An N-Heterocyclic Carbene Adduct of Diatomic Tin, :Sn=Sn:

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SUPPLEMENTARY INFORMATION

(13 pages)

Contents

1. Syntheses

General considerations. All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of high purity dinitrogen. Toluene and THF were distilled over molten potassium metal, while diethyl ether was distilled over Na/K (50:50) alloy. Melting points were determined in sealed glass capillaries under dinitrogen and are uncorrected. IR spectra were recorded using a Perkin Elmer RXI FT-IR spectrometer as Nujol mulls between NaCl plates. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on either Bruker DXP300 or AvanceIII 400 spectrometers and were referenced to the residual solvent resonances. A microanalysis for **3** could not be obtained due to its thermal instability at room temperature. [{(^{Mes}Nacnac)Mg}$_2$][1], [(IPr)SnCl$_2$][2] and IPr[3] were prepared by literature procedures. All other reagents were used as received.

Synthesis of [(IPr)Sn=Sn(IPr)] 3: Diethyl ether (10 cm^3) pre-cooled to -80 °C was added to a mixture of [(IPr)SnCl$_2$] (0.12 g, 0.21 mmol) and [{(^{Mes}Nacnac)Mg}$_2$] (0.15 g, 0.21 mmol) at -80 °C. Upon dissolution of the reactants the solution took on a deep red/brown color with concomitant precipitation of tin metal. After stirring the reaction mixture for 30 min, the suspension was left to warm to 0 °C, whereupon the soluble component of the reaction mixture became green. The suspension was concentrated *in vacuo* to *ca.* 4 cm^3, filtered and the filtrate stored at -30 °C to yield red crystals of **3** (yield 5%). M.p. 40-60 °C (decomp.); ^{1}H NMR (400 MHz, 243 K, C_7D_8): δ 1.09 (d, 24H, $^{3}J_{HH}$ = 6.4 Hz, CH(CH_3)$_2$), 1.28 (d, 24H, $^{3}J_{HH}$ = 6.4 Hz, CH(CH_3)$_2$), 3.01 (sept, 8H, $^{3}J_{HH}$ = 6.4Hz, CH(CH$_3$)$_2$), 6.67 (s, 4H, CH), 7.01-7.21 (m, 12H, Ar-CH); ^{13}C{^{1}H} NMR (100.6 MHz, 243K, C_7D_8): δ 23.6 (C(CH$_3$)$_2$), 25.9 (C(CH$_3$)$_2$), 29.2 (C(CH$_3$)$_2$), 124.1 (NCH), 125.6, 127.5, 138.9, 145.9 (Ar-*C*), 210.3 (N_2C); IR *v*/cm^{-1} (Nujol): 1661w, 1043w, 1569w, 1405m, 1374m, 1254m, 1102s, 1059m, 1017m, 802s, 759m.

N.B. Even at -30 °C in D_8-toluene solutions, compound **3** slowly decomposes, depositing tin metal.

Synthesis of [(IPr)PbBr$_2$]: THF (60 cm^3) was added to a mixture of IPr (0.50 g, 1.29 mmol) and $PbBr_2$ (0.47 g, 1.29 mmol) and the resultant suspension was stirred overnight at 20°C. During this time a colorless crystalline solid depsoited from solution. All volatiles were removed *in vacuo* and the residue was extracted into toluene (60 cm^3) and filtered. The filtrate was concentrated *in vacuo* to *ca.* 20 cm^3 and placed at -30°C freezer overnight yielding [(IPr)$PbBr_2$] as a colorless crystalline solid (yield 92%). M.p. 230-235°C; ^{1}H NMR (300 MHz, 298 K, C_6D_6): δ 1.06 (d, 12H, $^3J_{HH}$ = 5.1 Hz, CH(CH_3)$_2$), 1.36 (d, 12H, $^3J_{HH}$ = 5.1 Hz, CH(CH_3)$_2$), 2.86 (sept, 4H, $^3J_{HH}$ = 5.1 Hz, C*H*(CH$_3$)$_2$), 6.56 (s, 2H, C*H*), 7.13-7.26 (m, 6H, Ar-C*H*); ^{13}C{^{1}H} NMR (100.6 MHz, 298K, C_6D_6): δ 24.7 (C(*C*H$_3$)$_2$), 25.4 (C(*C*H$_3$)$_2$), 29.5 (*C*(CH$_3$)$_2$), 124.2 (N*C*H), 124.8, 130.8, 136.8, 146.7 (Ar-*C*), 218.9 (N_2C). IR *v*/cm^{-1} (Nujol): 1604m, 1074m, 1062, 945m, 934m, 924m, 808s, 802s, 757s, 697s, 687w; MS (+ve ESI/MeCN), *m*/*z* (%): 389.1 (IPrH$^+$, 100); MS (-ve ESI/MeCN), *m*/*z* (%): 446.8 ($PbBr_3^-$, 100).

