

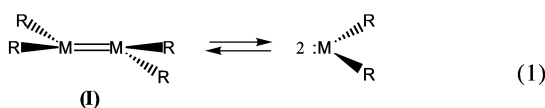
Characterization of $\text{Ar}'\text{Sn}(\mu\text{-Br})\text{Sn}(\text{Ar}')\text{CH}_2\text{C}_6\text{H}_4\text{-4-Pr}^i$ ($\text{Ar}' = \text{C}_6\text{H}_3\text{-2,6-Dipp}_2$; $\text{Dipp} = \text{C}_6\text{H}_3\text{-2,6-Pr}^i_2$): A Stable Structural Analogue for a Heavier Group 14 Element Monobridged Alkene Isomer $\text{HM}(\mu\text{-H})\text{MH}_2$ ($\text{M} = \text{Sn or Pb}$)

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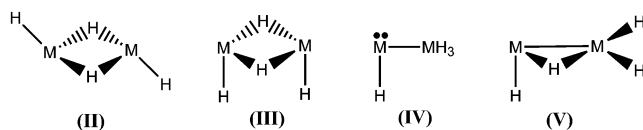
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Since the synthesis of R_2SnSnR_2 ($\text{R} = \text{CH}(\text{SiMe}_3)_2$) in 1973,¹ numerous examples of heavier group 14 element (tetrel) alkene analogues have been isolated and characterized.² The great majority of these possess trans pyramidal, dimeric structures (I) that display a preference for dissociation to monomers with increasing atomic number as shown by eq 1.



Nonetheless, in a series of computational studies^{3,4} on the simple hydrogen derivatives M_2H_4 in the early 1990s, Trinquier showed that a number of other structural minima (II–V) could exist as illustrated by the structures below.



Indeed, for tin and lead, the trans, doubly bridged isomer II was found to be the absolute minimum, with the cis isomer III lying slightly higher (ca. 2 kcal mol⁻¹) in energy.⁵ Furthermore, the unsymmetric isomer IV was only 5.0 kcal mol⁻¹ less stable. Through the use of these guidelines and a combination of substituents we have shown that organosubstituted tin derivatives of the doubly bridged and unsymmetric structures II⁶ and IV⁷ could be isolated and characterized. It was also shown that, although a trans pyramidal dimer (I, shown in eq 1) is preferred for germanium, it could be transformed into the unsymmetric form (IV) by reaction with a Lewis base.⁸ Despite this, a stable analogue of the singly bridged isomer V has proven to be elusive.⁵ Reference to the Trinquier calculations, however, shows that V lies just 0.9 kcal above IV, or 7.9 kcal mol⁻¹ above the absolute minimum II, which suggests that, energetically at least, a derivative of such a species should also be obtainable. We now show that by suitable manipulation of substituents the singly bridged derivative $\text{Ar}'\text{Sn}(\mu\text{-Br})\text{Sn}(\text{Ar}')(\text{CH}_2\text{C}_6\text{H}_4\text{-4-Pr}^i)$, **1**, ($\text{Ar}' = \text{C}_6\text{H}_3\text{-2,6-Dipp}_2$; $\text{Dipp} = \text{C}_6\text{H}_3\text{-2,6-Pr}^i_2$) can be isolated and characterized structurally and spectroscopically. For comparison, the characterization of the related symmetric trans pyramidal species $\{\text{Sn}(\text{Ar}')(\text{CH}_2\text{C}_6\text{H}_4\text{-4-Bu}^i)\}_2$, **2**, is also reported.⁹

Compound **1** can be isolated¹⁰ via the direct reaction of $\text{Ar}'\text{SnCl}^{11}$ with 0.5 equiv of $\text{BrMgCH}_2\text{C}_6\text{H}_4\text{-4-Pr}^i$, which yielded **1** as large orange crystals. ¹¹⁹Sn NMR spectroscopy of **1** in C_6D_6 solution afforded two signals of equal intensity at 1399.8 and 2274.3 ppm. X-ray crystal data¹² showed that the solid-state structure (Figure 1) features bromine bridging two tins, one of which (Sn(1)) is

