Supporting Information

A Neutral Low-Coordinate Heterocyclic Bismuth-Tin Species

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1. Experimental

General Information. All manipulations were carried under oxygen- and moisture free conditions using standard Schlenk and Drybox techniques.

Dichloromethane was purified according to a literature procedure¹, dried over P_4O_{10} , stored over CaH_2 and was freshly distilled prior to use. C_6H_5F was dried over CaH_2 and freshly distilled prior to use. Benzene was dried over Na/benzophenone and freshly distilled prior to use. ${}^{iPr}Ar^*NH_2$, ${}^{tBu}Ar^*NH_2$, ${}^{[1]}$ and $Sn\{N(SiMe_3)_2\}_2{}^{[2]}$ have been reported previously and were prepared according to modified literature procedures. $SbCl_3$ (99.99%, Merck) and BiCl₃ (99.9%, anhydrous, Alfa Aesar) were freshly sublimed prior to use.

NMR: ¹¹⁹Sn{¹H}, ¹³C{¹H}- and ¹H-NMR spectra were recorded on a BRUKER spectrometer AVANCE 300. The ¹H- and ¹³C-NMR chemical shifts were referenced to the solvent signals (CDHCl₂: δ (¹H) = 5.31; δ (¹³C) = 54.0). The ¹¹⁹Sn NMR chemical shift is referred to SnMe₄. CD₂Cl₂ was dried over P₄O₁₀ and was degased prior to use. C₆D₆ was dried over Na and freshly distilled prior to use.

CHN analysis: Analysator Flash EA 1112 from Thermo Quest.

IR: Nicolet 380 FT-IR with a Smart Orbit ATR module.

RAMAN: LabRAM HR 800 Horiba Jobin YVON equipped with a High Stability BX40 Microscope (Focus 1 μ m) or an Olympus Mplan 50xNA 0.70 lens, the laser is variable and was chosen prior to the measurement.

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

2. Structure elucidation

X-ray Structure Determination: X-ray quality crystals of **1***i***Pr**, **1***t***Bu**, **2**, **3**, **4**·CH₂Cl₂ and **4**·C₆H₅F were selected in Fomblin YR-1800 perfluoroether (Alfa Aesar) at ambient temperature. The data was collected on a Bruker Kappa Apex-II CCD diffractometer using graphite monochromated Mo-K α radiation ($\lambda = 0.71073$). The structures were solved by direct methods (*SHELXS-13*)³ and refined by full-matrix least squares procedures (*SHELXL-13*).⁴ Semi-empirical absorption corrections were applied (*SADABS*).⁵ All non-hydrogen atoms were refined anisotropically, hydrogen atoms were included in the refinement at calculated positions using a riding model.

The 4-*i*Pr group in the ^{*i*Pr}Ar*-moiety in **1***i*Pr was found to be disordered and was split in two parts. The occupation of each part was refined freely (0.59(3)/0.41(3). Moreover, two benzene molecules in the voids were found to be disordered and were split in two parts (0.643(6)/0.357(6)) or three parts (0.423(3)/0.378(3)/0.199(3)), respectively.

The 4-*t*Bu group in the ^{*t*Bu}Ar*-moiety in **1***t***Bu** was found to be disordered and was split in two parts. The occupation of each part was refined freely (0.539(4)/0.461(4)). Moreover, three disordered C₆H₅F molecules are present. Two of the molecules lie on a crystallographically imposed center of inversion, resulting in a 50 % occupancy of each part. The third molecule was split in three parts and the occupancy was refined freely (0.375(3)/0.391(3)/0.233(3)).

3 was found to contain two molecules of C_6H_5F , which are disordered on their respective positions. One molecule was split in four parts and the occupation of each part was refined freely (0.357(s)/0.237(3)/0.258(3)/0.147(3)). The second molecule was split in three parts and the occupancy of each part was refined freely (0.528(3)/0.247(3)/0.225(3)).

 $4 \cdot CH_2Cl_2$ was found to contain two molecules of CH_2Cl_2 , which are disordered on their respective positions. Each molecule was split in two parts and the occupation of each part was refined freely (0.888(6)/0.112(6); 0.54(2)/0.46(2)). The second molecule was split in three parts and the occupancy of each part was refined freely (0.528(3)/0.247(3)/0.225(3)).

