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Synthesis of Some Bridgehead (Trimethylsilyl)polycycloalkanes. Silicon-29 NMR Chemical Shifts and ^{29}Si–^{13}C Coupling Constants

Ernest W. Della* and John Tsanaktsidis

School of Physical Sciences, Flinders University, Bedford Park, South Australia 5042

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A series of polycycloalkanes substituted with the trimethylsilyl group at the bridgehead has been synthesized from the corresponding halide either by lithiation followed by treatment with fluorotrimethylsilane or by exposure of the bromide to (trimethylsilyl)sodium in HMPA. It is found that there is reasonable correlation between the ^{29}Si chemical shift and the state of hybridization of the attached carbon atom. One-bond carbon–silicon coupling is shown to be dependent on the degree of s character of the bridgehead carbon exocyclic orbital. While vicinal coupling between the ^{29}Si nucleus and the non-bridgehead γ carbon atoms appears to be governed by a Karplus expression, the values of $^3J(^{13}\mathrm{C}-^{29}\mathrm{Si})$ involving the bridgehead carbons in the bicyclo[*n*.1.1]alkyl systems are modified significantly by through-space orbital interactions.

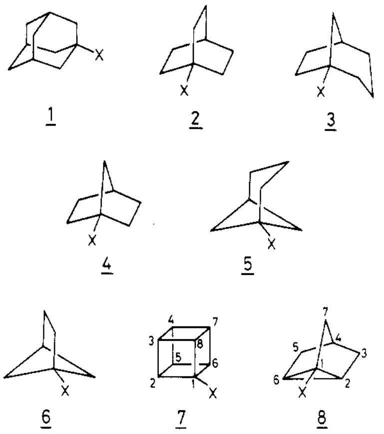
Introduction

The group IV elements represent a unique set because four of the five members have nuclei with spin $^1/_2$, viz., ^{13}C, ^{29}Si, ^{117,119}Sn, and ^{207}Pb, and these, of course, are amenable to nuclear magnetic resonance studies. An enormous amount of NMR spectral information on the carbon-13 nuclide has been accumulated over the past 20 years, in accordance with the important role of carbon in organic chemistry. Recently, however, considerably more attention has been given to NMR investigations of the "less common" group IV nuclei. In view of the widespread occurrence of silicon and its importance both chemically and industrially, an understanding of ^{29}Si NMR parameters is essential because such measurements provide information about bonding and molecular properties. The advent of Fourier transform spectrometers has led to a spectacular growth in silicon-29 NMR studies, and this is reflected in the appearance of several important reviews.[1,2] At this stage most of the data relate to ^{29}Si chemical shifts as well as couplings between ^{29}Si and elements such as hydrogen and fluorine; ^{29}Si–^{13}C coupling information other than that involving directly bonded carbon and silicon is still very limited.

Interestingly, although the ^{29}Si nuclide has a natural abundance of 4.7%, it possesses a relatively long spin–lattice relaxation time and a negative magnetogyric ratio; both of these contribute to greatly reduced signal intensities. Furthermore, as a result of its low natural abundance, ^{29}Si couplings appear as small satellites about the main peak of the coupled atom, thus making it difficult to locate coupling constants of small magnitude.

We recently completed the synthesis of the group of silanes **1a**–**8a** which were required principally for gas-phase acidity studies,[3] and we now wish to report details of the synthesis of these silanes as well as their NMR properties. As noted above, NMR investigations of this kind are important in their own right; at the same time we were interested to compare the results so obtained with those from earlier work on the corresponding stannanes **1**, **2**, **4**, and **7** (X = SnMe$_3$)[4] and ^{13}C-labeled methyl derivatives **1b**–**8b**.[5]

Chart I[a]



[a] **a**, X = SiMe$_3$; **b**, X = ^{13}CH$_3$; **c**, X = ^{1}H; **d**, X = Cl.

Results and Discussion

Syntheses. Despite the existence of a wide variety of methods which can be used to synthesize organosilanes,[6–9] the range of possibilites applicable to the synthesis of bridgehead silanes such as **1a**–**8a** is considerably restricted. Our objective was to devise a route that we hoped could be applied generally to the preparation of all of the substrates **1a**–**8a**, and one procedure that appealed to us in view of our previous experience in the synthesis of the metalated derivatives **1**–**4** and **6** (X = Li)[5] is the displacement reaction involving organometallic carbon nucleophiles and electrophilic silicon derivatives **9** (eq 1).

$$\mathrm{RLi} + \mathrm{Me_3Si}\text{–}\underset{\mathbf{9}}{\mathrm{X}} \rightarrow \mathrm{RSiMe_3} + \mathrm{LiX} \qquad (1)$$

Although chlorotrimethylsilane (Me$_3$SiCl) has been used extensively in coupling reactions of this type, West and Gornowicz[10] observed that Me$_3$SiCl is unsuitable for use

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(1) Marsmann, H. *NMR: Basic Princ. Prog.* **1981,** *17.*

(2) Williams, E. A. *Annu. Rep. NMR Spectrosc.* **1983,** *15,* 235–289.

(3) Damrauer, R.; Della, E. W.; DePuy, C. H.; Tsanaktsidis, J., work in progress.