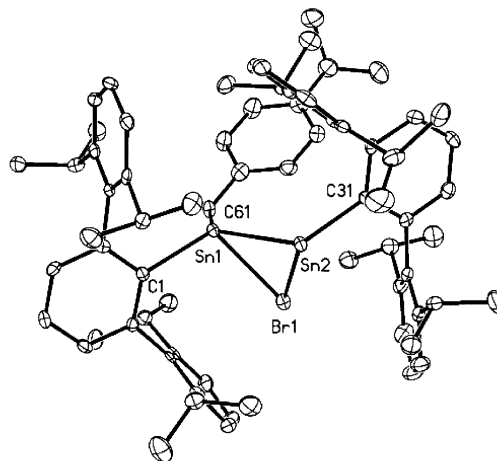


Figure 1. Selected bond lengths (Å) and angles (deg) for **1**. H atoms are not shown. Sn(1)–Sn(2) = 2.9407(4), Sn(1)–Br(1) = 2.7044(5), Sn(2)–Br(1) = 2.7961(5), Sn(1)–C(1) = 2.201(4), Sn(1)–C(61) = 2.196(3), Sn(2)–C(31) = 2.212(4), Sn(1)–Br(1)–Sn(2) = 64.61(1), Br(1)–Sn(1)–Sn(2) = 59.20(1), Br(1)–Sn(2)–Sn(1) = 56.18(1), Sn(1)–Sn(2)–C(31) = 107.83(9), Br(1)–Sn(2)–C(31) = 96.89(1), Sn(2)–Sn(1)–C(1) = 117.66(9), C(1)–Sn(1)–Br(1) = 103.8(1), C(1)–Sn(1)–C(61) = 104.6(1), Sn(2)–Sn(1)–C(61) = 133.96(9).

bonded to Ar' and $\text{CH}_2\text{C}_6\text{H}_4\text{-4-Pr}^i$ groups and the other to a single Ar' . The Sn–Sn distance is 2.9407(4) Å, and the bridged Sn–Br distances are unequal, having the values 2.7044(5) (Sn(1)) and 2.7961(5) Å. The three Sn–C bond lengths are in the narrow range 2.196(3)–2.212(4) Å. The interligand angles surrounding the tins display extreme variation and are provided in the caption of Figure 1. The reaction of $\text{Ar}'\text{SnCl}$ with 1 equiv of $\text{BrMgCH}_2\text{C}_6\text{H}_4\text{-4-Bu}^i$ afforded **2**, which has a trans pyramidal structure (Figure 2) found for most $(\text{SnR}_2)_2$ dimers.² The most prominent features of the structure are the Sn–Sn bond length of 2.7705(8) Å and an out of plane angle of 42°. ¹¹⁹Sn NMR spectroscopy of **2** in C_6D_6 afforded a signal at 1205.7 ppm.

The singly bridged structure of **1** is unique for low-coordinate tin(II) organometallic derivatives. The details of the structure and ¹¹⁹Sn NMR spectroscopy establish that it is bromide bridged rather than an unsymmetric species of the type $\text{Ar}'\text{SnSn}(\text{Br})(\text{Ar}')(\text{CH}_2\text{C}_6\text{H}_4\text{-4-Pr}^i)$. The chemical shifts obtained for Sn(1), 1399.8 ppm, and Sn(2), 2274.3 ppm, both lie in the Sn(II) rather than the Sn(IV) range and suggest that the structure in the solid state is retained in solution.^{9,13} The bridging Sn–Br distances differ by ca. 0.09 Å and are similar to the 2.81(2) Å bridging Sn–Br distance in $[\text{Fe}(\text{Sn}\{\text{N}(\text{Bu}^i)\}_2\text{SiMe}_2)_2\text{Br}_2]_2$.¹⁴ In addition, the disposition of the C(1) and C(61) ligands is toward the bromine side of the molecule. This is the same structural distortion as that predicted for **V** and, as further observed by Trinquier,⁴ is consistent with the