 $4 \cdot C_6 H_5 F$ was found to contain two molecules of $C_6 H_5 F$, of which one is disordered its position. The occupancy of each part was refined freely (0.55(3)/0.45(3)).

Compound	1 <i>t</i> Bu	1 <i>i</i> Pr	2
	$C_{72}H_{66}N_2Sn_2\cdot$	$C_{94}H_{86}Sn_2N_2$	
Chem. Formula	$4(C_{6}H_{5}F)$		$C_{72}H_{66}N_2Sb_2Cl_2$
Form. Wght. [g mol ⁻¹]	1581.04	1481.02	743.96
Colour	Red	Red	Colourless
Cryst. system	triclinic	triclinic	triclinic
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1
<i>a</i> [Å]	10.1387(5)	10.3114(6)	10.5945(2)
<i>b</i> [Å]	14.5652(8)	12.6833(6)	12.3644(3)
<i>c</i> [Å]	15.4070(8)	14.8438(6)	12.5871(3)
α [°]	109.721(3)	101.757(3)	98.608(1)
β [°]	103.913(2)	90.344(2)	105.285(1)
γ [°]	101.780(2)	99.280(3)	100.205(1)
V[Å ³]	1974.97(18)	1874.2(2)	1531.50(6)
Ζ	1	1	1
$\rho_{\text{calc.}} [\text{g cm}^{-3}]$	1.329	1.312	1.381
$\mu \text{ [mm}^{-1}\text{]}$	0.690	0.715	1.01
<i>T</i> [K]	173(2)	173(2)	173(2)
Measured reflections	66071	38164	51581
Independent reflections	13646	11805	10958
Reflections with $I > 2\sigma(I)$	10553	9160	8978
R _{int}	0.036	0.037	0.052
<i>F</i> (000)	812	764	648
$R_1(R[F^2>2\sigma(F^2)])$	0.042	0.042	0.044
$wR_2 (F^2)$	0.095	0.1079	0.0686
GooF	1.074	1.030	1.096
Parameters	529	457	355

Table S1. Crystallographic Details of 1tBu, 1iPr and 2

Compound	3	4·CH ₂ Cl ₂	4·C ₆ H ₅ F
	$C_{36}H_{33}Cl_4NSb_2\cdot$	$C_{72}H_{66}N_2BiCl_3Sn\cdot$	$C_{72}H_{66}N_2BiCl_3Sn\cdot$
Chem. Formula	$2(C_6H_5F)$	$2(CH_2Cl_2)$	$2(C_6H_5F)$
Form. Wght. [g mol ⁻¹]	1057.13	1563.14	1585.48
Colour	Colourless	Orange	Yellow
Cryst. system	monoclinic	triclinic	orthorhombic
Space group	$P2_{1}/n$	<i>P</i> -1	$Pna2_1$
<i>a</i> [Å]	16.2248(8)	10.5190(9)	21.3654(9)
<i>b</i> [Å]	10.8555(5)	14.757(1)	31.117(1)
<i>c</i> [Å]	26.4376(12)	22.906(2)	10.7124(4)
α [°]	90	75.620(2)	90
β [°]	106.2400(10)	86.231(2)	90
γ [°]	90	80.569(2)	90
V [Å ³]	4470.6(4)	3396.4(5)	7121.8(5)
Ζ	4	2	4
$\rho_{\text{calc.}} [\text{g cm}^{-3}]$	1.571	1.528	14791
$\mu [\mathrm{mm}^{-1}]$	1.49	3.27	2.98
<i>T</i> [K]	173(2)	173(2)	173(2)
Measured reflections	85218	100106	48842
Independent reflections	16169	20494	16347
Reflections with $I > 2\sigma(I)$	11230	13584	9163
R _{int}	0.058	0.093	0.117
<i>F</i> (000)	2104	1560	3184
$R_1(R[F^2>2\sigma(F^2)])$	0.038	0.046	0.066
$wR_2 (F^2)$	0.0952	0.0873	0.1232
GooF	1.023	1.005	0.980
Parameters	475	810	755

Table S2. Crystallographic Details of 3, $4 \cdot C_6 H_5 F$ and $4 \cdot C H_2 C l_2$





 Table S3. Selected bond lenghts (Å) angles (°) and torsion angles (°) of 1tBu.

