

Supporting Information

for

Monomeric Sn(II) and Ge(II) Hydrides Supported by Tridentate Pincer-based Ligand^{†‡}

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S1. Experimental Section

All manipulations were performed under a dry and oxygen free atmosphere (N_2) using standard Schlenk techniques or inside a MBraun MB 150-GI glove box maintained at or below 1 ppm of O_2 and H_2O . Compound **1** was prepared according to the literature procedure.^(S1) All solvents were distilled from Na/benzophenone prior to use. 1H , ^{13}C and ^{119}Sn solution NMR spectra were recorded on a Bruker Avance DRX instrument. ^{119}Sn solid-state NMR spectra were recorded at 9.4 T (400 MHz 1H larmor frequency) and at magic-angle spinning rates of 8.2 and 11 kHz. Elemental analyses was performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen. IR spectra were recorded on Bio-Rad Digilab FTS7 spectrometer in the range 4000-350 cm^{-1} . EI-MS were measured on a Finnigan Mat 8230 or a Varian MAT CH5 instrument. Melting points were measured in sealed glass tubes with a Büchi melting point B 540 instrument.

Synthesis of 2: nBuLi (8 mL, 20 mmol, 2.5 M solution in *n*-hexane) was added to a stirred solution of 2,6-bis[N-(2',6'-diisopropylphenyl)ketimino]phenyl-1-bromide (5.59 g, 10 mmol) in Et_2O (90 mL) at $-60\text{ }^\circ C$. The mixture turned to deep red and was stirred for additional 2 h at this temperature. This solution was then added to a precooled ($-60\text{ }^\circ C$) solution of $GeCl_2 \cdot dioxane$ (2.31 g, 10 mmol) in Et_2O (50 mL), and the reaction mixture was allowed to warm to room temperature gradually and stirred for additional 12 h. The solution was filtered through Celite and concentrated to ca. one-third. Concentration and storing of the solution at $-35\text{ }^\circ C$ in a freezer for one day afforded **2** as a orange-red crystalline product (2.47 g, 42.0 %). 1H NMR (200 MHz, $THF-d_8$, $25\text{ }^\circ C$): δ 1.01-1.43 (m, 24 H, CH_3), 2.09 (s, 6H, $CH_3-C=$), 2.79-2.93 (m, 2H, $CH(CH_3)_2$), 3.24-3.37 (m, 2H, $CH(CH_3)_2$), 7.13-7.39 (m, 7H, Ph), 7.68 (d, 2H, Ph) ppm; $^{13}C\{^1H\}$ NMR (125.75 MHz, $THF-d_8$, $25\text{ }^\circ C$): δ 17.83 ($=C-CH_3$), 24.53, 24.97 (CH_3), 28.72, 29.53 ($-CH$), 124.06, 124.78, 126.35, 130.69, 139.61, 141.23, 141.87, 142.75

(*Ph*), 168.82 (-C=N), 171.19 (C_{ipso}) ppm; EI-MS: m/z : 588.2 [M^+] (100%). Elemental analysis for $C_{34}H_{43}ClGeN_2$ (588.2): calcd C, 69.47; H, 7.37; N, 4.77; found C, 71.34; H, 7.78; N, 4.68.