2. X-Ray Crystallography

Crystals of **3**, [(IPr)$PbBr_2$], **2**·(benzene)$_2$ and **2**·(benzene)$_4$ suitable for X-ray structural determination were mounted in silicone oil. Crystallographic measurements were made using either Bruker Apex X8 or Oxford Gemini Ultra diffractometers using a graphite monochromator with Mo Kα radiation (λ = 0.71073 Å). All structures were solved by direct methods and refined on F^2 by full matrix least squares (SHELX97)[4] using all unique data. All non-hydrogen atoms are anisotropic with hydrogen atoms included in calculated positions (riding model). There are no significant geometric differences between the two new structural modifications of compound **2** reported here, and that previously reported.[5] Two crystallographically independent molecules of [(IPr)$PbBr_2$] were refined in the asymmetric unit of its crystal structure. There are no significant geometric differences between them. The Flack parameter for the structure of [(IPr)$PbBr_2$] was refined as -0.008(8). Crystal data, details of data collections and refinements for all structures can be found in their CIF files and are summarised in Table S1.

Table S1. Summary of Crystallographic Data for Compounds **3**, [(IPr)PbBr$_2$], **2**·(benzene)$_2$ and **2**·(benzene)$_4$.

	3	[(IPr)PbBr$_2$]	**2**·(benzene)$_2$	**2**·(benzene)$_4$
empirical formula	$C_{54}H_{72}N_4Sn_2$	$C_{27}H_{36}Br_2N_2Pb$	$C_{66}H_{84}Ge_2N_4$	$C_{78}H_{96}Ge_2N_4$
formula weight	1014.54	755.59	1078.55	1234.77
crystal system	monoclinic	monoclinic	triclinic	monoclinic
space group	$P2_1/n$	Pn	P-1	$P2_1/c$
a (Å)	13.8057(6)	10.628(2)	12.2068(2)	12.2533(7)
b (Å)	12.2283(5)	19.090(4)	13.3207(3)	22.8619(12)
c (Å)	15.4273(7)	14.334(3)	20.7196(4)	13.0395(7)
α (deg.)	90	90	92.467(1)	90
β (deg)	97.181(2)	102.91(3)	93.122(1)	108.371(1)
γ (deg.)	90	90	116.634(1)	90
vol (Å^3)	2584.01(19)	2834.6(10)	2998.5(1)	3466.6(3)
Z	2	4	2	2
ρ (calcd) (g.cm^{-3})	1.304	1.771	1.195	1.183
μ (mm^{-1})	1.003	8.787	1.044	0.911
F(000)	1048	1456	1144	1312
T (K)	123(2)	123(2)	123(2)	123(2)
reflections collected	40679	20502	99544	17684
unique reflections	4551	9186	17459	6102
R_{int}	0.0601	0.0706	0.0461	0.0815
R1 indices [I>2σ(I)]	0.0393	0.0574	0.0381	0.0492
wR2 indices (all data)	0.1034	0.1095	0.0859	0.1041
CCDC No.	892557	892554	892555	892556