N1—C1	1.394 (2)	C1—C2	1.411 (3)
N1—Sn1	2.0752 (16)	С2—С3	1.389 (3)
N1—Sn1 ⁱ	2.0897 (16)	C3—C4	1.393 (3)
Sn1—N1 ⁱ	2.0898 (16)	C4—C5	1.390 (3)
Sn1—Sn1 ⁱ	3.2318 (3)	С5—С6	1.392 (3)
C1—N1—Sn1	130.47 (12)	Sn1—N1—Sn1 ⁱ	101.78 (6)
C1—N1—Sn1 ⁱ	127.69 (12)	N1—Sn1—N1 ⁱ	78.22 (6)
Sn1—N1—C1—C6	91.3 (2)	Sn1 ⁱ —N1—C1—C2	88.2 (2)

Symmetry code: (i) -x+1, -y, -z+1.





Table S4. Selected bond lenghts (Å) angles (°) and torsion angles (°) of 1*i*Pr.

Sn1—N1	2.0788 (18)	C1—C2	1.408 (3)
Sn1—N1i	2.0859 (18)	C2—C3	1.395 (3)
Sn1—Sn1i	3.2304 (4)	C3—C4	1.391 (3)
N1—C1	1.401 (3)	C4—C5	1.385 (3)
N1—Sn1i	2.0859 (18)	С5—С6	1.395 (3)
C1—N1—Sn1	130.59 (14)	N1—Sn1—N1i	78.27 (7)
C1—N1—Sn1i	127.57 (15)	Sn1—N1—Sn1i	101.73 (7)
Sn1—N1—C1—C2	88.6 (3)	Sn1i—N1—C1—C6	93.8 (2)

Symmetry codes: (i) -x+1, -y+1, -z+1; (ii) -x, -y+1, -z+1; (iii) -x, -y, -z.

Scheme S3. Numbering scheme of 2.



Table S5. Selected bond lenghts (Å) angles (°) and torsion angles (°) of 2.

Sb1—N1	2.0299 (19)	Sb2—N1	2.0392 (18)
Sb1—Cl1	2.3709 (7)	Sb2—Cl3	2.3731 (7)
Sb1—Cl2	2.4338 (7)	Sb2—Cl4	2.4199 (7)
N1—C1	1.434 (3)	C1—C2	1.412 (3)
C4—C5	1.391 (3)	C2—C3	1.394 (3)
C5—C6	1.394 (3)	C3—C4	1.397 (3)
N1—Sb1—Cl1	95.78 (6)	N1—Sb2—Cl3	96.48 (6)
N1—Sb1—Cl2	89.04 (6)	N1—Sb2—Cl4	89.61 (6)
Cl1—Sb1—Cl2	95.26 (3)	Cl3—Sb2—Cl4	95.38 (3)
C1—N1—Sb1	123.05 (14)	Sb1—N1—Sb2	115.74 (10)
C1—N1—Sb2	121.19 (14)	Sb1—N1—C1—C6	80.0 (2)

Scheme S4. Numbering scheme of 3.



Table S6. Selected bond lenghts (Å) angles (°) and torsion angles (°) of 3.

Sb1—N1	2.0332 (18)	N1—C1	1.430 (3)
Sb1—N1i	2.0337 (16)	N1—Sb1i	2.0337 (16)
Sb1—Cl1	2.4327 (7)	C6—C5	1.388 (3)
Sb1—Sb1i	3.1749 (3)	C6—C1	1.415 (3)
C2—C1	1.400 (3)	C3—C4	1.380 (3)
С2—С3	1.403 (3)	C4—C5	1.398 (3)
N1—Sb1—N1i	77.36 (7)	C1—N1—Sb1	122.53 (13)
N1—Sb1—Cl1	97.60 (5)	C1—N1—Sb1i	134.66 (14)
N1i—Sb1—Cl1	98.09 (5)	Sb1—N1—Sb1i	102.64 (7)
Sb1—N1—C1—C2	77.6 (2)		

Symmetry code: (i) -x, -y+2, -z+1.

