Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

[[Hyp-Au-Sn_9(Hyp)$_3$-Au-Sn_9(Hyp)$_3$-Au-Hyp]$^-$: The longest intermetalloid chain compound of tin

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Experimental Section

All reactions were carried out under rigorous exclusion of air and moisture using Schlenk techniques under standard nitrogen atmosphere. All solvents were dried and purified by standard procedures. At -78°C $Ph_3PAuS(Hyp)$ (54 mg, 0.076 mmol) was dissolved in THF (ca. 20 mL) and transferred to precooled $[Li(tmeda)_2]_2Sn_{10}(Hyp)_4$ (200 mg, 0.076 mmol). The dark green reaction mixture was slowly warmed up to RT while stirring, leading to a dark red solution. The solvent was removed in vacuum to give a black residue which was washed with pentane and extracted in toluene. The black toluene extract was stored at -30 °C for 7d leading to the formation of dark red crystals of $[Li(TMEDA)_2][Au_3Sn_{18}(Hyp)_8]$. (yield: 32 mg, 0.007 mmol, 11 %). 1H-NMR (250 MHz, THF-d8): δ = 0.13 (s, 54 H, $AuSi(SiMe_3)_3$), 0.25 (s, $Si(SiMe_3)_4$), 0.41 (s, 162 H, $SnSi(SiMe_3)_3$), 2.15 (s, TMEDA), 2.31 (s, TMEDA) ppm; 7Li-NMR (97.2 MHz, THF-d8): 0.41 (s, $Li(tmeda)_2^+$) ppm.

The obtained single crystals (dark red blocks) are very sensitive and rapidly loose solvent molecules and disintegrate into thin plates or rods. Hence, the single crystal quality decreases rapidly when taken out of the mother liquor into mineral oil for selection and preparation of the single crystals for x-ray measurements. Also NMR measurements to get an idea of the amount of embedded solvent molecules failed as the single crystals were washed and evaporated before dissolving in THF-d_8 for NMR measurement. During this procedure the loosely bound solvent molecules within the crystal are completely removed so that no additional signals for the solvent molecules could be obtained within the proton NMR spectrum.

^{119}Sn Mössbauer spectroscopy

A $Ca^{119m}SnO_3$ source was used for the ^{119}Sn Mössbauer spectroscopic investigation. The sample was placed within a thin-walled glass container at a thickness of about 10 mg Sn/cm^2. A palladium foil of 0.05 mm thickness was used to reduce the tin K X-rays concurrently emitted by this source. The measurement (11 d total counting time) was conducted in the usual transmission geometry at 78 K. Fitting of the spectrum was done with the NORMOS-90 software package.[1]

Mass spectrometry

The anionic cluster compound **2** was brought into the gas phase by electrospraying a thf solution of **2**. Mass spectrometer: Thermo Fischer Q Exactive Hybrid Quadrupol Orbitrap mass spectrometer.

X-ray structural characterization

Crystals were mounted on the diffractometer at 180 K. The data were collected on a Bruker APEX II diffractometer employing monochromated MoKα (λ = 0.71073 Å) radiation from a sealed tube and equipped with an Oxford Cryosystems cryostat. A semi-empirical absorption correction was applied using the program SADABS. The structure was solved by Direct Methods and refined against F^2 for all observed reflections. Programs used: SHELXS and SHELXL[2] within the Olex2 program package.[3] CCDC-1551134 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.as.uk/data_request/cif.

$[Li(TMEDA)_2][Au_3Sn_{18}(Hyp)_8]$: $C_{84}H_{248}Au_3Si_{32}Sn_{18}Li_2N_4$; Mr = 4948.32 g mol_{-1}, crystal dimensions 0.279 × 0.079 × 0.067 mm3, space group P-1, *a* = 14.9081(6) Å, *b* = 16.3138(7) Å, *c* = 24.6890(10) Å, *α* = 81.862(2)°, *β* = 87.078(2)°, *γ* = 63.232(2)°, V = 5306.6(4) $Å^3$, *Z* = 1, $\rho_{calc.}$ = 1.47 g cm-3, μ_{Mo} = 4.3 mm-1, $2\theta_{max}$ = 52.97°, 109833 reflections measured, 21803 independent reflections (R_{int} = 0.0986), absorptions correction: semi-empirical (min./max. transmission 0.556/0.746), R_1 (I>2σ) = 0.0707, wR2 (all) = 0.2171, Bruker APEXII diffractometer ($Mo^{K\alpha}$ radiation (λ = 0.71073 Å), 180 K).

Details on the refinement:

During the structure solution large voids are present where the counter cation $[Li(TMEDA)_2]^+$ and solvent molecules are located. However, during structure solution we were not able to refine the cation or solvent molecules due to disorder. Although, some residual electron density (Q-peaks) show the form of a six membered ring, refinement as toluene molecules failed. Nevertheless, treatment of the residual electron density using SQUEEZE[4] leads to voids of 1412 $Å^3$ with 609 electrons which fits to $[Li(TMEDA)_2]^+$ together with 8 solvent (toluene) molecules.