(4) Della, E. W.; Patney, H. K. *Aust. J. Chem.* **1979,** *32,* 2243.

(5) Della, E. W.; Pigou, P. E. *J. Am. Chem. Soc.* **1984,** *106,* 1085.

(6) Armitage, D. A. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Store, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 2, pp 20–57 for references.

(7) Fleming, I. In *Comprehensive Organic Chemistry*; Barton, D. H. R., Ollis, Eds.; Pergamon: New York, 1979; Vol. 3, pp 608 for references.

(8) Yoshide, J.; Muraki, K.; Funahaski, H.; Keivabate, N. *J. Org. Chem.* **1986,** *57,* 3996 and ref 3–8 therein.

(9) Calas, R.; Dunogues, J. *J. Organomet. Chem. Lib.* **1976,** *2,* 277.

(10) (a) West, R.; Gornowicz, G. A. *J. Organomet. Chem.* **1971,** *28,* 25. (b) Gornowicz, G. A.; West, R. *J. Am. Chem. Soc.* **1968,** *90,* 4478.

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Table I. Conversion of the Bridgehead Chlorides into the Silanes

$RCl \rightarrow RLi \rightarrow RSiMe_3$

substr	time, h	temp, °C	RLi	$RSiMe_3$	yield (%)
1d	5	80	**1** (X = Li)[a]	**1a**	22[b]
2d	3	80	**3** (X = Li)	**2a**	49 (63[c])
3d	3	80	**2** (X = Li)	**3a**	52[b]
4d	3	80	**4** (X = Li)	**4a**	84
5d	8	65–80	**5** (X = Li)	NRO[d]	
6d	2–3	55	**6** (X = Li)	**6a**	39[b] (69[c])

[a] TMEDA added. [b] Isolated yield after preparative GC. [c] NMR/GC yield. [d] No reaction observed; starting material (**5d**) was recovered.

with tertiary reagents such as *tert*-butyllithium. In these cases coupling is unfavorable presumably as a result of increased steric hindrance to substitution that allows a competing metalation process to dominate. At the same time, however, West and Gornowicz[10] showed that other derivatives of **9**, e.g., X = F or OMe, function as excellent alternative silylating agents. Accordingly, we chose to use fluorotrimethylsilane, **9** (X = F), because it is readily available.[11] Interestingly, the substitution process represented in (eq 1) employing Me_3SiF is believed to proceed by frontside displacement, fostered by favorable interaction between the frontier orbitals of the reactants involving the HOMO of the carbanionic species and the LUMO of the fluorosilane.[12]

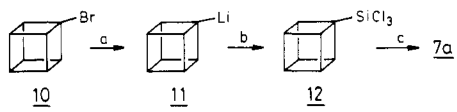
We find that lithiation of the bridgehead chlorides **1d**–**4d** and **6d** in boiling hexane/cyclohexane is facilitated by ultrasonic irradiation and that under these conditions metalation is complete in 2–5 h (Table I). Addition of Me_3SiF to the alkyllithium leads to rapid production of the corresponding silane, and, as the data in Table I demonstrates, modest yields of the silanes are obtained.

Several features of these syntheses are noteworthy. Me_3SiF is inert to lithium under these conditions, and it is therefore not necessary to remove the finely divided metal. Unlike the other bridgehead lithio derivatives 1-adamantyllithium is highly insoluble in hydrocarbon solvents[13] and requires the presence of TMEDA to enhance its solubility. Even then, however, the conversion of adamantyllithium to 1-(trimethylsilyl)adamantane (**1a**) is poor, with adamantane as the main contaminant. Reduction is much less of a problem in the case of the other silanes and yields are better, but the need to commit these to preparative GC in order to achieve the level of purity required for the gas-phase studies leads to significant losses of silane. The synthesis of **1a** has been reported previously by Weber and his associates[14] via a Wurtz coupling process between 1-chloroadamantane and Me_3SiNa (12% yield) and more recently by Sasaki and co-workers[15] (50% yield) by treatment of 1,3-dichloroadamantane with sodium in HMPA in the presence of the silylating agents **9** (X = H, $SiMe_3$, and $OSiMe_3$). The occurrence of 1,3-dehydroadamantane as an intermediate in the latter process has been suggested.[15] Comparable yields of the silane **2a** can be obtained[16] by treatment of 1-bromobicyclo[2.2.2]octane (**2**, X = Br) with Me_3SiNa following the method described by Shippey and Dervan (eq 2).[17] Reduction, however, is a significant competing process in this transformation.