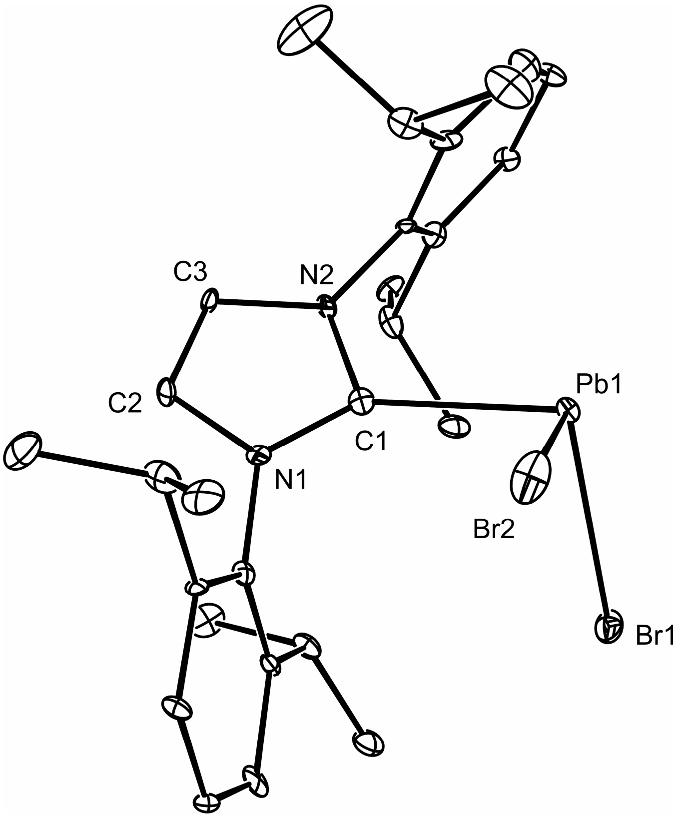


Fig. S1 Molecular structure of [(IPr)PbBr$_2$] (25% thermal ellipsoids; hydrogen atoms omitted). Selected bond lengths (Å) and angles (º): Pb(1)-C(1) 2.443(11), Pb(1)-Br(2) 2.6905(16), Pb(1)-Br(1) 2.6933(14), N(1)-C(1) 1.365(14), N(1)-C(2) 1.386(13), C(1)-N(2) 1.366(14), N(2)-C(3) 1.394(14), C(2)-C(3) 1.339(15), C(1)-Pb(1)-Br(2) 93.3(3), C(1)-Pb(1)-Br(1) 98.6(3), Br(2)-Pb(1)-Br(1) 93.79(5), N(1)-C(1)-N(2) 102.1(9).

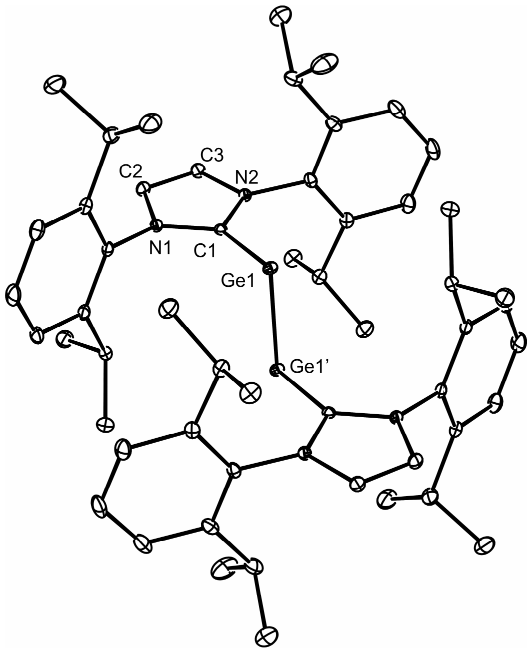


Fig. S2 Molecular structure of **2**, from the crystal structure of **2**·(benzene)$_2$ (25% thermal ellipsoids; hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): Ge(1)-C(1) 2.0241(16), Ge(1)-Ge(1)' 2.3400(3), C(1)-Ge(1)-Ge(1)' 92.48(4), N(2)-C(1)-N(1) 103.71(13), N(2)-C(1)-Ge(1) 127.24(11), N(1)-C(1)-Ge(1) 128.49(11). Symmetry operation: ' -x+1, -y+1, -z+1.

