Supporting

Synthesis and Structure of Bismuth-Nitrogen Cage Compounds and Heterocubanes: [Cl-Bi(μ_3-NTMP)]$_4$ – A Dimer of an 1,3-Dichloro-*cyclo*-Dibismadiazane

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1 General Information

All manipulations were carried out under oxygen- and moisture-free conditions under argon using standard Schlenk or drybox techniques.

Dichloromethane (CH_2Cl_2, CD_2Cl_2) was purified according to a literature procedure,[1] dried over P_4O_{10} and CaH_2 and freshly distilled prior to use. Tetrahydrofurane (thf, thf-d_8), and benzene (benzene, benzene-d_6) were dried over Na/benzophenone and freshly distilled prior to use.

TMP-NH_2 (ABCR, 98 %) was stirred for 8 h over KOH and distilled prior to use. TMP-NH_2 (ABCR, 98 %) was stirred for 8 h over KOH and distilled prior to use. $Sn[N(SiMe_3)_2]_2$ was prepared following a modified literature procedure.[2,3] $BiCl_3$ (ABCR, 99.9 %) was sublimed prior to use (200 °C, 1·10-3 mbar). *n*-Bu-Li (2.5 M in *n*-hexane, Sigma-Aldrich) and $SnCl_2$ (anhydrous, 97 %, Lancaster) were used as received.

NMR: ^{1}H, $^{13}C\{^{1}H\}$, ^{19}F, and ^{119}Sn-INEPT NMR spectra were recorded on a Bruker AVANCE 250, a Bruker AVANCE 300 or a Bruker AVANCE 500 spectrometer. The chemical shifts were referenced to solvent signals or protic impurities in the deuterated solvent (CD_2Cl_2: $\delta^{1}H = 5.32$, $\delta^{13}C = 54.0$; benzene-d_6: $\delta^{1}H = 7.16$, $\delta^{13}C = 128.4$; thf-d_8: $\delta^{1}H = 1.73$ or 3.58, $\delta^{13}C = 25.4$ or 67.6).

IR: Nicolet 380 FT-IR spectrometer with a Smart Orbit ATR unit was used.

Raman: A LabRAM HR 800 Horiba Jobin Yvon Raman spectrometer equipped with a High Stability BX41 Microscope (focus 1 µm) and Olympus Mplan 50xNA 0.70 objective was used. The samples were excited by an infrared laser (785 nm, 100 mW, air cooled diod laser), a red laser (633 nm, 17 mW, HeNe-laser), a green laser (532 nm, 50 mW, air cooled, doubled frequency Nd:YAG solid state laser) or a blue laser (473 nm, 20 mW, air cooled solid state laser).

CHN analyses: A vario Micro cube CHNS analyser from Elementar was used.

Melting points are uncorrected (EZ-Melt, Stanford Research Systems). Heating-rate 20 °C/min (clearing-points are reported).

X-ray: Single crystals were measured on a Bruker Kappa-APEX-II CCD diffractometer or a Bruker D8 Quest CMOS diffractometer using graphite monochromated Mo Kα

radiation (λ = 0.71073 Å). The structures were solved by direct methods (*SHELXS-2014*)[4] and refined by full-matrix least squares procedures (*SHELXL-2014*).[5] Semi-empirical absorption corrections were applied (SADABS).[6] Unless otherwise noted, all non-hydrogen atoms were refined anisotropically, hydrogen atoms were included in the refinement at calculated positions using a riding model.

2 X-ray Studies

Table S1: Crystallographic details of [Cl-Bi(μ_3-N-TMP)]$_4$, [Li(thf)$_4$]$_2$[Li$_9$(N-TMP)$_5$F]·8 thf, 3,5-[(CF$_3$)$_2$C$_6$H$_3$-NSn]$_4$·thf and **D**.