Synthesis of 3: To the solution of **1** (0.634 g, 1.00 mmol) in THF, solution of $K[B(\text{sec-Bu})_3H]$ (1.0 mL, 1M solution, 1.0 mmol) was added at room temperature. Immediately after addition, the reaction mixture turned to deep orange from yellowish orange in color. The resulting mixture was stirred for additional 2 h at room temperature and evaporated under reduced pressure. The residue was extracted with toluene (30 mL) and the insoluble material was filtered off. The deep orange filtrate was concentrated to about 5 mL and stored at $-32\text{ }^\circ\text{C}$ in a freezer to afford orange crystals of **3** (0.300 g, 50%). Mp ($^\circ\text{C}$): 140; ^1H NMR (500 MHz, C_6D_6 , $25\text{ }^\circ\text{C}$): δ 1.02 (m, 12 H, CH_3), 1.36 (m, 12 H, CH_3), 1.95 (s, 6H, $CH_3\text{-C=}$), 2.90-3.17 (m, 4H, $CH\text{-}$), 7.04-7.71 (m, 9H, Ph), 10.59 (s, 1H, Sn-H { $^1J_{\text{Sn-H}} = 112\text{ Hz}$ }) ppm; ^{13}C { ^1H } NMR (125.75 MHz, C_6D_6 , $25\text{ }^\circ\text{C}$): δ 17.82 (=C- CH_3), 23.87, 24.04, 24.67, 25.11 (CH_3), 28.07, 28.05 (-CH), 123.89, 124.01, 125.84, 128.5, 130.06, 138.76, 139.88, 143.69 (*Ph*), 171.69 (-C=N), 182.34 (C_{ipso}) ppm; ^{119}Sn NMR (C_6D_6 , $25\text{ }^\circ\text{C}$): δ - 114.27 ppm ($^1J_{\text{Sn-H}} = 112.9\text{ Hz}$). EI-MS: m/z : 599 [M^+] (100%). For the elemental analysis the crystals of $3 \cdot 2C_7H_8$ were kept under vacuum overnight to remove the two molecules of toluene. Elemental analysis for $C_{34}H_{44}N_2Sn$ (600.25): calcd C, 68.12; H, 7.40; N, 4.67; found C, 68.09; H, 7.11; N, 4.58. FT-IR (Nujol, cm^{-1}): wave number 1826 (s, Sn-H).

Synthesis of 4: To the solution of **2** (0.588 g, 1.00 mmol) in THF, solution of $K[B(\text{sec-Bu})_3H]$ (1.0 mL, 1M solution, 1.0 mmol) was added at room temperature. Immediately after addition, the reaction mixture turned to deep orange from yellowish orange in color. The resulting mixture was stirred for additional 2 h at room temperature and evaporated under reduced pressure. The residue was extracted with toluene (40 mL) and the insoluble material

was filtered off. The deep orange filtrate was concentrated to about 5 mL and stored at 0 °C in a freezer to afford orange crystals of **4** (0.250 g, 45%). Mp (°C): 184; ¹H NMR (500 MHz, THF-*d*₈, 25 °C): δ 1.08-1.21 (m, 24 H, CH₃), 2.30 (s, 6H, CH₃-C=), 2.76-2.84 (m, 4H, CH-), 6.69 (s, 1H, Ge-H), 7.11-7.17 (m, 7H, Ph), 8.08 (d, 2H, Ph) ppm; ¹³C{¹H} NMR (125.75 MHz, THF-*d*₈, 25 °C): δ 17.45 (=C- CH₃), 24.21, 24.96 (CH₃), 28.68, 28.88 (-CH), 123.95, 124.06, 126.35, 129.61, 139.63, 140.53, 141.13, 143.42 (*Ph*), 168.86 (-C=N), 176.48 (C_{ipso}) ppm; EI-MS: *m/z*: 553 [M⁺] (100%). Elemental analysis for C₃₄H₄₄ GeN₂ (553.37): calcd C, 73.80; H, 8.01; N, 5.06; found C, 73.69; H, 8.05; N, 4.98. FT-IR (Nujol, cm⁻¹): wave number 1985 (br, Ge-H).