Scheme S5. Numbering scheme of 4·(CH₂Cl₂)₂.



Table S7. Selected bond lenghts (Å) angles (°) and torsion angles (°) of 4·(CH₂Cl₂)₂.

Sn1—N1	2.094 (3)	Bi1—N1	2.106 (3)
Sn1—N2	2.107 (3)	Bi1—N2	2.108 (3)
Sn1—Cl1	2.3531 (10)	Bi1—C8	2.861 (4)
Sn1—Cl3	2.3874 (11)	N1—C37	1.425 (5)
Sn1—Cl2	2.4028 (11)	N2—C1	1.426 (5)
Sn1—Bi1	3.2631 (4)	N1—Bi1—N2	78.10 (12)
N1—Sn1—N2	78.41 (12)	C37—N1—Sn1	130.1 (2)
N1—Sn1—Cl1	107.32 (9)	C37—N1—Bi1	125.9 (2)

N2—Sn1—Cl1	106.84 (9)	Sn1—N1—Bi1	101.96 (13)
C1—N2—Sn1	126.7 (2)	Sn1—N2—Bi1	101.44 (13)
C1—N2—Bi1	125.4 (2)	Bi1—N2—C1—C6	115.8 (3)
Sn1—N2—C1—C2	82.7 (4)		

Scheme S5. Numbering scheme of 4·C₆H₅F.



Table S7. Selected bond lenghts (Å) angles (°) and torsion angles (°) of 4·(CH₂Cl₂)₂.

Sn2—N1	2.093 (10)	Bi1—N2	2.080 (11)
Sn2—N2	2.110 (11)	Bi1—N1	2.131 (11)
Sn2—Cl1	2.380 (4)	Bi1—C49	2.848 (14)
Sn2—Cl2	2.413 (4)	Bi1—C44	2.870 (15)
Sn2—Cl3	2.347 (4)	N1—C1	1.431 (15)
Bi1—Sn2	3.2604 (11)	N2—C37	1.430 (15)
N2—Bi1—N1	77.7 (4)	N1—Sn2—N2	77.9 (4)
C1—N1—Sn2	128.1 (8)	C1—N1—Sn2	128.1 (8)

C1—N1—Bi1	128.1 (8)	C1—N1—Bi1	128.1 (8)
Sn2—N1—Bi1	101.1 (4)	Sn2—N1—Bi1	101.1 (4)
Bi1—N1—C1—C2	63.5 (17)	Sn2—N1—C1—C6	81.0 (14)

3.1. Synthesis of $[Sn(\mu-N^{tBu}Ar^*)]_2$ (1*t*Bu)

$${}^{tBu}Ar^*NH_2 \xrightarrow{Sn[N(SiMe_3)_2]_2} 0.5 [Sn(\mu-N^{tBu}Ar^*)]_2 \\ \xrightarrow{160^{\circ}C} -2 HN(SiMe_3)_2}$$

^{*t*Bu}Ar*-NH₂ (1.008 g, 2.09 mmol) and Sn[N(SiMe₃)₂]₂ (0.940 g, 2.14 mmol) were combined in a 25 mL round-bottomed flask, which was evacuated and heated to 160 °C over a period of 30 minutes. During this time a deep red powder has formed and the volatiles are removed *in vacuo* at 80 °C to afford a crude red powder. The powder was extracted with C₆H₅F (100 mL) and filtered. The filtrate was concentrated to incipient crystallization and standing at r.t. for 12 h afforded [Sn(μ -N^tBuAr*)]₂·(C₆H₅F)₃ as red crystalline solid (1.006 g, 0.67 mmol; 64 % based on ^{tBu}Ar*-NH₂). Drying of the crystals did not result in complete removal of C₆H₅F

