

A Carbene–Stannylene Adduct with a Long Tin–Carbon Double Bond?

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Bis(2,4,6-triisopropylphenyl)stannylene, formed by thermolysis of the cyclotristannane **4**, reacts with 4,5-dimethyl-1,3-diisopropylimidazol-2-ylidene to furnish the adduct **8**; an X-ray structural analysis of this compound reveals the presence of a long tin–carbon ‘double bond’ with a length of 237.9(5) pm and a distinctly pyramidal tin centre.

Although germenes and stannenes with Ge=C and Sn=C double bonds are now relatively well established,¹ structurally characterised representatives of these classes of compounds are still extremely rare. The only two stannenes **1**² and **3**³ for which molecular structures have been determined concomitantly represent extreme cases with regard to the Sn=C bond lengths and the environments of the respective tin atoms. Thus, in spite of considerable twisting of the Sn=C double bond in **1**, its length is very short (202.5 pm).² On the other hand, the Sn=C bond length in the stannaketene **3**, prepared by addition of an isocyanide to a stannylene, of 239.7 pm is considerably longer than a corresponding single bond. In addition, the tin atom in **3** has a clear pyramidal environment of its substituents; this is comparable with the *trans*-bent structure of Lappert’s distannene **2**^{4,5} (Scheme 1).

According to theoretical studies, the *trans*-bent structure of distannenes is interpreted in terms of the bonding interactions between two singlet stannylenes in which the doubly occupied 5s orbital of one of the tin atoms overlaps with the empty 5p π orbital of the other tin atom and *vice versa*.^{5–8} The situation for the stannenes is not so clear cut since both angled as well as planar structures have been predicted.^{7–9}

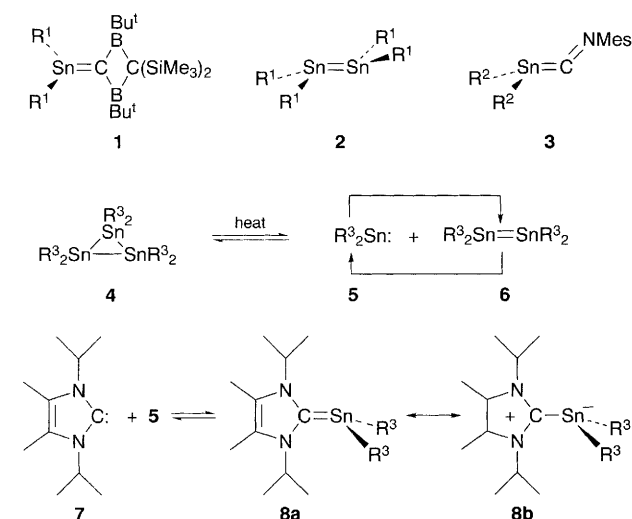
Stable singlet carbenes of the 4,5-dimethylimidazol-2-ylidene type¹⁰ have been known for a few years and open the possibility to check these theoretical calculations on the basis of the reactions of such carbenes with stannylenes. For this purpose, the 1,3-diisopropyl derivative **7**, which is easily accessible from the reaction of an imidazole-3(2*H*)-thione with potassium,¹¹ was treated with the bis(2,4,6-triisopropylphenyl)stannylene **5**, obtained in turn by thermolysis of the cyclotristannane **4**.^{12,13} The adduct **8** [mp 59–61 °C (dec.)] was obtained in the form of yellow, air-sensitive crystals in 37% yield. The proposed constitution is supported by complete elemental analyses and the ¹³C and ¹¹⁹Sn NMR spectroscopic data.[†]

As compared to that of the free stannylene [¹¹⁹Sn δ 1420],¹³ the ¹¹⁹Sn NMR signal of **8** is shifted by 710 ppm to higher field

and thus occurs in the region typical for the tricoordinated tin atoms in **2**¹⁴ or **6**.¹² The signal for the carbene carbon atom also experiences a shift to higher field in the ¹³C NMR spectrum, albeit of only 28 ppm. The X-ray crystal structure analysis provides more information about the bonding situation in **8** (Fig. 1).[‡]

The most conspicuous features of the structure of **8** are the pyramidal environment of the substituents about the tin atom, as reflected by the angle of 68.6° between the C(12)–Sn–C(27) plane and the Sn–C(1) vector, and the extremely large Sn–C(1) separation. With a length of 237.9(5) pm, this bond is considerably longer than the calculated 195–206 pm^{7–9} for the parent stannene H₂Sn=CH₂ and even exceeds the lengths of the also large single bonds Sn–C(12) and Sn–C(27). Although according to theoretical predictions a pyramidalisation at the tin atom should be accompanied by a lengthening of the Sn=C double bond, the geometry of the molecule observed here clearly indicates that the adduct **8** is better described by the limiting formula **8b** than by the stannene form **8a**. The similarities between **8** and an adduct recently isolated from the reaction of a stable carbene with germanium(II) iodide¹⁵ are immediately apparent although the ¹³C NMR data of the latter molecule are highly suggestive of an even stronger charge separation. The weakness of the central Sn–C bond of **8** is also reflected in its chemical behaviour. Although **8** is stable in the solid state, it decomposes rapidly in the gas phase—and slowly in solution—into its starting components where mainly 1,3,5-triisopropylbenzene is detected as the subsequent product from **5**.