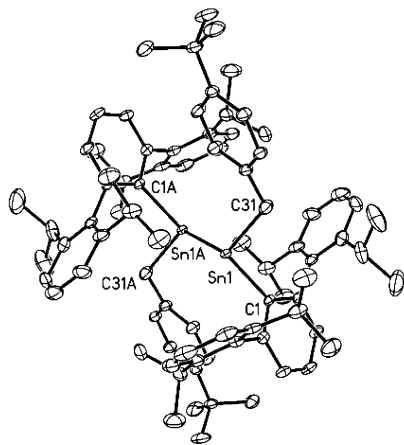


Figure 2. Selection bond lengths (Å) and angles (deg) for **2**. Sn(1)–Sn(1A) = 2.7705(8), Sn(1)–C(1) = 2.180(5), Sn(1)–C(31) = 2.175(6), C(1)–Sn(1)–C(31) = 101.4(2), Sn(1A)–C(1) = 112.1(1), Sn(1)–Sn(1)–C(31) = 116.2(2).

view that it represents the midpoint in the transformation of the trans pyramidal geometry in **1** to the unsymmetric structure **IV**, that is, from $\text{Ar}'(\text{Br})\text{SnSn}(\text{Ar}')\text{CH}_2\text{C}_6\text{H}_4\text{-4-Pr}^i$ to $\text{Ar}'\text{SnSn}(\text{Br})(\text{Ar}')\text{-CH}_2\text{C}_6\text{H}_4\text{-4-Pr}^i$. The Sn–Sn distance, 2.9407(4) Å, in **1** is longer than that calculated for **V**, 2.74 Å. However, similarly long distances have been observed for the unsymmetric $\text{Ar}^*\text{SnSnMe}_2\text{Ar}^{*6a}$ (Sn–Sn = 2.8909(2) Å, $\text{Ar}^* = \text{C}_6\text{H}_5\text{-2,6-Trip}_2$; $\text{Trip} = \text{C}_6\text{H}_2\text{-2,4,6-Pr}_3^i$) or $\text{Ar}^*\text{SnSnPh}_2\text{Ar}^*$ (Sn–Sn = 2.9688(5) Å).^{7b} Presumably, the large substituent size, the strained geometries at the tins, as well as the fact that bromine (and not hydrogen) is the bridging atom, contribute to Sn–Sn bond lengthening in **1**.¹⁵ The dimeric structure of **2** is also significant in that the Sn–Sn distance, 2.7705(8) Å, is among the shortest observed for R_2SnSnR_2 compounds^{1,2} and lends support to the idea that a species analogous to **V** is intermediate between R_2SnSnR_2 and RSnSnR_3 . The ¹¹⁹Sn NMR chemical shift of **2** (1205.7 ppm) indicates that the dimeric structure is retained in solution and does not coincide with either of the two ¹¹⁹Sn NMR signals seen for **1**.¹³

In summary, the isolation of **1** increases the number of structurally modelled isomers of a distannene to four. Only the cis, doubly bridged isomer **III** remains unmodelled.