$$RBr + Me_3Si\text{-}Na \rightarrow R\text{-}Me_3Si + NaBr \quad (2)$$

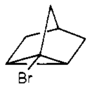
Surprisingly, all attempts to lithiate 1-chlorobicyclo[3.1.1]heptane (**5d**) met with failure despite the fact that the closely related chlorides **4d** and **6d** metalate readily. 1-Bromobicyclo[3.1.1]heptane (**5**, X = Br) was also observed to be inert to lithium, and, in view of the difficulty we had experienced previously[5] in generating cubyllithium from bromocubane, we decided to investigate whether the Shippey–Dervan procedure (eq 2) could be applied to the synthesis of the silanes **5a**, **7a**, and **8a** from their respective bromides. In the event, exposure of bromocubane (**10**) and 1-bromonortricyclene (**13**) to Me_3SiNa in HMPA gave the silanes **7a** and **8a**,[18] respectively, in acceptable yield (31%) after preparative GC. In an alternative synthesis of **7a**, we find that bromocubane undergoes metal–halogen exchange with *tert*-butyllithium quite readily and that the derived lithiocubane **11** is best silylated with silicon tetrachloride, giving the trichlorosilane **12** (Scheme I). In situ replacement of the chlorine atoms with methyl groups is effected by exposure of **12** to excess methylmagnesium halide. Overall, the process **10** → **11** → **12** → **7a** occurs in 34% yield. Interestingly, Eaton and his colleagues[20] have found that 1,4-bis(trimethylsilyl)cubanes are produced from metalation of amide-activated cubane with lithium tetramethylpiperidide followed by treatment with 2 equiv of chlorotrimethylsilane.

Scheme I[a]



[a] a, Bu-*t*-Li; b, $SiCl_4$; c, MeMgCl.

Unfortunately, treatment of 1-bromobicyclo[3.1.1]heptane (**5**, X = Br) with Me_3SiNa in HMPA failed to produce 1-(trimethylsilyl)bicyclo[3.1.1]heptane (**5a**); only complex mixtures of silicon-containing compounds were detected. Eventually, **5a** was prepared, albeit in low yield (preparative GC), from the dibromide **14** by treatment with sodium in HMPA containing trimethylsilane under the conditions employed by Sasaki[15] for the synthesis of **1a**. The mechanism of this reaction is uncertain, and whether [3.1.1]propellane is an intermediate in this case is impossible to say.



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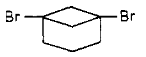

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Chemical Shifts. Carbon-13 and silicon-29 chemical shifts of the silanes **1a**–**8a** are assembled in Table II. Particular attention is drawn to the silicon-29 data. Despite the existence of quite an extensive tabulation of ^{29}Si shifts, a satisfactory theoretical description of the principles governing such shifts is not yet available, and indeed, the relative contributions of the diamagnetic and paramagnetic terms are controversial. Consequently, exami-

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(11) Della, E. W.; Tsanaktsidis, J. *Synthesis*, in press.

(12) (a) Suslick, K. S.; Johnson, R. E. *J. Am. Chem. Soc.* **1984**, *106*, 6856. (b) Suslick, K. S. *Adv. Organomet. Chem.* **1986**, *25*, 73 and references therein.

(13) Corriu, R. J. P.; Guerin, C.; Moreau, J. J. E. *Top. Stereochem.* **1984**, *15*, 43 and references therein.

(14) Pai, Y.-M.; Wanek, E.; Weber, W. P. *J. Organomet. Chem.* **1984**, *270*, 271.

(15) Sasaki, T.; Shimuzu, K.; Ohno, M. *Synth. Commun.* **1984**, *14*, 853.

(16) Adcock, W.; Gangodawila, H.; Kok, G. B.; Iyer, V. S.; Kitching, W.; Drew, G. M.; Young, D. *Organometallics* **1987**, *6*, 156.

(17) Shippey, M. A.; Dervan, P. B. *J. Org. Chem.* **1977**, *42*, 2654.

(18) The silane **8c** has been synthesized previously[19] from treatment of nortricyclylsodium (**8**, X = Na) with Me_3SiCl. Evidently steric hindrance is not a serious problem in this case.

(19) Hartmann, J.; Schlosser, M. *Helv. Chim. Acta* **1976**, *59*, 453.

(20) Eaton, P. E.; Higuchi, H.; Millikan, R. *Tetrahedron Lett.* **1987**, *28*, 1055.

Table II. Carbon-13 and Silicon-29 Chemical Shifts[a,b] in the Trimethylsilanes 1a–8a

compd	C1	C2	C3	C4	C5	C6	C7	C8	C_{Me}	^{29}Si
1a[c]	21.13 (−7.62)	37.22[d] (−1.02)	27.90 (−0.85)	37.81[d] (−0.43)					−5.58	3.89
2a[e]	15.60 (−8.40)	25.84 (−0.16)	26.00 (0.00)	23.89 (−0.11)					−4.77	4.57
3a	30.41 (−5.39)	33.53 (0.13)	20.15 (0.55)	33.26 (−0.14)	36.51 (0.71)	30.77 (1.37)	31.15 (1.75)	41.12 (1.02)	−4.12	4.03
4a	33.54 (−3.06)	32.02 (1.98)	30.93 (0.93)	38.30 (1.70)			40.74 (2.14)		−3.20	2.69
5a	31.38 (−2.75)	30.41 (1.05)	16.37 (0.40)	29.81 (0.45)	34.31 (0.18)	33.22 (0.02)			−4.64	0.02
6a	41.53 (2.03)	29.04 (2.74)	27.63 (1.33)	41.50 (2.00)	40.20 (1.20)				−3.36	−2.55
7a	46.1 (−1.30)	46.64 (−1.47)	48.27 (0.16)	48.27 (0.16)					−4.82	−7.41
8a[f]	6.64 (−3.66)	14.96 (4.66)	33.71 (0.31)	(30.34) (0.44)			35.00 (1.60)		−2.03	0.29

[a] ±0.02 ppm in $CDCl_3$. [b] Values in parentheses are the substituent-induced chemical shifts (SCS). [c] For literature values of ^{13}C shifts see Sasaki and co-workers.[15] [d] May be interchanged. [e] For literature values see Adcock and co-workers;[16] the C2 and C3 assignments have been reversed. [f] For literature values of ^{13}C shifts see Harmann and Schlosser;[19] the C4 and C7 assignments have been reversed.

