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COMMUNICATION

A planar chiral [2.2]paracyclophane derived N-heterocyclic stannylene†‡

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The reaction of *pseudo-ortho*-4,12-*N*,*N*′-diphenyldiamino-[2.2]paracyclophane ((±)-3) with $Sn[N(SiMe_3)_2]_2$ results in the formation of the monomeric planar chiral N-heterocyclic stannylene (±)-4, featuring a unique [2.2]paracyclophane backbone, which has been characterized by an X-ray diffraction study.

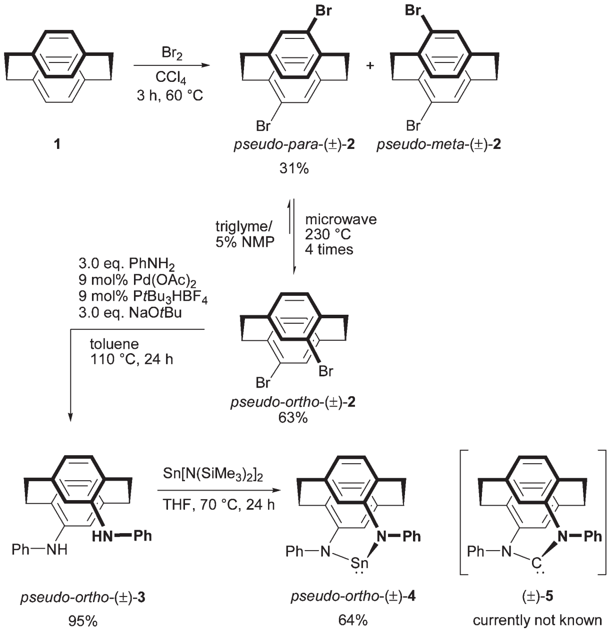
The [2.2]paracyclophane motif and heterocyclic compounds derived thereof have been known since the 1960s, but there has been a resurgence of interest in such compounds in the past decade.[1] The motivation for most studies in this field has been the desire to create heterocycles possessing either planar chirality, or the capacity for long-distance electronic communication, although this latter property has been discussed conversely in the literature.[2] The [2.2]paracyclophane motif offers the possibility for the generation of topological chirality which constitutes a key principle in overcoming the limits of traditional central chirality.[3]

N-Heterocyclic carbenes (NHCs) have attracted tremendous interest as ligands in organometallic chemistry[4] and as organocatalysts.[5] A number of NHCs bearing chiral substituents[6] but also planar chiral NHCs[7] are known, amongst which some cyclophane derived ones show promising properties in organocatalysis.[7e] The key to success seems to be the restriction of conformational flexibility, as Fürstner demonstrated with a carbene center being implemented in the stereogenic unit.[7f] While NHC-substituted [2.2]paracyclophanes have been described, no NHC is known in which the cyclophane moiety serves as the backbone, linking the two NHC ring nitrogen atoms with each other.

Compared to the large body of chemistry dealing with NHCs, their heavier germanium(II) (NHGe),[8] tin(II) (NHSn)[9] and lead(II) (NHPb)[10] analogues received less attention although some of these N-heterocyclic derivatives were known years before NHCs emerged.[11] Some NHGes and NHSns bearing chiral N-substituents have also been described.[12]

Combining the generally higher stability[11] of the diamido E^{II} derivatives with the interesting properties of expanded ring NHCs[13] we initiated a program to prepare cyclic diamido Sn^{II} compounds where two atoms of the paracyclophane backbone are amino functionalized and these two nitrogen atoms are bound to the same tin atom. Such derivatives are not only chiral but would also feature a very large (10-membered) heterocycle. The corresponding heterocyclic diaminocarbenes are not known yet. Herein we report on the first planar chiral N-heterocyclic stannylene (±)-**4** (Scheme 1) bearing a [2.2]paracyclophane backbone architecture.

Our investigation started from the readily available unsubstituted [2.2]paracyclophane (**1**). Initial bromination of **1** followed by a rearrangement under microwave conditions using a modified literature procedure resulted in the smooth formation of *pseudo-ortho*-dibromide (±)-**2** (Scheme 1, see also ESI‡).[14] A Buchwald–Hartwig amination of the *pseudo-ortho*-dibromide (±)-**2** with aniline led to the corresponding *pseudo-ortho*-diamine (±)-**3**,[15] which in a final step could be converted into the targeted NHSn (±)-**4** using $Sn[N(SiMe_3)_2]_2$.[16]



Scheme 1 Preparation of stannylene (±)-**4**.

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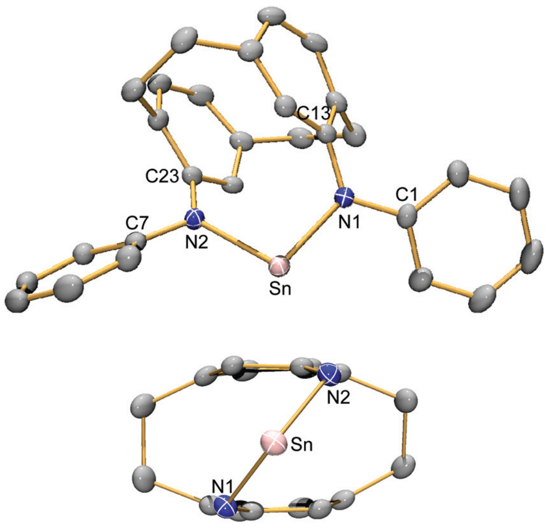

Fig. 1 Top: Molecular structure of one enantiomer of (±)-**4**. Ellipsoids are drawn at 50% probability and hydrogen atoms have been omitted for clarity; bottom part of the molecular structure of (±)-**4** with the *N*-phenyl substituents omitted to show the planar chirality. Selected bond lengths (Å) and angles (°): Sn–N1 2.1296(14), Sn–N2 2.1186(13), N1–C1 1.401(2), N1–C13 1.417(2), N2–C7 1.410(2), N2–C23 1.416(2); N1–Sn–N2 96.69(5), Sn–N1–C1 118.07(11), Sn–N1–C13 121.32(10), C1–N1–C13 120.17(14), Sn–N2–C7 115.30(10), Sn–N2–C23 125.42(11), C7–N2–C23 118.62(13).