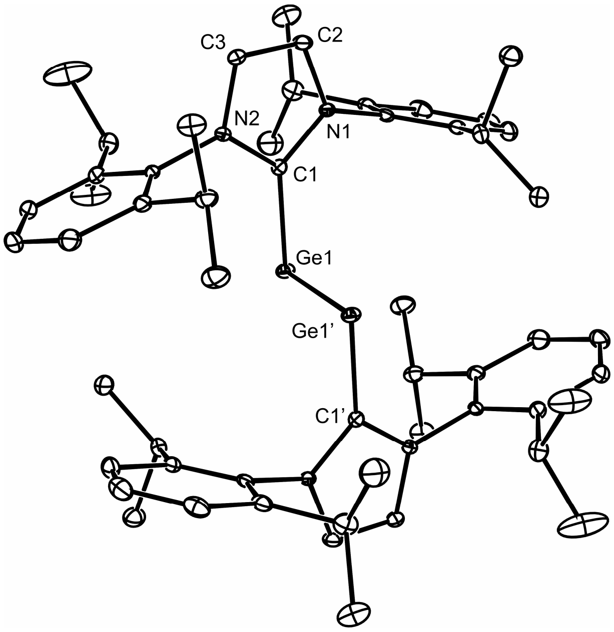


Fig. S3 Molecular structure of **2**, from the crystal structure of **2**·(benzene)$_4$ (25% thermal ellipsoids; hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): Ge(1)-C(1) 2.027(3), Ge(1)-Ge(1)' 2.3413(8), C(1)-Ge(1)-Ge(1)' 91.25(9), N(2)-C(1)-N(1) 103.7(3), N(2)-C(1)-Ge(1) 128.8(2), N(1)-C(1)-Ge(1) 127.4(2). Symmetry operation: ' -x, -y, -z+1.

3. Computational Studies

Geometry optimizations have been carried out using TurboMole 6.1 optimizer[6] and gradients at the BP86[7]/def2-TZVPP[8] level of theory. Stationary points were characterized as minima by calculating the Hessian matrix analytically at this level of theory. For all calculations the resolution-of-identity method has been applied.[9]

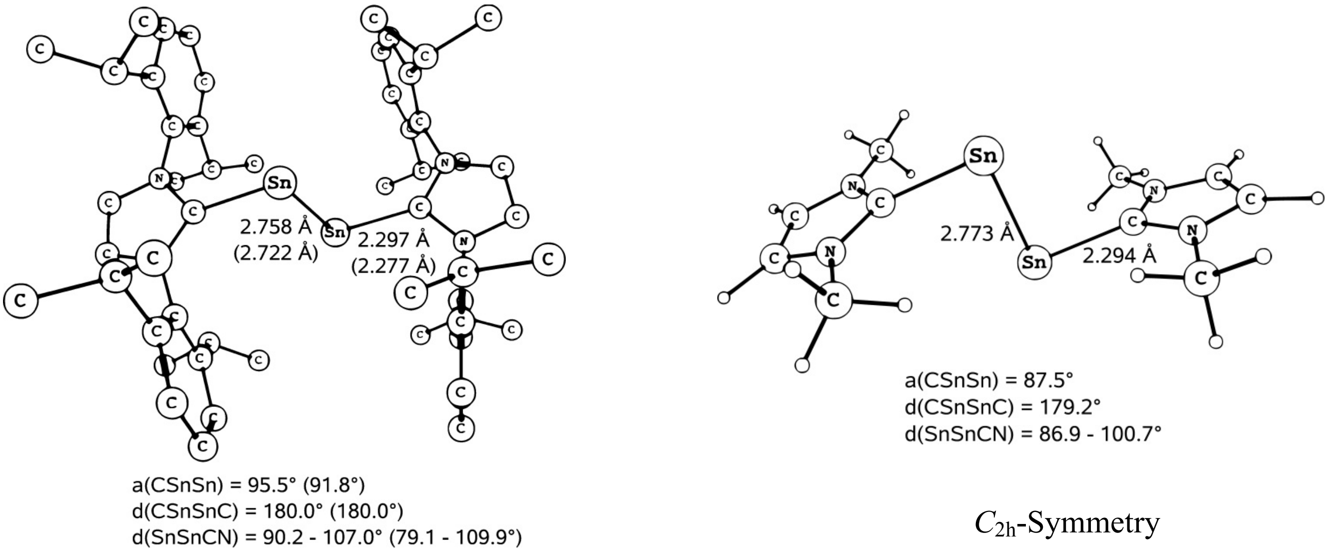
For the bonding analyses we optimized the molecule with the program package ADF2009.01.[10] BP86 was chosen applying uncontracted Slater-type orbitals (STOs) as basis functions.[11] The latter basis sets for all elements have triple-ζ quality augmented by two sets of polarization functions (ADF-basis set TZ2P). This level of theory is denoted BP86/TZ2P. An auxiliary set of s, p, d, f, and g STOs was used to fit the molecular densities and to represent the Coulomb and exchange potentials accurately in each SCF cycle.[12] Scalar relativistic effects have been incorporated by applying the zeroth-order regular approximation (ZORA) in all ADF calculations.[13]

