-BuOK in hexane gave rise to **13b**, which, again, could be cyclized by dichlorides XCl_2, affording propellanes **14** ($Y = CH_2$). The specification of X, the isolated yields and selected chemical shifts of **14** are collected in Table 2. Compound **14c** was obtained in 66% yield from **14b** by nucleophilic exchange of the silicon-bonded hydrogen by phenyllithium.

Disilane **15a** was the starting material for the synthesis of two further [3.1.1]propellanes. It was obtained in 68% yield from **7b** and two equivalents of chlorodimethylsilane. When treated with sodium in liquid ammonia, the substitution of amide for hydride was accomplished[20] and aza[3.1.1]propellane **14f** could be isolated in 7.8% yield. Furthermore, **15a** was converted to dibromide **15b** by bromine in pyridine. Remarkably, the bicyclo[1.1.0]butane unit of **15a** remained unchanged during this process. When **15b** was allowed to react with aqueous sodium hydroxide, the oxa-disila[3.1.1]propellane **14e** was formed in 11% yield.



16



17

The equimolar mixture of dibromosilane **15b** and anhydrous hydrazine in ether gave rise to a 2:1 substitution product (11% yield), which could have structure **16** or **17**. The ^1H-NMR chemical shifts of the bicyclo[1.1.0]butane protons appeared at δ 2.17. This value is closer to the chemical shifts of the corresponding protons of [4.1.1]propellanes **6**, **9c** and **d** than to those of [3.1.1]propellanes **9e** and **f**. Therefore, structure **16** seems more likely for the unknown compound than **17**. This was finally confirmed by an X-ray analysis.[21] The nitrogen atoms in **16** exhibit *trans* oriented pyramidal configurations. As a consequence, the two methyl groups at silicon are non-equivalent and show two separate signals in the ^1H- and ^{13}C-NMR spectrum of **16**.

Concluding remarks

The results presented in this paper have shown that bridging reactions from substituted tricyclo[4.1.0.0^{2,7}]heptanes allow the synthesis of hetero[*k*.1.1]propellanes without difficulty. This should be applicable to other bicyclo[1.1.0]butanes, thus making many new small-ring propellanes easily accessible.

EXPERIMENTAL

General remarks. M.ps and b.ps are uncorrected. ^1H-NMR spectra were recorded on a Varian A 60, a Varian EM-360 or a Bruker WP 80 CW instrument, ^{13}C-NMR spectra on a Bruker WP 80 FT spectrometer. $(CH_3)_4Si$ was used as internal standard. Mass spectra were obtained on a AEI-902 instrument, IR spectra on a Perkin–Elmer 125 spectrometer. Solvents were purified by standard procedures. Tetrahydrofuran and ether, when used as solvents for metalorganic reagents, were distilled from an excess of lithium aluminum hydride. All air-sensitive reactions were performed in flame-dried glassware under N_2.

n-BuLi was purchased from CHEMETALL as a 1.5 M soln in hexane. Compounds **7a**,[11,12] **13a**,[22] **8a**,[10] and bis(cyclopentadienyl)titanium dichloride[23] were prepared by reported procedures.

[4.1.1]*Propellanes*

General procedure. From 22.7 ml (34.7 mmol) of BuLi in hexane (1.53 M) the solvent was evaporated *in vacuo* and the remaining oil was dissolved in 20 ml of ether. To this soln 4.30 g (17.6 mmol) of **8a** in 10 ml of ether was added and the mixture was stirred for 5 d at room temp. The yellow soln of **8b** was diluted with 200–300 ml of ether and cooled to 0°, whereupon 17.4 mmol of dichloride XCl_2 was added dropwise during 30 min. The mixture was stirred for 18 h at room temp, poured into 200 ml of ice–water, and the layers were separated. The organic part was twice extracted with 100 ml of water, dried over $MgSO_4$, and the solvent was evaporated *in vacuo*. The product was then isolated by crystallization, high-vacuum distillation or sublimation of the residue.