Synthesis of 5: To the solution of **2** (0.500 g, 0.85 mmol) in THF (40 mL), a solution of LiAlD₄ (0.85 mL, 1M solution in THF, 0.85 mmol) was added at -78°C. This temperature was maintained for additional 1 h and then raised to room temperature very slowly. The resulting mixture was stirred for additional 5 h at room temperature and evaporated under reduced pressure. The residue was extracted with toluene (25 mL) and the insoluble material was filtered off. The deep orange filtrate was concentrated to 5 mL and stored at 0 °C in a freezer to afford orange crystals of **5** (0.180 g, 39%). ¹H NMR (500 MHz, THF-*d*₈, 25 °C): δ 1.08-1.22 (m, 24 H, CH₃), 2.31 (s, 6H, CH₃-C=), 2.75-2.84 (m, 4H, CH-), 7.10-7.17 (m, 7H, Ph), 8.07 (d, 2H, Ph) ppm; EI-MS: *m/z*: 555.3 [M⁺]. Elemental analysis for C₃₄H₄₃DGeN₂ (555.28): calcd C, 73.66; H, 8.18; N, 5.05; found C, 73.42; H, 8.34; N, 4.94. FT-IR (Nujol, cm⁻¹): wave number 1462 (Ge-D)

S2. Theoretical Calculations

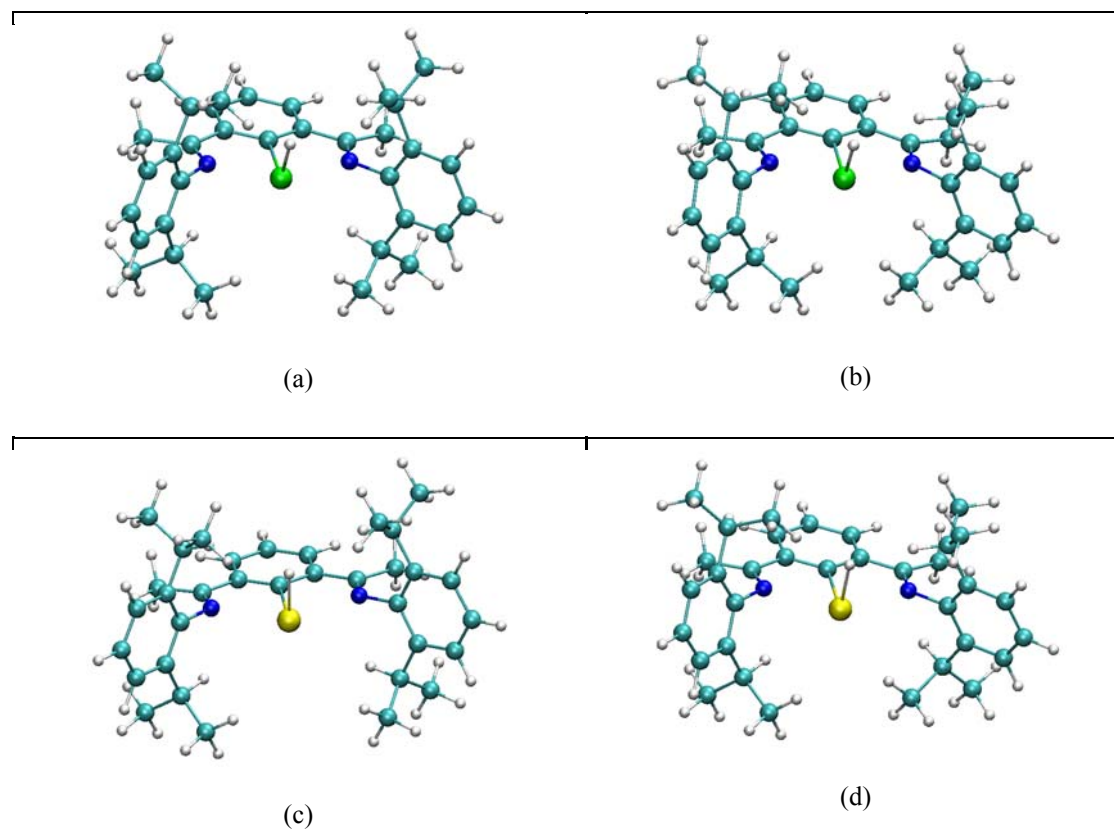


Figure 1. DFT optimized structures: (a) BP86/def2-SVP - compound **3**, (b) BP86-D/def2-SVP - compound **3**, (c) BP86/def2-SVP - compound **4**, (d) BP86-D/def2-SVP - compound **4**.