The interatomic interactions were investigated by means of an energy decomposition analysis (EDA, also known as extended transition state method - ETS) developed independently by Morokuma[14] and by Ziegler and Rauk.[15] The bonding analysis focuses on the instantaneous interaction energy ΔE_{int} of a bond A-B between two fragments A and B in the particular electronic reference state and in the frozen geometry of AB. This interaction energy is divided into three main components [Eq. (1)].

$$\Delta E_{int} = \Delta E_{elstat} + \Delta E_{Pauli} + \Delta E_{orb} \tag{1}$$

The term ΔE_{elstat} corresponds to the quasi-classical electrostatic interaction between the unperturbed charge distributions of the prepared atoms and is usually attractive. The Pauli repulsion ΔE_{Pauli} is the energy change associated with the transformation from the superposition of the unperturbed electron densities $\rho_A + \rho_B$ of the isolated fragments to the wavefunction $\Psi^0 = N\hat{A}[\Psi_A \Psi_B]$, which properly obeys the Pauli principle through explicit anti-symmetrization ($\hat{A}$ operator) and renormalization (N = constant) of the product wavefunction. ΔE_{Pauli} comprises the destabilizing interactions between electrons of the same spin on either fragment. The orbital interaction ΔE_{orb} accounts for charge transfer and polarization effects. The ΔE_{orb} term can be decomposed into contributions from each irreducible representation of the point group of the interacting system. Further details on the EDA/ETS method[10] and its application to the analysis of the chemical bond[16] can be found in the literature.

Lewis structure was obtained using NBO 3.1[17] as implemented in Gaussian 09 Rev. C.01.[18] NBO electron densities were generated from a single-point calculation of the molecule with BP86/def2-TZVPP basis sets in Gaussian09 from the TURBOMOLE 6.1 optimized geometry.



(a) (b)

Fig. S4 Optimised geometries of (a) **3** (experimental values in parentheses) and (b) **3a**.