	[Cl-Bi(μ_3-N-TMP)]$_4$	[Li(thf)$_4$]$_2$[Li$_9$(N-TMP)$_5$F]·8 thf	3,5-[(CF$_3$)$_2$C$_6$H$_3$-NSn]$_4$·thf	**D**
chem. formula	$C_{32}H_{12}Bi_4Cl_4F_{24}N_4 \cdot 5(C_6H_6)$	$C_{72}H_{79}F_{31}Li_9O_8^{2-} \cdot 2(C_{16}H_{32}LiO_4^+) \cdot 2(C_4H_8O)$	$C_{32}H_{12}F_{24}N_4Sn_4 \cdot 4(C_4H_8O)$	$C_{16}H_6Bi_5Cl_8F_{12}N_3 \cdot 5(C_6H_6) \cdot OC_4H_8$
M [g mol^{-1}]	2276.71	2528.77	1671.63	2220.33
color	yellow	colorless	colorless	yellow
crystal system	monoclinic	monoclinic	orthorhombic	triclinic
space group	*C*2/*c*	*P*2$_1$/*n*	*Ccc*2	$P\bar{1}$
a [Å]	28.323(2)	18.850(1)	23.2340(8)	8.2744(3)
b [Å]	14.5543(6)	21.919(2)	23.3343(8)	14.8960(6)
c [Å]	20.421(2)	30.974(2)	10.8266(3)	24.427(1)
α [°]	90	90	90	78.007(2)
β [°]	126.746(1)	98.983(2)	90	85.152(1)
γ [°]	90	90	90	80.932(1)
V [Å^3]	6745.1(7)	12640(2)	5869.6(3)	2904.0(2)
Z	4	4	4	2
$\rho_{calc.}$ [g cm^{-3}]	2.242	1.329	1.892	2.539
μ [mm^{-1}]	10.67	0.12	1.80	15.54
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073	0.71073
T [K]	123	123	123	123
measured reflexes	100452	345256	58017	191106
independent reflexes	11721	24786	10551	23675
reflexes with $I > 2\sigma(I)$	9844	15884	9931	18985
$R_{int.}$	0.044	0.081	0.033	0.055
F(000)	4232	5288	3232	2022
R_1 (R [$F^2 > 2\sigma(F^2)$])	0.022	0.065	0.034	0.040
wR_2 (F^2)	0.051	0.200	0.069	0.069
GooF	1.03	1.04	1.13	1.09
parameter	543	2685	527	1055
Flack parameter	-	-	-	-
res. density [*e* Å^{-3}]	$\Delta\rho_{max}$ = 1.56 *e* Å^{-3} $\Delta\rho_{min}$ = −1.30 *e* Å^{-3}	$\Delta\rho_{max}$ = 0.37 *e* Å^{-3} $\Delta\rho_{min}$ = −0.29 *e* Å^{-3}	$\Delta\rho_{max}$ = 1.17 *e* Å^{-3} $\Delta\rho_{min}$ = −1.08 *e* Å^{-3}	$\Delta\rho_{max}$ = 3.69 *e* Å^{-3} $\Delta\rho_{min}$ = −3.21 *e* Å^{-3}

Table S2: Crystallographic details of **E** (data based on .res-File) and **F**.

	E (only .res file)	**F**
chem. formula	-	$C_{32}H_{16}F_{24}N_4Sn_3Cl_4 \cdot 2(C_6H_6) \cdot 2(OC_4H_8)$
M [g mol^{-1}]	-	1710.78
color	yellow	colorless
crystal system	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a [Å]	12.738(1)	9.5017(5)
b [Å]	13.229(1)	12.1989(8)
c [Å]	14.431(1)	14.7132(9)
α [°]	102.527(3)	111.879(2)
β [°]	97.862(3)	104.035(2)
γ [°]	115.558(2)	93.120(2)
V [Å^3]	-	1515.34(16)
Z	4	1
$\rho_{calc.}$ [g cm^{-3}]	-	1.87459
μ [mm^{-1}]	-	1.52
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073
T [K]	123	123
measured reflexes	-	8832
independent reflexes	-	8832
reflexes with $I > 2\sigma(I)$	-	6876
$R_{int.}$	-	
$F(000)$	-	834
R_1 (R [$F^2 > 2\sigma(F^2)$])	0.125	0.0336
wR_2 (F^2)	-	0.0522
GooF	-	0.950
parameter	601	514
Flack parameter	-	-
res. density [e Å^{-3}]	$\Delta\rho_{max}$ = 6.61 e Å^{-3} $\Delta\rho_{min}$ = −3.07 e Å^{-3}	$\Delta\rho_{max}$ = 0.812 e Å^{-3} $\Delta\rho_{min}$ = −0.951 e Å^{-3}

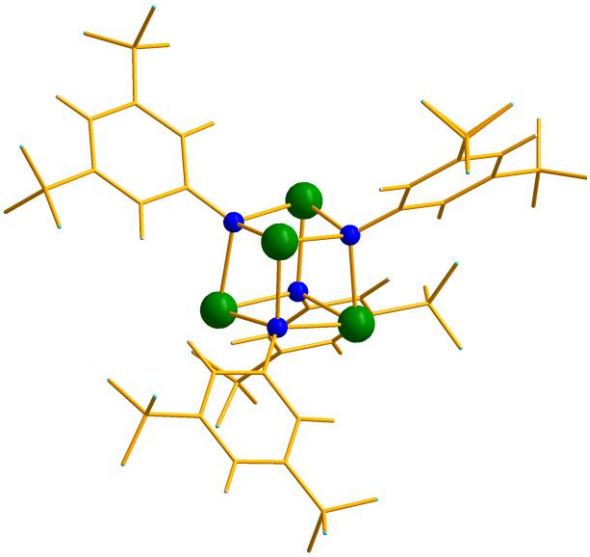


Figure S1. Ball-and-stick representation of [Sn(μ_3-N-TMP)]$_4$ (TMP substituent shown as wireframe).

