Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information for the Communication

Synthesis of a cyclopentadienyl(imino)stannylene and its direct conversion into halo(imino)stannylenes

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Contents

1.) Experimental Details

General considerations: All experiments and manipulations were conducted under dry anaerobic nitrogen using standard Schlenk techniques or in an MBraun inert atmosphere drybox containing an atmosphere of purified nitrogen. Solvents were dried by standard methods. NMR solvents: degassed by freeze-pump-thaw technique and stored over 3Å molecular sieves. The starting materials LiNIPr (NIPr = bis(2,6-di*iso*propylphenyl)imidazolin-2-iminato) and stannocene (Cp_2Sn (Cp = cyclopentadienyl)) were prepared according to literature procedures.[S1,S2] ^{1}H, ^{13}C and ^{119}Sn NMR spectra were recorded on Bruker Avance II 200 MHz and 400 MHz. H chemical shifts were referenced to the residual protons of C_6D_6 at 7.15 ppm or of THF-d_8 at 3.58 ppm, and ^{13}C chemical shifts were referenced to the carbon atoms of C_6D_6 at 128.00 ppm or THF-d_8 at 67.57 ppm. The $^{119}Sn\{^{1}H\}$ NMR spectra was referenced to $SnMe_4$ as an external standard. Mass spectra were recorded on a Finnigan Orbitrap MAT95S. Melting points were determined from vacuum sealed capillaries on an electronic “Melting point tester” device from BSGT company and are uncorrected. For this purpose samples were sealed off in capillaries under vacuum and heated slowly to observed decomposition or melting.

Experimental Procedure and Analytical Data for **1**

A mixture of LiNIPr (326 mg, 0.795 mmol) and $SnCp_2$ (198 mg, 0.795 mmol) was placed in a reaction tube with a magnetic stirring bar. Then dry oxygen-free THF (5 ml) was introduced into the reaction tube by canular at –78 C, and the reaction mixture was slowly warmed up to room temperature and stirred overnight. Then the solvent was removed under vacuum. The residue was recrystallized from THF and hexane (10:1) to afford **1** as pale-yellow crystals (103 mg, 22%).

^{1}H NMR (400.1 MHz, THF-d_8): δ = 1.21 (d, $^3J_{HH}$ = 8 Hz, 48H, CH(CH_3)$_2$), 2.98 (sept, $^3J_{HH}$ = 8 Hz, 8H, CH(CH$_3$)$_2$), 5.66 (s, 10H, Cp), 6.44 (s, 4H, NCH), 7.24-7.31 (br, 8H, m-Dip), 7.36-7.42 ppm (br, 4H, p-Dip). **^{13}C{^{1}H} NMR** (100.6 MHz, THF-d_8): δ = 23.9 (CH(*C*H$_3$)$_2$), 29.3 (*C*H(CH$_3$)$_2$), 106.9 (Cp), 114.4 (N*C*H), 115.0 (N*C*H), 124.5 (Ar-*C*), 125.0 (Ar-*C*), 129.8 (Ar-*C*), 130.4 (Ar-*C*), 132.7 (Ar-*C*), 134.1 (Ar-*C*), 148.3 (Ar-*C*), 149.2 (Ar-*C*), 155.1 ppm (N*C*N). **^{119}Sn{^{1}H} NMR** (149.2 MHz, THF-d_8): δ = −232.3 ppm. **APCI-HRMS** *m/z*: 588.2397 (*calc*. 588.2395 for [M/2 + H]$^+$). **M.p.** 251-254 ºC (dec.).

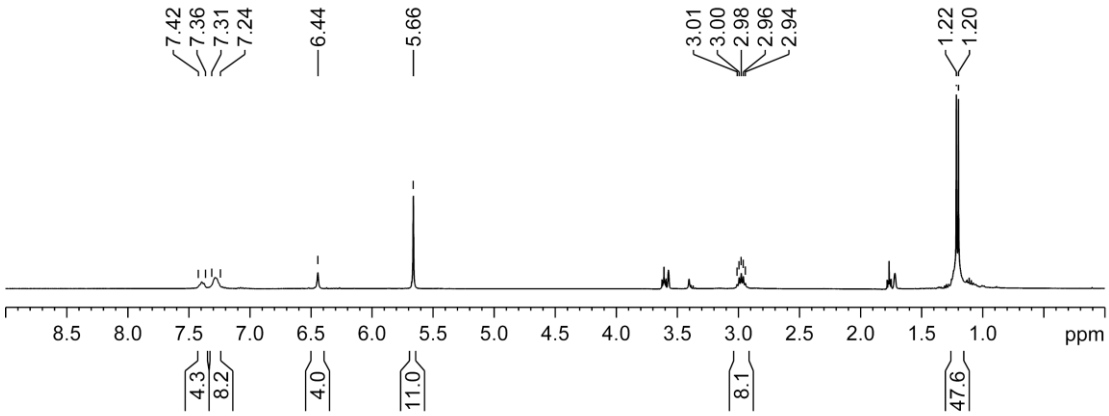

Figure S1. ^{1}H NMR spectrum (400.1 MHz, THF-d$_8$) of **1**.

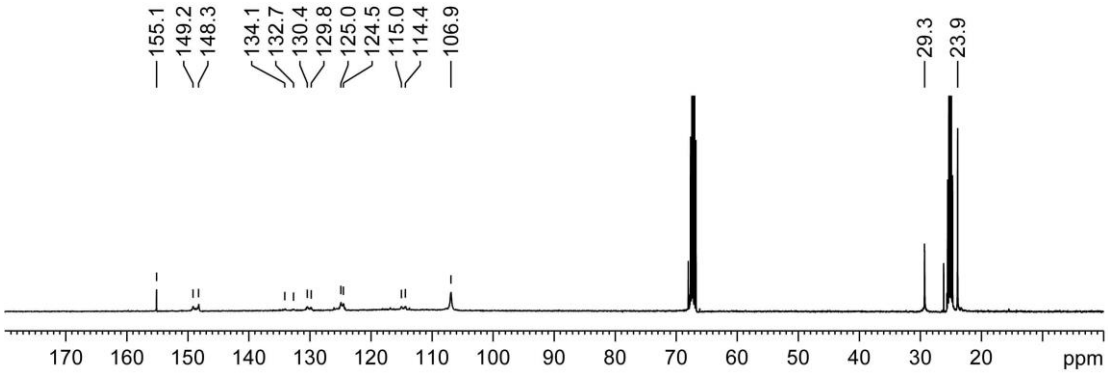

Figure S2. ^{13}C NMR spectrum (100.6 MHz, THF-d_8) of **1**.

