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UNUSUALLY LARGE DESHIELDING OF ^{29}Si IN 7-SILANORBORNADIENES AND RELATED COMPOUNDS[1)]

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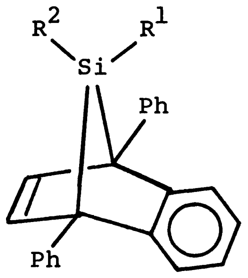
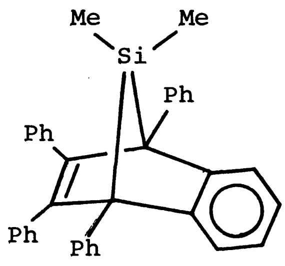
Bridge silicon atoms in [2.2.1] bicyclic systems display unusually large deshielding in ^{29}Si NMR. An explanation is given to account for the phenomena.

Recently we have prepared several derivatives of the so far elusive 2,3-benzo-1,4-diphenyl-7-silanorbornadienes (I), which serve as efficient silylene generators.[2)] The reaction of I is interesting in reference to the silylene chemistry and in fact we have found a novel silylene to disilene rearrangement in the reaction of $Me_3SiMe_2SiMeSi$:.[2)] However, these compounds are also interesting in the study of the structures, since 7-heteroatom-norbornadienes display sometimes unusual properties. In this paper, we will describe the extraordinary deshielding of ^{29}Si in 7-silanorbornadienes and related compounds.

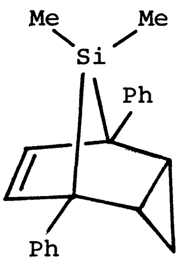
Table 1 lists ^{29}Si NMR data for five derivatives of 2,3-benzo-1,4-diphenyl-7-silanorbornadiene (I) and three other compounds, 2,3-benzo-1,4,5,6-tetraphenyl-7,7-dimethyl-7-silanorbornadiene (II),[3)] 1,5-diphenyl-8,8-dimethyl-8-silatricyclo-[3.2.1.0^{2,4}]oct-6-ene (III),[4)] and 3,3,10,10-tetramethyl-3,10-disilatricyclo-[5.2.1.0^{2,6}]deca-4,8-diene (IV).



(I)

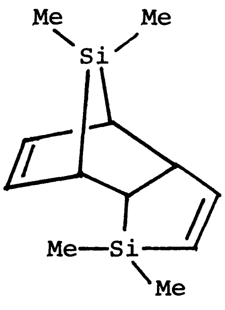


(II)



(III)

a : $R^1 = R^2 =$ Me
b : $R^1 =$ Me ; $R^2 = SiMe_3$
c : $R^1 =$ Me; $R^2 = SiMe_2Ph$
d : $R^1 =$Me; $R^2 = SiMe_2SiMe_3$
e : $R^1 = R^2 = SiMe_3$



(IV)

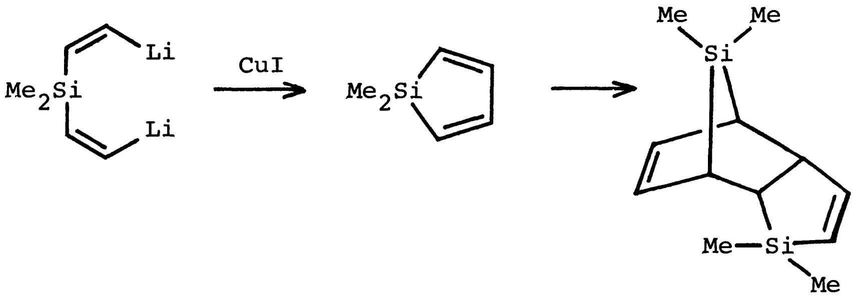
Table 1. ^{29}Si NMR Chemical Shifts of Some Cage Compounds (δ, ppm relative to Me_4Si)[a, b]

Compound	(Ia)	(Ib)	(Ic)	(Id)	(Ie)	(II)	(III)	(IV)
bridge Si	76.9	82.5	80.2	85.7	97.7	67.7	58.5	40.8
other Si		-19.3	-22.1	-47.6 -15.5	-18.7 -17.5			17.8

[a] In $CDCl_3$. [b] Spectra were taken with a JEOL FX-90Q spectrometer.

