Synthesis and structural characterization of (THF)$_3$Na{(SnC$_6$H$_3$–2,6-Trip$_2$)$_2$} (Trip = C$_6$H$_2$-2,4,6-i-Pr$_3$): effects of cation–anion association on Sn–Sn multiple bonding[☆]

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Abstract

The synthesis and structural characterization of the contact ion-pair species (THF)$_3$Na{(SnC$_6$H$_3$–2,6-Trip$_2$)$_2$} (**1**) are described. The compound **1** was synthesized by the reduction of Sn(Cl)C$_6$H$_3$–2,6-Trip$_2$ with sodium anthracenide in THF. Its UV–vis and EPR spectra are very similar to those previously reported for the solvent separated ion pairs [K(THF)$_6$] [(SnC$_6$H$_3$–2,6-Trip$_2$)$_2$] and [K(dibenzo–18–crown–6)(THF)$_3$] [(SnC$_6$H$_3$–2,6-Trip$_2$)$_2$]. The X-ray crystal structure of **1** reveals an Sn–Sn distance 2.8107(13)Å and an Na–Sn bond length of 3.240(7)Å with C–Sn–Sn angles of ca. 98°. The Sn–Sn distance and tin geometry are very similar to those previously observed. These similarities lead to the conclusion that the Sn–Sn bonding is affected only in a minor way by sodium coordination. Crystal data at 130 K with CuKα ($\lambda = 1.54178$Å) radiation; **1**, $a = 22.142(5)$, $b = 15.845(4)$, $c = 23.425(7)$Å, $\beta = 107.83(2)°$, Z = 4, monoclinic, space group C2/c, R1 = 0.0615 for 4872 ($I = 2\sigma(I)$) data. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

A recent publication has disclosed the synthesis and structure of the radical ion [(SnC$_6$H$_3$–2,6-Trip$_2$)$_2$]$^{-•}$ [1] which is the singly-reduced derivative (a) of the distannylene (b). The lattice species is a valence isomer of the distannyne (c) as shown by:

singly reduced distannylene   distannylene   distannyne

(a)   (b)   (c)
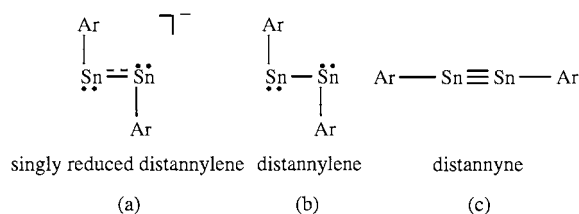
An important aspect of the structure was that the anion did not interact with either of the counter-cations [K(THF)$_6$]$^+$ or [K(dibenzo–18–crown–6)(THF)$_3$]$^+$ with which it can be crystallized. In principle, a counter-cation may interact with at least two different sites on the anion; with the aromatic substituents or with the center of the anionic charge (presumably the tins), unless it is coordinated to other donors, i.e. ether oxygens in this case. Numerous structures of salts featuring various terphenyl substituents have provided ample evidence that alkali metal ions can interact in various ways with the ortho-aryl rings of these ligands [2]. Furthermore, calculations [3] have shown that the hypothetical compound Na$_2${GaC$_6$H$_3$–2,6–Ph$_2$}$_2$ (which was used as a model for Na$_2$(GaC$_6$H$_3$–2,6–Trip$_2$)$_2$ [4]) features Na– –Ph bonding and a Ga–Ga distance 0.11 Å shorter than in Na$_2${GaPh}$_2$ which does not have these interactions. Apparently, anion–cation bonding may have a very large effect on the bonding in

the anion in some molecules. At present, however, there are no examples of species having a cation–anion interaction involving the central element(s) which is unsupported by bonding to the pendant aryl groups. In this paper the synthesis and characterization of such a compound as exemplified by $(THF)_3Na\{(SnC_6H_3-2,6-Trip_2)_2\}$, **1**, are reported.

2. Experimental

2.1. General procedures

All experiments were performed under a nitrogen atmosphere either by using modified Schlenk techniques or in a Vacuum atmospheres HE43-2 drybox, solvents were freshly distilled from sodium-potassium alloy and degassed twice prior to use. EPR spectra were recorded on a Bruker ECS-106 spectrometer. The electronic spectrum was obtained on a Hitachi-1200 instrument. $Sn(Cl)C_6H_3-2,6-Trip_2$ was synthesized as previously described [1].