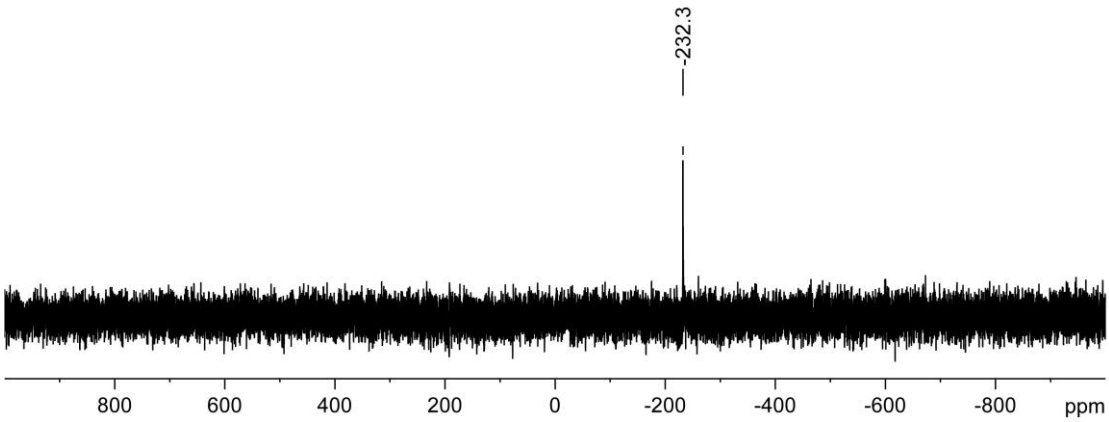

Figure S3. ^{119}Sn NMR spectrum (149.2 MHz, THF-d_8) of **1**.

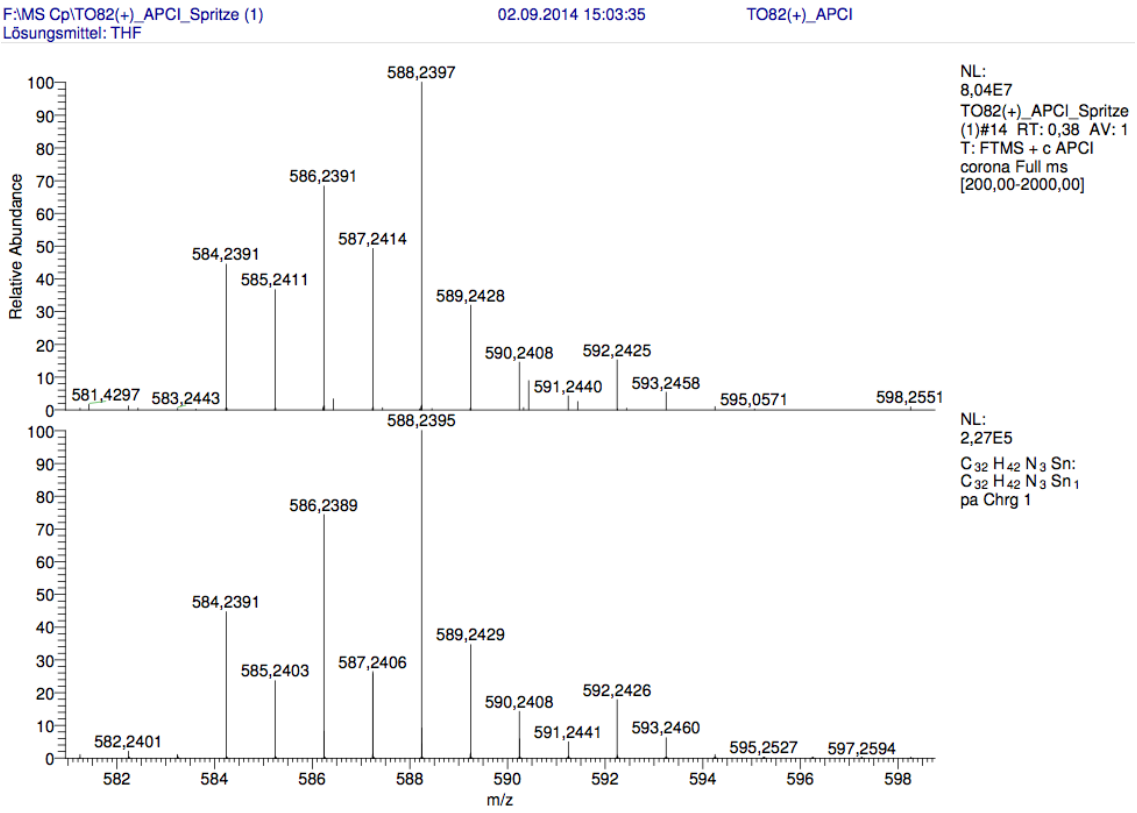

Figure S4. APCI-MS of $[M/2 + H]^+$ Signal of **1**. Top (expt.) Bottom (Theor.)

Experimental Procedure and Analytical Data for **2**

A THF solution (0.16 M) of CH_2Cl_2 (2.7 ml, 0.432 mmol) was added to a solution of **1** (103 mg, 0.0878 mmol) in THF (5 ml) via syringe and stirred for 1 h at ambient temperature. Then the solvent was removed under vacuum. The residue was recrystallized from CH_2Cl_2 at –30 ºC to afford **2** as pale yellow crystals (74 mg, 76%).

^{1}H NMR (200.1 MHz, THF-d_8): δ = 1.21 (d, $^3J_{HH}$ = 8.0 Hz, 48H, CH(CH_3)$_2$), 3.07 (sept, $^3J_{HH}$ = 8.0 Hz, 8H, CH(CH$_3$)$_2$), 6.39 (s, 4H, NCH), 7.22-7.35 (br, 12H, Ar-H). **^{13}C{^{1}H} NMR** (100.6 MHz, THF-d_8): δ = 24.1 (CH(*C*H$_3$)$_2$), 24.2 (CH(*C*H$_3$)$_2$)), 29.5 (*C*H(CH$_3$)$_2$), 114.5 (N*C*H), 124.6 (Ar-C), 129.8 (Ar-C), 146.2 (Ar-C), 149.2 (Ar-C), 155.0 (N*C*N). **^{119}Sn{^{1}H} NMR** (149.2 MHz, THF-d_8): δ = −125.2.

Experimental Procedure and Analytical Data for **3**

A THF solution (0.22 M) of 1,2-dibromoethane (2.0 ml, 0.440 mmol) was added to a solution of **1** (98 mg, 0.0836 mmol) in THF (5 ml) via syringe and stirred for 1 h at ambient temperature. Then the solvent was removed under vacuum. The residue was recrystallized from CH_2Cl_2 at –30 ºC to afford **3** as pale-yellow crystals (93 mg, 92%).

^{1}H NMR (200.1 MHz, THF-d_8): δ = 1.21 (dd, $^3J_{HH}$ = 8.0, $^4J_{HH}$ = 2.0 Hz, 48H, CH(CH_3)$_2$), 3.04 (sept, J_{HH} = 6.9 Hz, 8H, CH(CH$_3$)$_2$), 6.44 (s, 4H, NCH), 7.21-7.38 ppm (m, 12H, Ar-*H*). **^{13}C{^{1}H} NMR** (100.6 MHz, THF-d_8): δ = 24.1, 24.2 (CH(*C*H$_3$)$_2$), 29.5 (*C*H(CH$_3$)$_2$), 115.7 (N*C*H), 124.9, 130.5, 133.3, 148.7 (Ar-*C*), 153.7 ppm (N*C*N). **^{119}Sn{^{1}H} NMR** (149.2 MHz, THF-d_8): δ = –87.6 ppm. **APCI-HRMS** *m/z*: 1121.3028 (*calc*. 1121.3034 for $[M-Br]^+$).
M.p. 211-213 ºC (dec.).