1*t*Bu: Mp. 220 °C (dec.). Anal. calc. % (found): 72.79 (71.51), H 5.50 (5.42), N 1.89 (1.82) ¹H-NMR (25 °C, C₆D₆, 300.13 MHz): δ = 1.33 (s, 18H, CH(CH₃)₃), 6.77 (s, 2H, CH(C₆H₅)₂), 7.11-7.50 (Ar-CH). ¹³C{¹H} NMR (25 °C, C₆D₆, 75.46 MHz): δ = 32.3 (s, *p*-C(CH₃)₃), 34.5 (s, *p*-C(CH₃)₃), 54.9 (s, 2 CHPh₂), 125.1, 127.5, 129.8, 130.7, 137.8, 142.1, 147.0, 149.1 (C-Ar, some missing due to C₆D₆, see Figure SX); ¹¹⁹Sn{¹H}-NMR (25 °C, C₆D₆, 111.92 MHz): δ = 780.4. IR (ATR, 25°C, 32 scans, cm⁻¹): 3080 (w), 3059 (w), 3024 (w), 2956 (w), 2900 (w), 2862 (w), 1621 (w), 1595 (m), 1493 (m), 1472 (m), 1446 (m), 1425 (w), 1392 (w), 1361 (w), 1338 (w), 1321 (w), 1295 (w), 1242 (w), 1217 (m), 1182 (w), 1153 (w), 1117 (w), 1076 (w), 1063 (w), 1030 (w), 1003 (w), 910 (w), 893 (w), 866 (w), 852 (w), 830 (w), 805 (w), 754 (m), 737 (s), 696 (s), 685 (m), 633 (w), 621 (w), 606 (m), 586 (w), 573 (w).



Figure S1. Molecular structure of **1***t***Bu**. Thermal ellipsoids drawn at 50% probability and -100 °C. ^{*t*Bu}Ar* substituents rendered as wire-frame and H atoms omitted for clarity. Selected bond lengths and angles are shown in Table S3.



Figure S2. ¹H NMR spectrum of 1tBu in C₆D₆.



Figure S3. ¹³C NMR spectrum of 1tBu in C₆D₆.

3.2. Synthesis of $[Sn(\mu-N^{iPr}Ar^*)]_2$ (1*i*Pr)

$${}^{Pr}Ar^*NH_2 \xrightarrow{Sn[N(SiMe_3)_2]_2} 0.5 [Sn(\mu-NiPrAr^*)]_2$$

$$-2 HN(SiMe_3)_2$$

 iPr Ar*-NH₂ (0.465 g, 0.98 mmol) and Sn[N(SiMe₃)₂]₂ (0.440 g, 1.00 mmol) were combined in a 25 mL round-bottomed flask, which was evacuated and heated to 160 °C over a period of 30 minutes. During this time a deep red powder has formed and the volatiles were removed *in vacuo* at 80 °C to afford a crude red powder. The powder was extracted with hot C₆H₆ (50 mL) and filtered. The filtrate was concentrated to incipient crystallization and standing at r.t. for 12 h afforded minimal amounts (<0.025 g) of [Sn(μ -N^{*i*Pr}Ar*)]₂·(C₆H₆)₃ as red crystals, which were suitable for X-ray analysis.

¹**H-NMR** (25 °C, C₆D₆, 300.13 MHz): $\delta = 1.23$ (d, 12H, CH(CH₃)₂), 2.79 (sept, 2H, CH(CH₃)₂), 6.79 (s, 2H, CH(C₆H₅)₂), 7.06 (s, 2H, Ar-CH), 7.11-7.50 (Ar-CH). ¹³C{¹H} NMR (25 °C, C₆D₆, 75.46 MHz): $\delta = 25.3$ (s, *p*-CH(CH₃)₂), 34.1 (s, *p*-CH(CH₃)₂), 54.9 (s, 2 CHPh₂), 126.1, 127.5, 128.9, 129.8, 130.7, 138.3, 140.1, 147.0, 149.5 (C-Ar, some missing due to C₆D₆, see Figure SX); ¹¹⁹Sn{¹H}-NMR (25 °C, C₆D₆, 111.92 MHz): $\delta = 783.07$ (s).