Dimethyl(7,7′ - (2 - *silaprop* - 2 - *ylidene*) - *bis*(*tricyclo*-[4.1.0.0^{2,7}]*hept* - 1 - *yl*))*germanium* (**9a**)

Following the general procedure and aqueous work-up, from 4.30 g (17.6 mmol) of **8a** and 2.83 g (16.3 mmol) of dimethylgermanium dichloride, 0.327 g (5.8%) of **9a** was obtained by sublimation of the raw material at 110° (bath temp)/0.001 Torr as a white crystalline solid: m.p. 131–132°; ^{1}H-NMR ($CDCl_3$) δ 0.15 (s, 6H, $(C\underline{H}_3)_2Si$), 0.34 (s, 6H, $(C\underline{H}_3)_2Ge$), 1.30 (m, 12H, 3-H$_2$, 4-H$_2$, 5-H$_2$, 3′-H$_2$, 4′-H$_2$, 5′-H$_2$), 1.83 (m, 4H, 2-H, 6-H, 2′-H, 6′-H); ^{13}C-NMR ($CDCl_3$) δ -3.21 (q, $(\underline{C}H_3)_2Si$), -1.66 (q, $(\underline{C}H_3)_2Ge$), 7.63 (s, C-7), 15.72 (s, C-1), 20.96 (t, C-4), 21.62 (t, C-3, C-5), 46.43 (d, C-2, C-6); mass spectrum (rel. intensity) *m/e* 346, 344, 342 (M^+, 50%), 331, 329, 327 (100), 241 (80), 227 (50), 199 (20), 181 (30), 149 (33), 135 (27), 121 (17), 109 (16), 91 (13), 73 (67), 59 (69). (Found: C, 63.23; H, 8.60. Calc for $C_{18}H_{28}GeSi$: C, 62.65; H, 8.18%.)

Dimethyl(7,7′ - (2 - *silaprop* - 2 - *ylidene*) - *bis*(*tricyclo*-[4.1.0.0^{2,7}]*hept* - 1 - *yl*))*tin* (**9b**)

According to the general procedure followed by aqueous work-up, from 4.30 g (17.6 mmol) of **8a** and 3.70 g (16.8 mmol) dimethyltin dichloride, 0.628 g (9.6%) of **9b** was obtained by sublimation of the crude residue at 140° (bath temp)/0.001 Torr as white crystals: m.p. 125–126°; ^{1}H-NMR ($CDCl_3$) δ 0.16 (s, 6H, $(C\underline{H}_3)_2Si$), 0.28 (s, 6H, $(C\underline{H}_3)_2Sn$), 1.48 (m, 12H, 3-H$_2$, 4-H$_2$, 5-H$_2$, 3′-H$_2$, 4′-H$_2$, 5′-H$_2$), 2.14 (m, 4H, 2-H, 6-H, 2′-H, 6′-H); ^{13}C-NMR ($CDCl_3$) δ -10.81 (q, $(\underline{C}H_3)_2Sn$), -1.48 (q, $(\underline{C}H_3)_2Si$), 5.54 (s, C-1), 12.69 (s, C-7), 20.89 (t, C-4), 21.86 (t, C-3, C-5), 46.91 (C-2, C-6); mass spectrum (rel. intensity) *m/e* 393, 391, 389 (M^+, 7%, 5%, 3%), 375 (15), 232 (23), 151 (24), 149 (17), 145 (30), 118 (100), 97 (38), 90 (19), 59 (40). (Found: C, 55.40; H, 7.17. Calc for $C_{18}H_{28}Si\,Sn$: C, 55.27; H, 7.21%.)

Phenyl(7,7′ - (2 - *silaprop* - 2 - *ylidene*) - *bis*(*tricyclo*-[4.1.0.0^{2,7}]*hept* - 1 - *yl*))*phosphane* (**9c**)

The reaction of 4.30 g (17.6 mmol) of **8a** and 2.64 g (14.7 mmol) of dichlorophenylphosphane, according to the general procedure followed by aqueous work-up and sublimation of the raw material at 160° (bath temp)/0.001 Torr, afforded a white crystalline product, from which after purification from acetonitrile 0.485 g (9.4%) white crystals of **9c** were isolated: m.p. 131–132°; ^{1}H-NMR ($CDCl_3$) δ 0.11 and 0.49 (2s, 3H each, $C\underline{H}_3$-Si), 1.40 (m, 12H, 3-H$_2$, 4-H$_2$, 5-H$_2$, 3′-H$_2$, 4′-H$_2$, 5′-H$_2$), 2.03 and 2.29 (2m, 2H each, 2-H, 2′-H and 6-H, 6′-H, or reversed), 7.22–8.02 (m, 5H, $C_6\underline{H}_5$); ^{13}C-NMR ($CDCl_3$) δ (the ^{13}C–^{31}P coupling is omitted) -3.30 and -0.56 ($\underline{C}H_3Si$), 12.71 (C-7), 20.77, 21.35 and 21.47 (C-5, C-6, C-7, in unknown order), 23.06 (C-1), 50.84 and 52.65 (C-2, C-6, or reversed), 126.63, 127.95, 131.33, 142.84 (aromatic-C). (Found: C, 75.92; H, 7.65. Calc for $C_{22}H_{27}PSi$: C, 75.39; H, 7.76%.)