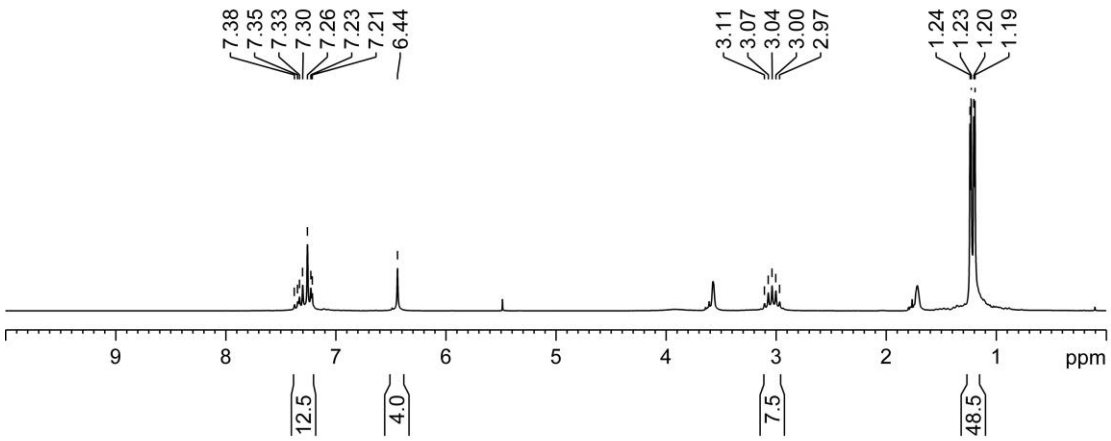

Figure S5. ^{1}H NMR spectrum (200.1 MHz, THF-d_8) of **3**.

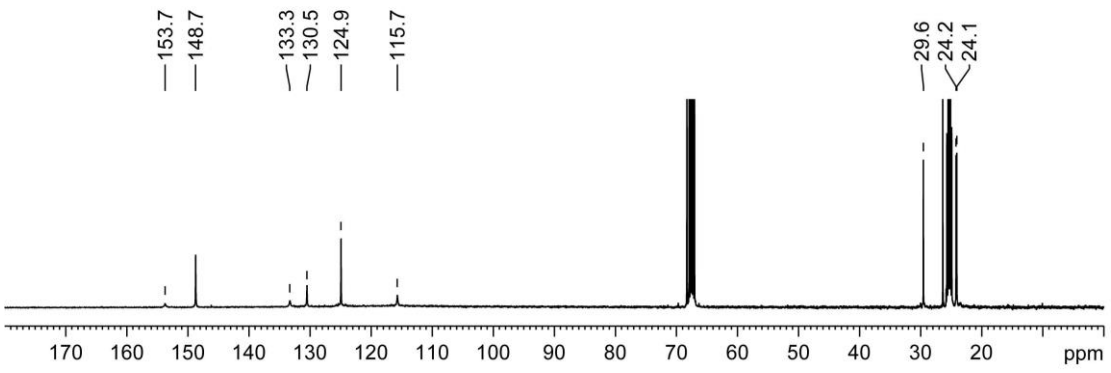

Figure S6. ^{13}C NMR spectrum (100.6 MHz, THF-d_8) of **3**.

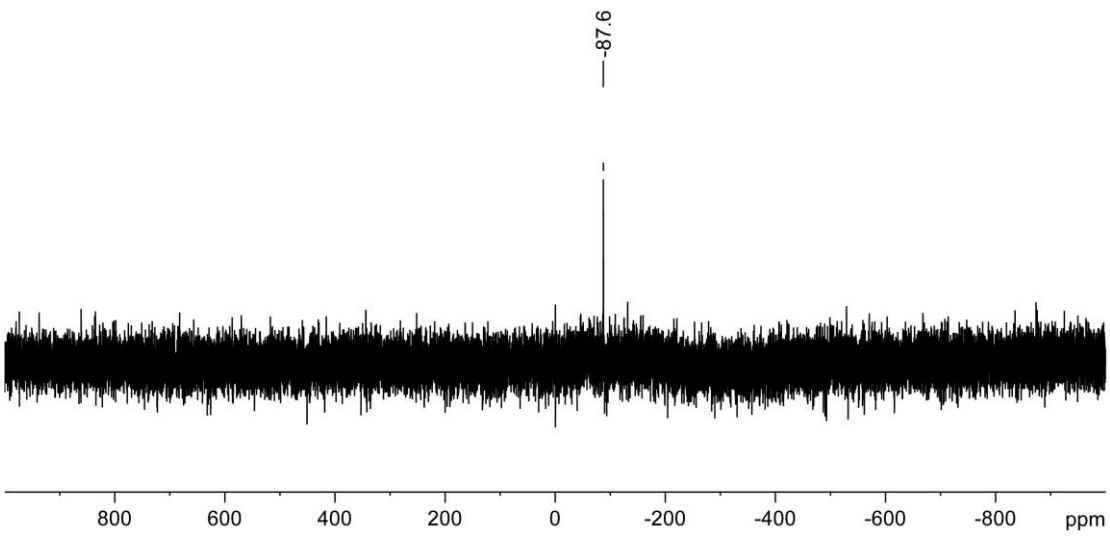

Figure S7. ^{119}Sn NMR spectrum (149.2 MHz, THF-d_8) of **3**.

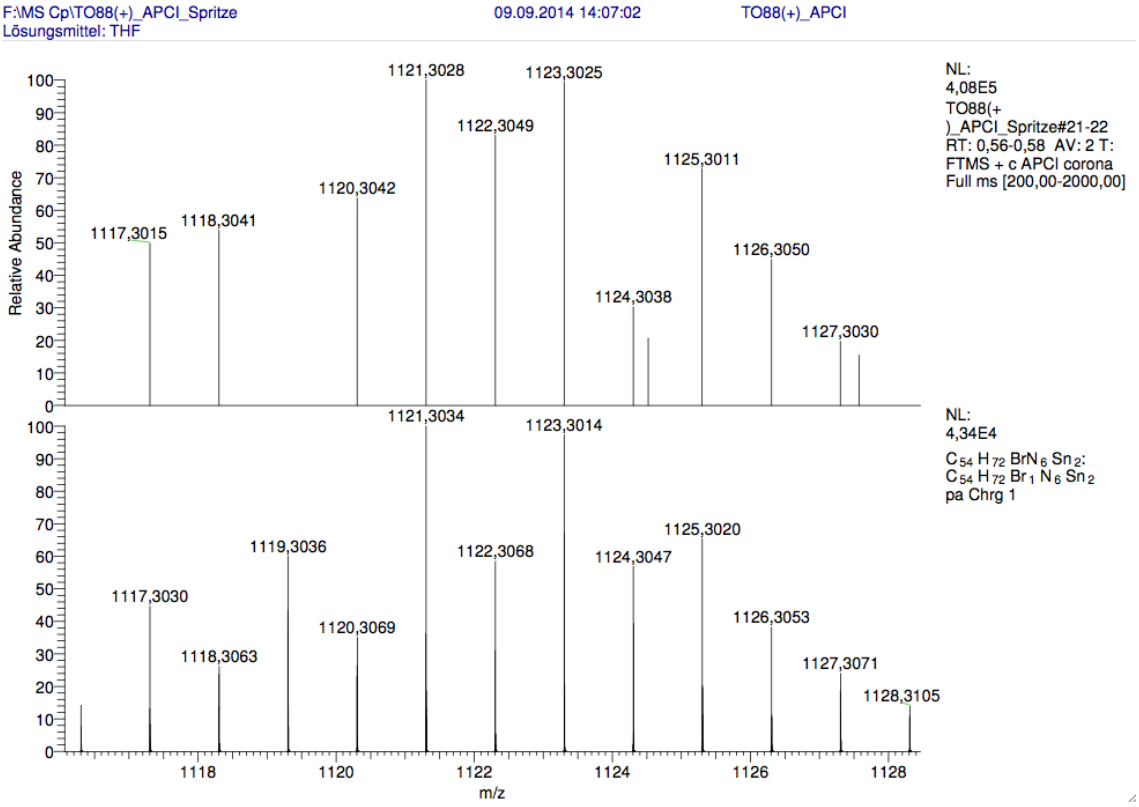

Figure S8. APCI-MS of $[M - Br]^+$ Signal of **3**. Top (expt.) Bottom (Theor.)