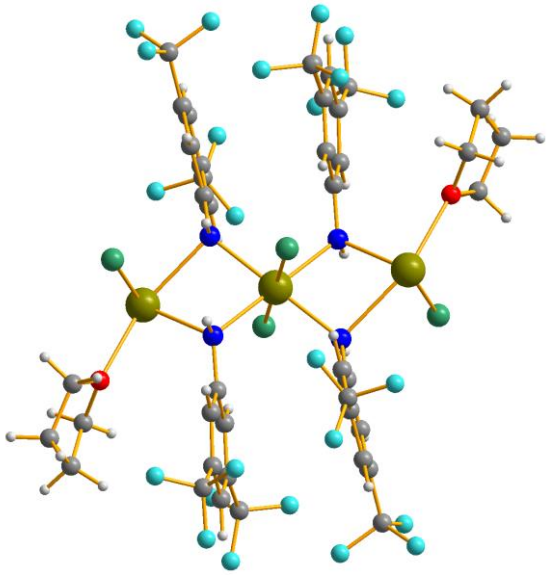
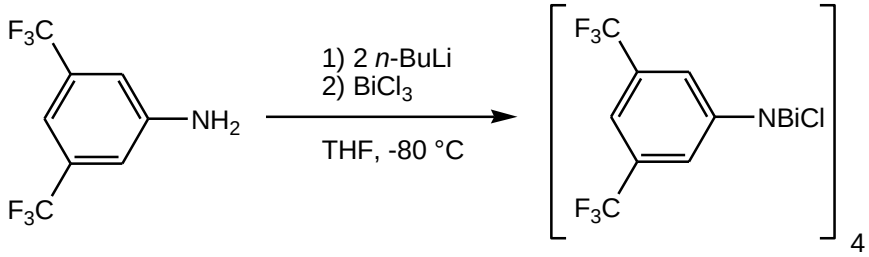


Figure S2. Ball-and-stick representation of spiro compound **E**.