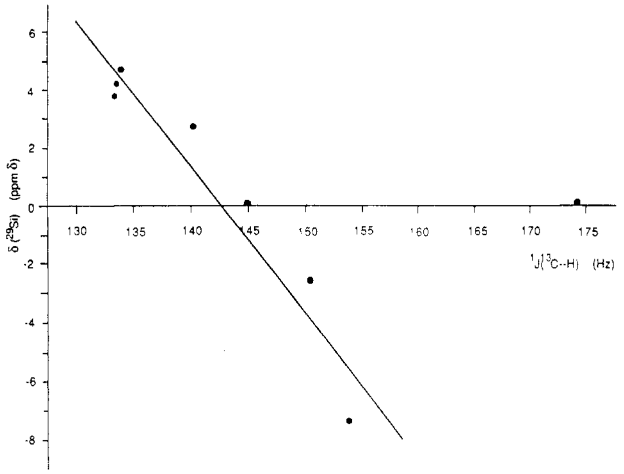

Figure 1. Silicon-29 chemical shifts versus s character of the attached carbon atom.

Table III. ^{13}C–^{29}Si Coupling Constants, $^{n}J(C\text{–}Si)$,[a] in the Trimethylsilanes 1a–8a

compd	$^{1}J^{b}$	^{2}J	$^{3}J(\phi)^{c}$	^{4}J	$^{1}J_{C_{Me}}$
1a	58.89 (133.4)	ncd[d]	4.61 (180°)	ncd	49.80
2a	60.42 (134.3)	ncd	5.08 (180°)	ncd	49.98
3a	59.76 (133.7)	ncd (C2) ncd (C7) ncd (C8)	5.35 (C3) (178°) 4.98 (C5) (165°) 4.98 (C6) (149°)	ncd	50.00
4a	61.70 (140.1)	1.63 (C2) ncd (C7)	4.90 (C3) (161°) 6.22 (C4) (180°)		50.30
5a	61.29 (144.9)	ncd (C2) ncd (C6)	4.09 (C3) (169°) 7.87 (C5) (144°)	ncd	49.92
6a	62.89 (150.5)	3.22 (C2) ncd (C5)	4.04 (C3) (180°) 10.46 (C4) (159°)		50.46
7a	no[d] (153.8)	2.44 (C2)	3.32 (C3) (135°)	ncd	50.57
8a	63.87 (174.3)	nc (C2) ncd (C7)	ncd (C3) (147°) 3.23 (C4) (164°)		51.78

[a] In Hz, ±0.02 Hz. [b] Numbers in parentheses refer to the values of $^{1}J(^{13}C\text{–}H)$ of the bridgehead carbon in the parent hydrocarbon **1c–8c** (data of Della, Cotsaris, and Hine[28]). [c] ϕ = SiCCC dihedral angle in the parent hydrocarbon (AM1 optimized geometry). [d] ncd = no coupling detected. no = not observed.

nation of model substrates such as **1a–8a** may prove to be of assistance in the development of theory.

The silanes **1a–8a** are arranged in order of increasing a character of the bridgehead carbon exocyclic bonding orbital, and it can be seen from Table II that, with the exception of the nortricyclene derivative **8a**, there is a reasonable correlation between the ^{29}Si shift and the hybridization of the carbon atom to which the silicon is attached. Figure 1 shows graphically the variation of δ_{Si} with the one-bond coupling constant, $^{1}J(C\text{–}H)$, of the parent hydrocarbon. Thus, in the larger, relatively unstrained molecules, viz., **1a–3a**, the silicon-29 signal occurs downfield from that in TMS, whereas in the more highly constrained systems, e.g., (trimethylsilyl)cubane (**7a**), it is located considerably upfield. It is interesting to compare these data with those in the corresponding methyl-substituted hydrocarbons **1b–8b** in which the ^{13}C shifts were observed[5] to occur randomly; the conclusion to be drawn regarding the types of compounds under study here is that there is little correspondence between the ^{29}Si and ^{13}C chemical shifts. The literature contains conflicting reports of the possible parallelism between ^{29}Si and ^{13}C shifts in analogous compounds. Harris and his colleagues[21] on the one hand suggest that there is no evidence for the existence of such a correlation. Mitchell[22] and Olah and Field,[23] however, believe that the results of their studies demonstrate that the type of structural features which influence ^{13}C shifts also have a large bearing on ^{29}Si shifts.