2.) Crystallographic Data for **1** and **3**

General Considerations: Data for the single crystal structure determinations of **1** and **3** were collected on an Agilent SuperNova diffractometer, equipped with a CCD area Atlas detector and a mirror monochromator utilizing CuK_α radiation (λ = 1.54184 Å). The crystal structures were solved by Direct Methods and refined on F^2 using full-matrix least squares with SHELXL-97[S3]. The positions of the H atoms at the carbon atoms were calculated by standard methods. CCDC deposition numbers: 1515971 for **1** and 1515070 for **3**.

Table S1. Crystal data and structure refinement for **1**.

Empirical formula	$C_{72}H_{98}N_6O_2Sn_2$	
Formula weight	1316.94	
Temperature	150(2) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 11.0955(3) Å	α = 90°.
	b = 23.0198(5) Å	β = 95.263(2)°.
	c = 25.7805(6) Å	γ = 90°.
Volume	6557.0(3) Å^3	
Z	4	
Density (calculated)	1.334 Mg/m^3	
Absorption coefficient	6.429 mm^{-1}	
F(000)	2752	
Crystal size	0.41 x 0.33 x 0.23 mm^3	
Theta range for data collection	3.94 to 67.50°.	
Index ranges	-13<=h<=12, -27<=k<=27, -22<=l<=30	
Reflections collected	26259	
Independent reflections	11821 [R(int) = 0.0503]	
Completeness to theta = 67.50°	99.8 %	
Absorption correction	Analytical	
Max. and min. transmission	0.3195 and 0.1780	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11821 / 0 / 755	
Goodness-of-fit on F2	1.158	
Final R indices [I>2sigma(I)]	R1 = 0.0915, wR2 = 0.2201	

R indices (all data)	R1 = 0.0994, wR2 = 0.2233
Largest diff. peak and hole	2.237 and -2.085 e.Å^{-3}

Table S2. Crystal data and structure refinement for **3**.

Empirical formula	$C_{54}H_{72}Br_2N_6Sn_2$	
Formula weight	1202.38	
Temperature	150.00(10) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 12.7203(2) Å	α = 90°.
	b = 13.7758(3) Å	β = 100.925(2)°.
	c = 15.8945(3) Å	γ = 90°.
Volume	2734.75(9) Å^3	
Z	2	
Density (calculated)	1.460 Mg/m^3	
Absorption coefficient	9.269 mm^{-1}	
F(000)	1216	
Crystal size	0.13 x 0.10 x 0.10 mm^3	
Theta range for data collection	4.09 to 67.50°.	
Index ranges	-14<=h<=15, -16<=k<=15, -19<=l<=13	
Reflections collected	10352	
Independent reflections	4927 [R(int) = 0.0373]	
Completeness to theta = 67.50°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.38634	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4927 / 8 / 316	
Goodness-of-fit on F2	1.020	
Final R indices [I>2sigma(I)]	R1 = 0.0367, wR2 = 0.0904	
R indices (all data)	R1 = 0.0452, wR2 = 0.0978	
Largest diff. peak and hole	0.749 and -0.741 e.Å^{-3}	

3.) Details to the DFT Calculations of **1** and **2**

General Considerations: DFT calculations of model compounds to *cis*/*trans*-**1** and *cis*/*trans*-**2** were carried out on the B3LYP/def2-SVP level of theory implementing the GAUSSIAN03 program.[S4] Cartesian coordinates of the optimized structures are shown in Table S3, S4, S5 and S6, respectively. The structures obtained by the reported X-ray analysis for **1** and **2**[S5] were used as input for these calculations.

3.1) DFT Calculations: Supplementary Data to *cis*-**1**

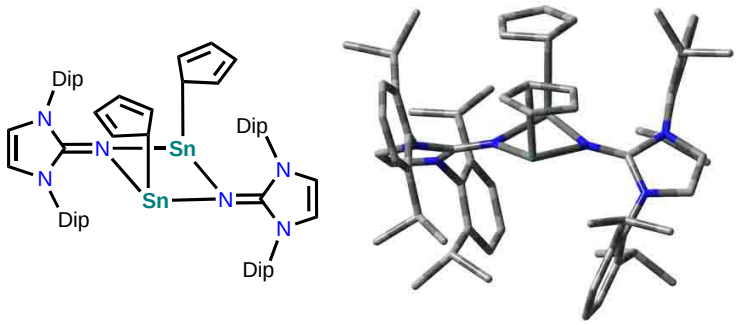

Figure S9. Lewis structure (left) and optimized structure (right) for *cis*-**1**.

Table S3. Cartesian coordinates (x, y, z) for the optimized structure of $[CpSnNIPr]_2$ **1** (Energy = –3243.44661773 A.U.).

Sn	-0.474016	1.689518	-0.393660
Sn	0.474025	-1.689250	-0.392535
N	1.401845	0.368305	-0.115670
N	2.949745	1.904776	0.973399
N	3.849026	0.302838	-0.274923
N	-1.401836	-0.368136	-0.115684
N	-2.949360	-1.904793	0.973739
N	-3.849048	-0.302818	-0.274254
C	2.593410	0.793896	0.158261
C	4.338726	2.059144	0.999952
C	4.883065	1.087509	0.245078
C	2.162955	2.497018	2.028881
C	1.653617	3.811742	1.883644

C	0.954425	4.365205	2.966866
C	0.782624	3.662110	4.157467
C	1.338428	2.393530	4.300583
C	2.052361	1.793097	3.253759
C	1.915706	4.657790	0.639828
C	0.754774	5.596789	0.281114
C	3.213268	5.478218	0.796102
C	2.759948	0.463730	3.504703
C	1.803583	-0.657268	3.934428
C	3.900738	0.641443	4.525240
C	4.195253	-0.820604	-1.111730
C	4.523833	-0.581474	-2.468780
C	5.059734	-1.641817	-3.214901
C	5.264233	-2.895355	-2.644659
C	4.927962	-3.115949	-1.310828
C	4.399758	-2.090385	-0.513853
C	4.367990	0.787551	-3.125009
C	3.649702	0.710835	-4.483496
C	5.728169	1.496146	-3.277078
C	4.145554	-2.345961	0.970834
C	5.428898	-2.118795	1.794887
C	3.570206	-3.741075	1.262492
C	-2.593286	-0.793830	0.158597
C	-4.338339	-2.059307	1.000530
C	-4.882904	-1.087659	0.245858
C	-2.162418	-2.496834	2.029243
C	-2.051767	-1.792773	3.254034
C	-1.337631	-2.393019	4.300826
C	-0.781725	-3.661563	4.157779
C	-0.953629	-4.364812	2.967284
C	-1.652988	-3.811530	1.884083
C	-2.759427	-0.463433	3.504929
C	-3.899654	-0.640968	4.526130

