E–E Triple Bonds

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Cleavage of the Sn–Sn Multiple Bond in a Distannyne by Cyclooctatetraene: Formation of the π-Bound Inverse Sandwich Complex [(Ar′Sn)$_2$(μ$_2$-η^2:η^3-cot)]**

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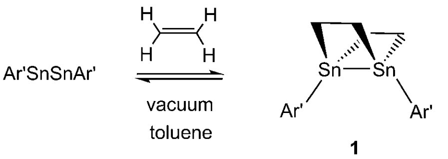
The syntheses of stable heavier group 14 element alkyne analogues have attracted considerable attention in the last decade.[1–8] Reactivity studies on these molecules have afforded insights into the nature of the E–E triple bonds (E = group 14 element), and have supported the existence of a multiplicity of resonance forms, including those with singlet diradical character.[9–12] Recently we have shown that the distannyne [Ar′SnSnAr′] (**1**) (Ar′ = C_6H_3-2,6-(C_6H_3-2,6-*i*Pr_2)$_2$) undergoes reversible complexation with two molecules of either ethylene or norbornadiene [Eq. (1)],[13] processes that are considered symmetry-forbidden for alkynes but are enabled by the higher reactivity caused by the strained geometry in the heavier analogues.



(1)

We present here studies of the reaction of **1** with cyclic polyolefinic molecules, in particular cyclooctatetraene (cot), 1,5-cyclooctadiene (cod), 1,4-cyclohexadiene and cyclohexene, and show that the reaction with cot results in the complete cleavage of the Sn≡Sn bond to give a new inverse-sandwich structure composed of mono aryl–stannyl units and a planar C_8H_8 ring. These types of cot-bridged molecules are known for f-block[14–17] and s-block elements,[18,19] whereas transition metal analogues isolated to date display olefinic or "semi-aromatic" cot character.[20–23] The inverse sandwich coordination archetype is unknown for cot derivatives of the p-block elements and no π-coordinated cot^{2-} complex of a p-block element has been characterized. Cyclized [2+1] derivatives of cot are known for phosphorus fragments but in these cases the cot rings remain non-planar with undelocalized π electrons and alternating C–C distances.[24,25]

Addition of cot to dark green **1** in toluene results in the immediate formation of red-orange [(Ar′Sn)$_2$(μ$_2$-η^2:η^3-cot)] (**2**), which was recrystallized in 76% yield [Eq. (2)]. Structural data obtained by X-ray diffraction[26] show an *anti*-bimetallic structure, with the cot ring unsymmetrically bridging the two Sn atoms in an approximate η^2:η^3 manner (Figure 1), demonstrating that the reaction has proceeded with the cleavage of the Sn–Sn bond in **1**. The cot ring has the almost planar geometry expected for the 10π aromatic form,[18] containing similar C–C distances and C-C-C angles averaging 1.411(6) Å and 134.4(4)° (cf. 1.39–1.42 Å and 135° in K_2-cot). The Sn atoms are bound on opposing faces of the cot ring but not on opposing edges; instead they are slipped slightly towards each other, which may account for the uniquely small C–C distance found on the side of the cot ring more distant from the Sn atoms (C7–C8 1.359(6) Å).

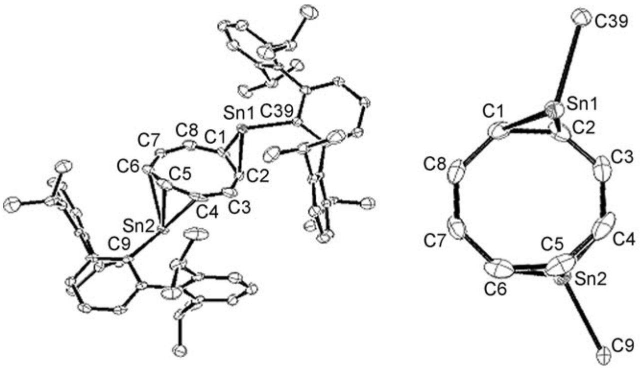


Figure 1. Thermal ellipsoid (50%) plots of **2** without H atoms. Selected bond lengths [Å] and angles [°]: C1–C2 1.420(5), C2–C3 1.390(6), C3–C4 1.434(6), C4–C5 1.407(6), C5–C6 1.419(6), C6–C7 1.418(6), C7–C8 1.359(6), C1–C8 1.440(6), Sn1-C39 2.231(4), Sn1–C2 2.366(4), Sn1–C1 2.506(4), Sn2–C9 2.242(4), Sn2–C4 2.541(4), Sn2–C5 2.364(4), Sn2–C6 2.590(4); C2-C1-C8 133.6(4), C3-C2-C1 133.8(4), C2-C3-C4 135.0(4), C5-C4-C3 134.3(4), C4-C5-C6 134.2(4), C7-C6-C5 132.7(4), C8-C7-C6 136.0(4), C7-C8-C1 135.1(4).