Carbon–Silicon Coupling Constants. Inspection of the coupling constants assembled in Table III shows that, of the one-bond couplings, viz., those between ^{29}Si and the methyl carbons, $^{1}J(Si\text{–}C_{Me})$, and those involving ^{29}Si and the bridgehead carbons, $^{1}J(Si\text{–}C1)$, the values of $^{1}J(^{29}Si\text{–}^{13}C_{Me})$ are compressed into a narrow range (49.8–51.8 Hz) scattered about the value (50.3 Hz) reported[24] for $^{1}J(Si\text{–}C_{Me})$ in tetramethylsilane. In contrast, coupling between silicon and the attached bridgehead carbon in **1a–8a**, while showing only a slightly larger spread, increases progressively along the series and shows a close correlation with values of $^{1}J(C\text{–}H)$ in the parent hydrocarbons **1c–8c**. The apparent dependence of $^{1}J(Si\text{–}C1)$ on the state of hybridization of the carbon atom agrees with previous experimental observations[25] and is also supported by calculation.[26] On the basis of INDO MO results, for example,

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[21] Harris, R. K.; Kimber, B. J. *J. Magn. Reson.* **1975**, *17*, 174.

[22] Mitchell, T. N. *J. Organomet. Chem.* **1983**, *255*, 279.

[23] Olah, G. A.; Field, L. D. *Organometallics* **1982**, *1*, 1485.

[24] Levy, G. C.; White, D. M.; Cargioli, J. D. *J. Magn Reson.* **1972**, *8*, 280.

[25] See (a) ref 2, pp 276–277, and (b) Harris, R. K.; Mann, B. E. *NMR and the Periodic Table*; Academic: New York, 1978 for leading references.

both Beer and Grinter[26a] and Summerhays and Deprez[26b] have shown that the Fermi contact term is the predominant contributor to the mechanism of directly bonded Si–C coupling, and hence the magnitude of ^{1}J(Si–C1) is a reflection of the s character of the carbon bonding orbital. It is noteworthy that no such correlation was found for ^{1}J(C–C) in the methyl analogues **1b**–**8b**[5] and that the stannanes **1**, **2**, **4**, and **7** (X = SnMe$_3$) behave differently again.[4] In the latter, the one-bond Sn–C1 couplings fall into a narrow range, whereas the ^{1}J(^{117,119}Sn–^{13}C$_{Me}$) values show significant spread.

As mentioned earlier, the detection of small Si–C couplings is difficult and it is not surprising to find that the literature dealing with experimentally determined long-range J(Si–C) values is not extensive. In accordance with this, only a limited number of two-bond ^{29}Si–^{13}C coupling constants in **1a**–**8a** were observed (Table III). However, vicinal Si–C coupling is readily detectable in these compounds and, indeed, is quite substantial in a number of cases. This is understandable if the magnitude of ^{3}J(Si–C) is governed by a Karplus-type expression as found for ^{3}J(Si–H),[25] ^{3}J(C–C),[5] and ^{3}J(Sn–C).[4] The relevant dihedral angles in the silanes **1a**–**8a** lie between 135° and 180°, and it can be seen from Table III that, in general terms, the coupling constants between ^{29}Si and the γ-carbon atoms in these systems range from 3.2 Hz in **7a** (SiCCC dihedral angle 135°) to 5.35 Hz in **3a** (dihedral angle 178°). Notable exceptions to this trend include couplings to the bridgehead γ-carbons in the bicycloalkyl silanes **4a**–**6a** in which the values of ^{3}J(Si–C) are somewhat enhanced. In (trimethylsilyl)bicyclo[2.2.1]heptane (**4a**), for instance, ^{3}J(^{29}Si–^{13}C bridgehead) is 6.22 Hz, and in the related species **5a** and **6a** the corresponding values are 7.87 and 10.46 Hz, respectively. Actually, the vicinal couplings in **5a** and **6a** are smaller than anticipated if allowance is made for the possibility that spin information can be transmitted via two three-bond pathways in these systems. The reduced values of ^{3}J(Si–C) in **5a** and **6a** may be attributed to the fact the couplings are angular dependent and simply reflect the magnitude of the relevant dihedral angles. An alternative explanation is that through-space contributions to coupling are significant in these compounds and that they oppose contributions transmitted through the σ framework. Through-space interactions are especially relevant in systems such as **5a** and **6a**, in which the proximity of the bridgehead carbons is conducive to favorable overlap of the rear lobes of the exocyclic bonding orbitals. MO calculations suggest that these effects account both for the enhancement of ^{13}C–^{19}F vicinal couplings[28] in bridgehead fluorides (where through-space and through-bond effects reinforce each other) and the decrease in three-bond ^{13}C–^{13}C couplings[5] (in which the effects are opposed). Unfortunately, we were unable to complement our experimental data with INDO calculations in the case of the silanes **1a**–**8a** because our FINITE program is restricted to elements in the first row.