C	-1.802968	0.657828	3.933756
C	-1.915202	-4.657684	0.640368
C	-3.212843	-5.477945	0.796775
C	-0.754373	-5.596810	0.281681
C	-4.195559	0.820500	-1.111086
C	-4.399985	2.090337	-0.513316
C	-4.928533	3.115748	-1.310256
C	-5.265274	2.894935	-2.643941
C	-5.060852	1.641338	-3.214078
C	-4.524556	0.581162	-2.467996
C	-4.145350	2.346102	0.971268
C	-5.428471	2.119122	1.795735
C	-3.569861	3.741237	1.262592
C	-4.368747	-0.787917	-3.124112
C	-3.650621	-0.711288	-4.482698
C	-5.728904	-1.496600	-3.275927
H	4.809886	2.842833	1.583535
H	5.920575	0.872351	0.011640
H	0.542582	5.371470	2.879277
H	0.231085	4.115593	4.985289
H	1.234083	1.864721	5.250838
H	2.056175	3.966494	-0.205011
H	-0.198325	5.055057	0.201489
H	0.945495	6.070291	-0.693558
H	0.637777	6.407928	1.018474
H	4.094002	4.842813	0.965935
H	3.135751	6.178493	1.644385
H	3.402438	6.070987	-0.113650
H	3.223719	0.144942	2.563257
H	1.011332	-0.822237	3.190667
H	1.318522	-0.436455	4.898788
H	2.352760	-1.605033	4.055067
H	4.615609	1.413463	4.200671

H	4.456086	-0.302257	4.650852
H	3.514963	0.936831	5.514675
H	5.322167	-1.480839	-4.262386
H	5.682411	-3.707697	-3.244482
H	5.091033	-4.103692	-0.876856
H	3.749975	1.404721	-2.456800
H	2.700537	0.159906	-4.413558
H	4.270708	0.214645	-5.246626
H	3.423824	1.723534	-4.851697
H	6.233873	1.629282	-2.308827
H	5.593767	2.494057	-3.725073
H	6.403467	0.921704	-3.932495
H	3.399852	-1.611195	1.308681
H	5.236632	-2.291067	2.866638
H	5.814669	-1.094948	1.683987
H	6.222645	-2.815777	1.479412
H	2.688642	-3.955793	0.640838
H	3.263639	-3.806351	2.318599
H	4.312623	-4.537394	1.092216
H	-4.809287	-2.843130	1.584101
H	-5.920477	-0.872609	0.012596
H	-1.233211	-1.864100	5.251013
H	-0.230029	-4.114895	4.985577
H	-0.541719	-5.371052	2.879769
H	-3.223760	-0.145019	2.563638
H	-4.614597	-1.413169	4.202156
H	-4.455045	0.302702	4.651755
H	-3.513323	-0.936018	5.515446
H	-1.011118	0.822590	3.189512
H	-1.317365	0.437411	4.897934
H	-2.352180	1.605581	4.054344
H	-2.055597	-3.966448	-0.204535
H	-4.093485	-4.842451	0.966739

H	-3.135299	-6.178251	1.645033
H	-3.402192	-6.070664	-0.112971
H	0.198702	-5.055089	0.201666
H	-0.945329	-6.070587	-0.692814
H	-0.637194	-6.407750	1.019225
H	-5.091517	4.103544	-0.876372
H	-5.683743	3.707157	-3.243723
H	-5.323664	1.480159	-4.261440
H	-3.399602	1.611344	1.309033
H	-5.814218	1.095219	1.685277
H	-6.222333	2.815969	1.480264
H	-5.235910	2.291741	2.867381
H	-2.688559	3.955909	0.640555
H	-3.262834	3.806581	2.318558
H	-4.312363	4.537538	1.092580
H	-3.750617	-1.405001	-2.455934
H	-2.701423	-0.160403	-4.412890
H	-4.271713	-0.215092	-5.245761
H	-3.424819	-1.724011	-4.850883
H	-6.234437	-1.629710	-2.307579
H	-5.594508	-2.494532	-3.723881
H	-6.404359	-0.922259	-3.931268
C	-0.566117	1.760746	-2.873719
C	0.748548	2.360863	-2.825091
C	0.587751	3.750132	-2.800174
C	-0.803454	4.044385	-2.871831
C	-1.510345	2.843116	-2.940747
H	-0.779467	0.731186	-3.160810
H	1.689285	1.816946	-2.830346
H	1.393329	4.483540	-2.738527
H	-1.242785	5.043420	-2.860916
H	-2.588208	2.733483	-3.028669
C	0.564419	-1.761234	-2.872191

C	-0.749799	-2.362471	-2.824102
C	-0.587935	-3.751543	-2.800049
C	0.803553	-4.044716	-2.871942
C	1.509499	-2.842930	-2.940123
H	0.776930	-0.731553	-3.159509
H	-1.690966	-1.819268	-2.828616
H	-1.392926	-4.485636	-2.738804
H	1.243610	-5.043442	-2.861683
H	2.587264	-2.732428	-3.028163

3.2) DFT Calculations: Supplementary Data to *trans*-**1**

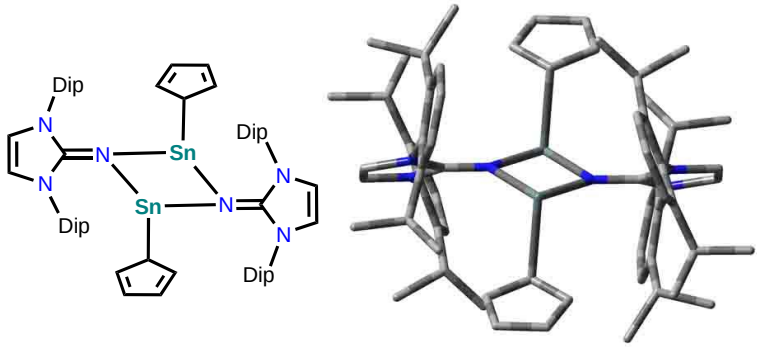

Figure S10. Lewis structure (left) and optimized structure (right) for *trans*-**1**.

Table S4. Cartesian coordinates (x, y, z) for the optimized structure of *trans*-[CpSnNIPr]$_2$ **1** (Energy = –3243.444468759 A. U.).