Sn–C(cot) distances show Sn1 bonded to C2 (2.366(4) Å) and less strongly with C1 (2.506(4) Å). The Sn1···C3 distance is significantly longer (2.679(4) Å). The other tin atom, Sn2, shows a different bonding pattern, and is primarily bound to C5 (Sn2–C5 2.364(4) Å) with more highly symmetric interactions to the adjacent carbons C4 and C6 (2.541(4) and 2.590(4) Å). Sn–C(*ipso*) terphenyl distances (Sn1–C39

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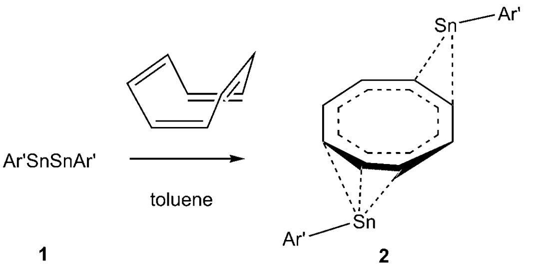

(2)

2.231(4), Sn2–C9 2.242(4) Å) are similar to other Sn−C bond lengths in tin terphenyl derivatives.[9,13,27] The angles observed are consistent with π interactions between the Sn atoms and the ring (angle between planes of cot ring and Sn1-C2-C3 86°; Sn2-C4-C5 87°). Additionally, a strongly bent coordination geometry is found at each Sn atom in the range found in two-coordinate tin(II) compounds (95–120°)[28] with angles C39-Sn1-C2 94.8(1)° and C9-Sn2-C5 95.6(1)° consistent with minimal s/p hybridization.

NMR data are consistent with fluxional, aromatic behavior of the cot unit: a single resonance for this moiety was found in both the ^{1}H and the ^{13}C{^{1}H} NMR spectra at $\delta = 5.66$ and 97.1 ppm respectively ([D$_6$]benzene) which do not decoalesce at temperatures as low as −60 °C ([D$_8$]toluene). These data are consistent with either a spinning carbocyclic ring or full η^8-coordination in solution. The ^{13}C NMR chemical shift of $\delta = 97.1$ ppm is shifted upfield with respect to uncoordinated cot ($\delta = 132.7$ ppm), approaching the shift found in K$_2$-cot ($\delta = 89.9$ ppm),[22] consistent with the increased ring current of the planar aromatic form. The corresponding cot coupling constant $^1J_{\text{C-H}}$ of 157 Hz is similar to those observed for [(Cp$^{i\text{Pr}4}$M)$_2$(μ_2-cot)] (M = Ca, Sr, Ba: 157, 157, and 158 Hz, respectively)[19] and uncoordinated cot (155 Hz), but larger than for K$_2$-cot (143 Hz).[22] A single resonance is found in the ^{119}Sn{^{1}H} NMR spectrum at $\delta = -85$ ppm, well upfield of the range generally observed for two-coordinate stannylenes (e.g. $\delta = 2235$ ppm in Sn(Ar′)$_2$),[27] but consistent with a higher coordination number and increased ^{119}Sn nuclear shielding (cf. $\delta = -2199$ ppm for [Sn(η^5-Cp)$_2$]).[29]

DFT calculations[30] carried out on the model compound [(MeSn)$_2$(μ-cot)] reproduced a very similar geometry to that of the structure of **2**, consistent with cot aromaticity. Additionally, a slightly smaller C7–C8 distance (1.370 Å), analogous to that found in **2** (1.359(6) Å), was calculated. The HOMO–LUMO gap was computed at 362.3 kJ mol^{-1} (330 nm), correlating well with the primary absorption found experimentally in the UV/Vis spectrum at 340 nm.