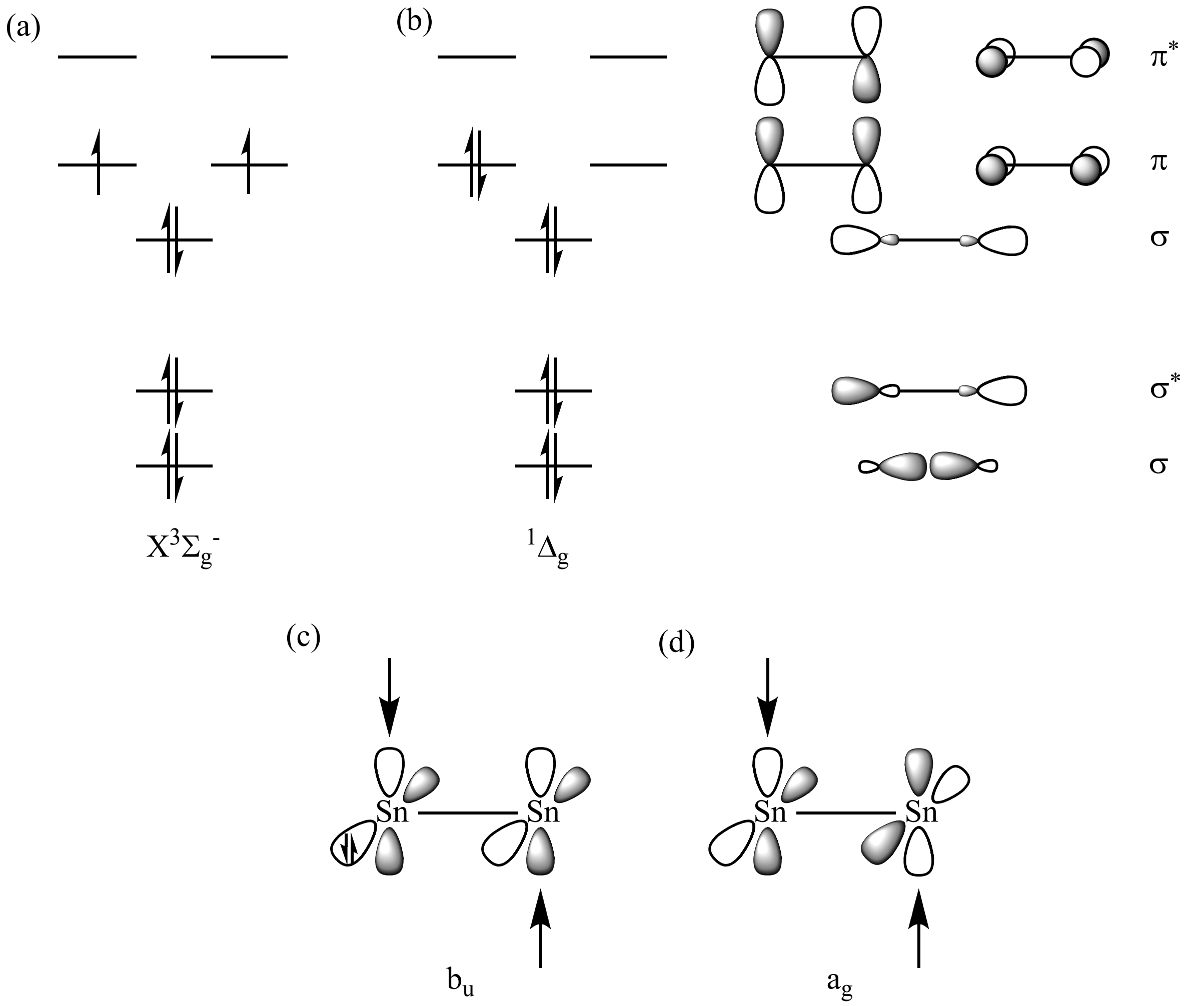
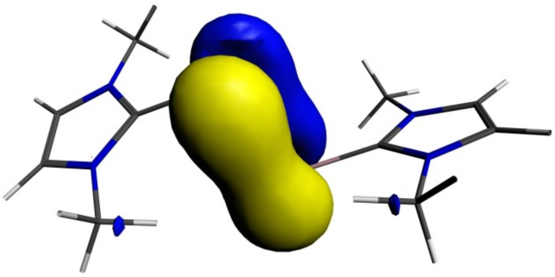
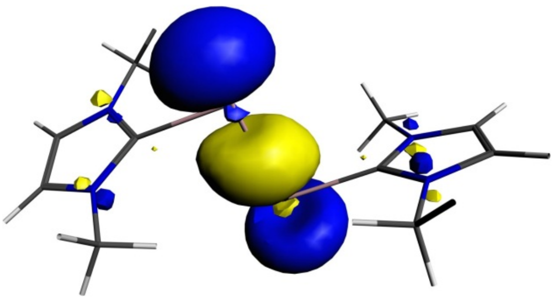


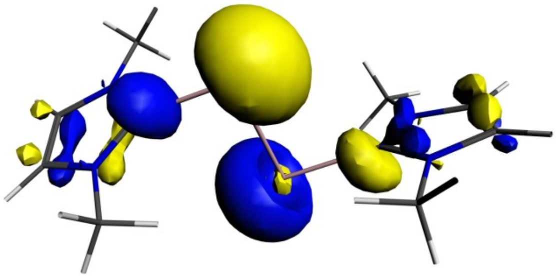
Fig. S5 Schematic representation of (a) the $X^3\Sigma_g^-$ ground state and (b) the $^1\Delta_g$ excited state of Sn_2. Pictorial description of the electron donation from the carbon σ-lone pair orbitals of the NHC ligands into the vacant orbitals of ($^1\Delta_g$)Sn_2. (c) Donation of the plus combination of the lone-pairs into the in-plane vacant π MO and (d) donation of the minus combination of the lone-pairs into the in-plane vacant π* MO.



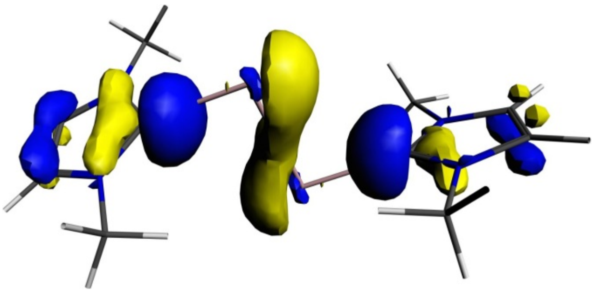
HOMO -0.1066 a.u.