A. Compound **3** coordinates

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BP86/def2-SVP

C	0.084442	0.002334	-0.047705
C	-0.114622	-1.258501	-0.663641
C	-0.741128	-1.337142	-1.931427
H	-0.900322	-2.308232	-2.424886
C	-1.165912	-0.166863	-2.580815
H	-1.646622	-0.231811	-3.568349
C	-0.976866	1.086635	-1.976321
H	-1.317693	1.989767	-2.505076
C	-0.352301	1.177469	-0.708275

C	0.361813	-2.464435	0.061510
C	0.143553	-3.832584	-0.540516
H	0.549434	-4.628607	0.109407
H	0.633575	-3.902208	-1.533242
H	-0.938012	-4.020629	-0.702580
C	-0.123414	2.478620	-0.027936
C	-0.608059	3.753952	-0.677093
H	-0.349084	4.639932	-0.069415
H	-1.708677	3.727701	-0.817128
H	-0.159272	3.871741	-1.684693
C	1.480928	-3.331578	2.007186
C	2.849416	-3.702377	1.851738
C	3.364458	-4.712587	2.687532
H	4.416230	-5.018807	2.571261
C	2.570265	-5.332498	3.661482
H	2.993648	-6.121510	4.302400
C	1.235755	-4.936002	3.818670
H	0.616548	-5.417678	4.592471
C	0.664258	-3.934283	3.008862
C	-0.792765	-3.522139	3.226042
H	-1.023626	-2.714659	2.500890
C	-1.011036	-2.933628	4.635521
H	-0.804758	-3.682652	5.428865
H	-2.061367	-2.596295	4.759380
H	-0.349987	-2.060839	4.809654
C	-1.767450	-4.686247	2.950316
H	-1.639132	-5.095933	1.927449
H	-2.820576	-4.349358	3.051663
H	-1.616067	-5.523491	3.664332
C	3.755731	-3.032589	0.817321
H	3.162181	-2.238469	0.320717
C	4.958816	-2.334212	1.483509
H	4.624323	-1.583026	2.226827
H	5.572338	-1.808411	0.722045
H	5.619941	-3.059404	2.003434
C	4.217530	-4.025860	-0.269383
H	4.845188	-4.836535	0.158042
H	4.823187	-3.509071	-1.043424
H	3.356406	-4.506230	-0.777092
C	0.785126	3.617176	1.887086
C	2.074067	4.215777	1.768218
C	2.361920	5.341554	2.564636
H	3.347721	5.824372	2.473407
C	1.424131	5.856630	3.469725
H	1.668455	6.739871	4.079916
C	0.175131	5.234965	3.597530
H	-0.555629	5.632352	4.320392
C	-0.171725	4.110490	2.822196
C	-1.536820	3.448093	3.016742
H	-1.602446	2.599217	2.305745
C	-1.675040	2.854311	4.434498
H	-1.619365	3.643169	5.214406
H	-0.873488	2.115681	4.637450
H	-2.651792	2.338756	4.548395
C	-2.700284	4.411321	2.699762
H	-2.722895	5.271366	3.401629
H	-3.676112	3.888475	2.785245
H	-2.624608	4.823054	1.673021
C	3.124680	3.672452	0.798733
H	2.732863	2.717637	0.392854
C	4.451753	3.342630	1.510400
H	4.934404	4.250369	1.929686

H	5.169208	2.885135	0.797607
H	4.292698	2.625271	2.340153
C	3.351380	4.633676	-0.387361
H	3.761601	5.607101	-0.045353
H	2.407749	4.845482	-0.930362
H	4.072455	4.202122	-1.113338
N	0.957866	-2.274955	1.208553
N	0.496709	2.451312	1.121659
Sn	0.844554	0.114132	2.017053
H	2.561925	0.267620	1.527677

