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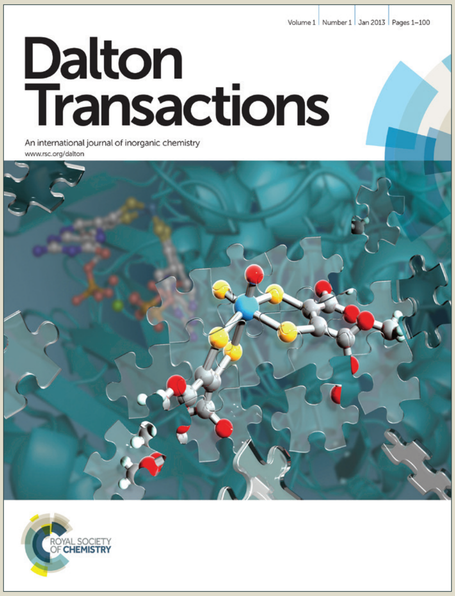

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Triphenylene-based tris-*N*-heterocyclic stannylenes

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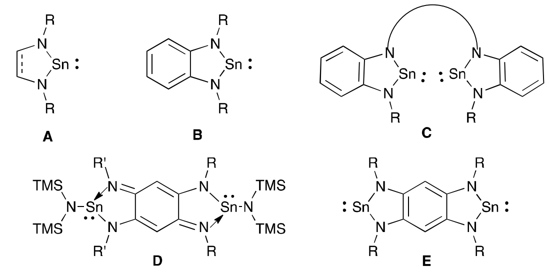
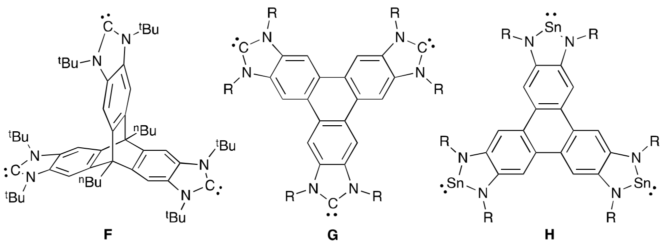
Two planar tridentate *N*-heterocyclic stannylenes are synthesized from the corresponding 2,3,6,7,10,11-hexaamino-triphenylene and $Sn[N(TMS)_2]_2$. Multinuclear NMR and absorption spectra of these tris-stannylenes are reported. Molecular structure of the *N*-benzhydryl-substituted tris-stannylene is also realized.

Being the heavier homologue of carbene, the synthesis and coordination chemistry of stannylene have also attracted much attention. Compared with carbene (H_2C:), stannylene adopts singlet ground state as a result of less effective s-p hybridization.[1-5] Among the reported stannylenes, we are most interested in the stable *N*-heterocyclic stannylenes for their potential to replace *N*-heterocyclic carbene ligands in metal complexes. The unsaturated and saturated *N*-heterocyclic stannylenes (NHSns) of type **A**[6-8] (Scheme 1) have been utilized as ligand to transition metals[9] or as precursor for low temperature atomic layer deposition of SnO_2 and SnS thin films.[10, 11] Benzo-fused NHSns featuring various *N*-substitutents have also been reported (**B**).[12-19] In recent years, several ditopic NHSns have also been reported. Stannylene **C** have proved to be effective in supporting transition metal centres[20-22] as well as main-group fragments such as SnO and PbO,[23] the heavier homologues of CO. Transamination between $Sn[N(TMS)_2]_2$ and 1,2,4,5-tetra(alkylamino)benzene resulted in the isolation of imine-coordinated ditopic NHSns (**D**).[24]



Scheme 1: Examples of mono- and bi-dentate *N*-heterocyclic stannylenes.

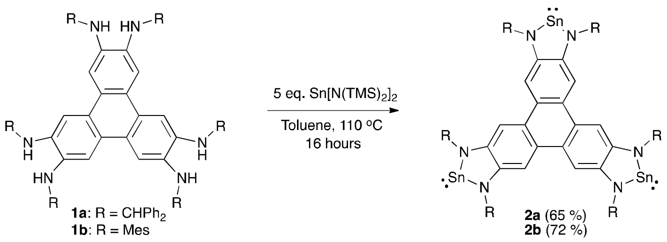
Although NHSns can be straightforwardly synthesized from the corresponding lithioamides and $SnCl_2$,[12, 25, 26] a majority of benzannulated NHSns are prepared from transamination of the corresponding di-amines and $Sn[N(TMS)_2]_2$.[27] However, bis-stannylene of type **E** could not be generated from transamination due to the facile oxidation of tetraaminobenzene by $Sn[N(TMS)_2]_2$ leading to the formation of 1,4-benzoquinonediimine and tin metal.[24] The extension of the π-conjugated molecular backbone from benzene to triphenylene may help to prevent such undesired redox reaction between poly-amines and Sn(II) centre.