2.2. $(THF)_3Na\{(SnC_6H_3-2,6-Trip_2)_2\}$ (1)

An ice-cold blue solution of sodium (0.031 g, 1.35 mmol) and anthracene (1.35 mmol, 0.178 g) in THF (35 ml) was added dropwise to a rapidly stirred solution of $Sn(Cl)C_6H_3-2,6-Trip_2$ (0.84 g, 1.32 mmol) in THF (20 ml) which was cooled in a dry-ice acetone bath. The reaction mixture became orange–brown in color and was allowed to warm to room temperature. Upon stirring for 24 h, the solvents were removed under reduced pressure and the residue was warmed (50°C) in the presence of a cold finger to remove the anthracene. The remaining material was extracted with pentane (40 ml). The cloudy solution was allowed to settle and the supernatant liquid was filtered through Celite. Reduction of the volume to ca. 20 ml under reduced pressure and storage in a −20°C freezer for several days afforded the product **1** as orange–red crystals. Yield: 0.35 g, 36%. Calc. for $C_{84}H_{122}NaO_3Sn_2$: C, 70.05, H, 8.54. Found: C 70.96, H 8.19.

2.3. X-ray data collection and refinement

The crystals were coated with a layer of hydrocarbon oil upon removal from the Schlenk tube. Suitable crystals were selected attached to a glass fiber and immediately placed in the low temperature N_2 stream [5]. X-ray data were collected on a Siemens P4 diffractometer equipped with a rotating anode, nickel filter and locally modified LT apparatus. Calculations were carried out using the SHELXTL-PLUS programs [6]. Scattering factors and the correction for anomalous scattering were taken from common sources [7]. The structure was

solved by direct methods and refined by full-matrix least squares refinement. An absorption correction was applied using the program XABS2 [8]. Crystal data for **1** ($C_{84}H_{122}NaO_3Sn_2$, MW 1440.19) at 130 K using Cu–K_α ($\lambda = 1.54178$ Å) radiation: $a = 22.142(5)$, $b = 15.845(4)$, $c = 23.425(7)$ Å, $\beta = 107.83(2)°$, $Z = 4$, monoclinic, space group $C2/c$, $d = 1.223$ Mg m^{-3}, abs. coefft. 5.464 mm^{-1}, $F_{000} = 3044$, Θ range = 3.49–56.42°, 20 scans, 5160 independent reflections of which 4872 had $I > 2(\sigma)I$ which afforded an $R1$ of 0.0615 and a wR_2 value of 0.1631. Crystallographic data for the structural analysis available have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 110871 for compound **1**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ [Fax: +44-(1223)-336-033 or e-mail: deposit@ccdc.cam.ac.uk].

3. Results and discussion

The reduction of $Sn(Cl)C_6H_3-2,6-Trip_2$ by sodium anthracenide proceeds smoothly in THF at low temperature. The stoichiometry of the reactants was 1:1 as it was intended to synthesize the neutral tin compound $(SnC_6H_3-2,6-Trip_2)_2$ which is a tin analogue of an alkyne. The previously available structures of the $[(SnC_6H_3-2,6-Trip_2)_2]^-$ ion [1] display a very bent geometry at tin, and this is expected to be retained in a putative neutral species which should have a single
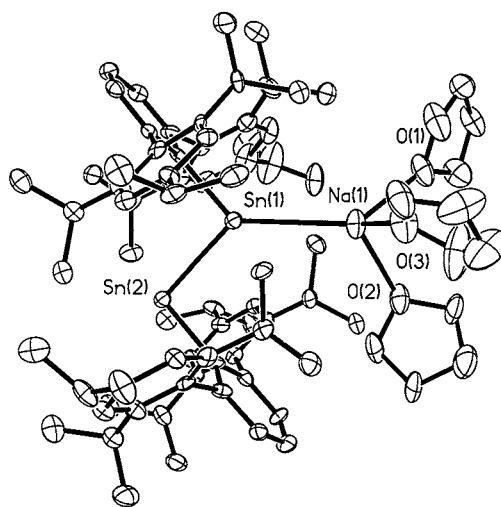

Fig. 1. Thermal ellipsoid (30%) drawing of **1**. H atoms are not shown for clarity. Selected bond distances (Å) and angles (°) not given in the text or Table 1 are: Na(1)–O(1) = 2.257(15), Na(1)–O(2) = 2.347(15), Na(1)–O(3) = 2.467(16), C(1)–Sn(1)–Na(1) = 113.3(4), Sn(2)–Sn(1)–Na(1) = 130.36(15), C(1)–Sn(1)–Sn(2) = 97.9(3), O(1)–Na(1)–O(3) = 84.3(6), O(1)–Na(1)–O(2) = 94.2(5), O(2)–Na(1)–O(3) = 92.1(6), O(1)–Na(1)–Sn(1) = 127.9(5), O(2)–Na(1)–Sn(1) = 114.1(4), O(3)–Na(1)–Sn(1) = 133.5(5), C(6)–C(1)–C(2) = 114.4(13), C(42)–C(37)–C(38) = 117.4(13).