The reaction reported here for the first time between a stannylene and a stable carbene, which in spite of the lacking ylidic character,¹⁶ still acts as a nucleophile, again illustrates the fascinating properties of the imidazol-2-ylidene system. It



Scheme 1 R¹ = CH(SiMe₃)₂, R² = 2,4,6-(CF₃)₃C₆H₂, R³ = 2,4,6-Pr₃C₆H₂

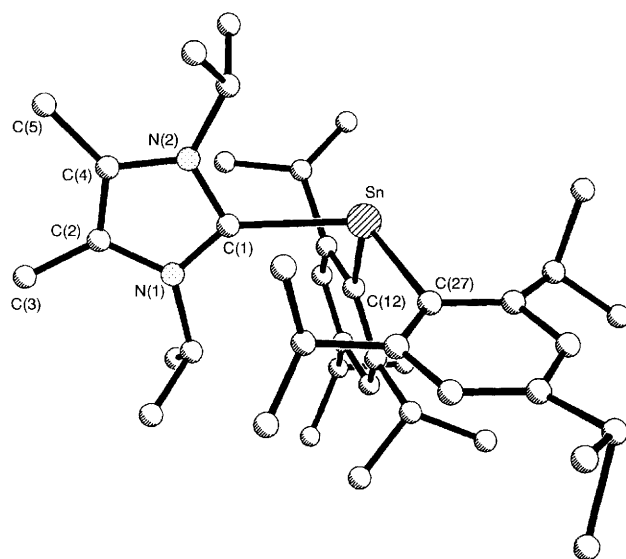


Fig. 1 Molecular structure of **8** (hydrogen atoms omitted). Selected bond lengths (pm) and angles (°): Sn–C(1) 237.9(5), Sn–C(12) 232.1(2), Sn–C(27) 230.8(2), C(1)–N(1) 136.5(6), C(1)–N(2) 136.1(6), N(1)–C(2) 138.8(7), N(2)–C(4) 138.8(7), C(2)–C(4) 134.6(9), C(12)–Sn–C(27) 106.7(1), C(12)–Sn–C(1) 92.6(1), C(27)–Sn–C(1) 109.4(1), N(1)–C(1)–N(2) 104.6(4).

remains to be seen whether or not the reactions of stannylenes with electrophilic carbenes will give rise to stannenes with the theoretically predicted properties.

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Footnotes

† NMR data were recorded at room temp. in C₆D₆ solution at 75.4 MHz (¹³C) and 111.9 MHz (¹¹⁹Sn). The ¹H NMR spectrum (300 MHz) reflects the steric congestion of the *ortho*-isopropyl groups. *Selected spectroscopic data for 8*: ¹³C NMR δ 10.10 (CH₃-C=C), 21.19, 24.05, 24.60, 25.67, 34.77, 37.2 (broad), 53.90 (N-CH-Me), 120.88 (CH arom), 125.99 (Me-C=C), 147.00, 156.2 (broad), 177.2 (Carbene); ¹¹⁹Sn NMR δ 710.0.

‡ *Crystal data for 8*: C₄₁H₆₆N₂Sn, *M* = 705.6, crystal size 0.40 × 0.30 × 0.15 mm, space group *P* $\bar{1}$, *a* = 1058.5(2), *b* = 1116.7(2), *c* = 1828.4(3) pm, α = 72.24(2), β = 89.09(3), γ = 85.93(2)°, *V* = 2.0530(6) nm³, *Z* = 2, *D_c* = 1.142 g cm⁻³, λ = (Mo-Kα) 71.073 pm, *T* = 296(2) K, 2θ_{max} 48°, unique reflections 6433, observed [*I* > 2σ(*I*)] 6430, variables 367. The structure was solved by direct phase determination using the SHELXL 93 program system and refined by full-matrix least-squares techniques. Hydrogen atoms were placed in calculated positions, and all other atoms were refined anisotropically. The carbon atoms C33 to C38 are occupying two positions, each with an occupancy factor of 0.5, *R* = 0.050, *wR*₂ = 0.1244. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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