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COMMUNICATION

Alkynyl-functionalised and linked bicyclo[1.1.1]pentanes of group 14†‡

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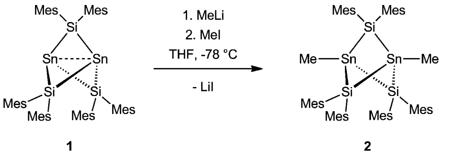
We report the synthesis and properties of alkynyl-functionalised and -bridged bicyclo[1.1.1]pentane derivatives consisting of the heavier group 14 elements silicon and tin.

Rod-like molecules have received considerable attention in recent years, in particular in view of their relevance in acting as elementary building blocks in investigations of long-range interactions such as charge and energy transfer, for instance.[1] Most commonly, carbon-rich species composed of polyynes or poly(aryleneethynylene)s have been investigated.[2] More rigid structures have been obtained by including all-carbon bicyclo[1.1.1]pentane cages in between the polyynes or by employing [*n*]staffane chains. It has been shown that these scaffolds have the ability to transmit electronic interactions over long distances, which is astonishing since they are saturated systems.[3] Even larger cages such as the 12-vertex carborane cluster 1,12-$C_2B_{10}H_{10}$ have been found to permit electronic communication between two metal centres over large distances.[4]

Recently, it has been proposed that heavy-core staffanes, *i.e.*, oligomers of heavy [1.1.1]propellanes of group 14,[5] could have interesting electronic and useful optoelectronic properties, since the atoms in these chains may couple.[6] Although few in number, some examples of heavy bicyclo[1.1.1]pentanes of group 14 have been reported in recent years.[7] Catenated versions have, to the best of our knowledge, only been described once so far. In a recent breakthrough paper, Iwamoto *et al.* reported the synthesis and characterisation of persilylated [*n*]staffanes (*n* = 1, 2, 3) and their remarkable conjugation between bicyclo[1.1.1]pentasilane units.[8]

As an extension of our studies on heavy [1.1.1]propellanes of group 14[7d–g] we became interested in utilising these cages for the well-directed synthesis of catenated bicyclo[1.1.1]pentanes. As a suitable entry point to this area we have chosen alkynyl moieties as bridging entities.[9] In this paper we report the synthesis and characterisation of alkynyl-functionalised heavy bicyclo[1.1.1]-pentanes and the first example of an alkynyl-bridged [1,1′]-bis(bicyclo[1.1.1]pentane).

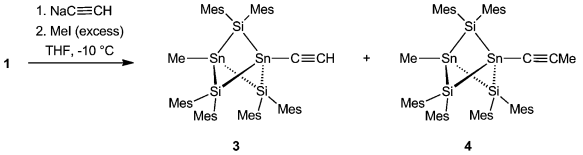


Scheme 1 Synthesis of **2**.

In order to get access to this new family of compounds, we employed the recently reported trisiladistanna[1.1.1]propellane (**1**).[7g] In a first test reaction, we checked the suitability of **1** to react with the simple nucleophile MeLi, followed by a treatment with MeI.[10] Indeed, when this simple two-step synthesis was conducted in THF at low temperature, the dimethyl substituted cage **2** was obtained after a short workup procedure as yellow crystals in 82% yield (Scheme 1). Compound **2** is remarkably stable towards air and moisture and decomposes only when heated above 200 °C. **2** has been completely characterised, including single crystal X-ray diffraction. However, several disordered solvent molecules in the crystal lattice prevented a detailed discussion of the structural parameters (see ESI‡).

Based on this general reactivity of **1**, and in order to access alkynyl-functionalised bicyclo[1.1.1]pentanes, we intended to employ alkynides of the alkali metals in the first step of the reaction.[11] Initially, we used sodium acetylide as alkynylation reagent. The reaction of **1** with *ca.* one equivalent of NaC≡CH was carried out in THF at −10 °C. The initial deep purple solution **1** became colourless and an excess of MeI was added to the reaction mixture. However, instead of clean formation of the Me/ethynyl terminated bicyclo[1.1.1]pentane **3** we also observed the formation of the propynyl substituted cage (**4**; Scheme 2).