Sn	0.229779	-1.673865	-0.508575
N	-1.428822	-0.123567	-0.164036
N	-3.574491	0.668809	-1.034996
N	-3.454988	-1.455679	-0.390725
C	-2.679368	-0.274250	-0.478146
C	-4.721180	-1.235383	-0.940349
C	-4.792448	0.051346	-1.330812
C	-3.178568	-2.649036	0.380913
C	-3.309158	-2.597665	1.795652

C	-3.068273	-3.770858	2.523901
C	-2.760591	-4.970300	1.886424
C	-2.705295	-5.018773	0.498960
C	-2.914018	-3.872738	-0.285136
C	-3.797728	-1.351888	2.532674
C	-5.339458	-1.280007	2.513578
C	-3.301201	-1.251486	3.982585
C	-2.921322	-4.023297	-1.805243
C	-4.293790	-4.526945	-2.300056
C	-1.820562	-4.963053	-2.322060
C	-3.399999	2.089324	-1.235026
C	-4.045038	2.992843	-0.349963
C	-3.913975	4.367252	-0.602727
C	-3.185098	4.838605	-1.689585
C	-2.588392	3.937429	-2.568161
C	-2.694262	2.553818	-2.373587
C	-4.918126	2.545760	0.822552
C	-4.706462	3.396563	2.087579
C	-6.414460	2.562345	0.446074
C	-2.127928	1.589767	-3.408504
C	-3.215296	1.172851	-4.419621
C	-0.900479	2.128892	-4.156070
Sn	-0.230223	1.673108	0.507962
N	1.428062	0.122775	0.164768
N	3.574878	-0.667974	1.034727
N	3.453114	1.456419	0.390501
C	2.678688	0.274297	0.478173
C	4.719784	1.237284	0.939569
C	4.792317	-0.049330	1.330182
C	3.176524	2.649106	-0.382175
C	3.309381	2.597188	-1.796672
C	3.070477	3.770301	-2.525739
C	2.762243	4.970119	-1.889225

C	2.704170	5.018983	-0.501886
C	2.910839	3.873072	0.282906
C	3.799171	1.351280	-2.532639
C	5.340893	1.279669	-2.510903
C	3.304863	1.250558	-3.983370
C	2.914633	4.024223	1.802916
C	4.285107	4.530629	2.300366
C	1.810813	4.962160	2.316530
C	3.401610	-2.088517	1.235500
C	4.047913	-2.991841	0.351162
C	3.918253	-4.366265	0.604589
C	3.189620	-4.837852	1.691498
C	2.591872	-3.936830	2.569530
C	2.696379	-2.553203	2.374320
C	4.920507	-2.544669	-0.821685
C	4.707478	-3.394980	-2.086847
C	6.417097	-2.562198	-0.446298
C	2.129999	-1.589405	3.409440
C	3.217526	-1.173037	4.420629
C	0.902587	-2.128716	4.156950
H	-5.460927	-2.026192	-0.992862
H	-5.596465	0.595734	-1.813455
H	-3.145302	-3.751926	3.611098
H	-2.581974	-5.873905	2.475123
H	-2.493090	-5.968937	0.007652
H	-3.411204	-0.474412	1.995219
H	-5.746050	-1.272733	1.492602
H	-5.685888	-0.364341	3.020322
H	-5.773002	-2.142689	3.045913
H	-3.764611	-2.016016	4.627064
H	-3.565607	-0.269999	4.402116
H	-2.209336	-1.352589	4.054361
H	-2.742243	-3.030831	-2.245011

H	-4.508081	-5.531100	-1.898409
H	-4.304087	-4.594853	-3.400024
H	-5.121234	-3.868504	-1.999264
H	-0.821868	-4.651764	-1.984660
H	-1.812420	-4.958598	-3.421303
H	-1.989575	-6.004602	-2.004339
H	-4.393648	5.081895	0.067989
H	-3.090267	5.914142	-1.860155
H	-2.038089	4.317298	-3.429503
H	-4.646640	1.507324	1.065449
H	-5.186718	2.912383	2.952820
H	-5.162778	4.394514	1.986412
H	-3.641676	3.530991	2.318496
H	-6.735957	3.582433	0.178994
H	-7.027765	2.229570	1.299345
H	-6.644228	1.906278	-0.404838
H	-1.809302	0.689405	-2.867530
H	-4.082133	0.706820	-3.928288
H	-2.807830	0.447224	-5.141871
H	-3.577009	2.047698	-4.985045
H	-1.164265	2.948128	-4.845012
H	-0.454507	1.324987	-4.760373
H	-0.128832	2.502374	-3.465383
H	5.458672	2.028931	0.991847
H	5.596819	-0.592884	1.812953
H	3.149682	3.750960	-3.612783
H	2.585307	5.873673	-2.478510
H	2.491342	5.969348	-0.011181
H	3.412143	0.473795	-1.995600
H	5.745225	1.264297	-1.489099
H	5.688707	0.368199	-3.024239
H	5.775325	2.146727	-3.035330
H	3.775122	2.010105	-4.628810

H	3.562862	0.266098	-4.399877
H	2.213912	1.359510	-4.057663
H	2.736571	3.031659	2.242860
H	4.498752	5.534786	1.898378
H	4.292850	4.599462	3.400297
H	5.114245	3.873189	2.001930
H	0.813503	4.648472	1.977236
H	1.800188	4.958697	3.415741
H	1.978298	6.003728	1.998037
H	4.398906	-5.080703	-0.065659
H	3.095939	-5.913397	1.862647
H	2.041951	-4.316799	3.431075
H	4.649445	-1.506012	-1.064061
H	5.184519	-2.909240	-2.952987
H	5.166057	-4.392085	-1.987476
H	3.642391	-3.531392	-2.315122
H	6.738025	-3.582344	-0.178776
H	7.030049	-2.230473	-1.300238
H	6.648001	-1.905725	0.403999
H	1.811512	-0.688744	2.868904
H	4.084429	-0.707059	3.929336
H	2.810271	-0.447524	5.143112
H	3.579096	-2.048131	4.985761
H	1.166799	-2.946632	4.847301
H	0.455396	-1.324384	4.759779
H	0.131789	-2.504052	3.466328
C	0.520387	-0.955055	-2.831519
H	0.511504	0.110592	-2.597661
C	1.735183	-1.702476	-3.082855
C	-0.525440	-1.632236	-3.570172
H	2.723285	-1.434841	-2.715816
C	1.419149	-2.805762	-3.866197
H	-1.563963	-1.310356	-3.645947

C	0.025248	-2.754269	-4.175996
H	2.112773	-3.581433	-4.194988
H	-0.513611	-3.482995	-4.782957
C	-0.520600	0.955224	2.830605
H	-0.512076	-0.110363	2.596300
C	0.525305	1.630618	3.571102
C	-1.735589	1.701602	3.084728
H	1.564061	1.309079	3.645241
C	-0.025531	2.750516	4.180423
H	-2.723675	1.434797	2.717012
C	-1.419664	2.802651	3.870979
H	0.513283	3.477669	4.789348
H	-2.113411	3.577229	4.202114

3.3) DFT Calculations: Supplementary Data to *trans*-**2**

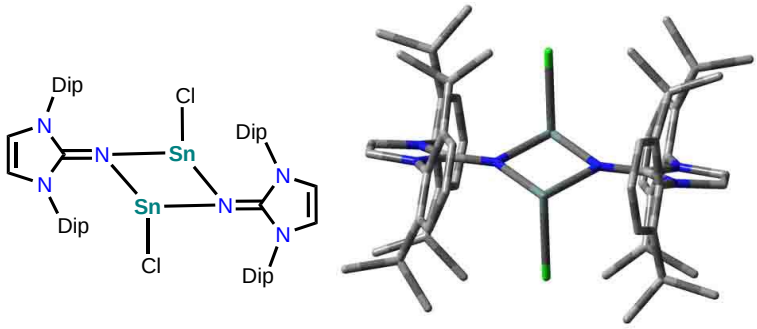

Figure S11. Lewis structure (left) and optimized structure (right) for *trans*-**2**.