Figure S4. Molecular structure of **1***i***Pr**. Thermal ellipsoids drawn at 50% probability and -100 °C. ^{*i*Pr}Ar* substituents rendered as wire-frame and H atoms omitted for clarity. Selected bond lengths and angles are shown in Table S4.



Figure S5. ¹H NMR spectrum of 1iPr in C₆D₆.



Figure S6. ¹³C NMR spectrum of 1iPr in C₆D₆.

3.3. Synthesis of $[ClSb(\mu-N^tBuAr^*)]_2$ (2)

$$[Sn(\mu-N^{tBu}Ar^*)]_2 \xrightarrow{2 \text{ SbCl}_3} [ClSb(\mu-N^{tBu}Ar^*)]_2$$

$$CH_2Cl_2 -2 \text{ SnCl}_2$$

 $[Sn(\mu-N'^{Bu}Ar^*)]_2$ (0.370 g, 0.25 mmol) and SbCl₃ (0.121 g, 0.52 mmol) were combined in a 25 mL round-bottomed flask and at room temperature CH₂Cl₂ (10 mL) was added to that mixture. The typical red colour of **1***t***Bu** disappeared immediately and stirring was continued overnight. After removal of the volatiles in vacuo the crude mixture was extracted with fresh CH₂Cl₂ (2x 10 mL), leaving behind an offwhite solid. The yellowish filtrate was concentrated to incipient crystallization and standing at 5 °C overnight afforded pale yellow crystals of $[ClSb(\mu-N'BuAr^*)]_2$ (0.250 g, 0.196 mmol; 78.4 % based on **1***t***Bu**), which were suitable for X-ray analysis.

Mp. 275 °C (dec). **Anal**. calc. % (found): C 67.89 (66.82); H 5.22 (5.22); N 2.20 (2.27). ¹**H-NMR** (25 °C, CD₂Cl₂, 300.13 MHz): δ 0.93 (s, 9H, p-C(CH₃)₃), 6.77 (s, 2H, CH(C₆H₅)₂), 6.80 (s, 2H, Ar-CH), 6.82-6.89 (m, 8H, Ar-CH), 7.08-7.36 (m, 32H, Ar-CH); ¹³C{¹H} NMR (25 °C, CD₂Cl₂, 75.46 MHz): δ = 31.3 (s, *p*-C(CH₃)₃), 34.6 (s, *p*-C(CH₃)₃), 51.6 (s, 2 CHPh₂), 126.7, 126.8, 127.8, 128.7, 130.1, 130.2, 130.9, 139.9, 140.7, 145.7, 145.9, 147.3 (C-Ar). **IR** (ATR, 25°C, 32 scans, cm⁻¹): 2991 (w), 2917 (w), 1653 (m), 1610 (w), 1570 (m), 1446 (w), 1406 (w), 1375 (m), 1288 (m), 1259 (m), 1207 (s), 1173 (s), 1093 (s), 1030 (w), 1001 (w), 943 (w), 889 (m), 852 (s), 810 (m), 793 (m), 760 (w), 746 (w), 722 (w), 708 (w), 685 (s), 644 (w), 567 (m), 534 (w). **Raman** (100 mW, 25 °C, 4 scans, cm⁻¹): 2990 (1), 2971 (1), 2945 (1), 2930 (1), 2907 (1), 2737 (1), 2722 (1), 1602 (6), 1582 (2), 1449 (3), 1441 (3), 1306 (2), 1288 (2), 1265 (4), 1245 (4), 1197 (2), 1181 (2), 1169 (3), 1120 (3), 1030 (4), 1000 (10), 953 (1), 924 (1), 892 (2), 833 (2), 776 (1), 761 (1), 745 (1), 704 (1), 693 81), 636 (2), 616 (2), 604 (1), 548 (1), 493 (1), 464 (3), 397 (1), 287 (6), 235 (8).



Figure S7. ¹H NMR spectrum of **2** in CD_2Cl_2 .



Figure S8. ¹³C NMR spectrum of 2 in CD₂Cl₂.