(7,7′ - (2 - *Silaprop* - 2 - *ylidene*) - *bis*(*tricyclo*[4.1.0.0^{2,7}]*hept* - 1 - *yl*))*sulfide* (**9d**)

Following the general procedure with aqueous work-up, from 4.30 g (17.6 mmol) of **8a** and 1.64 g (15.9 mmol) of sulfur dichloride, 0.517 g (12%) of **9d** was obtained as white crystals by sublimation of the raw material at 120° (bath temp)/0.001 Torr: m.p. 88–89°; ^{1}H-NMR ($CDCl_3$) δ 0.30 (s, 6H, $(C\underline{H}_3)_2Si$), 1.39 (m, 12H, 3-H$_2$, 4-H$_2$, 5-H$_2$, 3′-H$_2$, 4′-H$_2$, 5′-H$_2$), 2.03 (m, 4H, 2-H, 6-H, 2′-H, 6′-H); ^{13}C-NMR ($CDCl_3$) δ -1.54 (q, $\underline{C}H_3Si$), 1.54 (s, C-7), 20.32 (t, C-4), 21.11 (t, C-3, C-5), 33.13 (s, $\overline{C}$-1), 54.91 (d, C-2, C-6); mass spectrum (rel. intensity) *m/e* 274 (M^+, 100%), 259 (31), 231 (18), 215 (94), 167 (32), 141 (25), 91 (62), 59 (47), 43 (25); M^+ calc 274.121, obsd 274.124. (Found: C, 69.72; H, 7.85. Calc for $C_{16}H_{22}SSi$: C, 70.01; H, 8.08%.)

(7,7′ - (2 - *Silaprop* - 2 - *ylidene*) - *bis*(*tricyclo*[4.1.0.0^{2,7}]*hept* - 1 - *yl*))*ketone* (**9e**)

4.30 g (17.6 mmol) of **8a** was metalated by 22.7 ml (34.7 mmol) BuLi (1.53 M) in hexane and 3.80 g (32.7 mmol) of 1,2-bis(dimethylamino)ethane (TMEDA) within 3 d at room temp. The mixture was diluted with 200 ml of pentane. Subsequently, 10.0 ml of a soln of phosgene in toluene (1.93 M) was added dropwise under stirring. After 16 h, aqueous work-up afforded 0.428 g (9%) of **9e** by short-path distillation of the residual oil at 130° (bath temp)/0.001 Torr. **9e** solidified to a crystalline material of m.p. 129–131°: IR 1640 cm^{-1} (CO); ^{1}H-NMR ($CDCl_3$) δ 0.23 (s, 6H, $(C\underline{H}_3)_2Si$), 1.38 (m, 12H, 3-H$_2$, 4-H$_2$, 5-H$_2$, 3′-H$_2$, 4′-H$_2$, 5′-H$_2$), 3.03 (m, 4H, 2-H, 6-H, 2′-H, 6′-H); ^{13}C-NMR ($CDCl_3$) δ -3.30 (q, $\underline{C}H_3Si$), 20.08 (t, C-4), 20.74 (t, C-3, C-5), 32.19 and 33.89 (2s, C-7, C-1, or reversed), 51.06 (d, C-2, C-6), 213.11 (s, $\underline{C}O$); mass spectrum (rel. intensity) *m/e* 270 (M^+, 50%), 255 (25), 242 (75), 227 (50), 214 (25), 74 (100); M^+ calc 270.14399, obsd 270.144.

Bis(*cyclopentadienyl*)(7,7′ - (2 - *silaprop* - 2 - *ylidene*) - *bis*(*tricyclo*[4.1.0.0^{2,7}]*hept* - 1 - *yl*)*titanium* (**9f**)