Experimental Section

Routine ^{1}H NMR spectra were recorded on a Varian EM360A spectrometer, and precise ^{1}H spectra and all ^{13}C and ^{29}Si NMR spectra were measured on a JEOL FX90Q instrument operating at 89.56, 22.53, and 17.76 MHz, respectively. Unless otherwise specified, samples were dissolved in CDCl$_3$ which also served as internal lock; chemical shifts are referenced to TMS. For chemical shift measurements, ^{13}C spectra were normally run at 4000-Hz spectral width with 8K data points, corresponding to 0.04 ppm digital resolution. Accurate measurement of coupling constants was undertaken by running spectra at 200–400 Hz with 16K/32K data points, giving 0.02-Hz digital resolution. Mass spectra were obtained on an AEI MS30 spectrometer. Analytical GC was performed on a Perkin-Elmer Sigma 3B gas chromatograph and preparative GC on a Shimadzu GC-9A instrument using SE-30 as stationary phase. Microanalyses were performed by the Australian Microanalytical Service, Melbourne, Australia. 1-Chloroadamantane, 1-chlorobicyclo[2.2.2]octane, 1-chlorobicyclo[2.2.1]heptane, 1-chlorobicyclo[2.1.1]hexane, and bromocubane are known compounds and, together with 1-chlorobicyclo[3.2.1]octane, 1-chlorobicyclo[3.1.1]heptane, 1-bromobicyclo[3.1.1]heptane, and 1,5-dibromobicyclo[3.1.1]heptane, were synthesized as described.[29] 1-Bromonortricyclene was prepared from 1-bromobicyclo[2.2.1]heptan-2-one as reported.[5]

1-(Trimethylsilyl)adamantane (1a). A mixture of 1-chloroadamantane (**1d**) (2 g, 11.7 mmol) and lithium shot (2% Na, 1.5 g, 216 mmol) in dry cyclohexane (80 mL) was sonicated at reflux for 5 h. The resultant mixture was cooled to 0 °C and charged with fluorotrimethylsilane (5 mL) and *N,N,N′,N′*-tetramethylethylenediamine (3 mL). The vessel was sealed and the mixture stirred at room temperature for 90 h. Filtration of this mixture under nitrogen afforded a colorless filtrate that was washed with saturated ammonium chloride solution (50 mL) and water (3 × 100 mL) and then dried (MgSO$_4$). The solution was concentrated through a Vigreux column and the residue sublimed (75 °C (0.1 mm)) affording a 56:44 mixture (1.15 g) of the silane **1a** and adamantane. Purification by preparative gas chromatography furnished the pure silane **1a** (0.54 g, 22%): mp 47.5–48 °C (lit.[14] 48–49 °C); ^{1}H NMR (CDCl$_3$) δ −0.3 (9 H, s, CH$_3$Si), 1.22–1.89 (15 H, m, ring protons); ^{13}C NMR (CDCl$_3$) δ −5.58 (CH$_3$Si), 21.13 (C1), 27.90 (C3,5,7), 37.22 (C2,8,9 or C4,6,10), 37.81 (C4,6,10 or C2,8,9); ^{29}Si NMR (CDCl$_3$) δ 3.89.

1-(Trimethylsilyl)bicyclo[2.2.2]octane (2a). A mixture of 1-chlorobicyclo[2.2.2]octane (**2d**) (820 g, 5.67 mmol), lithium shot (2% Na, 0.5 g, 72 mmol), and dry cyclohexane (45 mL) was sonicated under reflux for 3 h in an argon atmosphere. The cooled (0 °C) mixture was treated with *N,N,N′,N′*-tetramethylethylenediamine (2.8 mL) and fluorotrimethylsilane (2 mL), then sealed, and stirred at room temperature for 24 h. Filtration of the resultant mixture gave a colorless filtrate that was washed successively with saturated ammonium chloride solution (50 mL) and water (3 × 50 mL) and then dried (MgSO$_4$). Evaporation of the solvent and distillation of the residue afforded the silane **2a** as a colorless solid (520 mg, 49%): mp 61–63 °C (lit.[16] 67–68 °C); ^{1}H NMR (CFCl$_3$) δ −0.19 (9 H, s, CH$_3$Si), 1.45 (13 H, br s, ring protons); ^{13}C NMR (CDCl$_3$) δ −4.77 (CH$_3$Si), 15.60 (C1), 23.89 (C4), 25.84 (C2,6,7), 26.00 (C3,5,7); ^{29}Si NMR (CDCl$_3$) δ 4.57.

1-(Trimethylsilyl)bicyclo[3.2.1]octane (3a). A mixture of 1-chlorobicyclo[3.2.1]octane (**3d**) (2 g, 13.8 mmol) and lithium shot (2% Na, 1.0 g, 144 mmol) in dry cyclohexane (80 mL) at reflux under an argon atmosphere was sonicated for 2.5 h, then cooled, and charged with fluorotrimethylsilane (3 mL). The reaction vessel was sealed and heated with stirring at 50 °C for 18 h. The cooled mixture was filtered and the filtrate washed with a portion of saturated ammonium chloride solution, then dessicated (MgSO$_4$), and concentrated by distillation through a Vigreux column. The residue was flash distilled at high vacuum (0.01 mm) to give two fractions that upon preparative gas chromatography gave the silane **3a** as a colorless liquid (1.3 g, 52%): ^{1}H NMR (CDCl$_3$) δ −0.08 (9 H, 5, CH$_3$Si), 1.20–1.63 (12 H, m, ring protons), 2.07–2.33 (1 H, br s, bridgehead proton); ^{13}C NMR (CFCl$_3$) δ −4.12 (CH$_3$Si), 20.15 (C3), 30.41 (C1), 30.77 (C6), 31.15 (C7), 33.26 (C4), 33.53 (C2), 36.51 (C5), 41.12 (C8); ^{29}Si NMR (CDCl$_3$) δ 4.03. Anal. Calcd for C$_{11}$H$_{22}$Si: C, 72.4; H, 12.2. Found: C, 72.0; H, 11.9.