3 Experimental Details

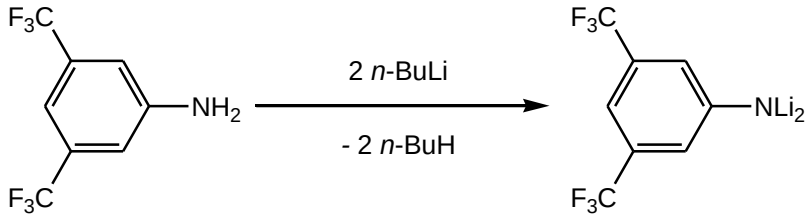
Heterocuban synthesis

Optimized reaction

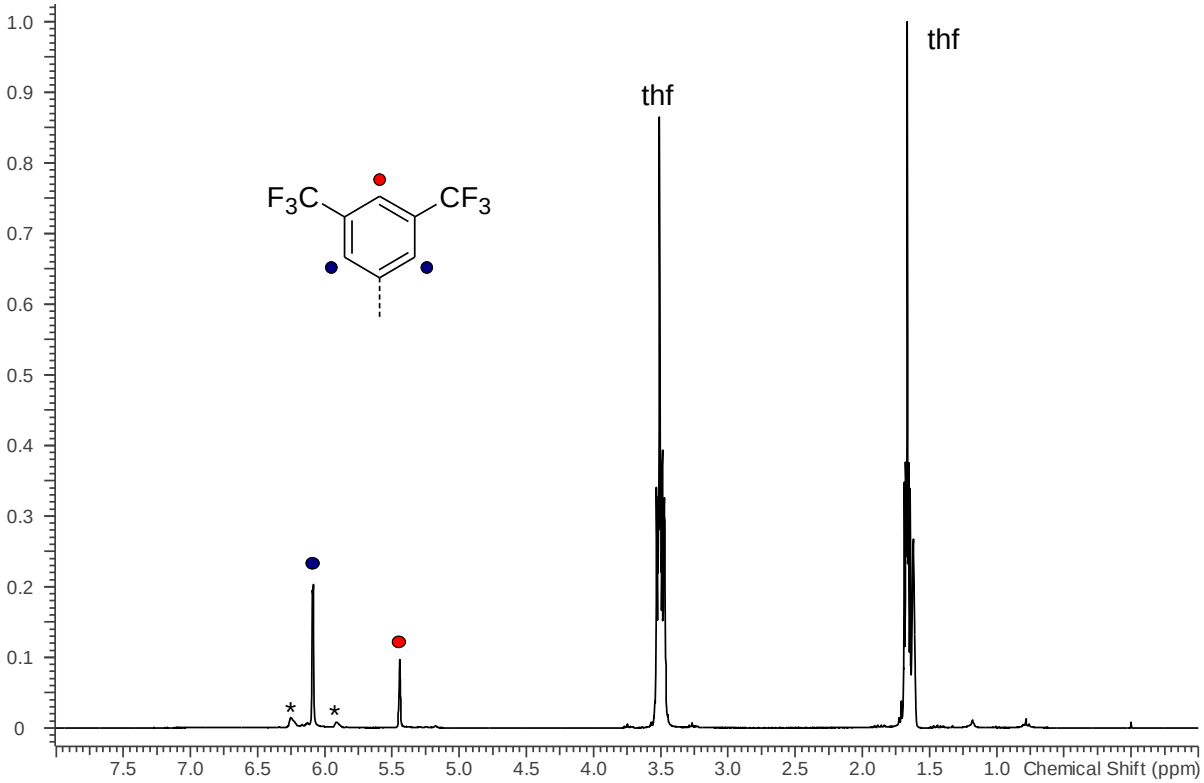


To a solution of *m*,*m*-$(CF_3)_2C_6H_3$-NH_2 (0.229 g, 1.00 mmol) in thf (5 mL) was added *n*-BuLi in hexane solution (0.88 mL, c = 2.5 M, 2.20 mmol) at −80 °C. After stirring at this temperature for 10 min, the reaction mixture was warmed to room temperature and added via syringe to a stirred suspension of $BiCl_3$ (0.347 g, 1.10 mmol) in thf (2 mL) at −80 °C. The now blackish suspension was warmed to room temperature over a period of 1 h and the solvent was removed *in vacuo* afterwards. Extraction with benzene (5 mL) and filtration (F4/celite padded) resulted in a reddish solution which was concentrated to induce crystallization. Yield: 0.103 g (0.06 mmol, 6.0%) of crystalline material, raw product (30%).
^{1}H NMR (298.2 K, benzene-d_6, 300.13 MHz): 6.78 (m, 8 H, *o*-C***H***), 7.45 (broad, 4 H, *p*-C***H***). **^{19}F{^{1}H} NMR** (298.2 K, benzene-d_6, 282.38 MHz): −62.8 (s). **IR** (ATR, 32 scans, cm^{-1}): 2957 (w), 2924 (w), 2870 (w), 2860 (w), 1622 (w), 1597 (w), 1461 (w), 1383 (m), 1356 (m), 1276 (s), 1173 (s), 1127 (s), 995 (w), 942 (m), 929 (m), 872 (m), 845 (m), 771 (w), 740 (w), 729 (m), 699 (m), 682 (s), 614 (w), 478 (s), 427 (s). Elemental analysis was tried several times but gave always deviation up to 5% due to hydrolysis and loss of benzene (solvate). Due to a bad solubility, no ^{13}C-NMR data could be obtained.

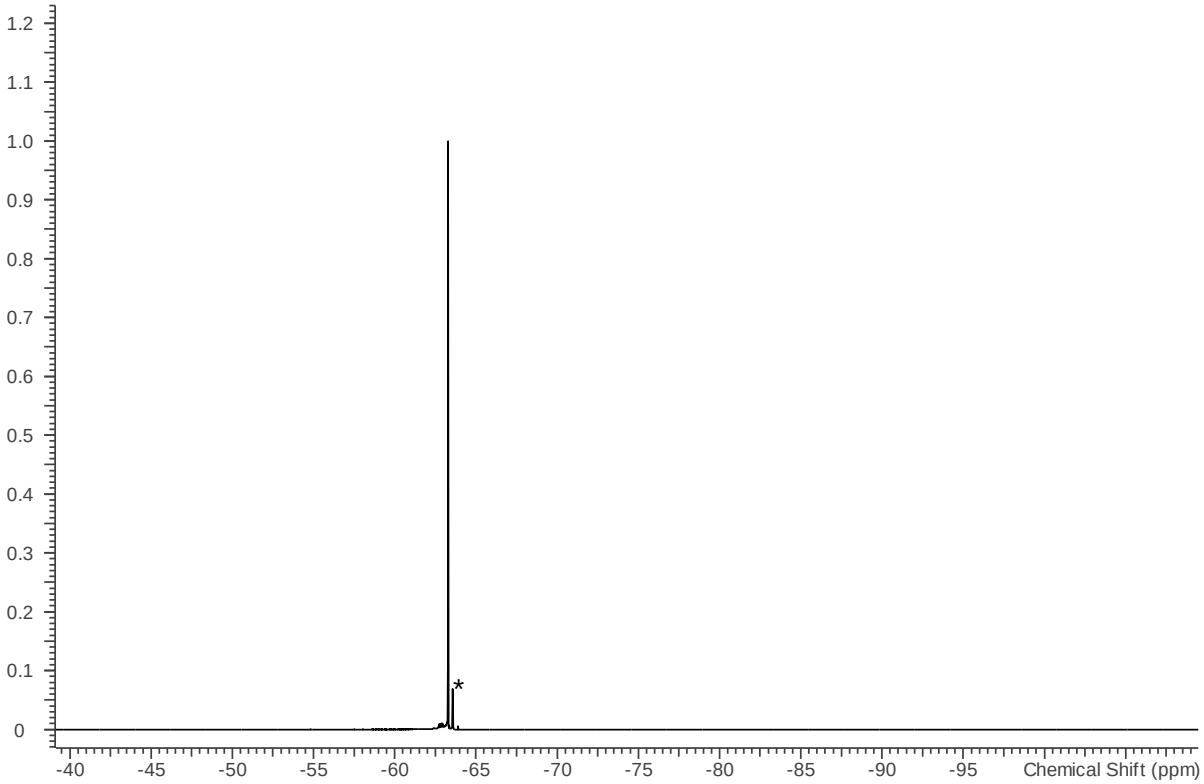
Attempted isolation of Li_2(N-TMP)