The void has thereby the form of a peanut and one part of the peanut is centered at -0.121 0.5 0.5 and is thus not positioned at a special position (Figure S1 shows the void from different directions). As Z is equal 1 only one $[Li(TMEDA)_2]^+$ is localized within this void and might reside in one side of the peanut while the other side is occupied by solvent molecules (toluene). As the space group is P-1, for the refinement we must solve the overlay of $[Li(TMEDA)_2]^+$ and

many toluene molecules, where all atoms should have an occupancy of 50% (50% of a lithium cation is nearly a hydrogen atom). Additionally, as the inversion center is in the middle of the peanut, which might not fit with a tetrahedral $[Li(TMEDA)_2]^+$ a further disorder is expected for the cation. All these aspects together lead to a smearing of the electron density so that a refinement is not possible.

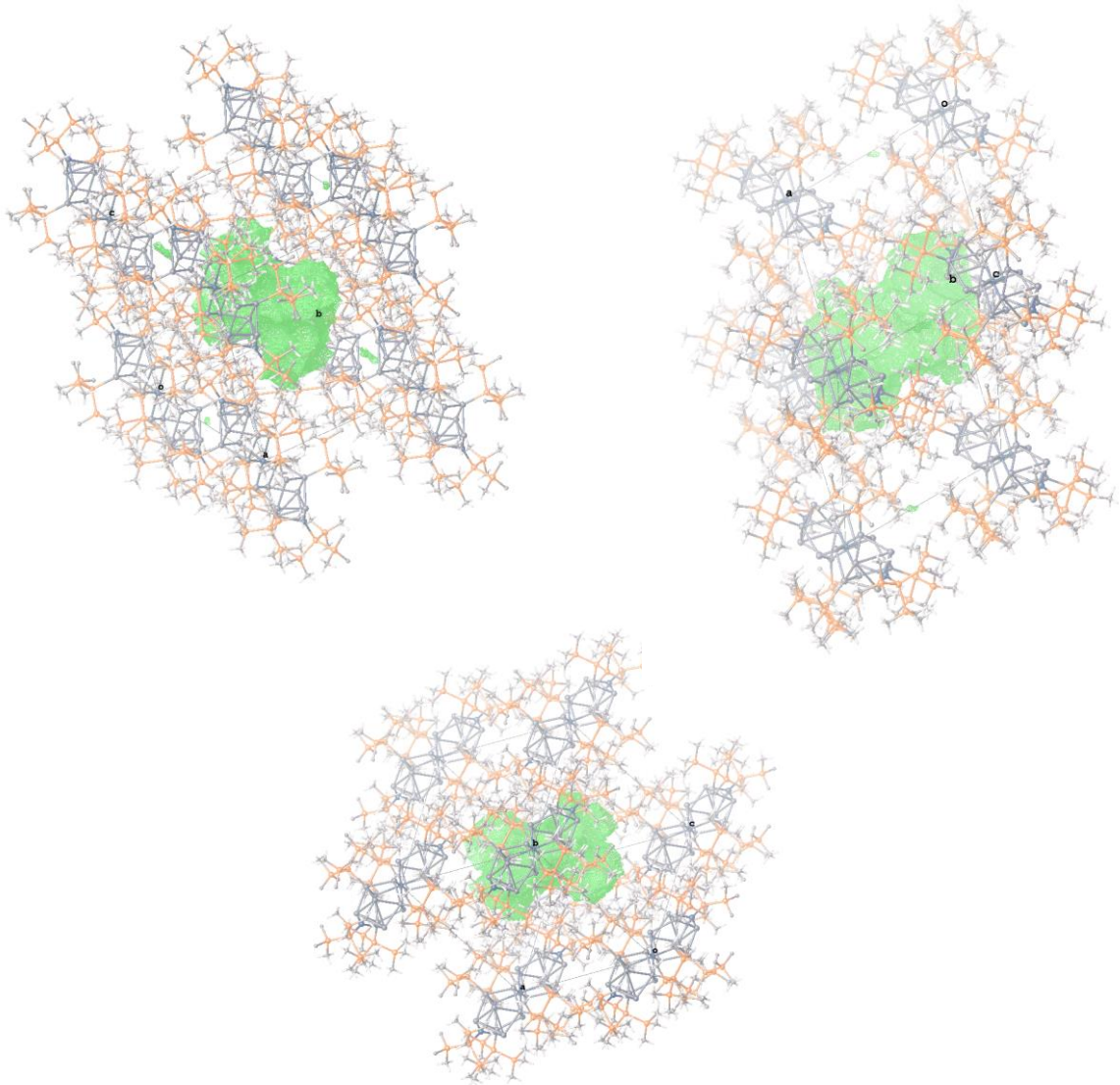

Figure S1: Picture of the void (green), localized at -0.121, 0.5, 0.5 within the solid state of $[Li(TMEDA)_2][Au_3Sn_{18}(Hyp)_8]$ **1**; view from different directions.