Using the sodium acetylide in excess, **4** can be obtained in up to 69% isolated yield. The formation of **4** can reasonably be explained by assuming that sodium acetylide is able to deprotonate the acidic C≡CH entity once coordinated to **3**; the resulting carbanion is subsequently converted to C≡CMe



Scheme 2 Synthesis of **3** and **4** using NaC≡CH.

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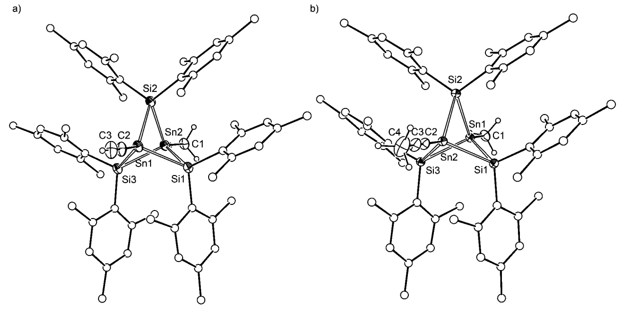


Fig. 1 Displacement ellipsoid plots (30% probability) of **3** (a) and **4** (b); Mes ligands without hydrogen atoms and with carbon atoms drawn with arbitrary radii for clarity (for bond lengths and angles, see ESI‡).

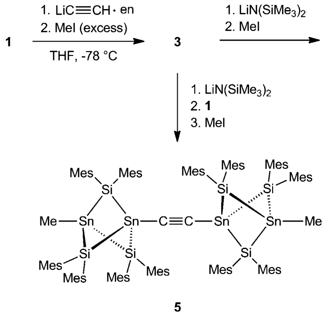
by the treatment with MeI. When changing from sodium acetylide to the less basic and more soluble lithium acetylide ethylenediamine complex ($\mathrm{LiC{\equiv}CH{\cdot}en}$), we were able to isolate **3** in similar yields (73%). In order to suppress the formation of **4**, the reaction was performed at ambient temperature with slow addition of a dilute THF solution of $\mathrm{LiC{\equiv}CH{\cdot}en}$. The addition was stopped precisely at the point when the deep purple solution of **1** became colourless; afterwards, an excess of methyl iodide was added.

Compounds **3** and **4** are colourless and pale yellow solids, respectively. The ^{1}H, ^{13}C, ^{29}Si, and ^{119}Sn NMR data are consistent with unsymmetrically 1,3-disubstituted bicyclo[1.1.1]-pentane structures (see ESI‡ and below for more details). As already observed for **2**, both cages are stable to air and moisture as well as thermally very stable. The molecular structures of **3** and **4** are shown in Fig. 1.

The distances between the bridgehead tin atoms were detected as follows: 315.7 pm for **3** and 315.8 pm for **4**. Compared to the starting material **1** [$d(\mathrm{Sn}\cdots\mathrm{Sn})$ = 309.7 pm],[7g] these values are increased by *ca.* 6 pm. The tin silicon distances of 260.5–262.5 pm, however, are similar to **1** (260.3–265.3 pm). As expected, the Sn–Si–Sn angles of 74.1–74.4° are slightly enlarged as compared to **1** (av. 72.1°). Overall, only small structural changes are observed confirming the structural integrity upon addition of organic substituents to the bridgehead tin atoms in **1**.

In order to employ the ethynyl-substituted cage **3** as starting material for the construction of catenated structures, we checked the suitability of the $-\mathrm{C{\equiv}CH}$ moiety in **3** to be employed for further manipulation. To this end, we treated **3** with 1 equiv. of a dilute THF solution of $\mathrm{LiN(SiMe_3)_2}$ and, in a second step, with MeI as alkylating reagent (Scheme 3). As expected, the propynyl substituted cage **4** was obtained in almost quantitative yield. Based on these results we performed another reaction, but this time we added the [1.1.1]propellane **1** to the deprotonated cage before treating the reaction mixture with MeI. This short synthetic sequence furnished the first alkynyl-bridged [1,1′]-bis(bicyclo[1.1.1]pentane) (**5**; Scheme 3). The use of the sterically demanding base $\mathrm{LiN(SiMe_3)_2}$ is crucial for the success of this reaction; no side reactions with **1** can occur.