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Supporting Information Available: X-ray data (CIF) for **1** and **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (9) Reaction of $\text{BrMgCH}_2\text{C}_6\text{H}_4\text{-4-Pr}^i$ with $\text{Ar}'\text{SnCl}$ afforded $[\text{Sn}(\text{Ar}')\text{CH}_2\text{C}_6\text{H}_4\text{-4-Pr}^i]_2$ (¹¹⁹Sn NMR $\delta = 1209$ ppm), which did not crystallize. The benzyl group $\text{CH}_2\text{C}_6\text{H}_4\text{-4-Bu}^i$ was used instead to obtain **2** with the assumption that substitution of Bu^i for Pr^i at the para position would not substantially alter its steric or electronic properties. X-ray-quality crystals of **2** could be grown with this substituent, which showed that it is dimeric with no bridging present. Its chemical shift, which differs significantly from those of **1**, indicates that **1** does not dissociate and supports the retention of the bridged structure in solution.
- (10) All manipulations were carried out under anaerobic and anhydrous conditions. **1**: To a solution of $\text{Ar}'\text{SnCl}$ (1.1 g, ca. 2 mmol) in THF (20 mL), cooled to ca. -78°C , was slowly added a freshly prepared THF solution (5 mL) containing isopropylbenzylmagnesium bromide (1.0 mmol), via syringe. The initial light yellow solution became orange and red upon warming to room temperature. The reaction was stirred at room temperature for 12 h, whereupon the solvent was removed and the solid residue was extracted with hexane (50 mL); filtration through Celite afforded a deep-red solution, which was concentrated to ca. 20 mL. After 24 h at ca. -20°C , large dark orange crystals were formed, which were suitable for X-ray analysis. Yield: 0.45 g (0.36 mmol, 36.1%). UV–vis (hexane) λ_{max} , ϵ ($\text{M}^{-1}\text{cm}^{-1}$): 405, 1900. ¹H NMR (399.77 MHz, C_6D_6 , 25°C): δ 0.95 [dd, ³ $J_{\text{HH}} = 6.4$ Hz, 24H, $o\text{-CH}(\text{CH}_3)_2(\text{Dipp})$], 1.09 [d, ³ $J_{\text{HH}} = 6.8$ Hz, 6H, $\text{CH}_2\text{C}_6\text{H}_4\text{-4-CH}(\text{CH}_3)_2$], 1.15 [d, ³ $J_{\text{HH}} = 6.8$ Hz, 6H, $o\text{-C}_6\text{H}_4\text{-4-CH}(\text{CH}_3)_2$], 1.20 [d, ³ $J_{\text{HH}} = 6.8$ Hz, 18H, $\text{CH}(\text{CH}_3)_2\text{C}(7)+\text{C}(19)(\text{Dipp})$], 2.16 (s, broad, 2H, $-\text{CH}_2\text{C}_6\text{H}_4\text{-4-CH}(\text{CH}_3)_2-$), 2.61 [sept, ³ $J_{\text{HH}} = 7.0$ Hz, 1H, $\text{CH}_2\text{C}_6\text{H}_4\text{-4-CH}(\text{CH}_3)_2$], 2.88 [sept, ³ $J_{\text{HH}} = 6.8$ Hz, 3H, $o\text{-CH}(\text{CH}_3)_2\text{C}(7)+\text{C}(19)(\text{Dipp})$], 3.05 [sept, ³ $J_{\text{HH}} = 6.8$ Hz, 5H, $\text{CH}(\text{CH}_3)_2\text{C}(7)$, $\text{C}(37)$, and $\text{C}(45)(\text{Dipp})$], 6.67 [dd, ³ $J_{\text{HH}} = 8.8$ Hz, 4H, $-\text{CH}_2-\text{C}_6\text{H}_4\text{-4-CH}(\text{CH}_3)_2$], 7.03 [d, ³ $J_{\text{HH}} = 8.8$ Hz, 6H, ($m\text{-C}_6\text{H}_3(\text{C}(1)$, $\text{C}(31)$, and $\text{C}(19)(\text{Dipp})$), 7.13–7.19 (br, m, 12H, Ar, H). ¹³C NMR (100.53 MHz, C_6D_6 , 25°C): δ 23.20 ($\text{CH}(\text{CH}_3)_2$, Dipp), 23.99 ($p\text{-CH}(\text{CH}_3)_2$, $\text{CH}_2\text{C}_6\text{H}_4\text{-4-CH}(\text{CH}_3)_2$), 24.45 ($-\text{CH}_2-$), 25.82 ($\text{CH}(\text{CH}_3)_2$, $\text{C}(7)$ Dipp), 25.86 ($\text{CH}(\text{CH}_3)_2$, $\text{C}(19)$ Dipp), 