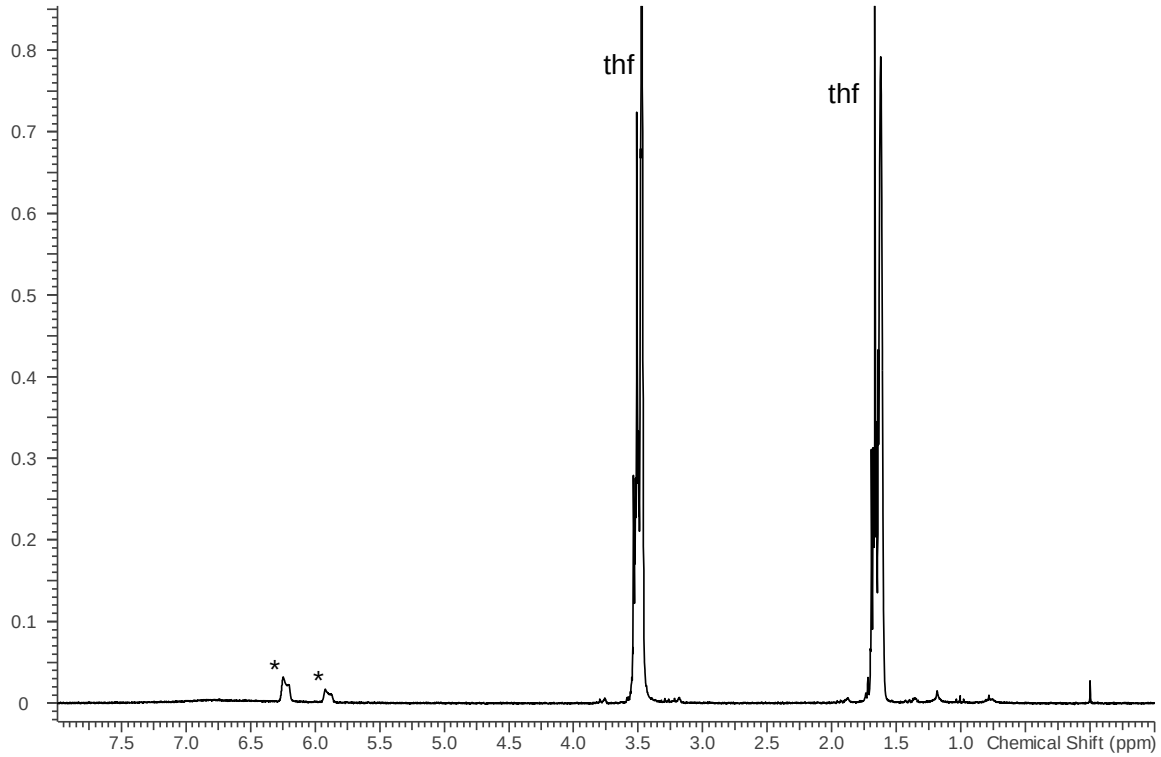
m,*m*-$(CF_3)_2C_6H_3$-NH_2 (0.379 g, 1.65 mmol) was dissolved in thf (3 mL) and cooled to 0 °C. Then a 2.5 M solution of *n*-BuLi in *n*-hexane (1.32 mL, 3.31 mmol) was added dropwise. Concentration to approximately 1 mL and storage at 5 °C for 1 h led to the deposition of colorless needle-like crystals suitable for single crystal X-ray studies. X-ray studies revealed the presence of $[Li(thf)_4]_2[Li_9(N\text{-}TMP)_5F]$ with $[Li_9(N\text{-}TMP)_5F]^{2-}$ = $LiF{\cdot}4\ Li_2[N\text{-}TMP]\ {\cdot}[N\text{-}TMP]^{2-}$. This salt was highly reactive and could not be stored in solution or as a solid at room temperature. Decomposition of the solid into a complex mixture was completed after ca. 12 h according to ^{1}H NMR data.



^{1}H NMR of TMP-NLi$_2$ measured in thf-d$_8$ directly after synthesis. Asterisk: beginning formation of TMP-NH$_2$ besides other decomposition products.



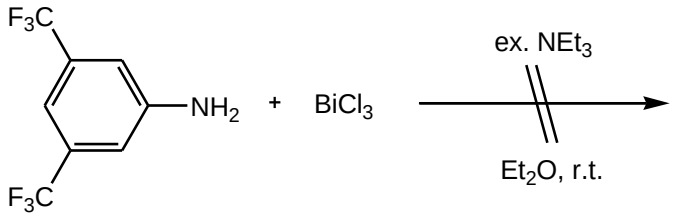
^{19}F NMR of TMP-NLi$_2$ measured in thf-d$_8$ directly after synthesis. Asterisk: beginning formation of TMP-NH$_2$ besides other decomposition products.



^{1}H NMR of the decomposition products of TMP-NLi_2 in thf-d_8. Asterisk: TMP-NH_2 besides other unknown decomposition products (broad signals).

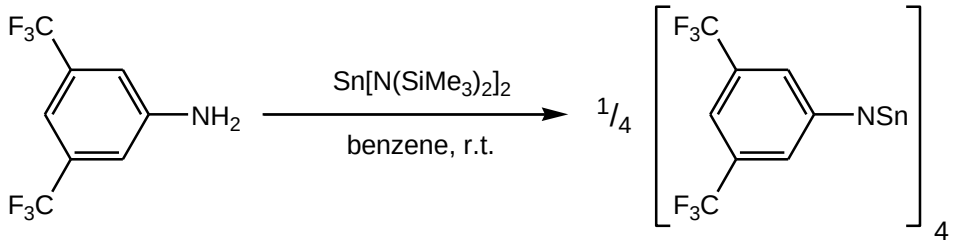
Experimental:
^{1}H NMR (298.5 K, thf-d_8, 300.13 MHz): 5.55 (m, 1 H, *o*-C***H***), 6.20 (broad, 2 H, *p*-C***H***).
^{19}F{^{1}H} NMR (298.9 K, thf-d_8, 282.38 MHz): −63.8 (s).

Attempted reaction with NEt_3



To a mixture of *m*,*m*-$(CF_3)_2C_6H_3$-NH_2 (0.229 g, 1.00 mmol) and $BiCl_3$ (0.347 g, 1.10 mmol) in Et_2O (5 mL) was added NEt_3 (0.304 g, 3.00 mmol) dropwise at room temperature. After stirring for 1 h, the solvent was removed and the residue was investigated by ^{1}H NMR spectroscopy. Only the starting material was observed.