NMR spectroscopy:

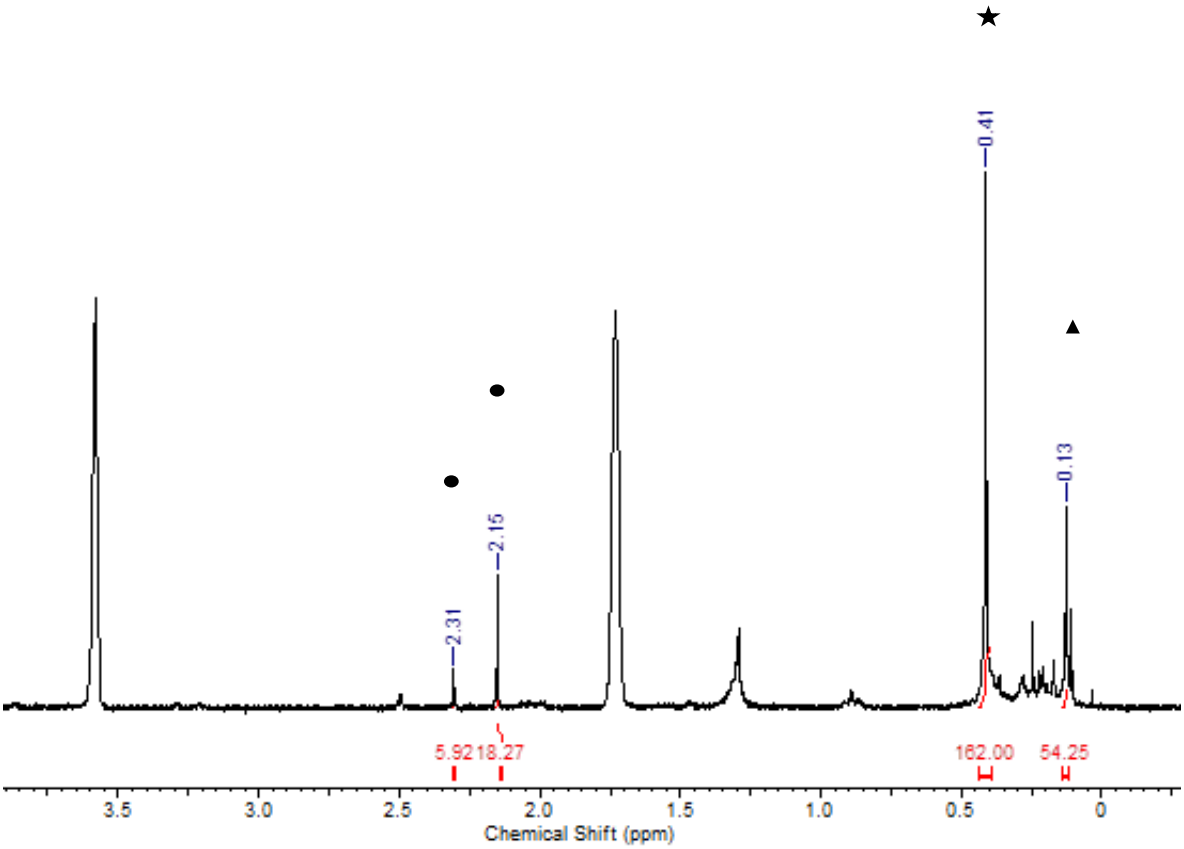

Figure S2: ^{1}H-NMR of $[Li(TMEDA)_2][Au_3Sn_{18}(Hyp)_8]$ **1** dissolved in THF-d_8. The signal at δ = 0.13 ppm shows the Hyp ligand bound to the gold atoms, whereas the signal at δ = 0.41 ppm could be assigned to the Hyp ligand bound to the tin atoms. The integrals shows a ratio of cluster to TMEDA of 1:1.5. (● TMEDA, ★ SnHyp, ▲ AuHyp).