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BP86-D/def2-SVP

Sn	-0.222959	0.020463	0.606853
H	1.519952	-0.098080	0.228939
N	-0.438944	-2.349060	-0.234920
C	-1.105353	-1.178620	-2.198255
C	-1.585522	-1.159781	-3.530410
H	-1.831755	-2.099021	-4.049367
C	-1.752577	0.064185	-4.201816
H	-2.124420	0.075744	-5.237436
C	-0.922220	-2.440901	-1.443507
C	-1.301983	-3.752635	-2.086954
H	-0.781664	-3.862382	-3.061529
H	-2.392655	-3.771019	-2.298565
H	-1.047394	-4.608735	-1.434125
C	-0.247142	-3.467354	0.612317
C	1.088239	-3.884613	0.871966
C	1.290820	-4.952371	1.766212
H	2.317021	-5.289638	1.973665
C	0.207874	-5.588598	2.392483
H	0.385649	-6.423237	3.088810
C	-1.101282	-5.158893	2.129354
H	-1.947140	-5.657007	2.625879
C	-1.358519	-4.096952	1.239335
C	-2.776568	-3.578022	1.028638
H	-2.836236	-3.134916	0.014136
C	-3.068551	-2.447722	2.036128
H	-2.328616	-1.624069	1.939080
H	-3.015303	-2.840458	3.074480
H	-4.084885	-2.028101	1.871619
C	-3.849251	-4.675050	1.110161
H	-4.840958	-4.257153	0.837329
H	-3.937209	-5.078595	2.141339
H	-3.621514	-5.521362	0.428740
C	2.239906	-3.215273	0.135123
H	1.979376	-2.137707	0.037351
C	3.584792	-3.312142	0.868107
H	4.348383	-2.708333	0.335314
H	3.954432	-4.360275	0.904344
H	3.505243	-2.936389	1.909274
C	2.361056	-3.788888	-1.292570
H	3.157597	-3.260246	-1.858413
H	1.410509	-3.683090	-1.853509
H	2.616997	-4.870136	-1.251351
C	-0.788110	0.032451	-1.534944
N	-0.141764	2.376980	-0.288857
C	-0.966319	1.259730	-2.220223
C	-1.449405	1.272836	-3.551628
H	-1.588452	2.225406	-4.086247

C	-0.643130	2.505591	-1.486351
C	-0.929539	3.842492	-2.125720
H	-2.002235	3.907947	-2.405775
H	-0.344924	3.948405	-3.064239
H	-0.673394	4.676713	-1.445002
C	0.194275	3.478720	0.535155
C	-0.666145	3.807536	1.615487
C	-0.283977	4.849829	2.482705
H	-0.951341	5.112206	3.319401
C	0.912860	5.552334	2.290358
H	1.196351	6.364268	2.978394
C	1.745012	5.223366	1.207335
H	2.678791	5.783443	1.053479
C	1.407652	4.192390	0.309943
C	2.330871	3.802697	-0.839700
H	1.692384	3.537585	-1.708948
C	3.140675	2.543708	-0.467189
H	2.471835	1.696846	-0.207938
H	3.791914	2.757844	0.407482
H	3.787001	2.232034	-1.316236
C	3.265887	4.934735	-1.290202
H	3.820026	4.626693	-2.201563
H	4.019248	5.166439	-0.507593
H	2.706624	5.867585	-1.514550
C	-2.006341	3.111652	1.816851
H	-2.079929	2.283486	1.081343
C	-2.119726	2.487090	3.217574
H	-3.104808	1.987857	3.338739
H	-2.027131	3.261301	4.009830
H	-1.323310	1.728849	3.370723
C	-3.166028	4.089726	1.542731
H	-4.145557	3.575797	1.652044
H	-3.102813	4.509813	0.516611
H	-3.141014	4.940220	2.258260