3.50 g (14.3 mmol) of **8a** was metalated by 28.7 mmol of BuLi in 20 ml of ether for 5 d at room temp. The mixture was diluted with 200 ml of ether, cooled to 0°, and 3.54 g (14.2 mmol) of bis(cyclopentadienyl)titanium dichloride was added as a solid in portions of approximately 100 mg. The suspension was then stirred for 3 h at 0°, the solvent was evaporated *in vacuo* at room temp, and the crude product was treated with 25 ml of benzene. The benzene soln was filtered from the insoluble residue and a ^{1}H-NMR spectrum was measured, which showed a 2 : 1 mixture of **8a** and **9f** yield of **9a** 7% by quant. ^{1}H-NMR with toluene as integration standard). Attempts to separate the mixture by crystallization or by chromatographic methods were unsuccessful. Attempted distillation of **8a** from **9f** at 60° (bath temp)/10^{-5} Torr led to decomposition of **9f**. NMR spectrum of **9f**: ^{1}H-NMR (C_6D_6) δ 0.38 (s, $(C\underline{H}_3)_2Si$), 1.40–1.52 (m, 3-H$_2$, 4-H$_2$, 5-H$_2$, 3′-H$_2$, 4′-H$_2$, 5′-H$_2$), 3.28 (m, 2-H, 6-H, 2′-H, 6′-H), 5.87 (s, $C_5\underline{H}_5$); ^{13}C-NMR (C_6D_6) δ 0.70 (q, $\underline{C}H_3Si$), 21.00 (t, C-4), 24.78 (t, C-3, C-5), 59.85 (d, C-2, C-6), 71.54 (s, C-1), 113.01 (d, $\underline{C}_5H_5$); the signal of C-7 could not be detected, it was probably covered by signals of **8a**.

(7,7′ - (2 - *Silaprop* - 2 - *ylidene*) - *bis*(*tricyclo*[4.1.0.0^{2,7}]*hept* - 1 - *yl*))*methanol* (**9g**)

2.00 g (8.18 mmol) of **8a**, 16.4 mmol of BuLi and 0.500 g (8.33 mmol) of methyl formate were brought to reaction according to the general procedure. Aqueous work-up and distillation of the remaining oil at 130–140° (bath temp)/0.001 Torr afforded 80 mg (4.8%) of **9g** as a waxy solid: ^{1}H-NMR ($CDCl_3$) δ 0.10 and 0.45 (2 s, 3H each, $C\underline{H}_3Si$), 1.35 (m, 12H, 3-H$_2$, 4-H$_2$, 5-H$_2$, 3′-H$_2$, 4′-H$_2$, 5′-H$_2$), 2.22 and 2.41 (2 m, 3H and 2H, $\underline{H}O$, 2-H, 2′-H and 6-H, 6′-H), 4.55 (s, 1H, $C\underline{H}OH$); ^{13}C-NMR ($CDCl_3$) δ -3.27 and -1.09 (2 s, $\underline{C}H_3Si$), 11.32 (s, C-7), 20.72 (t, C-4), 21.02 (t, C-3, C-5), 31.83 (s, C-1), 46.55 and 49.79 (2 d, C-2, C-6), 72.15 (d, $\underline{C}HOH$); mass spectrum (rel. intensity) *m/e* 272 (M^+, 15%), 257 (30), 197 (32), 75 (100). (Found: C, 74.54; H, 8.91. Calc for $C_{17}H_{24}OSi$: C, 74.94; H, 8.88%.)

(7,7′ - (2 - *Silaprop* - 2 - *ylidene*) - *bis*(*tricyclo*[4.1.0.0^{2,7}]*hept* - 1 - *yl*))*sulfone* (**9h**)

The mixture of 0.400 g (1.46 mmol) of **9d** and 4.56 g of 30% aq H_2O_2 (approx 40 mmol) in 40 ml of acetone was refluxed for 24 h. On cooling, 0.348 g (78%) of **9h** precipitated from the soln as white crystals: m.p. 126–127°; ^{1}H-NMR ($CDCl_3$) δ 0.39 (s, 6H, $(C\underline{H}_3)_2Si$), 1.46 (m, 12H, 3-H$_2$, 4-H$_2$, 5-H$_2$, 3′-H$_2$, 4′-H$_2$, 5′-H$_2$), 3.00 (m, 4H, 2-H, 6-H, 2′-H, 6′-H); ^{13}C-NMR ($CDCl_3$) δ -3.36 (q, $\underline{C}H_3Si$), 19.93 (t, C-3, C-4, C-5), 27.62 (s, C-7), 38.58 (s, C-1), 51.01 (d, C-2, C-6); mass spectrum (rel. intensity) *m/e* 306 (M^+, 10%), 291 (100), 227 (40), 199 (30), 167 (15), 92 (70), 75 (40), 49 (50); M^+ calc 306.110, obsd 306.113. (Found: C, 62.22; H, 7.75. Calc for $C_{16}H_{22}O_2SSi$: C, 62.70; H, 7.23%.)