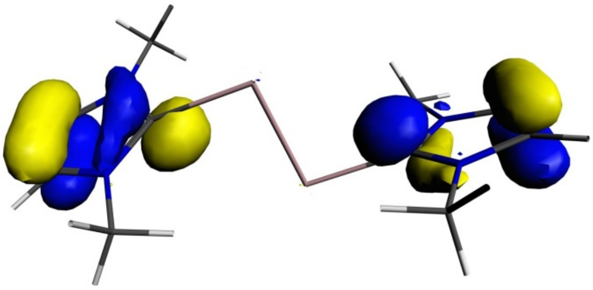
HOMO-1 -0.1135 a.u.



HOMO-2 -0.2050 a.u.



HOMO-3 -0.2084 a.u.



HOMO-4 -0.2265 a.u.

Fig. S6 Frontier molecular orbitals of **3a**.

Table S2. Cartesian coordinates for the calculated structure of **3**.

S_2-Symmetry

E(TURBOMOLE 6.1 RI-BP86/def2-TZVPP): -2749.922392855 a.u.

Sn	0.034861	1.041939	0.902897
N	-0.488592	-0.564359	3.728595
C	-1.070027	-0.080130	2.574693
N	-2.421909	-0.152272	2.845381
C	-1.445721	-0.912074	4.675785
H	-1.176252	-1.306094	5.646728
C	-2.658710	-0.653429	4.121944
H	-3.659600	-0.775671	4.514009
C	0.929811	-0.647805	3.996451
C	1.551829	0.431387	4.658589
C	2.908122	0.294988	4.984333
H	3.418278	1.112398	5.494879
C	3.612601	-0.862074	4.665059
H	4.667986	-0.946946	4.926893
C	2.972528	-1.911831	4.009230
H	3.536668	-2.809611	3.758729
C	1.618570	-1.832845	3.659776
C	0.807441	1.703087	5.044079
H	-0.191855	1.658947	4.589420
C	1.495694	2.963241	4.492688
H	2.500179	3.098082	4.919454
H	0.906474	3.856230	4.745021
H	1.584473	2.909259	3.399467
C	0.626391	1.796408	6.571578
H	0.091286	0.923877	6.970750
H	0.054139	2.696995	6.836703
H	1.598366	1.853348	7.082113
C	0.924248	-3.005115	2.979234
H	0.048407	-2.602780	2.449571
C	1.805797	-3.691500	1.925919
H	2.177658	-2.964727	1.191993
H	1.218113	-4.446336	1.385676
H	2.663614	-4.208811	2.379745
C	0.429356	-4.028885	4.021093
H	1.275445	-4.450659	4.582693
H	-0.095470	-4.858059	3.525293
H	-0.263073	-3.577106	4.744385
C	-3.491570	0.300154	1.984460
C	-3.887250	1.652664	2.058864
C	-4.963272	2.056229	1.257371
H	-5.291803	3.095394	1.290096
C	-5.620251	1.154147	0.425019
H	-6.453669	1.490323	-0.193065
C	-5.217646	-0.178422	0.383460
H	-5.740679	-0.875433	-0.270637
C	-4.147807	-0.639290	1.161619
C	-3.234916	2.651238	3.006479
H	-2.315468	2.193750	3.397108
C	-2.819925	3.950480	2.297732
H	-2.125677	3.737730	1.474060
H	-2.312192	4.619883	3.006373
H	-3.687427	4.492915	1.895074
C	-4.161603	2.947092	4.202232
H	-5.098842	3.414281	3.867079
H	-3.673638	3.636409	4.906024
H	-4.422629	2.030810	4.749549

