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Metal-Substituted Silacyclobutanes. 2. Derivatives of Silicon, Germanium, and Tin

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Silacyclobutanes bearing a wide variety of organic substituents at silicon have been known for some time,[1] whereas transition-metal-substituted derivatives were unknown until very recently.[2,3] We now describe silacyclobutanes containing silicon–silicon, silicon–germanium, or silicon–tin bonds.

There are relatively few ways of synthesizing compounds $R_3M{-}MR'_3$ containing group 4B–group 4B metal–metal bonds.[4] Of these, the most useful involves treatment of a halide R_3MX with an alkali metal (M′) derivative R_3MM', in a salt (M′X)-elimination reaction. Triphenylsilyllithium reacts with trimethylchlorosilane at room temperature in THF to yield $Ph_3SiSiMe_3$ in good (79%) yield.[5] In this synthesis, the silyllithium reagent is added to the chlorosilane solution and the mixture is hydrolyzed before workup. Phenyllithium also reacts with 1,1-dimethyl-1-silacyclobutane to open the ring in two ways, depending on the reaction conditions:[1] if the silacyclobutane is added to the phenyllithium, $CH_3CH_2CH_2SiMe_2Ph$ is obtained in 71% yield on hydrolysis; if the inverse addition is used, nucleophilic polymerization predominates and only small amounts of monomeric product are isolated. It was thus clear at the outset that while it may be possible to couple triphenylsilyllithium with 1-chloro-1-methyl-1-silacyclobutane to yield the desired product, **1**, such a process could be critically dependent on reaction conditions if ring opening of silacyclobutane starting material or product was to be avoided.

Results and Discussion

Addition of $ClSi(Me)CH_2CH_2CH_2$ to $Na[Fe(\eta\text{-}C_5H_5)(CO)_2]$ in THF at room temperature gave $[Fe(\eta\text{-}C_5H_5)(CO)_2\{Si(Me)CH_2CH_2CH_2\}]$ in reasonable (56%) yield;[1] a similar reaction using Ph_3SiLi gave (after a hydrolysis step) only a viscous involatile polymeric oil containing no detectable (^1H NMR) or isolable (chromatography) quantity of compound **1**. Since silyllithium/chlorosilacyclobutane coupling is likely to be more facile than ring opening, a low-temperature synthesis employing addition of Ph_3SiLi to $Cl(Me)SiCH_2CH_2CH_2$ in THF was investigated. In this case, after chromatographic and crystallization procedures, a low (2%) yield of the required $Ph_3SiSi(Me)CH_2CH_2CH_2$ (**1**) was obtained. Omission of the hydrolysis (neutral water) step in the workup raised the yield to 15%. Disilanes are known to be cleaved by base in some cases.[6] Since the aqueous product mixture would have been either neutral or (assuming slight adventitious hydrolysis of the silyllithium reagent prior to use) faintly alkaline, this observation is probably a further manifestation of the enhanced susceptibility of constrained endocyclic silicon to nucleophilic attack.[1,3]

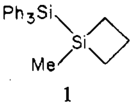
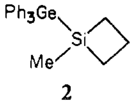
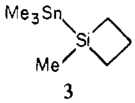
$Ph_3SiSi(Me)CH_2CH_2CH_2$ (**1**) is a white, apparently air-stable, crystalline compound melting at 69 °C and soluble in common solvents. IR and ^1H NMR spectroscopic characteristics (see Table I) confirm the proposed structure. The compound is monomeric in chloroform and showed a molecular ion in its mass spectrum. It rapidly reduced an ethanolic solution of silver nitrate, this being a diagnostic, although not specific, test for the silacyclobutane group.[1]

The brown color of trimethylsilylsodium in HMPA[7] was discharged upon addition to an approximately equimolar amount of 1-chloro-1-methyl-1-silacyclobutane in HMPA at ca. 0 °C. However, removal of volatile material in vacuo gave $CH_2CH_2CH_2Si(Me)O(Me)SiCH_2CH_2CH_2$ and unchanged chlorosilacyclobutane but no detectable (GLC, ^1H NMR) coupled product.