[3.1.1]*Propellanes*

1,1′ - (7,7′ - (2 - *Silaprop* - 2 - *ylidene*))*bi*(*tricyclo*[4.1.0.$0^{2,7}$] - *heptane*) (**11**)

Attempted synthesis of **11** *from* **9e**. A soln of 200 mg (0.739 mmol) of **9e** in 300 ml of cyclohexane was irradiated with a 150 W mercury high-pressure lamp for 16 h at room temp under N_2. After evaporation of the solvent *in vacuo*, the ^{1}H-NMR spectrum of the remaining oil showed only signals of ketone **9e**.

Attempted synthesis of **11** *from* **9h**. 0.200 g (0.653 mmol) of the sulfone **9h** was distilled at 0.05 Torr through a quartz tube (length 40 cm), placed in an oven and heated to 370°. The volatile material was condensed in a trap cooled by dry ice/acetone. The ^{1}H-NMR spectrum of the condensed product showed signals of **9h** only. The pyrolysis reaction was repeated with 0.150 g (0.489 mmol) of **9h** at an oven temp of 470°. The complex ^{1}H-NMR spectrum of the condensed material did not show signals of **9d** or of **11**.

Synthesis of **11** *from* **9f**. 1.50 g of a 2:1 mixture (by ^{1}H-NMR) of **8a** and **9f** (containing 1.64 mmol of **9f**) and 2.54 g (14.3 mmol) of diphenylacetylene in 350 ml of benzene were irradiated with a 150 W mercury high-pressure lamp for 18 h at room temp. The benzene was evaporated *in vacuo*, and the residue was bulb-to-bulb distilled at 10^{-5} Torr at a bath temp of 60–110°. According to NMR analysis, the volatile material was composed of diphenylacetylene, **8a** and **11** (yield of **11** by quant. ^{1}H-NMR 1.14 mmol = 70%). Isolation of pure **11** from the mixture was not achieved. Spectroscopic data of **11**: ^{1}H-NMR (C_6D_6) δ 0.22 (s, $(C\underline{H}_3)_2Si$); signals of 3-H_2, 4-H_2, 5-H_2, 3′-H_2, 4′-H_2, and 5′-H_2 are covered by corresponding signals of CH_2 of **8a**; 3.46 (m, 2-H, 6-H, 2′-H, 6′-H); ^{13}C-NMR (C_6D_6) δ −2.70 (q, $\underline{C}H_3Si$), 20.78 (t, C-4, C-4′), 21.45 (t, C-3, C-5, C-3′, C-5′), 38.23 (s, C-7, C-7′), 46.00 (s, C-1, C-1′), 55.85 (d, C-2, C-6, C-2′, C-6′); M^{+} calc 242.14908, obsd 242.149. The photolysis of mixtures of **8a** and **9f** in benzene were repeated several times. In the absence of diphenylacetylene, the yield of **11** remained under 40%. ^{1}H-NMR spectra of **11** in C_6D_6, recorded at intervals of 6 h and keeping the sample at room temp, showed a constant intensity of the signal of **11** at δ 3.46 within the first 24 h; subsequently, the intensity of this signal decreased steadily; after 72 h, only 20% of its original intensity was observed.

8,8,10,10 - *Tetramethyl* - 8,10 - *disilatetracyclo* - [5.3.0.$0^{1,6}$.$0^{2,7}$]*decane* (**14a**)

To a suspension of 21.6 g (192 mmol) of t-BuOK and 16.0 g (96.2 mmol) of **13a** in 20 ml of hexane, 125 ml (193 mmol) of BuLi in hexane (1.54 M) was added within 30 min. The mixture was stirred for 4 d at room temp, diluted with 300 ml of pentane, and chilled in an ice bath. After addition of 12.4 g (96.1 mmol) of dichlorodimethylsilane the suspension was stirred for 16 h at ambient temp, and, subsequently, poured on 1 l of 2 N NaOH aq. The organic layer was washed twice with 200 ml of water. After drying over $MgSO_4$ the solvent was evaporated. Distillation of the resulting brown oil gave 3.60 g (17%) of **14a** as a colorless liquid, b.p. 60–70° (bath temp)/0.001 Torr: ^{1}H-NMR ($CDCl_3$) δ 0.07 (s, 2H, 9-H_2), 0.16 (s, 12H, $(C\underline{H}_3)_2Si$), 1.37 (m, 6H, 3-H_2, 5-H_2), 2.40 (m, 2H, 2-H, 6-H); ^{13}C-NMR ($CDCl_3$) δ −0.45 (q, $\underline{C}H_3Si$), 8.81 (t, C-9), 17.62 (s, C-1, C-7), 20.68 (t, C-4), 21.32 (t, C-3, C-5), 50.37 (d, C-2, C-6); mass spectrum (rel. intensity) *m/e* 222 (M^{+}, 42%), 207 (46), 179 (38), 131 (100), 75 (53), 73 (52), 59 (23), 43 (15); M^{+} calc 222.1260, obsd 222.125. (Found: C, 64.56; H, 10.10. Calc for $C_{12}H_{22}Si_2$: C, 64.79; H, 9.97%.)

