Supporting Information

for

Theoretical investigation of the N→Sn coordination in $(Me_3SnCN)_2$

by

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S1. Geometrical configurations of $(Me_3SnCN)_2$

The geometrical configurations presented in Fig. 3 were optimized at the SCS-MP2/aug-cc-pVQZ computational level. However, the corresponding harmonic frequency calculations were performed only for configuration C1 because of the prohibitive computational cost of such calculations (resulting from the large size of the aug-cc-pVQZ basis set and numerical second derivatives available to SCS-MP2 in TURBOMOLE). In order to verify that all geometrical configurations are local minima on the potential energy surface of $(Me_3SnCN)_2$, we decided to carry out an additional set of optimizations at the SCS-MP2/def2-TZVPP level of theory. This level of theory allowed us to perform harmonic frequency calculations for all configurations. The number of configurations detected by SCS-MP2/def2-TZVPP and their order with respect to their energies (see Table S1) are exactly the same as those predicted by SCS-MP2/aug-cc-pVQZ (see Table 4). The SCS-MP2/def2-TZVPP calculations confirm that all the configurations are local minima. On this basis, we assumed that the positive verification of the $(Me_3SnCN)_2$ configurations at the SCS-MP2/def2-TZVPP level would be also valid at the SCS-MP2/aug-cc-pVQZ level.

Table S1 Selected distances and angle in four geometrical configurations of $(Me_3SnCN)_2$ optimized at the SCS-MP2/def2-TZVPP level of theory. These geometrical configurations are denoted the same as in Fig. 3 and are ordered with respect to the energy of the most stable configuration, ΔE. The distances and the angle are marked in Fig. 2

$(Me_3SnCN)_2$ configuration	$d_{N\rightarrow Sn}$	$d_{C\equiv N}$	$d_{Sn\text{-}CN}$	d_{Sn-CH_3}	$a_{N\rightarrow Sn-CH_3}$	ΔE
C1	3.149	1.171	2.154	2.126	78.16	0.0000
C2	3.150	1.171	2.154	2.126	78.16	0.0084
C3	2.938	1.171	2.159	2.128	77.59	0.1550
C4	2.938	1.171	2.159	2.128	77.59	0.1646

Distances in Å, angles in deg and energy differences in kcal/mol.

S2. Details of the extrapolation to the CBS limit

The two-point extrapolation procedure of Halkier et al. was employed to calculate the total energies of the Me_3SnCN molecules and the $(Me_3SnCN)_2$ dimer at four levels of theory: MP2, SCS-MP2, CCSD and CCSD(T). For each of these levels the extrapolated total energies were determined using the following expressions:

$$E_{\mathrm{CBS}(2,3)}^{\mathrm{tot}} = \frac{e^{\alpha}}{e^{\alpha}-1}E_3^{\mathrm{HF}} - \frac{1}{e^{\alpha}-1}E_2^{\mathrm{HF}} + \frac{\frac{27}{8}}{\frac{27}{8}-1}E_3^{\mathrm{corr}} - \frac{1}{\frac{27}{8}-1}E_2^{\mathrm{corr}} \qquad \text{(S1)}$$

$$E_{\mathrm{CBS}(3,4)}^{\mathrm{tot}} = \frac{e^{\alpha}}{e^{\alpha}-1}E_4^{\mathrm{HF}} - \frac{1}{e^{\alpha}-1}E_3^{\mathrm{HF}} + \frac{\frac{64}{27}}{\frac{64}{27}-1}E_4^{\mathrm{corr}} - \frac{1}{\frac{64}{27}-1}E_3^{\mathrm{corr}} \qquad \text{(S2)}$$

where the coefficient α was equal to 1.63. In Eq. (S1) the Hartree-Fock energies E^{HF} and the correlation energies E^{corr} were calculated using a pair of double- and triple-ζ basis sets, whereas in Eq. (S2) a pair of triple- and quadruple-ζ basis sets was employed. E_2, E_3 and E_4 refer to the energies computed with double-, triple- and quadruple-ζ basis sets, respectively. The frozen-core approximation was used in the calculations of E^{corr}. Counterpoise corrections for the BSSE were taken into account in the extrapolated total energies of the Me_3SnCN molecules in the dimer, so the resulting extrapolated E_{int} values are free from the BSSE. The MP2, SCS-MP2, CCSD and CCSD(T) energies used in the extrapolations were calculated by means of TURBOMOLE 6.3.1.