1-(Trimethylsilyl)bicyclo[2.2.1]heptane (4a). To a sonicated mixture of lithium shot (2% Na, 0.5 g, 72 mmol) in dry cyclohexane (40 mL) at reflux, under an argon atmosphere, was added

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(26) (a) Beer, M. D.; Grinter, R. *J. Magn. Reson.* **1978**, *31*, 187. (b) Summerhays, K. D.; Deprez, D. A. *J. Organomet. Chem.* **1976**, *118*, 19. (c) Kovačevič, K.; Makoič, Z. B. *J. Mol. Struct.* **1973**, *17*, 203. (d) Kovačevič, K.; Krmpotic, K.; Maksič, Z. B. *Inorg. Chem.* **1977**, *16*, 1421. (e) Jansen, H. B.; Meeuwis, A.; Pyykko, P. *Chem. Phys.* **1979**, *38*, 173.

(27) Grignon-Dubois, M.; Laguerre, M.; Barbe, B.; Petraud, M. *Organometallics* **1984**, *3*, 359, 1060.

(28) Della, E. W.; Cotsaris, E.; Hine, P. T. *J. Am. Chem. Soc.* **1981**, *103*, 4131.

(29) Della, E. W.; Tsanaktsidis, J. *J. Org. Chem.*, manuscript in preparation.

a solution of 1-chlorobicyclo[2.2.1]heptane (**4d**) (1.0 g, 7.66 mmol) in dry cyclohexane (4 mL) in a steady stream. The resultant mixture was sonicated under reflux for a further 3 h, then cooled and charged with fluorotrimethylsilane (3 mL), sealed, and allowed to stir at 35–40 °C for 19 h. The cooled mixture was then centrifuged and the supernatant washed with an aqueous solution of saturated ammonium chloride (2 × 25 mL) and then dried ($MgSO_4$) and concentrated by distillation through a Vigreux column. Kugelrohr distillation of the residue gave the silane **4a** as a colorless liquid (1.1 g, 86%): bp 100–105 °C (30 mm) which was contaminated with cyclohexane (~2%, ^{1}H NMR); ^{1}H NMR ($CFCl_3$) δ 0.03 (9 H, s, CH_3Si), 0.86–1.8 (10 H, m, ring protons), 2.15–2.57 (1 H, br s, bridgehead proton); ^{13}C NMR ($CDCl_3$) δ -3.20 CH_3Si), 30.93 (C3,5), 32.02 (C2,6), 33.54 (C1), 38.30 (C4), 40.74 (C7); ^{29}Si NMR ($CDCl_3$) δ 2.69. Preparative GC yielded a pure sample. Accurate mass ($C_{10}H_{20}Si$): M calcd 168.1334, found 168.1326.

1-(Trimethylsilyl)bicyclo[3.1.1]heptane (5a). A dry two-necked round-bottom flask equipped with a dry ice condenser, nitrogen inlet, magnetic stirring bar, and a rubber septum was charged with sodium metal (2.5 g, 108 mmol) and dry hexamethylphosphoramide (40 mL) and trimethylsilane (5 mL, 43 mmol, 2.6 equiv). A solution of 1.5-dibromobicyclo[3.1.1]heptane[29] (**14**) (4.15 g, 16.35 mmol) in dry hexamethylphosphoramide (5 mL) and dry diethyl ether (15 mL) was added dropwise over about 2 h such that the blue color of the mixture persisted. The resultant mixture was allowed to stir at room temperature overnight, before being separated from the excess sodium metal, and was then diluted with pentane (150 mL) and carefully treated with glacial acetic acid until it was decolorized. The solution was then washed with water (3 × 100 mL) and the washings back extracted with pentane (50 mL). The combined organic portions were dried ($MgSO_4$) and concentrated by distillation through a packed column, and the residue was flash distilled (20 °C (0.01 mm)). Preparative gas chromatography of the distillate afforded the silane **5a** as a colorless liquid (270 mg, 10%): ^{1}H NMR (CCl_4) δ -0.2 (9 H, s, CH_3Si), 0.96–1.38 (2 H, m), 1.56–2.49 (8 H, m), 2.27–2.54 (1 H, m); ^{13}C NMR ($CDCl_3$) δ -4.64 (CH_3Si), 16.37 (C3), 29.81 (C4), 30.41 (C2), 31.38 (C1), 33.22 (C6,7), 34.31 (C5); ^{29}Si NMR (CCl_4) δ 0.02. Anal. Calcd for $C_{10}H_{20}Si$: C, 71.3; H, 12.0. Found: C, 71.0; H, 11.9.