8,8,10 - *Trimethyl* - 8,10 - *disilatetracyclo*[5.3.0.$0^{1\ 6}$.$0^{2,7}$] - *decane* (**14b**)

7.93 g (47.7 mmol) of **13a** was metalated to give **13b** by a mixture of 10.7 g (95.4 mmol) of t-BuOK and 57.8 ml (96.5 mmol) of BuLi in hexane (1.67 M) as described above for the synthesis of **14a**. Addition of 5.49 g (47.7 mmol) of dichloromethylsilane afforded, after a reaction time of 16 h at room temp and after work-up as for **14a**, 800 mg (8%) of **14b** as a colorless liquid, b.p. 40° (bath temp)/0.001 Torr: ^{1}H-NMR ($CDCl_3$) δ 0.20 and 0.24 (2 s, 3H each, $C\underline{H}_3Si$), 0.28 (d, 3H, $C\underline{H}_3SiH$), 1.37 (m, 6H, 3-H_2, 4-H_2, 5-H_2), 2.47 (m, 2H, 2-H, 6-H), 4.26 (m, 1H, $\underline{H}Si$); the signal pattern of 9-H_2 is covered by the methyl signals; ^{13}C-NMR ($CDCl_3$) δ −3.36, 0.58 and 0.94 (3 q, $\underline{C}H_3Si$), 6.60 (t, C-9), 15.90 and 17.26 (2 s, C-1 and C-7, or reversed), 20.65 (t, C-4), 21.17 (t, C-3, C-5), 50.09 and 52.30 (2 d, C-2, C-6, or reversed); mass spectrum (rel. intensity) *m/e* 208 (M^{+}, 29%), 193 (47), 180 (18), 165 (30), 117 (100), 73 (80), 59 (33); M^{+} calc 208.11035, obsd 208.111.

8,8,10 - *Trimethyl* - 10 - *Phenyl* - 8,10 - *disilatetracyclo* - [5.3.0.$0^{1,6}$.$0^{2,7}$]*decane* (**14c**)

1.95 ml (4.00 mmol) of phenyllithium in benzene/ether (2.05 M) was added to a soln of 200 mg (0.96 mmol) of **14b** in 3 ml of ether. The mixture was stirred for 5 h at 0°. Aqueous work-up and distillation of the remaining oil of the organic layer afforded 0.181 g (66%) of **14c** as colorless liquid, b.p. 90° (bath temp)/0.001 Torr: ^{1}H-NMR ($CDCl_3$) δ 0.17, 0.23 and 0.33 (3 s, 3H each, $C\underline{H}_3Si$), 0.42 and 0.51 (AB system, 9-H_2), 1.44 (m, 6H, 3-H_2, 4-H_2, 5-H_2), 2.40 (m, 1H, 6-H), 2.70 (m, 1H, 2-H), 7.15–7.76 (m, 5H, $\underline{H}_5C_6$); ^{13}C-NMR ($CDCl_3$) δ −0.93, −0.75 and 0.00 (3 q, $\underline{C}H_3Si$), 7.66 (t, C-9), 16.62 (s, C-7), 17.68 (s, C-1), 20.05, 20.80 and 21.23 (3 t, C-4, C-3, C-5), 49.37 (d, C-6), 52.49 (d, C-2), 127.66, 128.87, 134.15, 139.14 (aromatic-C); mass spectrum (rel. intensity) *m/e* 284 (M^{+}, 35%), 269 (30), 256 (20), 241 (30), 203 (40), 191 (70), 177 (50), 135 (100), 73 (90); M^{+} calc 284.14166, obsd 284.143.