S3. Details of the SAPT calculation of the interaction energy between the Me_3SnCN molecules in the dimer

The first stage of the SAPT calculation is to compute the integrals involving one-electron basis functions and to proceed to calculate the SCF orbitals and the orbital energies for the Me_3SnCN molecules. This stage was performed using DALTON 2.0 [1] that was interfaced to SAPT2012.2. We made use of the aug-cc-pVDZ basis set in the SAPT calculation. The aug-cc-pVDZ-PP version of this basis set was assigned to tin so that the core of the Sn atoms would be described by a pseudopotential. The dimer-centered basis set approach was employed. In the post-SCF stage of the SAPT calculation, the SAPT expansion was truncated and took account of the energy correction terms up to the second order with respect to intermolecular interaction operator:

$$\begin{aligned} E_{\text{int}} = {} & E_{\text{elst}}^{(10)} + E_{\text{exch}}^{(10)} + E_{\text{ind,resp}}^{(20)} + E_{\text{exch-ind,resp}}^{(20)} + \varepsilon_{\text{elst,resp}}^{(1)}(3) + \varepsilon_{\text{exch}}^{(1)}(\text{CCSD}) \\ & + {}^{\text{t}}E_{\text{ind}}^{(22)} + {}^{\text{t}}E_{\text{exch-ind}}^{(22)} + E_{\text{disp}}^{(20)} + \varepsilon_{\text{disp}}^{(2)}(2) + E_{\text{exch-disp}}^{(20)} + \delta E_{\text{int,resp}}^{\text{HF}} \end{aligned} \tag{S3}$$

The right side of Eq. (S3) is a sum of perturbative energy correction terms that are the consequences of various physical interaction forces (for a detailed description of SAPT energy decomposition and possible interpretation of individual energy correction terms, see the review paper by Jeziorski et al. [2]). These energy correction terms, except for the very last one, were collected into four fundamental physical components: electrostatic (E_{elst}), exchange (E_{exch}), induction (E_{ind}), and dispersion (E_{disp}) ones as follows:

$$E_{\text{elst}} = E_{\text{elst}}^{(10)} + \varepsilon_{\text{elst,resp}}^{(1)}(3) \tag{S4}$$

$$E_{\text{exch}} = E_{\text{exch}}^{(10)} + \varepsilon_{\text{exch}}^{(1)}(\text{CCSD}) \tag{S5}$$

$$E_{\text{ind}} = E_{\text{ind,resp}}^{(20)} + E_{\text{exch-ind,resp}}^{(20)} + {}^{\text{t}}E_{\text{ind}}^{(22)} + {}^{\text{t}}E_{\text{exch-ind}}^{(22)} \tag{S6}$$

$$E_{\text{disp}} = E_{\text{disp}}^{(20)} + \varepsilon_{\text{disp}}^{(2)}(2) + E_{\text{exch-disp}}^{(20)} \tag{S7}$$

The assignment of the energy correction terms to four fundamental components of the interaction energy seems to be, to a certain extent, arbitrary and, therefore, a number of possible grouping schemes were proposed in the literature. The $\delta E_{\text{int,resp}}^{\text{HF}}$ term was calculated as the subtraction of the correction energy terms of the zeroth order in intramonomer

correlation operator from the supermolecular interaction energy at the Hartree-Fock level of theory, $E_{\mathrm{int}}^{\mathrm{HF}}$.

$$\delta E_{\mathrm{int,resp}}^{\mathrm{HF}} = E_{\mathrm{int}}^{\mathrm{HF}} - E_{\mathrm{elst}}^{(10)} - E_{\mathrm{exch}}^{(10)} - E_{\mathrm{ind,resp}}^{(20)} - E_{\mathrm{exch-ind,resp}}^{(20)} \quad \text{(S8)}$$

In the manuscript in the paragraph where the SAPT results are discussed, the value of the dipole moment for Me_3SnCN is mentioned. Its value was obtained for the free Me_3SnCN molecule using the SCS-MP2/aug-cc-pVQZ level of theory.

S4. Details of NMR calculations

The determination of the chemical shifts of the ^{119}Sn nuclei, $\delta(^{119}Sn)$, in the Me_3SnCN molecule and in the $(Me_3SnCN)_2$ dimer, both optimized at the SCS-MP2/aug-cc-pVQZ level of theory, required the isotropic shielding constants of these nuclei, $\sigma(^{119}Sn)$. In the case of the dimer only the nucleus of the Sn atom of **2** was taken into consideration. The $\sigma(^{119}Sn)$ values were calculated using the gauge including atomic orbital (GIAO) method [3,4] at the MP2/IGLO-II [5] level of theory. The values of $\delta(^{119}Sn)$ in the molecule and in the dimer were obtained using the following formulas:

$$\delta(^{119}Sn; Me_3SnCN) = \sigma(^{119}Sn; ref) - \sigma(^{119}Sn; Me_3SnCN) \quad (S9)$$

$$\delta(^{119}Sn; (Me_3SnCN)_2) = \sigma(^{119}Sn; ref) - \sigma(^{119}Sn; (Me_3SnCN)_2) \quad (S10)$$

where $\sigma(^{119}Sn; ref)$ stands for the isotropic shielding constant of the ^{119}Sn nucleus in a reference molecule. In the case of $\delta(^{119}Sn)$, tetramethyltin Me_4Sn was the reference molecule. The $\sigma(^{119}Sn)$ value for the SCS-MP2/aug-cc-pVQZ-optimized geometry of Me_4Sn was calculated at the MP2/IGLO-II level of theory. All NMR calculations were performed using TURBOMOLE 6.3.1.