5 is stable against air and moisture, has a high decomposition temperature of > 270 °C, and is accessible in 65% yield in analytically pure form. The symmetrical $\nu(\mathrm{C{\equiv}C_{stretch}})$ vibration was observed in the Raman spectrum (powder) at 2043 cm^{-1}. This frequency is in good accordance with the values obtained for $\mathrm{Me_3Sn{-}C{\equiv}C{-}SnMe_3}$ (*cf.* 2065 cm^{-1}).[12] The NMR data were consistent with the structure shown in Scheme 3 (for a further discussion, see below). Single crystals suitable for X-ray diffraction were obtained from a concentrated toluene solution, which was layered with acetonitrile. The molecular structure of **5** is shown in Fig. 2. Each individual molecule is located on a special crystallographic position. By inspecting a space-filling model of the molecular structure of **5** it becomes evident that the alkynyl bridge is comfortably lodged in between both $\mathrm{Sn_2Si_3}$ moieties [$d(\mathrm{C{\equiv}C})$ = 116.1 pm; $d(\mathrm{Sn{-}C})$ = 213.8(4) pm]. The tin–silicon distances fall within the expected ranges and are only slightly different as compared to **1**. The Sn–Si–Sn angles of 74.9–75.0° and the interbridgehead distance of 318.7 pm are similar to that determined for **3** or **4**.



Scheme 3 Synthesis of **3**, **4**, and **5** using $\mathrm{LiC{\equiv}CH{\cdot}en}$.

^{119}Sn NMR investigations of **2–5** in $\mathrm{C_6D_6}$ and d_8-thf (**5**) revealed that the unsymmetrically 1,3-disubstituted bicyclo-[1.1.1]pentanes **3** and **4** consist of two signals (δ = −245 and −282 ppm for **3**; −241 and −281 ppm for **4**) and the dimethyl derivative **2**, as expected, consists of only one with a chemical shift of δ = −222 ppm. The symmetrical *vs.* unsymmetrical substitution pattern is also reflected in the ^{1}H and ^{13}C NMR data. Interestingly, the alkynyl-bridged compound **5** gave *three* ^{119}Sn NMR signals at δ = −237, −295, and −296 ppm in d_8-thf at room temperature. The latter two resonances (integration ∼1 : 1) differ only slightly. Our current interpretation is that different stereoisomers of **5** are present in solution, which differ in the relative orientation of the mesityl substituents in both bicyclopentane subunits. Note that in Mes-substituted cages of this type, the aryl rings adopt a propeller-type arrangement (D_3 symmetry; Scheme 4 (left) and Fig. 2b). If two of these cages are connected by a bridge ($\mathrm{C{\equiv}C}$ in the case of **5**), different relative orientations of the Mes substituents of the two $\mathrm{Sn_2Si_3}$ subunits are possible. The resulting pairs of

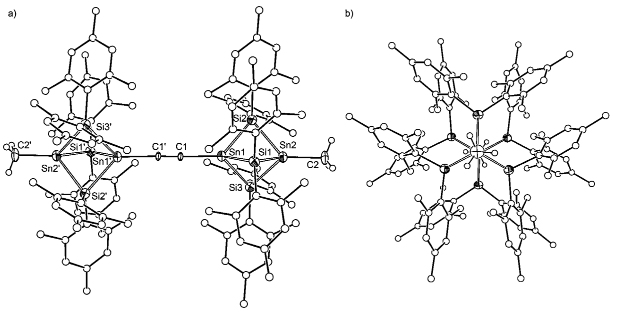
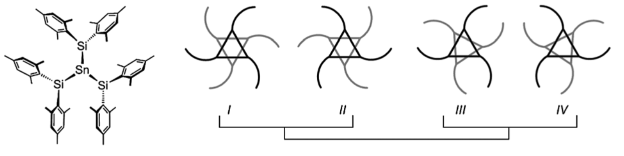


Fig. 2 (a) Displacement ellipsoid plot (50% probability) of **5**; Mes ligands without hydrogen atoms and with carbon atoms drawn with arbitrary radii for clarity (see also ESI‡); (b) view along the C_3 axis.