3.4. Synthesis of ^{tBu}Ar*N(SbCl₂)₂

Procedure 1:

$$[Sn(\mu-N^{tBu}Ar^*)]_2 \xrightarrow{4 \text{ SbCl}_3} 2 \stackrel{tBu}{\longrightarrow} 2 \stackrel{tBu}{\longrightarrow} 2 \text{ CH}_2\text{Cl}_2 \\ -2 \text{ SnCl}_2$$

 $[Sn(\mu-N^RAr^*)]_2$ (0.370 g, 0.25 mmol) and SbCl₃ (0.228 g, 1.00 mmol) were combined in a 25 mL round-bottomed flask and at room temperature CH₂Cl₂ (10 mL) was added to that mixture. The typical red colour of **1***t***Bu** disappeared immediately and stirring was continued overnight. After removal of the volatiles in vacuo the crude mixture was extracted with C₆H₅F (2x 10 mL), leaving behind an off-white solid. The yellowish filtrate is concentrated to incipient crystallization and standing at 5 °C overnight afforded crystals of ${}^{tBu}Ar^*N(SbCl_2)_2 \cdot (C_6H_5F)$ (0.112, 0.12 mmol; 24 % based on **1***t***Bu**).

Procedure 2:

$$[\text{CISb}(\mu-\text{N}^{t\text{Bu}}\text{Ar}^*)]_2 \xrightarrow{2 \text{ SbCl}_3} 2 \ t^{\text{Bu}}\text{Ar}^*\text{N}(\text{SbCl}_2)_2$$

 $[ClSb(\mu-N^RAr^*)]_2$ (0.327 g, 0.26 mmol) and SbCl₃ (0.135 g, 0.58 mmol) were combined in a 25 mL round-bottomed flask and at room temperature CH₂Cl₂ (10 mL) was added to that mixture and stirring was continued overnight. After removal of the volatiles *in vacuo* the crude mixture was extracted with C₆H₅F (10 mL). The yellowish filtrate was concentrated to incipient crystallization and standing at room temperature overnight afforded crystals of ^{*t*}BuAr*N(SbCl₂)₂·(C₆H₅F) (0.325, 0.33 mmol; 65 % based on **2**), which were suitable for X-ray analysis.

Mp. 236 °C. **Anal.** calc. % (found): 52.49 (52.06), H 3.99 (3.88), N 1.46 (1.49). ¹H NMR (25 °C, CD₂Cl₂, 300.13 MHz): δ 0.99 (s, 9H, p-C(CH₃)₃), 6.44 (s, 2H, CH(C₆H₅)₂), 6.68 (s, 2H, Ar-CH), 7.02-7.41 (m, 20H, Ar-CH) ; ¹³C{¹H} NMR

(25 °C, CD₂Cl₂, 75.46 MHz): $\delta = 31.5$ (s, *p*-C(CH₃)₃), 34.9 (s, *p*-C(CH₃)₃), 53.2 (s, 2 CHPh₂), 115.6, 115.9, 124.7, 126.4, 127.5, 128.5, 129.2, 130.2, 130.3, 130.6, 130.7, 131.4, 139.7, 144.2, 144.7, 149.1 (*C*-Ar, including C₆H₅F); ¹⁹F{¹H} NMR (25 °C, CD₂Cl₂, 282.40 MHz) $\delta = -113.8$. **IR (ATR, 32 scans, cm⁻¹):** 3030 (w), 2960 (w), 1643 (w), 1595 (w), 1512 (m), 1495 (w), 1460 (s), 1412 (w), 1373 (w), 1365 (w), 1273 (w), 1255 (w), 1217 (w), 1176 (w), 1082 (m), 1032 (w), 976 (s), 928 (w), 912 (w), 883 (w), 843 (m), 804 (w), 770 (m), 754 (m), 725 (w), 700 (m), 683 (m), 660 (m), 644 (w), 631 (w), 621 (w), 604 (m), 588 (w), 572 (w), 559 (w).



Figure S9. ¹H NMR spectrum of 3 in CD₂Cl₂.



Figure S10. ¹³C NMR spectrum of **3** in CD_2Cl_2 .