Table S5. Cartesian coordinates (x, y, z) for the optimized structure of *trans*-[ClSnNIPr]$_2$ **2** (Energy = –3777.00427646).

Sn	0.008099	1.685120	-0.387004
Cl	-0.005223	1.139876	-2.890181
N	1.432625	-0.020192	-0.060902
N	3.550728	-1.152329	-0.432763
N	3.613838	1.042569	-0.213642

C	2.719944	-0.042132	-0.218573
C	4.923945	0.591586	-0.395124
C	4.885196	-0.749190	-0.532568
C	3.302280	2.393512	0.160941
C	3.218435	2.707381	1.539446
C	2.903565	4.028198	1.888804
C	2.712478	5.004668	0.912801
C	2.852807	4.685540	-0.436616
C	3.153319	3.378592	-0.847506
C	3.560281	1.692036	2.628302
C	4.973859	1.972010	3.177836
C	2.528935	1.627377	3.763214
C	3.377157	3.067715	-2.327109
C	4.843080	3.343556	-2.721475
C	2.432501	3.826039	-3.271502
C	3.144372	-2.523833	-0.555202
C	3.322074	-3.391482	0.549413
C	2.954573	-4.736205	0.386269
C	2.438848	-5.200080	-0.820725
C	2.288496	-4.330947	-1.901699
C	2.640826	-2.978881	-1.799862
C	3.948266	-2.932712	1.865668
C	3.141433	-3.355289	3.104621
C	5.404922	-3.426988	1.970733
C	2.524147	-2.047513	-3.005016
C	3.856186	-1.980874	-3.778950
C	1.376539	-2.413858	-3.955709
Sn	-0.008082	-1.685170	0.386826
Cl	0.005105	-1.140468	2.890103
N	-1.432578	0.020223	0.060988
N	-3.550670	1.152406	0.432719
N	-3.613870	-1.042463	0.213308
C	-2.719913	0.042184	0.218527

C	-4.923994	-0.591401	0.394461
C	-4.885193	0.749349	0.532112
C	-3.302416	-2.393444	-0.161254
C	-3.218928	-2.707412	-1.539765
C	-2.904338	-4.028295	-1.889121
C	-2.713073	-5.004716	-0.913109
C	-2.852888	-4.685457	0.436328
C	-3.153202	-3.378463	0.847217
C	-3.560740	-1.692055	-2.628621
C	-4.974369	-1.971857	-3.178110
C	-2.529431	-1.627548	-3.763587
C	-3.376180	-3.067456	2.326923
C	-4.842241	-3.341649	2.721905
C	-2.432058	-3.827072	3.270823
C	-3.144263	2.523863	0.555514
C	-3.321880	3.391819	-0.548876
C	-2.954356	4.736489	-0.385340
C	-2.438658	5.200017	0.821798
C	-2.288369	4.330579	1.902537
C	-2.640764	2.978559	1.800323
C	-3.948020	2.933431	-1.865298
C	-3.140901	3.356000	-3.104069
C	-5.404534	3.428113	-1.970452
C	-2.524225	2.046847	3.005229
C	-3.856517	1.979485	3.778665
C	-1.377125	2.413267	3.956506
H	5.763209	1.278759	-0.399559
H	5.680682	-1.466939	-0.703667
H	2.823000	4.299802	2.943545
H	2.466588	6.028443	1.206939
H	2.722931	5.467152	-1.186822
H	3.582926	0.695275	2.166599
H	5.732134	1.956783	2.379236

H	5.254335	1.212581	3.925822
H	5.022996	2.959462	3.665860
H	2.429327	2.589592	4.291693
H	2.838791	0.876389	4.507172
H	1.542403	1.318675	3.391405
H	3.184450	1.993811	-2.470902
H	5.088086	4.411428	-2.596389
H	5.012123	3.080321	-3.778237
H	5.555661	2.765423	-2.115450
H	1.378210	3.648044	-3.021141
H	2.583244	3.473337	-4.303891
H	2.627006	4.911204	-3.267819
H	3.076115	-5.430312	1.220425
H	2.154288	-6.250571	-0.923673
H	1.889915	-4.713501	-2.842337
H	3.973540	-1.832973	1.856334
H	3.631246	-2.973504	4.015233
H	3.083406	-4.451504	3.204632
H	2.119887	-2.948514	3.084277
H	5.448412	-4.528282	2.001135
H	5.876112	-3.047089	2.891812
H	6.016452	-3.095263	1.117394
H	2.300984	-1.038350	-2.628976
H	4.686544	-1.634362	-3.146003
H	3.769943	-1.284611	-4.628896
H	4.126953	-2.972184	-4.179415
H	1.584337	-3.334986	-4.525568
H	1.225171	-1.601037	-4.681777
H	0.429352	-2.550961	-3.414455
H	-5.763310	-1.278511	0.398495
H	-5.680683	1.467131	0.703053
H	-2.824095	-4.299981	-2.943863
H	-2.467384	-6.028540	-1.207246

H	-2.722751	-5.466997	1.186559
H	-3.583216	-0.695278	-2.166941
H	-5.732486	-1.957625	-2.379345
H	-5.255199	-1.211768	-3.925289
H	-5.023348	-2.958840	-3.667105
H	-2.429037	-2.590137	-4.291228
H	-2.839885	-0.877464	-4.508211
H	-1.543147	-1.317749	-3.392022
H	-3.182124	-1.993804	2.470784
H	-5.088907	-4.408989	2.595543
H	-5.010141	-3.079608	3.779147
H	-5.554388	-2.761595	2.117224
H	-1.377668	-3.651623	3.019095
H	-2.580796	-3.473203	4.303096
H	-2.628950	-4.911818	3.268201
H	-3.075847	5.430835	-1.219304
H	-2.154077	6.250472	0.925045
H	-1.889812	4.712864	2.843293
H	-3.973570	1.833698	-1.856146
H	-3.631406	2.975645	-4.014907
H	-3.081421	4.452217	-3.203157
H	-2.119879	2.947874	-3.084262
H	-5.447706	4.529413	-2.001118
H	-5.875855	3.048133	-2.891430
H	-6.016144	3.096783	-1.117016
H	-2.300560	1.037876	2.628957
H	-4.686692	1.633634	3.145123
H	-3.770573	1.282379	4.627949
H	-4.127366	2.970414	4.180018
H	-1.585544	3.334040	4.526711
H	-1.225681	1.600182	4.682265
H	-0.429789	2.551044	3.415681

3.4) DFT Calculations: Supplementary Data to *cis*-**2**

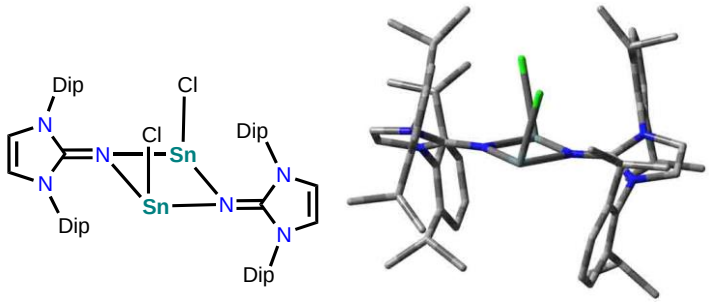

Figure S12. Lewis structure (left) and optimized structure (right) for *cis*-**2**.