C	-3.761821	-2.112690	1.137792
H	-2.742629	-2.195011	1.542296
C	-3.737572	-2.701418	-0.280874
H	-4.740573	-2.729875	-0.730499
H	-3.364525	-3.734497	-0.249323
H	-3.074776	-2.121841	-0.937968
C	-4.700915	-2.935050	2.044127
H	-4.691510	-2.574536	3.081246
H	-4.399917	-3.992221	2.049782
H	-5.737155	-2.880210	1.680138
Sn	-0.034861	-1.041939	-0.902897
N	0.488592	0.564359	-3.728595
C	1.070027	0.080130	-2.574693
N	2.421909	0.152272	-2.845381
C	1.445721	0.912074	-4.675785
H	1.176252	1.306094	-5.646728
C	2.658710	0.653429	-4.121944
H	3.659600	0.775671	-4.514009
C	-0.929811	0.647805	-3.996451
C	-1.551829	-0.431387	-4.658589
C	-2.908122	-0.294988	-4.984333
H	-3.418278	-1.112398	-5.494879
C	-3.612601	0.862074	-4.665059
H	-4.667986	0.946946	-4.926893
C	-2.972528	1.911831	-4.009230
H	-3.536668	2.809611	-3.758729
C	-1.618570	1.832845	-3.659776
C	-0.807441	-1.703087	-5.044079
H	0.191855	-1.658947	-4.589420
C	-1.495694	-2.963241	-4.492688
H	-2.500179	-3.098082	-4.919454
H	-0.906474	-3.856230	-4.745021
H	-1.584473	-2.909259	-3.399467
C	-0.626391	-1.796408	-6.571578
H	-0.091286	-0.923877	-6.970750
H	-0.054139	-2.696995	-6.836703
H	-1.598366	-1.853348	-7.082113
C	-0.924248	3.005115	-2.979234
H	-0.048407	2.602780	-2.449571
C	-1.805797	3.691500	-1.925919
H	-2.177658	2.964727	-1.191993
H	-1.218113	4.446336	-1.385676
H	-2.663614	4.208811	-2.379745
C	-0.429356	4.028885	-4.021093
H	-1.275445	4.450659	-4.582693
H	0.095470	4.858059	-3.525293
H	0.263073	3.577106	-4.744385
C	3.491570	-0.300154	-1.984460
C	3.887250	-1.652664	-2.058864
C	4.963272	-2.056229	-1.257371
H	5.291803	-3.095394	-1.290096
C	5.620251	-1.154147	-0.425019
H	6.453669	-1.490323	0.193065
C	5.217646	0.178422	-0.383460
H	5.740679	0.875433	0.270637
C	4.147807	0.639290	-1.161619
C	3.234916	-2.651238	-3.006479
H	2.315468	-2.193750	-3.397108
C	2.819925	-3.950480	-2.297732
H	2.125677	-3.737730	-1.474060
H	2.312192	-4.619883	-3.006373

H	3.687427	-4.492915	-1.895074
C	4.161603	-2.947092	-4.202232
H	5.098842	-3.414281	-3.867079
H	3.673638	-3.636409	-4.906024
H	4.422629	-2.030810	-4.749549
C	3.761821	2.112690	-1.137792
H	2.742629	2.195011	-1.542296
C	3.737572	2.701418	0.280874
H	4.740573	2.729875	0.730499
H	3.364525	3.734497	0.249323
H	3.074776	2.121841	0.937968
C	4.700915	2.935050	-2.044127
H	4.691510	2.574536	-3.081246
H	4.399917	3.992221	-2.049782
H	5.737155	2.880210	-1.680138

Table S3. Cartesian coordinates for the calculated structure of **3a**.

C_{2h}-Symmetry
E(TURBOMOLE 6.1 RI-BP86/def2-TZVPP): -1038.825358249 a.u.

Sn	0.523580	1.285027	0.000000
Sn	-0.523580	-1.285027	0.000000
C	2.589863	0.304349	0.000000
C	-2.589863	-0.304349	0.000000
N	3.375817	-0.006070	-1.079193
N	-3.375817	0.006070	1.079193
N	-3.375817	0.006070	-1.079193
N	3.375817	-0.006070	1.079193
C	4.606633	-0.505342	0.681316
C	-4.606633	0.505342	-0.681316
C	-4.606633	0.505342	0.681316
C	4.606633	-0.505342	-0.681316
C	2.944529	0.143099	-2.461692
C	-2.944529	-0.143099	2.461692
C	-2.944529	-0.143099	-2.461692
C	2.944529	0.143099	2.461692
H	5.368105	-0.809818	-1.387924
H	-5.368105	0.809818	1.387924
H	-5.368105	0.809818	-1.387924
H	5.368105	-0.809818	1.387924
H	3.826517	0.141175	-3.112876
H	-3.826517	-0.141175	3.112876
H	-3.826517	-0.141175	-3.112876
H	3.826517	0.141175	3.112876
H	2.263999	-0.670729	-2.743449
H	-2.263999	0.670729	2.743449
H	-2.263999	0.670729	-2.743449
H	2.263999	-0.670729	2.743449
H	2.401843	1.091651	-2.567870
H	-2.401843	-1.091651	2.567870
H	-2.401843	-1.091651	-2.567870
H	2.401843	1.091651	2.567870

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