Scheme 4 Relative orientations of the aryl rings of the D_3-symmetric Sn_2Si_3 subunits in **5**; formation of pairs of enantiomers and diastereomers.

enantiomers and diastereomers may be visualised as shown in Scheme 4. It is reasonable to assume that the diastereomeric forms give slightly different ^{119}Sn NMR resonances. The Sn atoms bonded to the alkynyl bridge are obviously more affected (signals at $\delta = -295$ and -296 ppm), whereas the resonances of the Sn–Me moieties overlap. Note that we also observed different ^{1}H NMR signals (likewise in other solvents like C_6D_6), albeit not clearly resolved (see ESI‡). Currently we are not able to comment on whether these isomers are in equilibrium or not. The single crystal used for the X-ray structure analysis of **5**, however, only contained the forms III and IV (Scheme 4 and Fig. 2b).

The ^{29}Si NMR chemical shifts of the bridging silicon groups of **2–5** are almost equal ($\delta = -56$ to -59 ppm), but clearly different from **1** ($\delta = 98$ ppm).[7g] Interestingly, we found an (almost) linear correlation when the ^{117}Sn,^{119}Sn coupling constants between the bridgehead atoms are correlated with the interbridgehead distance. As can be seen from Table 1, a larger distance is associated with a smaller ^{117}Sn,^{119}Sn coupling constant.[13] Without going into too much details, this correlation nicely shows the significance of the interbridgehead distance for the strength of the interaction between the bridgehead atoms – even in these cases, where both are formally not bonded and "simply" arranged in the same region of space. For all-carbon bicyclo[1.1.1]pentanes, the term "back-lobe-to-back-lobe" interaction has been coined for this phenomenon.[1,14] In this line of thought, similar effects are observable for **3** and **4**: the alkyne proton in **3** consists of two pairs of $^{117/119}$Sn satellites, the smaller one of which (5 Hz) belongs to a coupling to the tin bridgehead on the opposite side of the cage (most likely "through cage"). For **4**, the corresponding coupling is only evident as shoulders flanking the central signal.

In order to shed some light on conceivable conjugation effects in **5**,[15] a density functional theory (DFT) calculation was conducted on **q5** (a Ph-substituted model for **5**) at the (RI)-DFT/BP86/def2-TZVP level (see ESI‡). The highest occupied molecular orbitals are of π-type and located on both the C$\equiv$C bridge and the Sn_2Si_3 entities (Fig. S26, ESI‡). The lowest unoccupied orbital was found to be of σ*-type. Most importantly, the calculations revealed that the HOMO–LUMO gap decreases by 0.23 eV when going from **q2** to **q5**.[16] In order to confirm this calculated decrease, we tried to extract the relevant experimental data from the UV/Vis spectra of **2** and **5**. However, since these π–σ* transitions are too high in energy, they are covered by other transitions of the Mes rings in the UV region.

Table 1 Comparison of the interbridgehead distances detected by X-ray diffraction and the ^{117}Sn,^{119}Sn coupling constants of **2–5**[a]

Compound	d(Sn···Sn) [pm]	$J(^{117}\text{Sn},^{119}\text{Sn})$ [Hz]
2	319.4(1)[b]	4877
3	315.71(9)	7127
4	315.75(9)	6942
5	318.7(2)	6770

[a] Note that the $^{1}J(^{29}\text{Si},^{119}\text{Sn})$ coupling constants do not show a linear correlation with the interbridgehead distance. [b] Some uncertainties due to the quality of the refinement, see ESI.

To conclude, we report the first alkynyl-functionalised bicyclo[1.1.1]pentanes of heavy group 14 elements, including a linked member of this new family. NMR investigations revealed that the title compounds show significant "through cage" communication effects, which can most likely be attributed to "back-lobe-to-back-lobe"[1,14] interactions. For the bridged [1,1′]-bis(bicyclo[1.1.1]pentane) **5**, quantum chemical calculations predicted some conjugation along the rod-like scaffold. Studies in our lab continue to further explore the catenations of bicyclopentanes of this type.

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