B. Compound 4 coordinates

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BP86/def2-SVP

Ge	-0.403125	0.017285	0.217945
H	1.183412	-0.046860	0.195772
N	-0.454503	-2.221417	-0.398746
C	-1.200434	-1.147193	-2.358909
C	-1.733286	-1.101276	-3.667629
H	-1.992646	-2.027500	-4.203608
C	-1.937976	0.138349	-4.300459
H	-2.346873	0.168951	-5.321398
C	-0.970495	-2.387506	-1.593086
C	-1.342065	-3.729450	-2.172639
H	-0.831321	-3.887125	-3.144733
H	-2.432926	-3.782052	-2.371819
H	-1.067242	-4.554513	-1.490711
C	-0.163577	-3.295941	0.489696
C	1.166711	-3.807737	0.530536
C	1.456138	-4.840950	1.443541
H	2.475647	-5.256764	1.477346
C	0.476679	-5.346832	2.308930
H	0.723810	-6.156052	3.013802
C	-0.817660	-4.811391	2.275590

H	-1.582859	-5.201970	2.965079
C	-1.166856	-3.782229	1.377993
C	-2.584026	-3.206621	1.399189
H	-2.656722	-2.459622	0.581635
C	-2.856103	-2.449278	2.716167
H	-2.125370	-1.627899	2.858194
H	-2.789854	-3.125148	3.595187
H	-3.873572	-2.005179	2.708716
C	-3.656153	-4.285495	1.142121
H	-4.666462	-3.828609	1.092542
H	-3.678271	-5.046157	1.951474
H	-3.478107	-4.822423	0.187657
C	2.260390	-3.271422	-0.393694
H	1.841005	-2.388479	-0.918037
C	3.491815	-2.781366	0.393653
H	4.239427	-2.335382	-0.295051
H	3.994102	-3.610829	0.934564
H	3.210843	-2.010244	1.138482
C	2.658566	-4.310345	-1.463600
H	3.410394	-3.888495	-2.163747
H	1.783479	-4.637110	-2.061042
H	3.102700	-5.217368	-1.002071
C	-0.866898	0.058101	-1.689551
N	-0.271546	2.257459	-0.335806
C	-1.098505	1.304634	-2.325806
C	-1.631777	1.338932	-3.634932
H	-1.812483	2.297696	-4.145656
C	-0.769129	2.499236	-1.525638
C	-1.028356	3.883165	-2.065677
H	-2.108184	4.024115	-2.280887
H	-0.488870	4.032730	-3.023480
H	-0.705098	4.663218	-1.352777
C	0.101994	3.280700	0.582653
C	-0.855726	3.792097	1.506341
C	-0.432159	4.766509	2.432196
H	-1.161562	5.176407	3.148819
C	0.891652	5.224333	2.459804
H	1.198075	5.991325	3.188377
C	1.824675	4.694321	1.558705
H	2.867199	5.049496	1.588413
C	1.460146	3.713644	0.614891
C	2.510649	3.143313	-0.338457
H	2.020121	2.341604	-0.927298
C	3.677230	2.486754	0.426893
H	3.313438	1.691458	1.108060
H	4.238040	3.226072	1.036940
H	4.396626	2.026302	-0.282187
C	3.023706	4.208994	-1.329040
H	3.741124	3.764390	-2.050926
H	3.548515	5.034580	-0.803249
H	2.193926	4.660953	-1.909529
C	-2.305037	3.303866	1.530234
H	-2.429986	2.579227	0.699204
C	-2.614825	2.539787	2.834661
H	-3.657524	2.159170	2.826448
H	-2.501301	3.192795	3.725975
H	-1.935640	1.672127	2.955119
C	-3.308941	4.452377	1.302370
H	-4.346648	4.061368	1.254333
H	-3.105313	4.994753	0.355881
H	-3.275005	5.197806	2.125534