Scheme 2: Tritopic *N*-heterocyclic carbenes and stannylene with D_{3h} symmetry.

In the past few years, several benzannulated rigid tri-dentate *N*-heterocyclic carbene ligands featuring triptycene (**F**)[28] or triphenylene (**G**)[29-31] backbones have been reported (Scheme 2). Catalysis studies of the tri-nuclear metal complexes of **G** suggest that the presence of triphenylene backbone enhances the catalyst performance via inclusion of favourable π–π interaction between aromatic substracts and the carbene ligand.[29] Ligand **G** has also been incorporated into three-dimensional porous organometallic polymers.[32] However, poly-dentate stannylenes featuring such D_{3h} molecular scaffold have never been reported. In this work, we report the syntheses and characterisations of two planar tridentate *N*-heterocyclic stannylenes (**H**).

The 2,3,6,7,10,11-hexa(*N*-benzhydrylamine)triphenylene (**1a**) was synthesized from hydride reduction of the corresponding hexa-diphenylimine derivative and was isolated as an orange-yellow solid.[33] The mesityl-substituted amine (**1b**) was prepared according to the reported procedure.[31] While **1b** is prone to oxidation, **1a** is stable under ambient condition for several weeks. Hexaamines **1a** and **1b** were allowed to react with five equivalents of $Sn[N(TMS)_2]_2$ in toluene at 110 °C under inert atmosphere for 16 hours. Upon heating, the reaction mixture gradually turned from yellowish brown to dark red. After removal of all volatiles, residuals were washed with hexane to yield the anticipated tris-stannylenes (**2a** and **2b**) as red solids in moderate yield (Scheme 3).



Scheme 3: Synthesis of tris-*N*-heterocyclic stannylenes.

The formation of the D_{3h} symmetrical tridentate *N*-heterocyclic stannylenes was verified with multi-nuclear NMR spectroscopies. The ^1H NMR spectra of **2a** and **2b** contained only one set of signals arisen from the triphenylene backbone and the *N*-substituents, indicating the existence of three-fold symmetrical molecule in the solution. The shift of the methine proton (N-C*H*Ph$_2$) signal from 5.48 ppm of **1a** to 6.61 ppm of **2a** suggested the presence of aromatic character of the C_2N_2Sn ring. The presence of Sn(II) centre was verified with ^{119}Sn NMR spectroscopy. The ^{119}Sn NMR resonances of **2a** and **2b** were respectively detected at 226.4 ppm and 257.1 ppm in C_6D_6. These observed chemical shifts are comparable to that determined for the related *N*-(1-phenylethyl) (δ = 250.4 ppm) and *N*-mesityl NHSns (δ = 236.2 ppm),[16] confirming the formation of tris-NHSns.

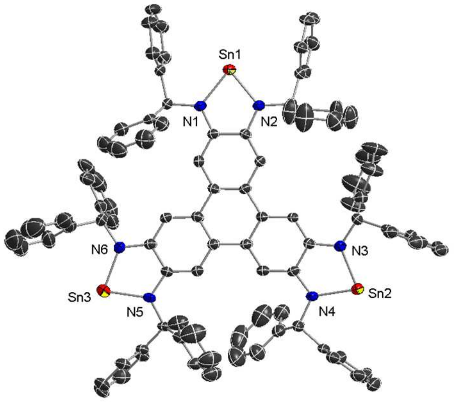


Figure 1: Molecular structure of **2a** with thermo ellipsoids set at 50% probability level. Hydrogen atom and solvent molecules are omitted for clarity. Selected bond distances (Å) and angles (deg): Sn(1)-N(1) 2.079(4), Sn(1)-N(2) 2.082(4), Sn(2)-N(4) 2.079(5), Sn(2)-N(3) 2.080(4), Sn(3)-N(6) 2.069(4), Sn(3)-N(5) 2.074(5), N(1)-Sn(1)-N(2) 78.11(17), N(4)-Sn(2)-N(3) 78.06(17), N(6)-Sn(3)-N(5) 78.48(17).