Synthesis of Sn_4N_4-Heterocuban

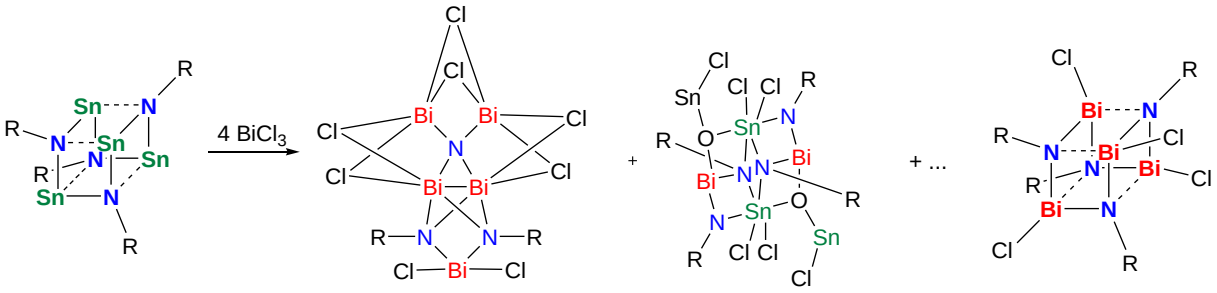


a) To a stirred solution of 1-amino-3,5-bis(trifluoromethyl)benzene (0.229 g, 1.00 mmol) in benzene (5 mL) a solution of $Sn[N(SiMe_3)_2]_2$ (0.549 g, 1.25 mmol) in benzene (2 mL) was added dropwise at room temperature. The resulting yellowish suspension was stirred for 15 min at r.t. and the solvent was removed *in vacuo* afterwards. Subsequent recrystallization from a minimum amount of thf and drying *in vacuo* yielded 0.244 g (0.17 mmol, 68.2%) 3,5-$[(CF_3)_2C_6H_3$-$NSn]_4$ • 0.7 THF in three crops as colorless needles.
Mp.: 288 °C (orange melt). **CHN** calc. (found) in %: C 29.08 (28.505), H 1.22 (1.265), N 3.92 (3.918). **^{1}H NMR** (298.5 K, thf-d_8, 300.13 MHz): 1.78 (m, 5.4 H, 0.7 thf), 3.62 (m, 5.4 H, 0.7 thf), 7.47 (m, 4 H, *p*-C***H***), 7.63 (m, 8 H, *o*-C***H***). **^{13}C{^{1}H} NMR** (299.4 K, thf-d_8, 75.48 MHz): 26.5 (s, thf), 68.4 (s, thf), 113.7 (broad, *p*-***C***H), 121.9 (broad, *o*-C***H***), 125.0 (q, $^1J\{^{13}C$-$^{19}F\}$ = 273 Hz, ***C***F_3), 132.8 (q, $^2J\{^{13}C$-$^{19}F\}$ = 32 Hz, ***C***(CF_3)), 157.7 (s, *i*-***C***). **^{19}F{^{1}H} NMR** (298.8 K, thf-d_8, 282.38 MHz): −63.7 (s, C***F***$_3$). **^{119}Sn{^{1}H} NMR** (298.4 K, thf-d8, 111.92 MHz): 293.7 (s, $[RNSn]_4$). **IR** (ART-IR, 16 scans, cm^{-1}): 3508 (w), 3419 (w), 3228 (w), 3086 (w), 3022 (w), 2874 (w), 2575 (w), 2519 (w), 2438 (w), 1763 (w), 1639 (w), 1628 (w), 1595 (m), 1458 (m), 1394 (w), 1350 (s), 1273 (s), 1215 (m), 1165 (s), 1117 (s), 993 (m), 935 (s), 881 (m), 868 (m), 845 (m), 729 (m), 696 (m), 683 (m), 656 (w), 636 (w), 606 (w), 553 (w). **Raman** (633 nm, accumulation time: 10 s, 20 scans, cm^{-1}): 3086 (1), 3024 (1), 2981 (1), 2961 (1), 2941 (1), 2882 (1), 2624 (1), 2576 (1), 2522 (1), 1758 (1), 1748 (1), 1597 (5), 1485 (1), 1460 (1), 1447 (1), 1372 (3), 1355 (5), 1315 (1), 1236 (2), 1226 (4), 1181 (1), 1137 (1), 1108 (1), 1097 (1), 1052 (1), 1036 (1), 996 (8), 964 (1), 956 (1), 945 (1), 939 (1), 915 (1), 894 (1), 890 (1), 736 (1), 731 (1), 699 (1), 631 (4), 607 (1), 558 (1), 537 (1), 449 (1), 438 (1), 399 (1), 360 (1), 345 (1), 319 (1), 287 (1), 259 (1), 215 (10), 178 (1), 163 (5).

b) To a stirred solution of 1-amino-3,5-bis(trifluoromethyl)benzene (0.916 g, 4.00 mmol) in benzene (5 mL) a solution of $Sn[N(SiMe_3)_2]_2$ (1.802 g, 4.10 mmol) in *n*-hexane (10 mL) was added dropwise at room temperature. The resulting yellowish

suspension was stirred for 30 min at r.t. and the solvent was removed afterwards. Subsequent drying *in vacuo* yielded 1.412 g (0.99 mmol, 99.4%) 3,5-[$(CF_3)_2C_6H_3$-NSn]$_4$ • 0.2 benzene.
CHN calc. (found) in %: C 30.12 (30.023), H 1.12 (1.426), N 3.90 (3.863). **^{1}H NMR** (298.5 K, thf-d_8, 300.13 MHz): 7.30 (s, 1 H, $^1/_6$ C_6H_6) 7.47 (m, 4 H, *p*-C***H***), 7.63 (m, 8 H, *o*-C***H***).