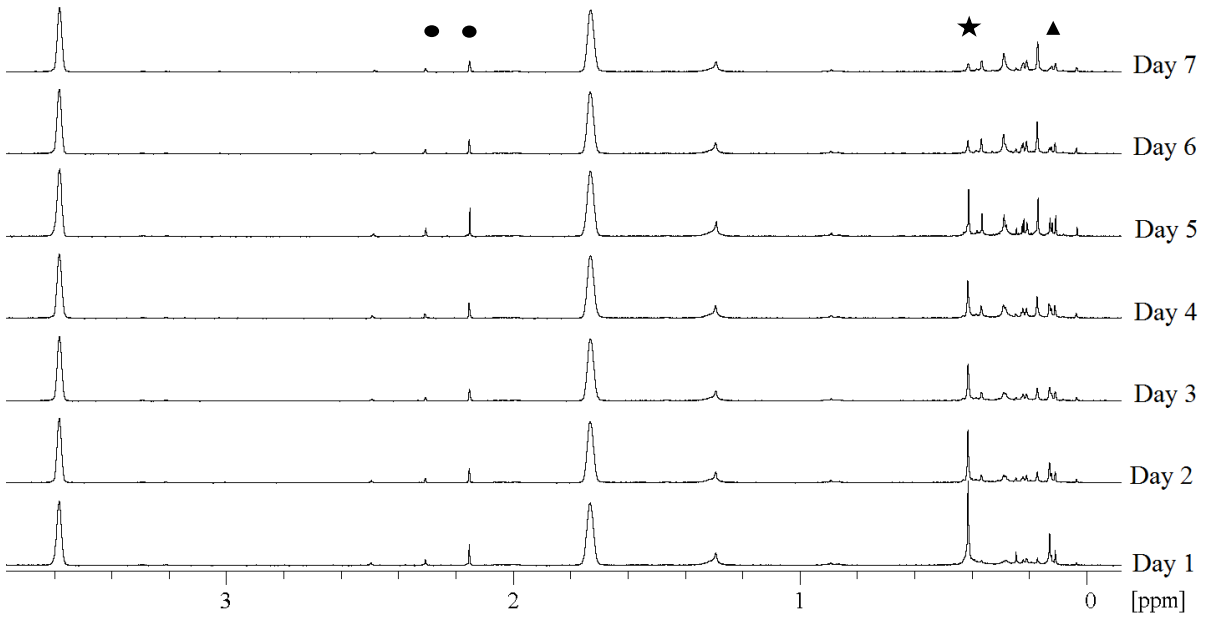

Figure S3: ^{1}H-NMR of $[Li(TMEDA)_2][Au_3Sn_{18}(Hyp)_8]$ **1** dissolved in THF-d_8 shows a fast degradation of **1** within 7 days. The TMEDA signals at δ = 2.15 ppm and δ = 2.13 ppm doesn't change during that period, whereas the two Hyp signals at δ = 0.13 ppm and δ = 0.41 ppm nearly disappeares at day 7.

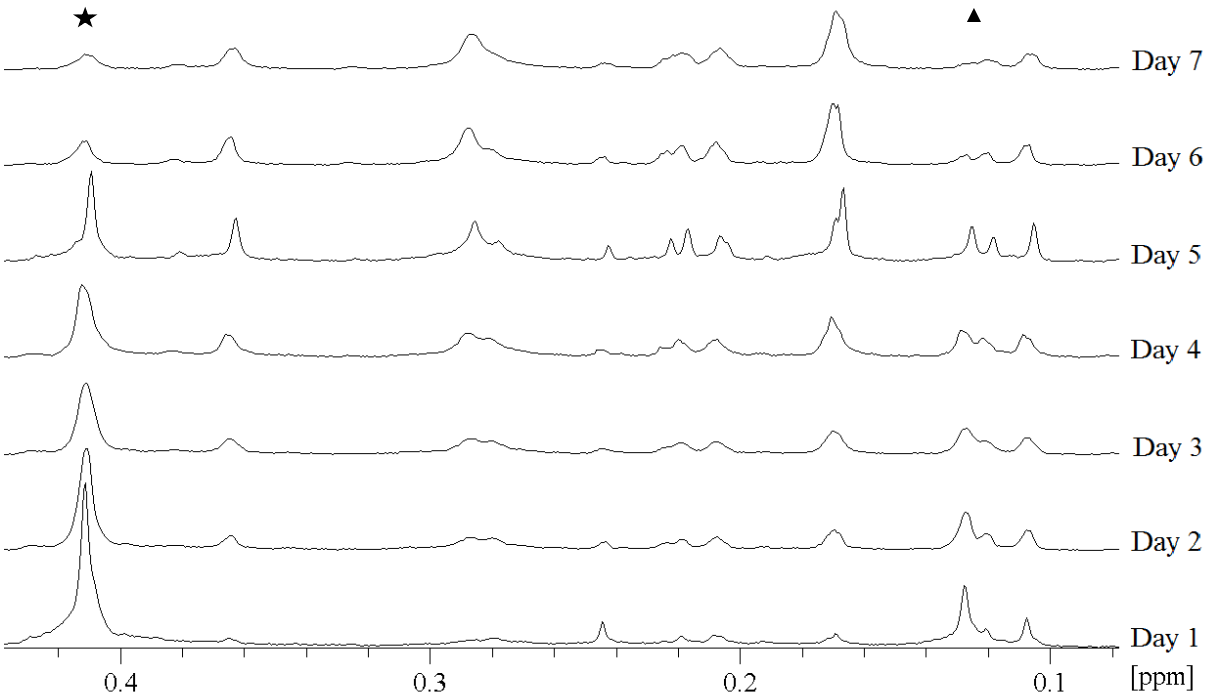

Figure S4: Enlargment of the ^{1}H-NMR spectra of $[Li(TMEDA)_2][Au_3Sn_{18}(Hyp)_8]$ **1**. The Hyp ligand signals at δ = 0.13 ppm and δ = 0.41 ppm show a fast degradation of **1** within the first two days. After 7 days the signals are nearly vanished and the spectrum gets more and more complex.