1-(Trimethylsilyl)bicyclo[2.1.1]hexane (6a). A mixture of 1-chlorobicyclo[2.1.1]hexane (**6d**) (2 g, 17 mmol) and lithium shot (2% Na, 1.2 g, 170 mmol) in dry cyclohexane (60 mL) was heated at 55 °C with ultrasonic irradiation for 2 h under an argon atmosphere. The mixture was cooled, charged with fluorotrimethylsilane (4 mL), sealed, and stirred at 60 °C for 4 h and then at room temperature overnight. The filtrate was washed with a solution of saturated ammonium chloride (80 mL) and then with brine (80 mL) and dried ($MgSO_4$). Concentration by distillation through a packed column and distillation (90 °C (40 mm)) of the residue at atmospheric pressure afforded a colorless distillate (2.3 g) which was shown by ^{1}H NMR to be a 1:2 mixture of cyclohexane and the silane **6a**. Preparative gas chromatography gave pure silane **6a** (1 g, 38%): ^{1}H NMR ($CFCl_3$) δ -0.13 (9 H, s, CH_3Si), 0.59–0.97 (2 H, m, ring protons), 1.60–1.77 (6 H, m, ring protons), 2.50–2.73 (1 H, br s, bridgehead proton); ^{13}C NMR ($CDCl_3$) δ -3.36 (CH_3Si), 27.63 (C3), 29.04 (C2), 40.20 (C5,6), 41.50 (C4), 41.53 (C1); ^{29}Si NMR ($CDCl_3$) δ -2.55. Accurate mass ($C_9H_{18}Si$): M calcd 154.1178, found 154.1184.

(Trimethylsilyl)cubane (7a). Method A. To a stirred suspension of sodium methoxide (3.9 g, 72 mmol) in dry hexamethylphosphoramide (60 mL) at room temperature under a nitrogen atmosphere was added hexamethyldisilane (20 mL, 93 mmol). A deep red solution resulted. The mixture was let stand at 1.5 h at room temperature and then heated to 60 °C for 30 min before being cooled (0 °C). Bromocubane (**10**) (2.5 g, 13.6 mmol) in hexamethylphosphoramide (3 mL) was then added dropwise to this mixture over 15 min. The resultant mixture was allowed to stir at room temperature overnight. Workup was effected by carefully quenching the cooled (0 °C) solution with saturated ammonium chloride (20 mL) followed by dilution with water (100 mL), extraction with pentane (2 × 50 mL), and back-extraction with water (3 × 50 mL). The combined organic extracts were dried ($MgSO_4$) and concentration by distillation through a Vigreux column. The residue was flash distilled and the distillate subjected to preparative gas chromatography furnishing the pure silane **7a** as a colorless liquid (750 mg, 31%): ^{1}H NMR ($CDCl_3$) δ 0.33 (9 H, s, CH_3Si), 3.62–4.22 (7 H, m, ring protons); ^{13}C NMR ($CDCl_3$) δ -4.82 (CH_3Si), 46.64 (C2,4.6), 46.81 (C1), 48.27 (C3,5,7,8); ^{29}Si NMR ($CDCl_3$) δ -7.4. Accurate mass ($C_{11}H_{18}Si$): M calcd 176.1021, found 176.1030.

Method B. A solution of bromocubane (0.5 g, 2.7 mmol) in dry diethyl ether (10 mL) at -78 °C was treated with a solution of *tert*-butyllithium (3.8 mL of a 1.6 M solution in pentane, 6.1 mmol, 2.5 equiv) in a dropwise fashion over 5 min. The resultant mixture was allowed to stir between -60 and -50 °C for 4 h by which time a white precipitate had formed. The mixture was then cooled to -78 °C and treated with tetrachlorosilane (0.8 mL, 2.6 equiv) in one portion and the solution allowed to warm to room temperature. After 30 min methylmagnesium chloride (11 mL, 3 M in THF) and dry ether (20 mL) was added and the mixture stirred under reflux overnight. Standard workup gave a residue which upon chromatography through a short column of silica gel (pentane elution) and careful distillation (Kugelrohr, 90–100 °C (20 mm)) gave a middle fraction (200 mg) which was shown by GC to be 80% pure, corresponding to an overall yield of ca. 34%. A pure sample was obtained by preparative GC as described above.

1-(Trimethylsilyl)nortricyclene (8a). 1-Bromonortricyclene (**13**) (2.3 g, 13.3 mmol) was treated in the manner described above for the preparation of **7a** from **10**. Preparative gas chromatography of the product furnished the silane **8a** (680 g, 31%) as a colorless liquid whose spectral data were in accord with those published:[19] ^{1}H NMR ($CDCl_3$) δ -0.003 (9 H, s, CH_3Si), 0.87–1.33 (8 H, m), 1.87–2.1 (1 H, br s); ^{13}C NMR ($CDCl_3$) δ -2.03 (CH_3Si), 6.64 (C1), 14.96 (C2,6), 30.34 (C4), 33.71 (C3,5), 35.01 (C7); ^{29}Si NMR ($CDCl_3$) δ 0.29.

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Registry No. **1a**, 66791-07-9; **1d**, 935-56-8; **2a**, 105253-32-5; **2d**, 2064-03-1; **3a**, 113451-40-4; **3d**, 35589-14-1; **4a**, 113451-41-5; **4d**, 765-67-3; **5a**, 113451-42-6; **5d**, 113451-45-9; **6a**, 113451-43-7; **6d**, 22907-75-1; **7a**, 113451-44-8; **8a**, 59518-11-5; **10**, 59346-69-9; **13**, 31991-53-4; ^{29}Si, 14304-87-1; fluorotrimethylsilane, 420-56-4; 1,5-dibromobicyclo[3.1.1]heptane, 75328-56-2; hexamethyldisilane, 1450-14-2.