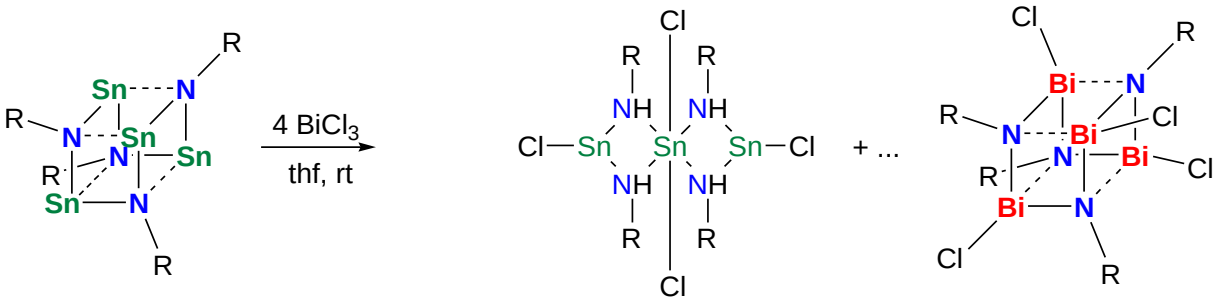
Transmetallation of Sn_4N_4-Heterocuban with $BiCl_3$ in benzene



D **E** **not observed**

The Sn_4N_4 heterocubane (0.168 g, 0.12 mmol) and $BiCl_3$ (0.189 g, 0.60 mmol) were combined in a flask and benzene (3 mL) was added. After stirring the brown suspension for 3 h at room temperature, the reaction mixture was filtered thru a celite padded frit. The orange filtrate was then concentrated. Overnight storage at room temperature resulted in the deposition of yellow crystals. By x-ray diffraction two different compounds (**D** and **E**) could be identified by X-ray studies. Attempts to separate both species by fractional crystallization from benzene or thf failed.

Transmetallation of Sn_4N_4-Heterocuban with $BiCl_3$ in THF



F **not observed**

The Sn_4N_4 heterocubane (0.278 g, 0.20 mmol) and $BiCl_3$ (0.315 g, 1.00 mmol) were combined in a flask and thf (5 mL) was added. After stirring the black suspension for 3 h at room temperature, the solvent was removed *in vacuo*. The blackish-greenish residue was extracted with benzene (10 mL) and filtered (F4). Concentrating and storage over 8 h at room temperature led to the deposition of yellow and colorless crystals. The colorless crystals could be identified as a spiran **F**, while the structure of the yellow substance remained elusive. Also, recrystallization form thf did not led to x-ray quality crystals of the yellow substance, but a Raman spectrum of a crystal could be recorded. All attempts to separate the two species failed.

Spiran colorless:
Raman (633 nm, accumulation time: 20 s, 20 scans, cm^{-1}): 3069 (1), 2979 (1), 2946 (1), 2892 (1), 1620 (1), 1380 (2), 1342 (1), 1312 (1), 1243 (1), 1179 (1), 1135 (1), 1108 (1), 1036 (1), 1001 (5), 992 (6), 947 (1), 918 (1), 866 (1), 808 (5), 747 (3), 731 (5), 605 (1), 541 (1), 380 (1), 334 (3), 303 (5), 285 (10), 203 (3), 182 (4), 157 (7), 115 (7).

Yellow crystals
Raman (633 nm, accumulation time: 20 s, 20 scans, cm^{-1}): 3065 (1), 1606 (1), 1368 (2), 1306 (1), 1214 (2), 1196 (2), 993 (10), 946 (2), 808 (2), 748 (1), 668 (1), 637 (1), 622 (2), 607 (1), 563 (1), 548 (1), 482 (1), 449 (1), 399 (1), 370 (1), 334 (1), 303 (3), 265 (1), 218 (1), 180 (9).

4 Computational Details

All calculations were carried out for isolated molecules in the gas phase using the Gaussian G09 Rev. E0.1 software package.[7] The structures – except for **2'**[$GaCl_4$] (structure for NRT analysis) – were optimized at the PBE0-D3(BJ)/def2svp[8–11] level of theory and confirmed as energetic minima by frequency analysis. NBO and NLMO calculations were carried out using the standalone version of the NBO 6.0 software package[12].

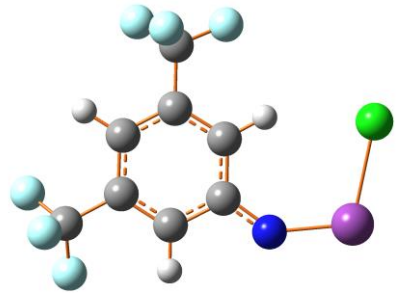
Table S3. Absolute (a.u.) and relative energies (kcal/mol, see Figure S3).