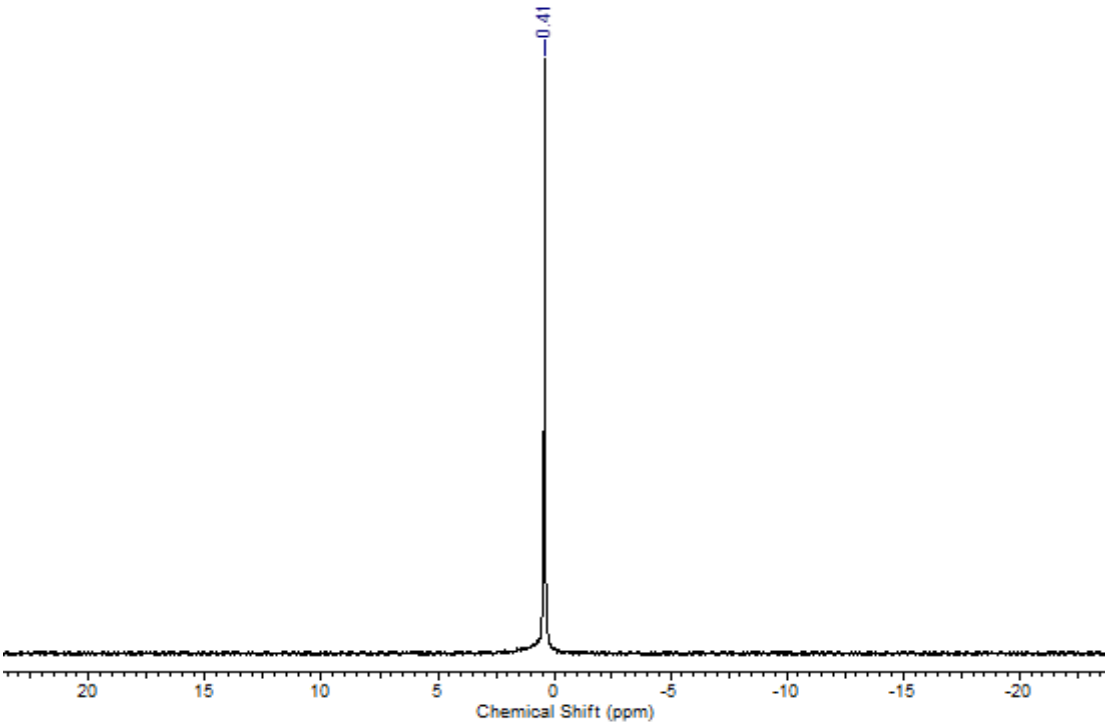

Figure S5: ^{7}Li-NMR of $[Li(TMEDA)_2][Au_3Sn_{18}(Hyp)_8]$ **1** dissolved in THF-d_8 shows a singlet at δ = 0.41 ppm, which can be seen as prove for the presence of $[Li(TMEDA)_2]^+$ in the crystals.

Mass spectrometry:

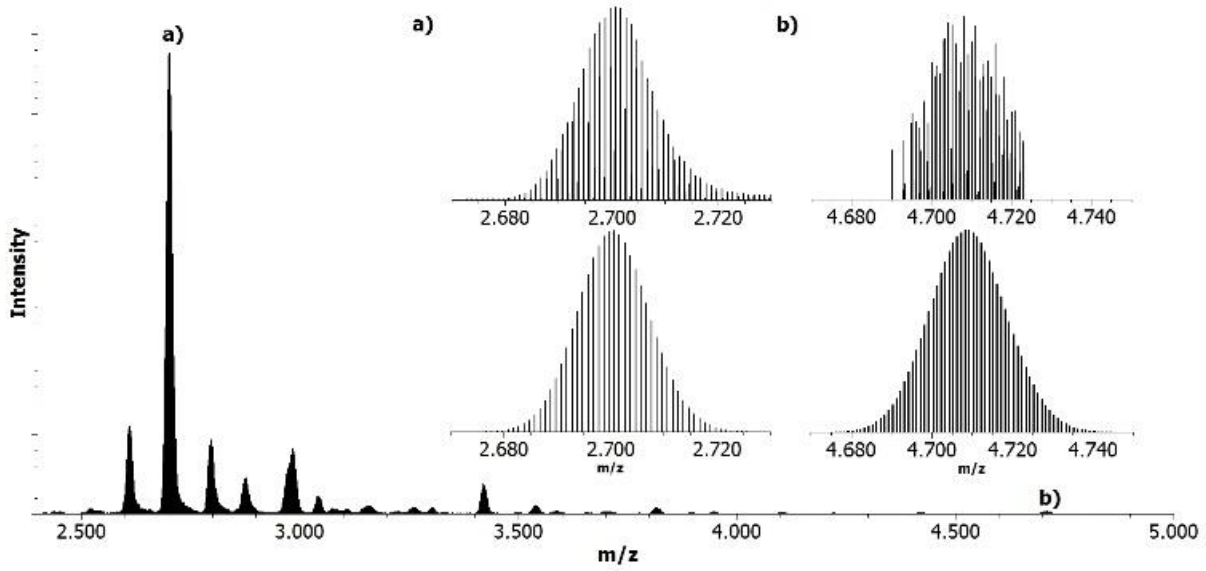

Figure S6: Mass spectrum of a solution of $[Au_3Sn_{18}(Hyp)_8]^-$ **1** in THF after electronspray ionization (ESI). Inset measured and calculated isotopic pattern for a) $[Au_3Sn_{18}(Hyp)_8]^-$ **1** and b) $[Au_2Sn_9(Hyp)_5]^-$