The preparation of IV, a dimer of 1,1-dimethyl-1-silacyclopentadiene (V), requires some comments. Recently, two groups have independently succeeded in the preparation of C-unsubstituted siloles including V,5) which is very reactive giving a dimer (IV) on standing. At almost the same time, we also have prepared V and IV by an entirely different method. Being no ^{29}Si NMR data given in the preceding papers, we used our own sample for the ^{29}Si NMR measurement. Taking this opportunity, we describe our method of preparation briefly.

Bis(2-lithioethenyl)dimethylsilane (VI)6) was the precursor to V. Copper iodide-catalyzed coupling of VI gave V, the formation of which was confirmed by GC-MS. However, V could not be isolated and after work-up, only IV was obtained in low yield. Physical data of IV agreed well with those reported.5)



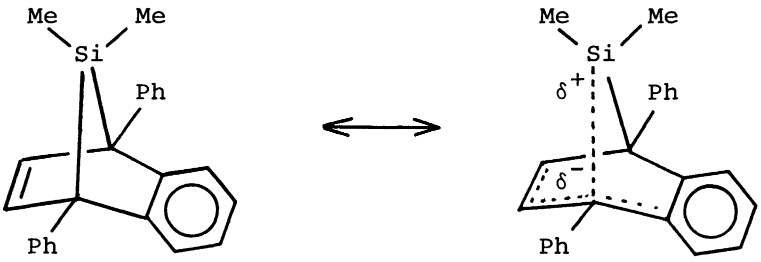
(VI) (V) (IV)

It is apparent that 7-silabicyclo[2.2.1]heptadienes and related compounds display a ^{29}Si resonance at very low field. Rather surprisingly, these resonances appear at far lower field than sp^2-hybridized silicon atoms of recently prepared disilene (63.6 ppm)7) and silene (54.3 ppm)8) derivatives. Indeed, Ie has the most deshielded ^{29}Si resonance except for an iron cluster compound with a dimethylsilandiyl bridge.9)

Such an anomal deshielding for the 7-atoms of similar norbornadiene and norbornene systems has been reported recently on 7-phosphanorbornenes[10,11] and 7-phosphanorbornadiene complexes.[12] The ^{13}C resonances of 7-C atoms of norbornane (38.4),[13] norbornene (48.5) and norbornadiene (75.1) also display increasing deshielding for the bridge carbon atoms.[14]

The angle strain at the 7-atoms may be a factor to the phenomena but should not be regarded as a sole factor to this anomal deshielding, since ^{29}Si resonances of 1,1-dimethyl-1-silacyclopentane (16.4)[13,15] 1,1-dimethyl-1-silacyclo-2-pentene (17.4),[16] and 1,1-dimethyl-1-silacyclo-3-pentene (16.5)[16] do not change the position of the chemical shifts by decreasing the ring size to 1,1-dimethyl-1-silacyclobutane (18.4).[15] On the contrary, dimethylsilacyclopropanes have ^{29}Si resonances at extremely high field.[17]

An enhanced polarization at the ground state of the molecules seems to be a good reason to this deshielding effect. Such a polarization shown below shoud be associated to σ-π conjugation which must be very important in the rigid framework. The importance of σ-π conjugation in strained cage systems and in organometallic compounds are well documented.[18]



In this connection, it is worthwhile mentioning that the magnitude of the deshielding effect is in the order of I > II > III > IV. In 2,3-benzo-1,4,5,6-tetraphenyl-7,7-dimethyl-7-silanorbornadienes (II), the bridge-head phenyl groups are perpendicular to the benzo group and the Si-C(bridge-head) σ bond lies in the nodal plane of the phenyl group.[19] Therefore, the degree of π conjugation of the C-Si bond with the π system in II must be smaller than in I. It is interesting to discuss the lesser stability of I than II toward nucleophiles as well as in the thermolysis[2] in terms of the deshielding effect, but it may be wise to wait for the pertinent kinetic data.

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