	E_0	H_{298}	G_{298}	ΔE_0	ΔH_{298}	ΔG_{298}
mono	-1633.371390	-1633.248091	-1633.316520			
cis_dimer	-3266.848477	-3266.599599	-3266.715450	0.00	0.00	0.00
trans_dimer	-3266.853624	-3266.604515	-3266.720581	-3.23	-3.08	-3.22
tetramer_cubane	-6533.811783	-6533.312044	-6533.510731	0.00	0.00	0.00
tetramer_ring	-6533.766487	-6533.267298	-6533.461109	28.42	28.08	31.14
tetramer_ring_iso1	-6533.724264	-6533.225617	-6533.419654	54.92	54.23	57.15
tetramer_ring_iso2	-6533.770300	-6533.270537	-6533.466234	26.03	26.05	27.92

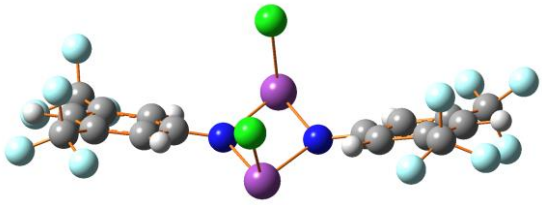
Table S4. Oligomerization energies (kcal/mol, see Figure S3).

oligomerization	ΔE_0	ΔH_{298}	ΔG_{298}
2 mono → cis_dimer	-66.33	-64.90	-51.71
2 mono → trans_dimer	-69.56	-67.98	-54.93
4 mono → tetramer_cubane	-204.71	-200.60	-153.52
2 trans_dimer → tetramer_cubane	-65.60	-64.64	-43.66
4 mono → tetramer_ring	-176.28	-172.52	-122.38
2 trans_dimer → tetramer_ring	-37.17	-36.56	-12.52

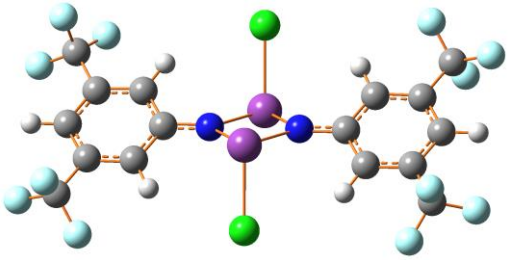
Figure S3. Computed structures of [Cl-Bi-N-TMP]$_n$ with n = 1-4.



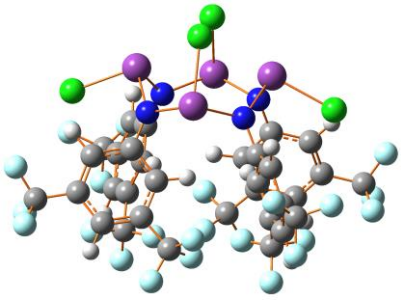
monomer



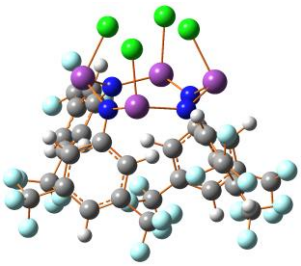
cis-dimer



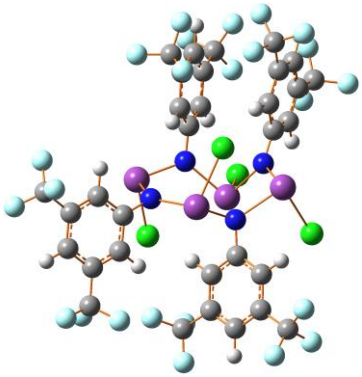
trans-dimer



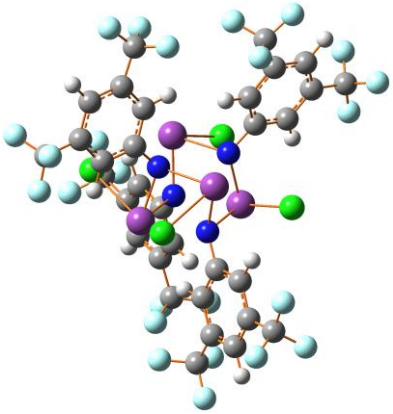
tetramer ring



isomer1



isomer2



tetramer cubane

Table S5. Selected NBO data (q = partial charge in e, Q_{CT} = charge transfer in e, LP = lone pair – s-character in %, σ(Bi-N) localization at Bi in %, π(Bi-N), localization at Bi in %).

species	q(Bi)	q(N)	q(Cl)	q(TMP-N)	Q_{CT}(Cl)	Q_{CT}(TMP)	Q_{CT}_sum	LP(Bi) s%	σ(Bi-N), %Bi	π(Bi-N), %Bi
mono	1.216	-0.896	-0.489	-0.727	0.511	1.273	1.784	92	23	35%
cis_dimer	1.575	-1.168	-0.467	-1.108	0.533	0.892	1.425	90	19	-
trans_dimer	1.604	-1.176	-0.488	-1.116	0.512	0.884	1.396	90	19	-
tetramer_cubane	1.650	-1.248	-0.509	-1.140	0.491	0.860	1.351	93	11	-
tetramer_ring	1.600	-1.210	-0.472	-1.127	0.528	0.873	1.401	91	17	

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