The presence of three divalent tin centres in **2a** was further confirmed with X-ray diffraction analysis on single crystals of **2a**. Dark red single crystals of **2a** were obtained from diffusion of hexane into a toluene solution of **2a** in a glove-box at room temperature. Tris-stannylene **2a** crystalized in triclinic P-1 space group as a toluene and hexane solvate (Figure 1). Although the molecule lost its high symmetry in solid state as a result of the differences in orientation of the *N*-benzhydryl substituents and the ruffled triphenylene backbone, numerical parameters of the three NHSn moieties are essentially identical. The averaged Sn-N bond distance of 2.077 Å and the N-Sn-N angle of 78.2° are comparable to that of mono- and bi-dentate benzannulated NHSns.[16, 17, 21, 22] However, the commonly observed intermolecular interactions of benzannulated NHSns in solid state were not identified in the crystal data of **2a**.[12, 15, 17] This could be attributed to the inclusion of a large amount of solvent molecules in the crystal lattice that prevent effective intermolecular interactions.

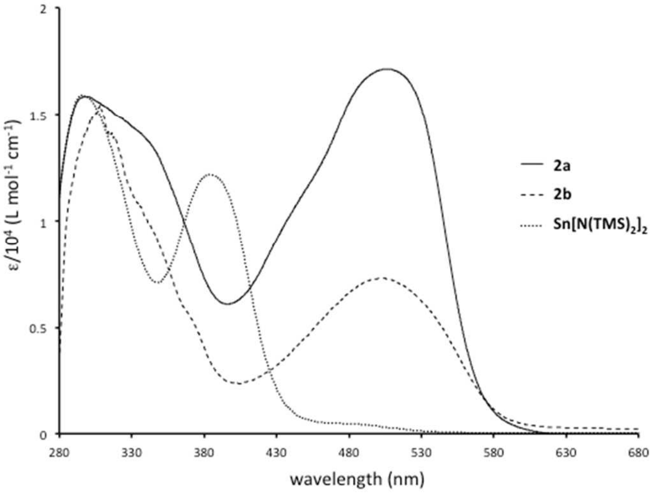


Figure 2: UV-vis absorption spectra of **2a**, **2b**, and $Sn[N(TMS)_2]_2$ in toluene.

Stannylenes are mostly coloured in hydrocarbon solution due to their symmetry forbidden n-p transition in the visible region.[34-42] As shown in Figure 2, both **2a** and **2b** feature two broad absorption bands. The absorption profiles in the UV region are similar to that of **1a** and **1b**, and can be assigned to the π–π* transitions of the central triphenylene ring and the *N*-substituents. The emerged absorption peak in the vision region (**2a**: 504 nm; **2b**: 499 nm) is ascribed to the n-p transition and is not affected by the nature of the *N*-substituents. The observed λ_{max} of the reported tris-NHSn is 120 nm longer than that of Sn[N(TMS)$_2$]$_2$ (λ_{max} = 381 nm). Similar bathochromic shift has also been observed in silylene chemistry, where the absorption maximum shifted from 292 nm of the saturated NHSi[43] to 344 nm of the benzannulated NHSi.[44, 45]

Unfortunately, preliminary reactivity investigations on the newly prepared tris-NHSns were unsuccessful. No reactions between **2** and S_8, Pd(PPh$_3$)$_4$, diphenylacetylene, B(C$_6$F$_5$)$_3$ and TMSOTf were observed. On the other hand, introduction of H_2 and BH$_3$-THF resulted in decomposition of tris-NHSns to hexamines and tin metal. These results suggested that further modification on the steric and electronic properties of the *N*-substituents are required to achieve accessible and reactive Sn(II) centres.

In summary, two planar tritopic *N*-heterocyclic stannylenes were synthesized and characterised. The symmetrical structure of the two tris-NHSns in solution was verified with multinuclear NMR spectroscopies. Structural connectivity of the benzhydryl-substituted tris-stannylene has been accomplished. UV-vis spectroscopy measurement of the two tris-NHSns revealed that the *N*-substituent has negligible effect on the energy of the lowest electronic transition of the molecule. Modification of the *N*-substituents and the extension of the chemistry to germylene and plumbylene are currently under investigation.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental details and spectroscopic data of **1a**, **2a**, and **2b**. See DOI: 10.1039/c000000x/

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