S5. Additional tables

Table S2 RMSD for the $(Me_3SnCN)_2$ geometries obtained by MP2 and its variants in combination with four double-ζ basis sets[a]

Method	Basis set			
	cc-pVDZ	aug-cc-pVDZ	def2-SVP	def2-SVPD
MP2	3.669	3.915	3.686	3.155
SCS-MP2	0.476	0.569	0.443	0.367
SOS-MP2	1.465	1.477	1.470	1.358
FE2-MP2	3.342	3.682	3.366	2.964
SCS(MI)-MP2	2.124	1.751	1.970	1.412
S2-MP	2.933	3.268	2.945	2.608
OO-MP2	5.884	7.048	6.305	6.016
OO-SCS-MP2	2.256	3.397	2.571	2.641
OO-SOS-MP2	0.749	1.492	0.984	0.993
OO-FE2-MP2	5.487	6.750	5.981	5.763
OO-SCS(MI)-MP2	3.907	4.216	3.680	3.306
OO-S2-MP	5.034	6.303	5.508	5.346

RMSD values in 10^{-2} Å.

[a] The values of RMSD were calculated for the $(Me_3SnCN)_2$ geometries optimized by each of the MP2-based methods with respect to the geometry optimized at the CCSD level of theory.

S6. Additional figures

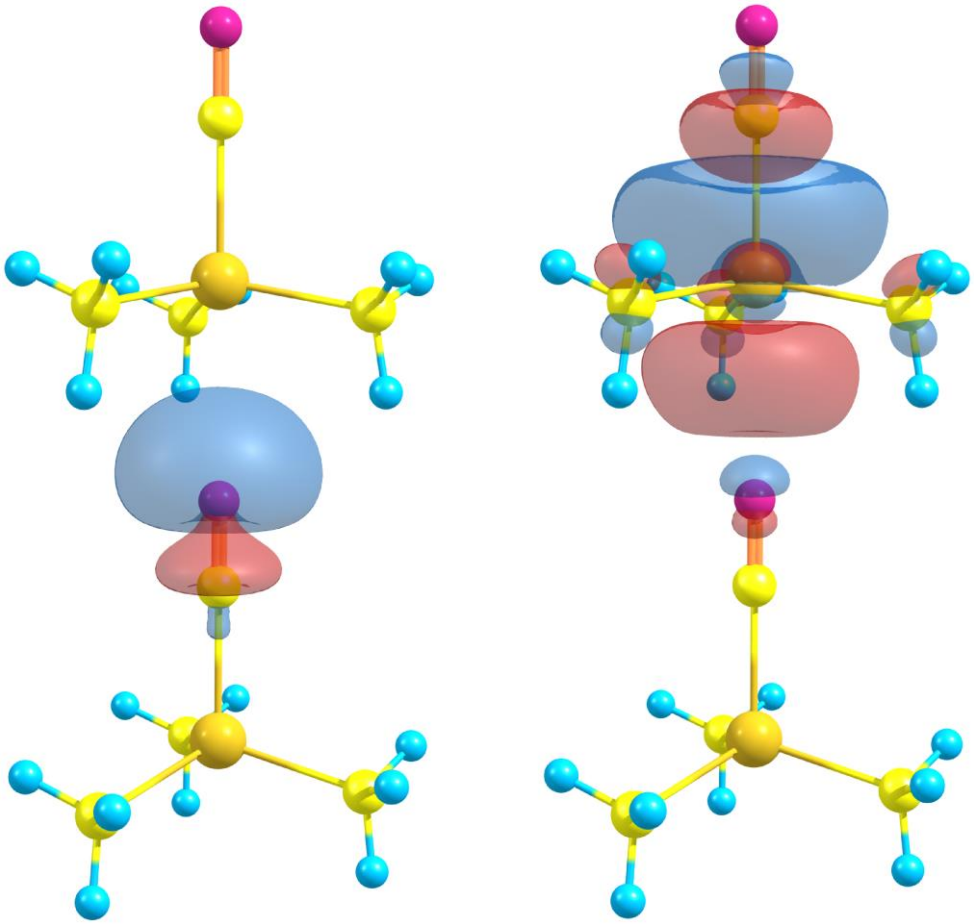

Fig. S1 NBOs for which the greatest $\Delta E^{(2)}$ stabilization energy is observed in $(Me_3SnCN)_2$. The donor NBO (on the left) corresponds to the lone pair on the N atom of **1**, whereas the antibonding σ^*(Sn-CN) orbital of **2** is the acceptor NBO (on the right). The NBOs are drawn with a contour value of 0.03 atomic unit

References

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