Trimethylsilylsodium, as made by the above method, does not appear to be a simple reagent, usually giving rather low yields in coupling reactions.[7] However, hexamethyldisilane has been made from Me_3SiLi/HMPA and Me_3SiCl.[8]

The preparation of 1-methyl-1-triphenylgermyl-1-silacyclobutane (**2**) was investigated using the same reaction conditions as for the Si_2 analogues, **1**. An encouraging precedent was the reaction of triphenylgermyllithium with triethylchlorosilane in THF to give $Ph_3Ge{-}SiEt_3$ in 52.5% yield.[9] The germylsilacyclobutane **2** was produced in 55% yield in a reaction so clean that no chromatographic separation step was necessary in the workup. Such a step is obligatory in the isolation of the disilane **1** to free the compound from involatile, oily by-products. Compounds **1** and **2** are very similar in their

Table I. Physical Data for Compounds

Compound	Mp, °C	Silacyclobutane ring vibrations,[a] cm^{-1}	τ(Si-CH_3)[b,c]	$\tau(\alpha\text{-}CH_2)$ (4 H, t)[b,d] $\tau(\beta\text{-}CH_2)$ (2 H, quintet)	Other resonances (τ)[b]
 1	69	1183 w[e] 1118 m 935 w	9.47	8.86 7.89	2.4–2.9 (15 H, complex m, aromatic C*H*)
 2	79	1183 w[e] 1117 m 932 w	9.38	8.92 7.82	2.4–2.9 (15 H, complex m, aromatic C*H*)
 3		1185 w[f] 1120 m 930 w	9.45	8.87 7.82	9.85 s (9 H,[g] Sn(CH_3)$_3$)

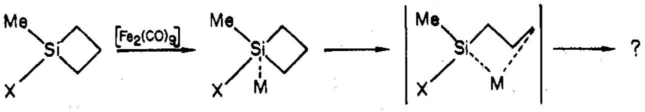
[a] See ref 1. [b] CCl_4 (Me_4Si τ 10.00). [c] Singlet. [d] ^3J(HH) = 8 Hz in all cases: spectrum interpreted in first-order terms, although second-order interactions clearly apparent. [e] Nujol. [f] Thin film. [g] Allowing for Sn–C–H satellites.

physical characteristics. As with **1**, compound **2** rapidly reduced ethanolic silver nitrate.

In an attempt to prepare the tin analogue $Ph_3Sn\overline{Si(Me)CH_2CH_2CH_2}$ of compounds **1** and **2** the dark color of Ph_3SnLi was not discharged upon addition to $Cl(Me)\overline{SiCH_2CH_2CH_2}$ in THF at low temperature. None of the coupled product was isolated from the reaction mixture. Similar results have been reported for the reaction between Ph_3SnLi and Me_3SiCl, where isolation of Ph_6Sn_2 in 69% yield from the resulting black suspension showed that metal–halogen exchange had taken place.[10]

Unlike trimethylsilyllithium, trimethylstannyllithium is easily prepared in THF solution.[11] Treatment of $Cl(Me)\overline{SiCH_2CH_2CH_2}$ with this reagent under conditions similar to those used in the preparation of **1** and **2** gave $Me_3Sn\overline{Si(Me)CH_2CH_2CH_2}$ (**3**) in 53% yield. The compound $Bu_3Sn{-}SiMe_3$ has been made (78%) similarly.[11] The stannylsilacyclobutane **3** rapidly reduced[1] ethanolic silver nitrate and showed the expected spectroscopic properties (see Table I).

It is known that members of the series $[Fe(\eta\text{-}C_5H_5)(CO)_x(PMePh_2)_{2-x}\overline{Si(Me)CH_2CH_2CH_2}]$ ($x = 0\text{–}2$) show increasing reactivity toward $[Fe_2(CO)_9]$ with increasing phosphine substitution at iron.[3] Thus, the dicarbonyl complex does not react, and although discrete products were not isolated in the other cases, reactions did occur. This is in marked contrast to the reactions[12,13] between $[Fe_2(CO)_9]$ and a silacyclobutane carrying organic substituents at silicon, where silaferracyclopentanes, e.g., $[\overline{Fe(CH_2CH_2CH_2Si}Me_2)(CO)_4]$, are formed in high yield. The germylsilacyclobutane, **2**, reacted with $[Fe_2(CO)_9]$ in a complex manner, mostly (^{1}H NMR) being polymerized; no tractable product was isolated. It is difficult to rationalize the marked difference in behavior toward $[Fe_2(CO)_9]$ found between metal-substituted silacyclobutanes and the simpler compounds, except on steric grounds, although the trends within the cyclopentadienyliron series follow from electronic arguments.[3] The reaction is known[12] to be highly regioselective when ring substituents are present, the iron entering the ring at the least hindered position. If ring opening does occur, strain energy release, together with steric resistance to recyclization, may explain the apparent formation of polymeric products:



M = attacking electrophile derived from $[Fe_2(CO)_9]$

Experimental Section

Experimental procedures and instrumentation were as described previously,[13] except that molecular weights were here measured osmometrically in chloroform. $Cl\overline{Si(Me)CH_2CH_2CH_2}$ was prepared from $Cl(CH_2)_3SiMeCl_2$ by reaction with magnesium.[1] Mass spectra are described elsewhere.[14]

A solution of triphenylsilyllithium[5] in THF was made from hexaphenyldisilane (8.60 g, 16.6 mmol), lithium wire (1.70 g, 246 mmol), and THF (100 cm^3). A solution of 1-chloro-1-methyl-1-silacyclobutane (0.84 g, 6.95 mmol) in THF (20 cm^3) was cooled to −50 °C and the clear red-brown Ph_3SiLi/THF solution added slowly with stirring until the color was just no longer discharged (35 cm^3). After stirring for a further 2 h at −50 °C, THF was removed in vacuo and the residue extracted with *n*-hexane (60 cm^3) and concentrated. Chromatography on "Florisil" in hexane followed by recrystallization from absolute ethanol gave white needles of 1-methyl-1-triphenylsilyl-1-silacyclobutane (**1**) (0.37 g, 15%). Anal. Calcd for $C_{22}H_{24}Si_2$: C, 76.7; H, 7.0; Si, 16.3; mol wt, 344. Found: C, 77.1; H, 7.15; Si, 16.5; mol wt, 359 ($CHCl_3$) or 344 (MS).

A dark red solution of triphenylgermyllithium[9] [from triphenylbromogermane (3.84 g, 10.0 mmol), lithium powder (0.69 g, 100 mmol), and THF (10 cm^3)] was added dropwise to a stirred solution of 1-chloro-1-methyl-1-silacyclobutane (1.58 g, 13.1 mmol) in THF (10 cm^3) at −50 °C; the color was discharged. THF was then removed in vacuo and the residue extracted with *n*-hexane. Removal of hexane in vacuo left a white powder which was crystallized from absolute ethanol to give pure 1-methyl-1-triphenylgermyl-1-silacyclobutane (**2**) (2.12 g, 55%). Anal. Calcd for $C_{22}H_{24}GeSi$: C, 67.9; H, 6.2; mol wt, 388. Found: C, 68.3; H, 6.2; mol wt, 407 ($CHCl_3$) or 388 (MS).

A solution of trimethylstannyllithium[11] [from trimethylchlorostannane (1.66 g, 8.34 mmol), lithium (0.58 g, 83.8 mmol), and THF (12.5 cm^3)] was added dropwise to a stirred solution of 1-chloro-1-methyl-1-silacyclobutane (1.19 g, 10.0 mmol) in THF (10 cm^3) at −50 °C. After stirring for 1 h at −50 °C, THF was removed from the cold solution at ca. 10 mmHg. Molecular distillation of the residual oil gave pure (GLC), colorless, liquid 1-methyl-1-trimethylstannyl-1-silacyclobutane (**3**) (1.09 g, 53%). Anal. Calcd for $C_7H_{18}SiSn$: C, 33.8; H, 7.3; mol wt, 248. Found: C, 33.7; H, 7.4; mol wt, 247 ($CHCl_3$) or 248 (MS).

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Registry No. **1**, 59395-10-7; **2**, 59395-11-8; **3**, 59395-12-9; $Cl\overline{Si(Me)CH_2CH_2CH_2}$, 2351-34-0; hexaphenyldisilane, 1450-23-3; triphenylbromogermane, 3005-32-1; trimethylchlorostannane, 1066-45-1.

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Organometallic Heterocyclic Chemistry. 2.[1] Spectral and Electrochemical Properties of Pyridazine, Pyrazine, and Pyrimidine Complexes of Tungsten Pentacarbonyl

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There has been a recent growing interest in the electronic spectral properties of transition-metal carbonyl complexes.[2]