The sensitivity of **1** in solution is also obvious from mass spectrometric investigations on dissolved crystals of **1**. Hence, electrospraying a thf solution of dissolved crystals gives a complicated mass spectrum (figure S6) where the signal of **1** is barely observable (figure S6 inset). While transferring the dissolved crystals to the mass spectrometer you can see a color change from dark purple to a brownish color, which indicates the fast decomposition of $[Au_3Sn_{18}(Hyp)_8]^-$ in thf and also explains the barely visible molecular peak. However, besides the signal of **1** the decomposition product with the highest intensity (signal at m/z = 2699) could be identified as $[Au_2Sn_9(Hyp)_5]^-$ by its mass and isotopic pattern (figure S6 inset) and which might form from **1** by the elimination of the neutral group $AuSn_9Hyp_3$. The NMR and mass spectrometric investigations thus show that **1** is quite unstable in solution and decomposes into smaller fragments.

Quantum chemical calculations:[5]

The model compound $[Au_3Sn_{18}(SiH_3)_8]^-$ **1a** was calculated with additional C_3 symmetry to get a good and comparable structural arrangement.

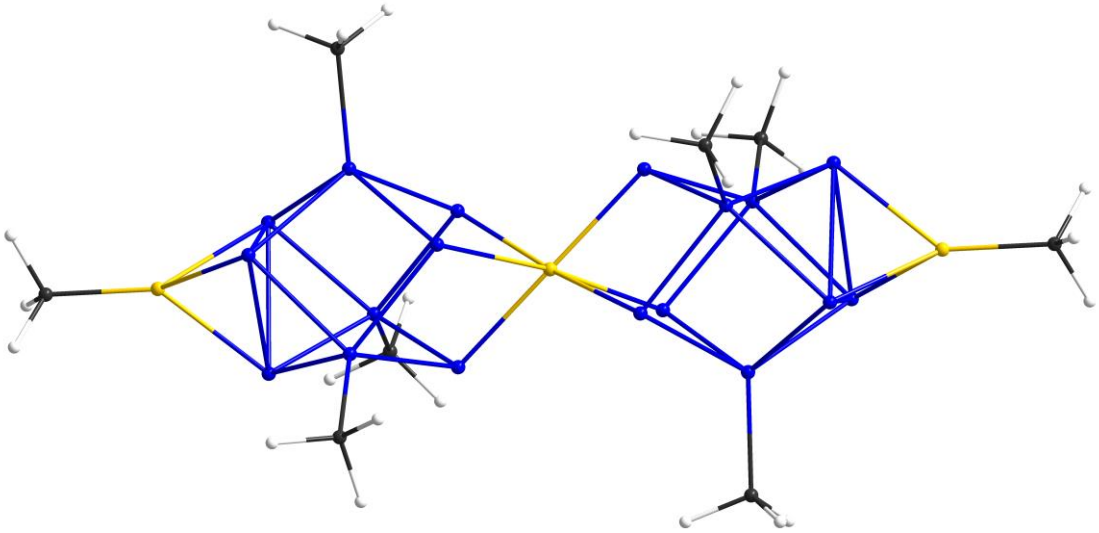

Figure S7: Optimized structure of **1a** with constrained C_3 symmetry.

Total energy: -2799.97123443018

HOMO-LUMO-gap: 0.962 eV

Coordinates of **1a**:

Au1 -0.000000 0.000000 -0.033634
Sn2 1.836398 -0.853312 -2.164582
Sn3 -1.657189 -1.163712 -2.164582
Sn4 -0.179210 2.017023 -2.164582
Sn5 0.211863 -2.389683 -4.164329
Sn6 -2.175457 1.011363 -4.164329
Sn7 1.963594 1.378320 -4.164329
Sn8 1.774836 -0.824811 -6.233140
Sn9 -1.601725 -1.124648 -6.233140
Sn10 -0.173111 1.949458 -6.233140
Au11 0.000000 -0.000000 -8.468265
Sn12 -1.644320 1.177787 2.099489
Sn13 1.842153 0.835129 2.099489
Sn14 -0.197834 -2.012916 2.099489
Si15 0.459488 -5.000398 -4.097402
Si16 -4.560215 2.102271 -4.097402
Si17 4.100728 2.898127 -4.097402
Sn18 0.235385 2.389026 4.104019
Sn19 -2.186650 -0.990664 4.104019
Sn20 -1.592144 1.140465 6.166454
Sn21 1.783744 0.808604 6.166454
Si22 0.518295 4.997561 4.146674
Sn23 -0.191600 -1.949070 6.166454
Si24 -4.587162 -2.049924 4.146674
Sn25 1.951265 -1.398362 4.104019
Au26 0.000000 0.000000 8.401301
Si27 4.068867 -2.947637 4.146674
Si28 -0.000000 0.000000 10.814252