Table S6. Cartesian coordinates (x, y, z) for the optimized structure of *cis*- $[ClSnNIPr]_2$ **2** (Energy = –3776.99444057 A.U.).

Sn	0.061256	1.736071	0.128819
Sn	-0.061538	-1.736515	0.129242
N	1.416952	-0.046023	0.123906
N	3.604398	0.928535	0.556948
N	3.561047	-1.032188	-0.455919
N	-1.417212	0.045721	0.123204
N	-3.605336	-0.928097	0.555080
N	-3.560499	1.032415	-0.458106
C	2.716168	-0.048981	0.073220
C	4.925802	0.525100	0.346110
C	4.897692	-0.671700	-0.274525
C	3.269164	2.053703	1.385505
C	3.267336	3.359298	0.831067
C	2.942122	4.424231	1.684386
C	2.639306	4.212124	3.028240
C	2.690732	2.926030	3.562008
C	3.025704	1.824958	2.761650
C	3.670394	3.634272	-0.617180
C	2.862981	4.759131	-1.283201
C	5.177114	3.954628	-0.709180

C	3.188355	0.448833	3.402250
C	1.913585	-0.029834	4.110848
C	4.399327	0.430544	4.354344
C	3.182720	-2.236758	-1.147269
C	2.939399	-2.176436	-2.540865
C	2.647987	-3.379250	-3.197982
C	2.610843	-4.589753	-2.509616
C	2.866646	-4.628516	-1.140628
C	3.160963	-3.457206	-0.427807
C	3.035353	-0.867939	-3.322610
C	2.038096	-0.771901	-4.486002
C	4.473660	-0.641190	-3.831167
C	3.512847	-3.537407	1.057354
C	4.964212	-4.018364	1.254943
C	2.544884	-4.417840	1.864767
C	-2.716396	0.048970	0.071777
C	-4.926439	-0.524284	0.343023
C	-4.897423	0.672416	-0.277774
C	-3.271108	-2.053367	1.383878
C	-3.028971	-1.824771	2.760287
C	-2.695054	-2.925977	3.560897
C	-2.643322	-4.212034	3.027069
C	-2.944778	-4.423975	1.682883
C	-3.268962	-3.358916	0.829330
C	-3.192152	-0.448681	3.400838
C	-4.404898	-0.430135	4.350684
C	-1.918546	0.029301	4.111976
C	-3.670582	-3.633672	-0.619362
C	-5.177231	-3.953936	-0.712923
C	-2.862596	-4.758493	-1.284740
C	-3.181120	2.236816	-1.149179
C	-3.159498	3.457263	-0.429715
C	-2.863764	4.628403	-1.142249

C	-2.606382	4.589452	-2.510930
C	-2.643282	3.378926	-3.199285
C	-2.936132	2.176310	-2.542481
C	-3.512563	3.537611	1.055170
C	-4.963233	4.021007	1.251799
C	-2.543718	4.416148	1.863625
C	-3.031714	0.867821	-3.324250
C	-2.033175	0.771409	-4.486518
C	-4.469579	0.641682	-3.834297
H	5.762005	1.132822	0.674173
H	5.704589	-1.307380	-0.623416
H	2.922284	5.440190	1.287023
H	2.377660	5.058969	3.668156
H	2.484440	2.776179	4.624515
H	3.478283	2.716816	-1.192715
H	1.782289	4.571316	-1.232985
H	3.129083	4.818586	-2.350025
H	3.080241	5.744442	-0.838482
H	5.805571	3.147397	-0.305956
H	5.417335	4.874839	-0.150797
H	5.470751	4.111709	-1.759692
H	3.399528	-0.272564	2.601149
H	1.068784	-0.068490	3.409368
H	1.631731	0.630340	4.947280
H	2.057996	-1.041958	4.522411
H	5.324240	0.727746	3.835627
H	4.551420	-0.580486	4.766367
H	4.255897	1.119287	5.202896
H	2.436495	-3.366102	-4.267737
H	2.376137	-5.513085	-3.045639
H	2.840707	-5.586289	-0.616738
H	2.783598	-0.047657	-2.634992
H	1.017463	-1.000387	-4.150196

H	2.300104	-1.452013	-5.314312
H	2.044316	0.252932	-4.887682
H	5.209235	-0.621281	-3.013051
H	4.542191	0.320359	-4.365593
H	4.771626	-1.438591	-4.532612
H	3.447176	-2.518202	1.468159
H	5.225645	-4.034682	2.325939
H	5.688046	-3.366814	0.742705
H	5.097750	-5.039077	0.860371
H	1.500256	-4.101239	1.726262
H	2.782250	-4.354376	2.939255
H	2.619289	-5.479691	1.579743
H	-5.763108	-1.131673	0.670516
H	-5.703806	1.308333	-0.627414
H	-2.489824	-2.776271	4.623630
H	-2.382492	-5.058974	3.667192
H	-2.924717	-5.439904	1.285461
H	-3.401517	0.272985	2.599507
H	-5.328976	-0.726786	3.830167
H	-4.557325	0.580832	4.762740
H	-4.263307	-1.119223	5.199266
H	-1.072317	0.067614	3.412201
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H	-2.063293	1.041461	4.523330
H	-3.477840	-2.716143	-1.194575
H	-5.806077	-3.146735	-0.310254
H	-5.418032	-4.874203	-0.154881
H	-5.469815	-4.110894	-1.763748
H	-1.781930	-4.570829	-1.233364
H	-3.127607	-4.817720	-2.351849
H	-3.080471	-5.743859	-0.840445
H	-2.837898	5.586182	-0.618373
H	-2.370561	5.512636	-3.046719

H	-2.430415	3.365599	-4.268771
H	-3.448926	2.518168	1.465722
H	-5.687827	3.370984	0.738704
H	-5.094638	5.042143	0.857594
H	-5.225473	4.037301	2.322593
H	-1.499542	4.097706	1.725921
H	-2.782090	4.352842	2.937899
H	-2.616038	5.478194	1.578805
H	-2.780996	0.047461	-2.636357
H	-1.012892	0.999737	-4.149539
H	-2.294062	1.451442	-5.315243
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H	-5.206010	0.622116	-3.016933
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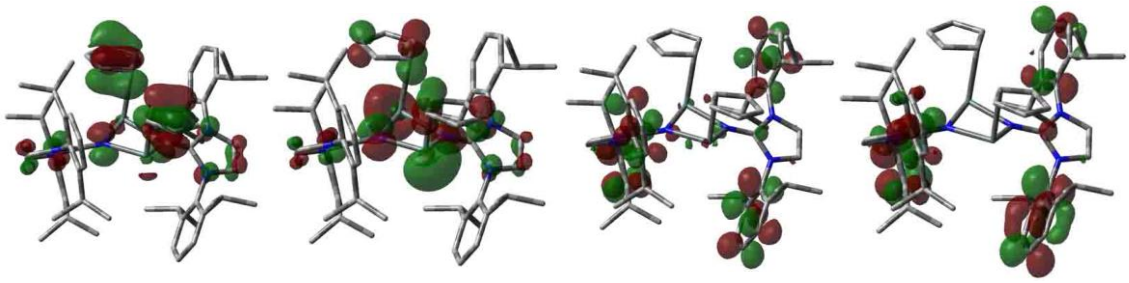

Figure S13. Kohn-Sham depictions of molecular orbitals of **1**.

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