Table 1
Comparison of the CSnSnC core bond distances (Å) and angles (°) in [(SnC$_6$H$_3$–2,6-Trip$_2$)$_2$]$^-$ species

	Sn–Sn (Å)	Sn–C (°)	Sn–Sn–C (°)
[K(THF)$_6$][(SnC$_6$H$_3$–2,6-Trip$_2$)$_2$][a]	2.8123(9)	2.236(5)	95.20(13)
[K(dibenzo-18-crown-6)(THF)$_3$][(SnC$_6$H$_3$–2,6-Trip$_2$)$_2$][a]	2.7821(14)	2.293(13), 2.269(14)	93.6(4), 95.0(4)
	2.8236(14)	2.226(7)	97.3(2)
(THF)$_3$Na(SnC$_6$H$_3$–2,6-Trip$_2$)$_2$ (**1**)[b]	2.8107(13)	2.216(16)	97.9(3)
		2.190(14)	98.0(4)

[a] Ref. [1].
[b] This work.

rather than triple tin–tin bond with a lone pair of electrons located at each tin as depicted by (b). However, only **1** could be isolated from solution. Apparently, reduction of the neutral dimer to give a monoanion takes place very easily (presumably owing to the presence of low-lying empty p-orbitals on each tin) to afford the mono-reduced species **1**. The EPR spectrum of **1** in THF solution at room temperature displays a signal at $g = 2.0068$ with hyperfine coupling to the ^{117}Sn and ^{119}Sn nuclei with $a(^{117}$Sn) and $a(^{119}$Sn) values of 8.3 and 8.5 G. The latter values indicate that the unpaired electron is located in an orbital of essentially π-character.

The structure of **1** is illustrated in Fig. 1. It consists of well separated molecules which are composed of a contact ion pair involving {Na(THF)$_3$}$^+$ and {(SnC$_6$H$_2$–2,6-Trip$_2$)$_2$}$^-$ moieties It features an Na–Sn distance of 3.240(7) Å. This value is considerably longer than the 3.070(5) Å distance seen in (η^6-PhMe)NaSn(SiMe$_3$)$_3$ [9], which is the only other structurally characterized species having a Na–Sn bond. The difference is probably connected with the different co-ligands; three THF's in the case of **1** and a π-interacting toluene for (η^6-PhMe)NaSn(SiMe$_3$)$_3$. The Na$^+$ ion has very distorted tetrahedral geometry (O–Na–O angles are in the range 84.3(6)–94.2(5)°) with Na–O distances averaging 2.36(2) Å, which is within the range found for ether coordinated organosodium compounds [10]. The closure of the O–Na–O angles is probably due to the high steric encumbrance of the –C$_6$H$_3$–2,6–Trip$_2$ ligands which tends to displace the THF ligands toward each other.

In the {(SnC$_6$H$_3$–2,6–Trip$_2$)$_2$}$^-$ moiety the C(1)Sn(1)Sn(2)C(37) array is essentially coplanar. The Na$^+$ lies very slightly out of this plane. A comparison of the structural parameters of the CSnSnC array in **1** and the previously published solvent separated analogues is provided in Table 1. It can be seen readily that there is very little change in the Sn–Sn, Sn–C bond lengths or in the Sn–Sn–C angles when the ion associates with the {Na(THF)$_3$} moiety in **1**. The Sn–Sn–C angle becomes slightly (2–3°) wider but the Sn–Sn distance is virtually the same as those previously observed. In other words, the original bonding model proposed for the ions [1], i.e. formal Sn–Sn bond order of 1.5, an unpaired electron in a π-orbital perpendicular to the CSnSnC plane, and

a lone pair of electrons at each tin, remains valid. Furthermore, the coordination of the sodium ion at a position where the lone pair of electrons is expected to be lends further credence to this bonding model. A research program to study doubly-reduced [11] and neutral analogues of **1** is underway.

Acknowledgements

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