H29 0.371852 1.340374 11.425311
H30 -1.346724 -0.348154 11.425311
H31 0.974872 -0.992221 11.425311
Si32 0.000000 -0.000000 -10.881816
H33 -0.470007 -1.309166 -11.492930
H34 1.368774 0.247545 -11.492930
H35 -0.898767 1.061621 -11.492930
H36 1.931227 5.425346 3.822096
H37 -0.394680 5.679516 3.153183
H38 0.185955 5.547385 5.514965
H39 5.306380 2.216217 -4.703238
H40 3.897186 4.193652 -4.849110
H41 4.453464 3.254145 -2.671405
H42 -5.664101 -1.040181 3.822096
H43 3.732874 -4.385165 3.822096
H44 -4.721265 -3.181561 3.153183
H45 5.115946 -2.497955 3.153183
H46 -4.897153 -2.612651 5.514965
H47 4.711199 -2.934734 5.514965
H48 -4.572490 3.487352 -4.703238
H49 -0.733890 -5.703568 -4.703238
H50 -5.580402 1.278236 -4.849110
H51 1.683216 -5.471888 -4.849110
H52 -5.044904 2.229740 -2.671405
H53 0.591441 -5.483885 -2.671405

Ahlrichs-Heinzmann population analysis:[6]

Two-center-SEN:[7]

shared electron number for the pair	1 au	- 2 sn	=	0.3278
shared electron number for the pair	1 au	- 12 sn	=	0.3242
shared electron number for the pair	2 sn	- 3 sn	=	0.5544
shared electron number for the pair	2 sn	- 5 sn	=	0.9445
shared electron number for the pair	2 sn	- 7 sn	=	0.9516
shared electron number for the pair	2 sn	- 8 sn	=	0.1377
shared electron number for the pair	2 sn	- 9 sn	=	-0.0141
shared electron number for the pair	2 sn	- 10 sn	=	-0.0151
shared electron number for the pair	2 sn	- 13 sn	=	0.0209
shared electron number for the pair	5 sn	- 8 sn	=	0.9057
shared electron number for the pair	5 sn	- 9 sn	=	0.9053
shared electron number for the pair	5 sn	- 15 si	=	1.2067
shared electron number for the pair	8 sn	- 9 sn	=	0.6830
shared electron number for the pair	8 sn	- 11 au	=	0.2236
shared electron number for the pair	11 au	- 32 si	=	0.7916
shared electron number for the pair	12 sn	- 13 sn	=	0.5587
shared electron number for the pair	12 sn	- 18 sn	=	0.9406
shared electron number for the pair	12 sn	- 19 sn	=	0.9371
shared electron number for the pair	12 sn	- 20 sn	=	0.1378
shared electron number for the pair	12 sn	- 21 sn	=	-0.0149
shared electron number for the pair	12 sn	- 23 sn	=	-0.0139
shared electron number for the pair	15 si	- 49 h	=	1.3119
shared electron number for the pair	15 si	- 51 h	=	1.3133
shared electron number for the pair	15 si	- 53 h	=	1.3211
shared electron number for the pair	18 sn	- 20 sn	=	0.9138
shared electron number for the pair	18 sn	- 21 sn	=	0.9172
shared electron number for the pair	18 sn	- 22 si	=	1.2077

shared electron number for the pair 20 sn - 21 sn = 0.6790
shared electron number for the pair 20 sn - 26 au = 0.2228
shared electron number for the pair 22 si - 36 h = 1.3119
shared electron number for the pair 22 si - 37 h = 1.3152
shared electron number for the pair 22 si - 38 h = 1.3199
shared electron number for the pair 26 au - 28 si = 0.7931
shared electron number for the pair 28 si - 29 h = 1.3173
shared electron number for the pair 32 si - 33 h = 1.3174

Three- and Four-center-SEN:

n(1 2 3) = 0.1035
n(1 2 3 4) = 0.0567
n(1 2 3 5) = -0.0166
n(1 2 3 12) = -0.0247
n(1 2 3 13) = -0.0222
n(1 2 5) = -0.0234
n(1 2 7) = -0.0236
n(1 2 8) = -0.0117
n(1 2 12) = -0.1302
n(1 2 12 13) = -0.0222
n(1 2 12 14) = -0.0249
n(1 2 13) = -0.0210
n(1 2 14) = -0.0412
n(1 12 13) = 0.1020
n(1 12 13 14) = 0.0561
n(1 12 13 18) = -0.0168
n(1 12 18) = -0.0234
n(1 12 19) = -0.0232
n(1 12 20) = -0.0118
n(2 3 4) = 0.1523
n(2 3 5) = 0.1753
n(2 3 6) = -0.0171
n(2 3 7) = -0.0174
n(2 5 7 8) = 0.0327
n(2 5 8) = 0.0751
n(2 5 9) = -0.0343
n(2 7 8) = 0.0753
n(2 7 10) = -0.0343
n(2 8 11) = -0.0111
n(5 8 9) = 0.1924
n(5 8 9 10) = -0.0114
n(5 8 10) = -0.0230
n(5 8 11) = -0.0195
n(5 9 10) = -0.0229
n(5 9 11) = -0.0193
n(5 15 49) = -0.0192
n(5 15 51) = -0.0189
n(5 15 53) = -0.0168
n(8 9 10) = 0.2046
n(8 9 10 11) = 0.0335
n(8 9 11) = 0.0608
n(8 9 11 32) = -0.0659
n(8 11 32) = -0.1840
n(11 32 33) = -0.0215
n(12 13 14) = 0.1543
n(12 13 18) = 0.1729
n(12 13 19) = -0.0179
n(12 13 25) = -0.0183
n(12 18 19 20) = 0.0332
n(12 18 20) = 0.0757
n(12 18 21) = -0.0346
n(12 19 20) = 0.0752
n(12 19 23) = -0.0350
n(12 20 26) = -0.0110
n(18 20 21) = 0.1954
n(18 20 23) = -0.0218
n(18 20 26) = -0.0197
n(18 21 23) = -0.0218
n(18 21 26) = -0.0197
n(18 22 36) = -0.0193
n(18 22 37) = -0.0179
n(18 22 38) = -0.0174
n(20 21 23) = 0.2035
n(20 21 23 26) = 0.0335
n(20 21 26) = 0.0606
n(20 21 26 28) = -0.0654
n(20 26 28) = -0.1832
n(26 28 29) = -0.0215

Atomic charges:

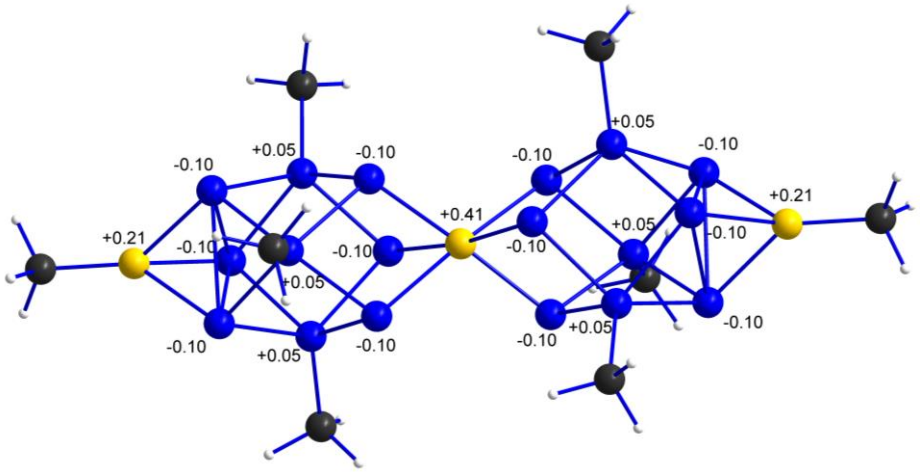

Figure S8: Atomic charges of the Sn and Au atoms in **1a**

atom	charge
1 au	0.4182
2 sn	-0.1018
3 sn	-0.1018
4 sn	-0.1018
5 sn	0.0551
6 sn	0.0551
7 sn	0.0551
8 sn	-0.1012
9 sn	-0.1012
10 sn	-0.1012
11 au	0.2060
12 sn	-0.1003
13 sn	-0.1003
14 sn	-0.1003
15 si	0.0183
16 si	0.0183
17 si	0.0183
18 sn	0.0509
19 sn	0.0509
20 sn	-0.0994
21 sn	-0.0994
22 si	0.0185
23 sn	-0.0994
24 si	0.0185
25 sn	0.0509
26 au	0.2066
27 si	0.0185
28 si	-0.0981
29 h	-0.0564
30 h	-0.0564
31 h	-0.0564
32 si	-0.0979
33 h	-0.0561
34 h	-0.0561
35 h	-0.0561
36 h	-0.0313
37 h	-0.0279
38 h	-0.0269
39 h	-0.0309
40 h	-0.0307
41 h	-0.0250
42 h	-0.0313
43 h	-0.0313
44 h	-0.0279
45 h	-0.0279
46 h	-0.0269
47 h	-0.0269
48 h	-0.0309
49 h	-0.0309
50 h	-0.0307
51 h	-0.0307
52 h	-0.0250
53 h	-0.0250

References:

[1] R. A. Brand, *Normos Mössbauer Fitting Program, University of Duisburg, Duisburg (Germany)* **2002**.

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[6] E. R. Davidson, *J. Chem. Phys.*, 1967, **46**, 3320–3324; K. R. Roby, *Mol. Phys.*, 1974, **27**, 81–104; R. Heinzmann, R. Ahlrichs, *Theor. Chim. Acta*, 1976, **42**, 33–45; C. Erhardt, R. Ahlrichs, *Theor. Chim. Acta*, 1985, **68**, 231–245.

[7] Shared electron numbers (SENs) for bonds are a reliable measure of the strength of covalent bonding. For example, the SEN for the Sn–Sn single bond in the model compound $Me_3SnSnMe_3$ is 1.07.