26.50 ($\text{CH}(\text{CH}_3)_2$, $\text{C}(19)$ Dipp), 26.54 ($\text{CH}(\text{CH}_3)_2$, $\text{C}(19)$ Dipp), 30.87 ($\text{CH}(\text{CH}_3)_2$, $\text{C}(19)$ and $\text{C}(7)$ Dipp), 30.96 ($\text{CH}(\text{CH}_3)_2$, $\text{C}(7)$ Dipp), 31.07 ($\text{CH}(\text{CH}_3)_2$, $\text{C}(31)$ Dipp), 31.98 ($\text{CH}(\text{CH}_3)_2$, $\text{CH}_2\text{C}_6\text{H}_4\text{-4-CH}(\text{CH}_3)_2$, $\text{C}(7)$ and $\text{C}(19)$ Dipp), 124.14 ($m\text{-C}(31)$ Dipp), 125.78 ($p\text{-C}_6\text{H}_3$), 125.84 ($m\text{-C}(7)$ Dipp), 127.35 ($p\text{-CH}_2\text{C}_6\text{H}_4\text{-4-CH}(\text{CH}_3)_2$), 127.51 ($p\text{-C}(1)$ Dipp), 127.58 ($p\text{-C}(31)$ Dipp), 127.62 ($p\text{-C}(7)$ Dipp), 129.14 ($o\text{-p-C}(7)$ Dipp), 129.57 ($m\text{-C}(31)$ Dipp), 130.02 ($p\text{-Dipp}$), 130.43 ($m\text{-Bn}$), 130.75 ($m\text{-Ph}$), 136.94 ($o\text{-Ph}$), 137.02 ($ipso\text{-Bn}$), $\text{CH}_2\text{C}_6\text{H}_4\text{-4-CH}(\text{CH}_3)_2$, 137.45 ($o\text{-C}(31)$ Dipp), 138.96 ($i\text{-C}(31)$ Dipp), 145.54 ($o\text{-C}(7)$ Dipp), 147.21 ($o\text{-C}(1)$ and $\text{C}(7)$ Dipp), 147.64 ($o\text{-C}(31)$ Dipp), 184.82 ($i\text{-C}(37)$ and $\text{C}(48)$), 191.85 ($i\text{-C}_6\text{H}_3(\text{C}(1))$). ¹¹⁹Sn NMR (C_6D_6 , 149.24 MHz): 1399.8 (tetracoordinated Sn), 2274.3 (tricoordinated tin). **2**: To a solution of $\text{Ar}'\text{SnCl}$ (0.55 g, ca. 1 mmol) in THF (20 mL), pre-cooled to ca. -78°C , was slowly added 4 mL of a freshly prepared THF solution (2.5 M) of $p\text{-tert-butylbenzylmagnesium bromide}$ (2.5 M) via syringe. The solution became amber immediately and deep red upon warming to room temperature. The reaction was stirred for a further 12 h, and the solvent was pumped off. The residue was extracted with hexane (40 mL), and the solution was allowed to settle for ca. 3 h. It was then decanted, concentrated to about half of the initial volume, and let stand in a ca. -20°C freezer overnight. Orange crystals were formed, which were suitable for single-crystal X-ray analysis. Yield: 0.28 g, 0.42 mol, 42.1%. UV–vis (hexane) λ_{max} , ϵ ($\text{M}^{-1}\text{cm}^{-1}$): 320 nm (sh). ¹H NMR (C_6D_6 , 399.77 MHz, 25°C): δ 1.01 (d, ³ $J_{\text{HH}} = 6.4$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 1.14 (d, ³ $J_{\text{HH}} = 6.4$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 1.23 (s, 9H, $t\text{-C}(\text{CH}_3)_3$), 2.08 (s, 2H, $\text{CH}_2\text{C}_6\text{H}_4\text{-4-Bu}^i$), 6.97–7.07 (m, 11H, aromatic Hs). ¹³C NMR (100.53 MHz, C_6D_6 , 25°C): δ 23.05 ($\text{CH}(\text{CH}_3)_2$), 26.57 ($\text{C}(\text{CH}_3)_3$), 31.98 ($\text{C}(\text{CH}_3)_3$), 34.11 ($-\text{CH}_2-$), 123.99 ($m\text{-Dipp}$), 125.72 ($m\text{-C}_6\text{H}_3$), 126.78 ($p\text{-C}_6\text{H}_4$), 126.99 ($m\text{-C}_6\text{H}_4$), 129.99 ($m\text{-Dipp}$), 125.72 ($m\text{-C}_6\text{H}_3$), 126.78 ($p\text{-C}_6\text{H}_4$), 126.99 ($m\text{-C}_6\text{H}_4$), 129.19 ($p\text{-Dipp}$), 129.79 ($o\text{-C}_6\text{H}_4$), 137.54 ($i\text{-C}_6\text{H}_4$), 140.49 ($p\text{-C}_6\text{H}_3$), 144.56 ($o\text{-C}_6\text{H}_3$), 145.81 ($i\text{-Dipp}$), 147.21 ($o\text{-Dipp}$), 199.20 ($i\text{-C}_6\text{H}_3$). ¹¹⁹Sn NMR (C_6D_6 , 149.20 MHz, 25°C): δ 1205.7.
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