Analysis by ^{1}H NMR spectroscopy provides evidence for the formation of stannylene (±)-**4**.‡ For example, the ^{1}H NMR spectrum of diamine derivative (±)-**3** in THF-d_8 shows a resonance for the N–H protons at δ = 5.48 ppm, which is absent in the ^{1}H NMR spectrum of stannylene (±)-**4**. The ^{119}Sn NMR spectrum (±)-**4** features a resonance at δ = 41.8 ppm compared to δ = 766 ppm (in C_6D_6)[17a] and δ = 601 ppm (in THF-d_8)[17b] for di{[bis(trimethylsilyl)]amido}tin(II).

Unequivocal evidence for the formation of a monomeric diaminostannylene with a paracyclophane backbone and a 10-membered heterocycle comes from an X-ray diffraction analysis (Fig. 1).§ As expected for a racemic mixture, (±)-**4** crystallizes in the centrosymmetric space group $P2_1/n$ with both enantiomers present in the same crystal. Due to the steric protection of the tin atom, the individual stannylenes in the crystal lattice show no intermolecular interactions of the type often observed for diaminostannylenes.[9] The N1–Sn–N2 angle (96.69(5)°) in the cyclic compound (±)-**4** is only slightly smaller than the N–Sn–N angle found in acyclic diaminostannylenes which fall in the range of about 100°–110°.[16c,17a,18] Only one acyclic diaminostannylene ($Sn(NHAr)_2$, Ar = C_6H_2-2,4,6-tBu$_3$, N–Sn–N 89.6(5)°)[19] features a smaller N–Sn–N angle than (±)-**4**. Among the known cyclic diaminostannylenes the N–Sn–N angle expands with the size of the heterocycle. Stannylenes derived from a four-membered heterocycle feature smaller N–Sn–N angles (73.2(4)° and 74.62(10)°)[20] than those obtained from five-membered heterocycles (range 77.12(7)° to 78.5 (2)°).[9b–d] A further expansion of the N–Sn–N angle to 92.63(6)° was found for a cyclic diaminostannylene derived from a six-membered heterocycle.[20b] A distannylene derived from a 12-membered heterocycle is also known (angle N–Sn–N 98.3(3)°)[21] and the N–Sn–N angle observed in (±)-**4** (10-membered heterocycle) fits perfectly in this series of expanding angles at the tin atom depending on the size of the heterocycle.

In spite of the monomeric nature of (±)-**4** in the solid state, the molecular structure determination indicates that the Lewis-acidic tin(II) center might still be accessible for small basic molecules. This is also indicated by the high-field resonance in the ^{119}Sn NMR spectrum at δ = 41.8 ppm (in THF-d_8). This resonance is significantly shifted high-field when compared to the resonances recorded for related cyclic diaminostannylenes where chemical shifts of about 200 ppm have been recorded for various derivatives.[9] The chemical shift in the ^{119}Sn NMR spectra has been shown to depend on the solvent used with basic solvents like THF leading to an upfield shift relative to hydrocarbon solvents like benzene or toluene. The upfield shift in THF results from coordination of the solvent molecules to the Lewis-acidic p-orbital at the tin center which has been demonstrated by X-ray diffraction for some derivatives.[9e,f] We assume that the upfield resonance recorded for (±)-**4** results from the combination of an electron-rich backbone and the use of THF as the solvent for the NMR experiment. Unfortunately, (±)-**4** is not soluble enough to record the ^{119}Sn NMR spectrum in benzene or toluene.

While we were able to prepare the planar chiral stannylene (±)-**4**, so far all attempts to synthesize the closely related amidinium salt precursors or the NHC (±)-**5** from diamine (±)-**3** were unsuccessful (Scheme 1). The distance between the two amino groups of the *pseudo-ortho*-diamine (±)-**3** is presumably too large to convert this diamine into the corresponding carbene precursor, whereas the larger tin(II) atom is more suitable for ring formation leading to (±)-**4**.

In summary we have prepared and characterized a [2.2]paracyclophane derived *N*,*N*′-disubstituted N-heterocyclic stannylene (±)-**4** by ^{1}H, ^{13}C and ^{119}Sn NMR and X-ray diffraction techniques. While the sterically demanding substituents prevent intermolecular interactions, the tin centre in (±)-**4** is most likely still accessible for Lewis bases like THF.

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Notes and references

§ Crystal data for (±)-**4**: $C_{28}H_{24}N_2Sn$, M = 507.18, T = 153(2) K, λ = 0.71073 Å, μ(Mo-Kα) = 1.205 mm^{-1}, monoclinic, a = 11.6317(3), b = 10.4920(3), c = 17.6728(5) Å, β = 93.7083(4)°, V = 2152.27(10) Å^3, space group $P2_1/n$, Z = 4, 25 504 measured intensities, 6557 unique intensities, all reflections used in refinement against F^2, R = 0.0238, wR = 0.0611 ($I \geq 2\sigma(I)$), wR_2 = 0.0643 (for all data).

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