3.5. Synthesis of $[BiSnCl_3(\mu-N^{tBu}Ar^*)_2]$ (4)

$$[Sn(\mu-N^{tBu}Ar^*)]_2 \xrightarrow{BiCl_3} [BiSnCl_3(\mu-N^{tBu}Ar^*)_2]$$

or
$$CH_2Cl_2$$

or
$$C_6H_5F$$

-Sn

 $[Sn(\mu-N'^{Bu}Ar^*)]_2$ (0.315 g, 0.21 mmol) and BiCl₃ (0.067 g, 0.21 mmol) were combined in a 25 mL round-bottomed flask and at room temperature CH₂Cl₂ (10 mL) is added to that mixture. The typical red colour of **1***t***Bu** disappeared and a black suspension formed immediately. Stirring was continued overnight and after removal of the volatiles in vacuo the crude mixture was extracted with fresh CH₂Cl₂ (10 mL) and filtered through a celite-padded frit. The clear orange filtrate was concentrated to incipient crystallization and standing at 5 °C overnight afforded minimal amounts (< 0.025g) of orange crystals of [BiSnCl₃(μ -N'^{Bu}Ar*)₂]·(CH₂Cl₂)₂, which were suitable for X-ray analysis. In order to exclude chloride migration in CH₂Cl₂ the synthesis was repeated in C₆H₅F, which afforded after work up and recrystallization from C₆H₃F some crystals [BiSnCl₃(μ -N'^{Bu}Ar*)₂]·(C₆H₅F)₂, which were suitable for X-ray analysis.

The isolated crystals of $[BiSnCl_3(\mu-N'^{Bu}Ar^*)_2] \cdot (CH_2Cl_2)_2$ were used for NMR experiments, which allowed to assign the relevant signals for the *p*-*t*Bu, the CHPh₂ and inner aryl protons in the ¹H NMR as well as in the ¹³C NMR spectrum (see Figure S11 and S12).

¹**H-NMR** (25 °C, CD₂Cl₂, 300.13 MHz): δ 1.00 (s, 9H, p-C(CH₃)₃), 6.75 (s, 4H, CH(C₆H₅)₂), 6.77 (s, 4H, Ar-CH). ; ¹³C{¹H} NMR (25 °C, CD₂Cl₂, 75.46 MHz): $\delta = 32.1$ (s, *p*-C(CH₃)₃), 34.2 (s, *p*-C(CH₃)₃), 51.3 (s, 2 CHPh₂). ¹¹⁹Sn{¹H} NMR (25 °C, CD₂Cl₂, 111.92 MHz): $\delta = 115.5$ (s).



Figure S11. ¹H NMR spectrum of 2 (blue) and 4 (red, with integrals and signals) in CD_2Cl_2 .



Figure S12. ¹³C NMR spectrum of 4 in CD₂Cl₂.



Figure S13. ¹¹⁹Sn NMR spectrum of 4 in CD_2Cl_2 .

4. Computational Details

To study the electronic situation in carbenoid species **4**, MO, NBO⁶ and ELF⁷ computations were carried out. Utilizing the experimental (Xray) structural data and for the model compound [BiSnCl₃(μ -NPh)₂], all calculations were carried out with the Gaussian 09 package of molecular orbital programs at the B3LYP level of theory.⁸ The wave functions for crystal structures were optimized with a 6-31G(d,p) (C, H, N, Cl), an aug-cc-pVDZ-PP basis set for Sn (pseudopotential: SN-ECP 4 28, MDF) and Bi (BI-ECP 5 60, MDF).^{9,10}

It should be emphasized that the computation was carried out for a single, isolated (gas-phase) molecule.

4.1. Electron Localization Function (ELF)



Figure S14. 3D depiction of the Electron Localization Function (ELF @ 0.7) of the model compound $[BiSnCl_3(\mu-NPh)_2]$.



Figure S15. 2D section of the Electron Localization Function in the N₂SnBi-plane of the model compound [BiSnCl₃(μ -NPh)₂].

4.2. Selected Molecular Orbitals (MOs)

Table S8. π -MOs calculated for the model compound [BiSnCl₃(μ -NPh)₂].

LUMO	
HOMO-13	

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