The cot dianion has been shown by Lappert et al. to reduce [Sn(CH(SiMe$_3$)$_2$)$_2$Cl$_2$] to give the stannylene and free cot.[31] It is interesting to note that for the reaction reported here, monovalent **1** acts as the reducing agent towards neutral cot. The electrochemical reduction of cot requires moderately strong reducing potentials (−1.99 V vs. SCE)[32] and therefore the tin(I) compound **1** clearly demonstrates its powerful reducing character, reminiscent of classical metal-type redox reactivity.[15,18,33] Mixing **1** with anthracene, which has a similar first electron redox potential to cot (−1.98 V)[32] gave no reaction even with heating in benzene (60 °C). A principal difference between anthracene and cot, despite the similar 1e redox waves, is that the former is a 14π aromatic unit and reduction occurs with population of a π* orbital, whereas cot is 8π olefinic and 2e reduction forms a planar 10π aromatic unit by filling the non-bonding HOMO. **1** also failed to react with 1,5-cyclooctadiene, 1,4-cyclohexadiene, and cyclohexene. These observations support the view that **1** is generally reactive toward strained (activated) or unsubstituted olefins, as previously reported.[13]

The reaction between **1** and cot is distinct from previous studies with unsaturated systems, because of the irreversible coordination and formal reduction of the polyolefin in contrast to a reversible cycloaddition process [Eq. (1)]. Additionally, scission of the Sn≡Sn bond was observed from a substrate lacking electronegative donor atoms. Cleavage of homonuclear group 14 multiple bonds has been shown for Si and Ge triple bonds following the three-fold addition of an olefin,[7a,10,12] and also recently for an aromatic C−C bond using a tungsten complex.[34]

In conclusion, we have demonstrated that the triple bond in **1** can be completely cleaved by an olefinic hydrocarbon to give the first p-block π-complex of cot. The driving force for this unique transformation is likely to be the formation of the 10π aromatic cot dianion, which may follow an initial [2+2] cycloaddition of one of the unsaturated C=C bonds to the Sn≡Sn bond.

Experimental Section

All manipulations were carried out under anaerobic and anhydrous conditions. ^{1}H, ^{13}C and ^{119}Sn NMR spectra were recorded on a Varian 300 spectrometer and referenced to known standards.

[(Ar′Sn)$_2$(cot)] (**2**): To a solution of [Ar′SnSnAr′][3] (0.23 g, 0.22 mmol) in 50 mL toluene, cyclooctatetraene (50 μL, 0.44 mmol) was added through a syringe, resulting in an immediate color change from deep green to red. The solution was stirred for 5 min, reduced to ca. 25 mL under reduced pressure, and stored at −20 °C for 2 d to afford orange crystals of **2** (0.19 g, 0.17 mmol, 76 % yield). m.p. 200 °C (dec); ^{1}H NMR (300 MHz, C$_6$D$_6$, 298 K): $\delta = 1.04$ (d, 24 H, *o*-CH-(CH$_3$)$_2$, $^3J_{\text{HH}} = 6.9$ Hz), 1.22 (d, 24 H, *o*-CH(CH$_3$)$_2$, $^3J_{\text{HH}} = 6.9$ Hz), 2.98 (sept, 8 H, CH(CH$_3$)$_2$, $^3J_{\text{HH}} = 6.9$ Hz), 5.66 (s, 8 H, C$_8$H$_8$) 7.20–7.47 ppm (m, 18 H, *m*-C$_6$H$_3$, *p*-C$_6$H$_3$, *m*-Dipp, and *p*-Dipp; Dipp = 2,6-*i*Pr$_2$C$_5$H$_3$); ^{13}C{^{1}H} NMR (C$_6$D$_6$, 100.6 MHz, 298 K): $\delta = 23.4$ (CH(CH$_3$)$_2$), 27.0 (CH(CH$_3$)$_2$), 31.7 (CH(CH$_3$)$_2$), 97.2 (C$_8$H$_8$), 124.3 (*m*-Dipp), 127.1 (*p*-C$_6$H$_3$), 129.7 (*o*-Dipp), 130.4 (*m*-C$_6$H$_3$), 140.8 (*p*-Dipp), 146.6 (*i*-Dipp), 147.8 (*o*-C$_6$H$_3$), 182.7 ppm (*i*-C$_6$H$_3$); ^{119}Sn{^{1}H} NMR (C$_6$D$_6$, 186.3 MHz, 298 K): $\delta = -85$ ppm; $\lambda_{\max}$ (ε): 340 nm (600 L mol^{-1} cm^{-1}).

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