8,8,10,10 - *Tetramethyl* - 8 - *germa* - 10 - *silatetracyclo* - [5.3.0.$0^{1,6}$.$0^{2,7}$]*decane* (**14d**)

The suspension of **13b** in hexane, prepared from 1.74 g (10.5 mmol) of **13a**, 2.32 g (20.7 mmol) of t-BuOK and 12.6 ml (21.0 mmol) of BuLi in hexane (1.67 M) as described for **14a**, was treated in the usual manner with 1.79 g (10.3 mmol) of dimethylgermanium dichloride. Aqueous alkaline work-up and distillation of the remaining oil afforded 121 mg (4.4%) of **14d** as colorless liquid, b.p. 40° (bath temp)/0.001 Torr, which solidified to a white wax: ^{1}H-NMR ($CDCl_3$) δ 0.06 (s, 2H, 9-H_2), 0.15 and 0.35 (2 s, 6H each, $C\underline{H}_3Si$ and $C\underline{H}_3Ge$), 1.35 (m, 6H, 3-H_2, 4-H_2, 5-H_2), 2.45 (m, 2H, 2-H, 6-H); ^{13}C-NMR ($CDCl_3$) δ −0.73 and −0.36 (2 q, $\underline{C}H_3Ge$ and $\underline{C}H_3Si$, or reversed), 10.02 (t, C-9), 16.75 and 22.29 (2 s, C-1 and C-7, or reversed), 20.74 (t, C-4), 21.59 (t, C-1, C-5), 51.34 (d, C-2, C-6); mass spectrum (rel. intensity) *m/e* 268 (M^{+}, 38%), 266 (27), 264 (20), 253 (100), 251 (79), 249 (61), 177 (20), 161 (27), 73 (94).

Propellanes from 1,7 - *bis*(*dimethylsilyl*)*tricyclo*[4.1.0.$0^{2,7}$] - *heptane* (**15a**)

Synthesis of **15a**. 4.00 g (42.5 mmol) of **7a** was metalated by a mixture of 19.6 g (175 mmol) of t-BuOK and 111 ml (170 mmol) of BuLi in hexane (1.53 M) for 4 d at room temp under stirring, affording **7b**. The suspension was cooled to 0°, 15.8 g (167 mmol) of chlorodimethylsilane was added dropwise, and the reaction mixture was stirred for 3 h at ambient temp. Aqueous work-up and distillation of the remaining oil of the organic layer, after evaporation of hexane *in vacuo*, gave 5.90 g (68%) of **15a** as colorless liquid, b.p. 40°/0.001 Torr: ^{1}H-NMR ($CDCl_3$) δ 0.12 (d, J = 4 Hz, 12H, $C\underline{H}_3Si$), 1.36 (m, 6H, 3-H_2, 4-H_2, 5-H_2), 2.00 (m, 2H, 2-H, 6-H), 4.28 (spt, J = 4 Hz, 2H, $\underline{H}Si$); ^{13}C-NMR ($CDCl_3$) δ −3.69 (q, $\underline{C}H_3Si$), 11.17 (s, C-1, C-7), 21.29 (t, C-3, C-4, C-5), 42.40 (d, C-2, C-6); mass spectrum (rel. intensity) *m/e* 210 (M^{+}, 20%), 195 (15), 151 (24), 135 (30), 115 (35), 73 (70), 59 (100); M^{+} calc 210.1260, obsd 210.126.

1,7-*Bis*(*bromodimethylsilyl*)*tricyclo*[4.1.0.$0^{2,7}$)*heptane* (**15b**)

To a soln of 1.94 g (9.22 mmol) of **15a** in 10 ml of pyridine was added 4.60 g (18.7 mmol) of Br_2 at 80° under stirring. The mixture was allowed to cool to room temp, the ppt was filtered, and the pyridine soln was concentrated *in vacuo*. The remaining brown oil consisted mostly of **15b** and of pyridine. It was used without further purification. Spectroscopic properties of **15b**: ^{1}H-NMR ($CDCl_3$) δ 0.66 (s, 12H, $(C\underline{H}_3)_2Si$), 1.38 (m, 6H, 3-H_2, 4-H_2, 5-H_2), 2.30 (m, 2H, 2-H, 6-H); ^{13}C-NMR ($CDCl_3$) δ 2.81 (q, $\underline{C}H_3Si$), 16.83 (s, C-1, C-7), 20.08 (t, C-3, C-5), 20.26 (t, C-4), 41.77 (d, C-2, C-6); mass spectrum *m/e* 368 (M^{+}, 0.5%).

