This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
Triphenylene-based tris-N-heterocyclic stannylenes

Chen-Yuan Hsu, Li-Wei Chan, Gene-Hsiang Lee, Shie-Ming Peng and Ching-Wen Chiu*

Two planar tridentate N-heterocyclic stannylenes are synthesized from the corresponding 2,3,6,7,10,11-hexamino-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 (H₂C:), stannylene adopts singlet ground state as a result of less effective s-p hybridization. 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 (Scheme 1) have been utilized as ligand to transition metals or as precursor for low temperature atomic layer deposition of SnO₂ and SnS thin films. Benzo-fused NHSns featuring various N-substituents have also been reported (B). In recent years, several ditopic NHSns have also been reported. Stannylene C have proved to be effective in supporting transition metal centres as well as main-group fragments such as SnO and PbO₂, 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).

Although NHSns can be straightforwardly synthesized from the corresponding lithioamides and SnCl₄, a majority of benzannulated NHSns are prepared from transamination of the corresponding di-amines and Sn[N(TMS)₂]₂. 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-benzoquinonedimine and tin metal. 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.
In the past few years, several benzannulated rigid tri-dentate N-heterocyclic carbene ligands featuring triptycene (F) or triphenylene (G) 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 substrates and the carbene ligand. Ligand G has also been incorporated into three-dimensional porous organometallic polymers. However, polydentate stannylenes featuring such D₃ₙ 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 hexadiphenylimine derivative and was isolated as an orange-yellow solid. The mesityl-substituted amine (1b) was prepared according to the reported procedure. 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 to yield the anticipated tris-stannylenes (2a and 2b) as red solids in moderate yield (Scheme 3).

The formation of the D₃ₙ 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-CHPh₂) signal from 5.48 ppm of 1a to 6.63 ppm of 2a suggested the presence of aromatic character of the C₅N₂Sn ring. The presence of Sn(II) centre was verified with ¹¹⁹Sn NMR spectroscopy. The ¹¹⁹Sn NMR resonances of 2a and 2b were respectively detected at 226.4 ppm and 257.1 ppm in C₅D₅. These observed chemical shifts are comparable to that determined for the related N-(α-phenylethyl) (δ = 250.4 ppm) and N-mesityl NHSns (δ = 236.2 ppm), confirming the formation of tris-NHSns.

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. Tristannylenes 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 2.075 Å and the N-Sn-N angle of 78.2° are comparable to that of mono- and bi-dentate benzannulated NHSns. However, the commonly observed intermolecular interactions of benzannulated NHSns in solid state were not identified in the crystal data of 2a. This could be attributed to the inclusion of a large amount of solvent molecules in the crystal lattice that prevent effective intermolecular interactions.

Stannylenes are mostly coloured in hydrocarbon solution due to their symmetry forbidden n-p transition in the visible region. As shown in Figure 2, both 2a and 2b feature two broad absorption

![Figure 1](image1.png)

**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) 2.037(1), Sn(1)-N(2) 2.082(1), Sn(2)-N(4) 2.079(1), Sn(2)-N(3) 2.080(1), Sn(3)-N(6) 2.069(1), N(1)-Sn(1)-N(2) 78.11(1), N(4)-Sn(2)-N(3) 78.06(1), N(6)-Sn(3)-N(5) 78.48(1).

![Figure 2](image2.png)

**Figure 2:** UV-vis absorption spectra of 2a, 2b, and Sn[N(TMS)]₂ in toluene.
bands. The absorption profiles in the UV region are similar to that of 1a and 2b, 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–π 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 (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 to 344 nm of the benzannulated NHSi.†4-6

Unfortunately, preliminary reactivity investigations on the newly prepared tris-NHSns were unsuccessful. No reactions between 1 and S_n, Pd[PPh_3]_4, diphenylacetylene, B(C_6F_5)_3, and TMSOTf were observed. On the other hand, introduction of H_2 and BH_3·THF resulted in decomposition of tris-NHSn 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 stannylene 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.

This work was supported by the Ministry of Science and Technology of Taiwan (MOST 103-2113-M-002-005 and NSC 101-2113-M-002-013).

Notes and references

Department of Chemistry, National Taiwan University, No. 1, Sec. 4, Roosevelt Rd., Taipei, Taiwan, 10617. Fax: +886-2-2363-6359; Tel: +886-2-3366-8191; E-mail: cwchiu@ntu.edu.tw
† Electronic Supplementary Information (ESI) available: Experimental details and spectroscopic data of 1a, 2a, and 2b. See DOI: 10.1039/c000000x/