8,8,10,10 - *Tetramethyl* - 9 - *aza* - 8,10 - *disilatetracyclo* - [5.3.0.0^{1,6}.0^{2,7}]*decane* (**14f**)

To a stirred soln of 2.0 g (87.0 mmol) of Na, dissolved in 250 ml of liquid ammonia and cooled in a dry ice/acetone bath, 1.50 g (7.13 mmol) of **15a** was added by syringe. The mixture was stirred for 3 h at −78°, the cooling bath was then removed and the liquid ammonia was allowed to evaporate. The residue was treated with 200 ml of ether, the soln filtered and the solvent removed *in vacuo*. Distillation of the remaining oil at 0.001 Torr afforded 0.125 g (7.8%) of **14f** as a colorless liquid, which solidified to a white waxy material. ^{1}H-NMR ($CDCl_3$) δ 0.14 (s, 12 H, $(C\underline{H}_3)_2Si$), 1.38 (m, 6H, 3-H_2, 4-H_2, 5-H_2), 1.99 (broad s, 1H, N$\underline{H}$), 2.56 (m, 2H, 2-H, 6-H); ^{13}C-NMR ($CDCl_3$) δ 1.30 (q, $\underline{C}H_3Si$), 15.32 (s, C-1, C-7), 20.53 (t, C-4), 21.23 (t, C-3, C-5), 50.15 (d, C-2, C-6); mass spectrum (rel. intensity) *m/e* 223 (M^+, 25%), 208 (100), 192 (9), 180 (13), 133 (18), 74 (25), 59 (16); M^+ calc 223.12125, obsd 223.123.

8,8,10,10 - *Tetramethyl* - 9 - *oxa* - 8,10 - *disilatetracyclo* - [5.3.0.0^{1,6}.0^{2,7}]*decane* (**14e**)

From 1.94 g (9.22 mmol) of **15a** the dibromosilane **15b** was prepared as described above. The crude oil of **15b** was dissolved in 200 ml of ether, 50 ml of a 2 N NaOH aq soln was added and the mixture stirred vigorously for 3 h at room temp. The layers were separated, the organic part was dried over $MgSO_4$, the ether was removed *in vacuo*, and the remaining oil was distilled, affording 231 mg (11%) of **14e**, b.p. 80° (bath temp)/0.001 Torr, which solidified to a crystalline product of m.p. 113–114°: ^{1}H-NMR ($CDCl_3$) δ 0.21 (s, 12H, $(C\underline{H}_3)_2Si$), 1.42 (m, 6H, 3-H_2, 4-H_2, 5-H_2), 2.65 (m, 2H, 2-H, 6-H); ^{13}C-NMR ($CDCl_3$) δ −0.60 (q, $\underline{C}H_3Si$), 17.78 (s, C-1, C-7), 20.38 (t, C-4), 20.83 (t, C-3, C-5), 50.79 (d, C-2, C-6); mass spectrum (rel. intensity) *m/e* 224 (M^+, 24%), 209 (43), 207 (16), 181 (18), 133 (100), 117 (11), 73 (17); M^+ calc 224.10526, obsd 224.107. (Found: C, 59.28; H, 8.90. Calc for $C_{11}H_{20}OSi_2$: C, 58.87; H, 8.98%.)

2,2,4,4,12,12,14,14 - *Octamethyl* - 3,13 - *diaza* - 2,4,12,14 - *tetrasilaoctacyclo*[14 . 4 . 0 . 0^{1,15} . 0^{3,13} . 0^{5,10} . 0^{5,11} . 0^{6,11} . 0^{15,20}] - *eicosane* (**16**)

To a soln of **15b**, prepared from 1.93 g (9.17 mmol) of **15a** as described above, in 250 ml of ether, 0.29 g (9.05 mmol) of anhyd hydrazine was added and the mixture stirred for 18 h at room temp. The soln was extracted with 50 ml of water, dried over $MgSO_4$, and the solvent was removed *in vacuo*. From the remaining oil, 225 mg (11%) of **16** crystallized as a white solid: m.p. 126–127° (from hexane); ^{1}H-NMR ($CDCl_3$) δ 0.09 and 0.24 (2 s, 12H each, CH_3Si), 1.34 (m, 12H, 7-H_2, 8-H_2, 9-H_2, 17-H_2, 18-H_2, 19-H_2), 2.17 (m, 4H, 6-H, 10-H, 16-H, 20-H); ^{13}C-NMR ($CDCl_3$) δ 0.82 and 2.06 (2 q, $\underline{C}H_3Si$), 8.66 (s, C-1, C-5, C-11, C-15), 20.84 (t, C-8, C-18), 21.32 (t, C-7, C-9, C-17, C-19), 45.40 (d, C-6, C-10, C-16, C-20); mass spectrum (rel. intensity) *m/e* 444 (M^+, 100%), 429 (9), 337 (8), 247 (5), 130 (14), 116 (6), 73 (11), 59 (7); M^+ calc 444.22687, obsd 444.228. (Found: C, 58.72; H, 9.00. Calc for $C_{22}H_{40}N_2Si_4$: C, 59.39; H, 9.06%.)

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