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BP86-D/def2-SVP

Ge	-0.300385	0.006376	0.201889
H	1.280722	-0.067520	0.211719
N	-0.373149	-2.196495	-0.345578
C	-1.025132	-1.199311	-2.369931
C	-1.515599	-1.190158	-3.695907
H	-1.770456	-2.134071	-4.203191
C	-1.684512	0.033214	-4.372146
H	-2.059867	0.038476	-5.406547
C	-0.862634	-2.405227	-1.544892
C	-1.307269	-3.755224	-2.042970
H	-0.959289	-3.920500	-3.083391
H	-2.418985	-3.807398	-2.055026
H	-0.928483	-4.565368	-1.390461
C	-0.209838	-3.228543	0.612817
C	1.109591	-3.682540	0.886927
C	1.281386	-4.664414	1.880147
H	2.294174	-5.031827	2.102042
C	0.183205	-5.174047	2.592096
H	0.337555	-5.939726	3.368821
C	-1.108080	-4.700466	2.317998
H	-1.965666	-5.092276	2.886259
C	-1.333199	-3.723351	1.327414
C	-2.728995	-3.152638	1.106179
H	-2.751369	-2.661425	0.112367
C	-3.013275	-2.058577	2.155894
H	-2.265651	-1.239891	2.080893
H	-2.968850	-2.488908	3.179914
H	-4.025279	-1.624484	2.002381
C	-3.825037	-4.230655	1.115133
H	-4.808256	-3.778547	0.866159
H	-3.923704	-4.699177	2.117741
H	-3.608930	-5.036261	0.381965
C	2.275100	-3.137030	0.072024
H	2.045251	-2.068207	-0.134618
C	3.622962	-3.202511	0.803802
H	4.404204	-2.690328	0.204462
H	3.953490	-4.253647	0.951301
H	3.566915	-2.714126	1.798474
C	2.362251	-3.864723	-1.286292
H	3.172001	-3.430027	-1.910964
H	1.410101	-3.784613	-1.848657
H	2.580439	-4.943860	-1.130565
C	-0.696720	0.020300	-1.724216
N	-0.161028	2.252706	-0.408485
C	-0.901953	1.248033	-2.402201
C	-1.391312	1.251326	-3.728111
H	-1.548498	2.202142	-4.261592
C	-0.622806	2.461270	-1.616006
C	-0.923858	3.825340	-2.181663
H	-2.003316	3.903808	-2.433539
H	-0.360823	3.979400	-3.126741
H	-0.655888	4.625583	-1.465305
C	0.148134	3.295996	0.498147
C	-0.727877	3.539583	1.589175
C	-0.362362	4.519628	2.533741
H	-1.038644	4.712944	3.382158
C	0.828176	5.246666	2.404524
H	1.097341	6.008320	3.153264
C	1.674474	5.005165	1.308814
H	2.604111	5.583244	1.205773

C	1.357150	4.036502	0.337817
C	2.298183	3.733773	-0.824584
H	1.673553	3.557583	-1.725964
C	3.080299	2.432335	-0.550619
H	2.389266	1.584420	-0.365530
H	3.724886	2.560166	0.345785
H	3.730336	2.178101	-1.415870
C	3.261870	4.883065	-1.156416
H	3.831914	4.642430	-2.078144
H	3.999810	5.035609	-0.340086
H	2.722974	5.841214	-1.313343
C	-2.047339	2.794303	1.752369
H	-2.172698	2.117200	0.882440
C	-2.028308	1.911746	3.012372
H	-2.994927	1.375933	3.126140
H	-1.860641	2.526300	3.923747
H	-1.218710	1.154786	2.939802
C	-3.238509	3.770082	1.773243
H	-4.196108	3.211727	1.851569
H	-3.269389	4.391773	0.853011
H	-3.174980	4.457701	2.644632

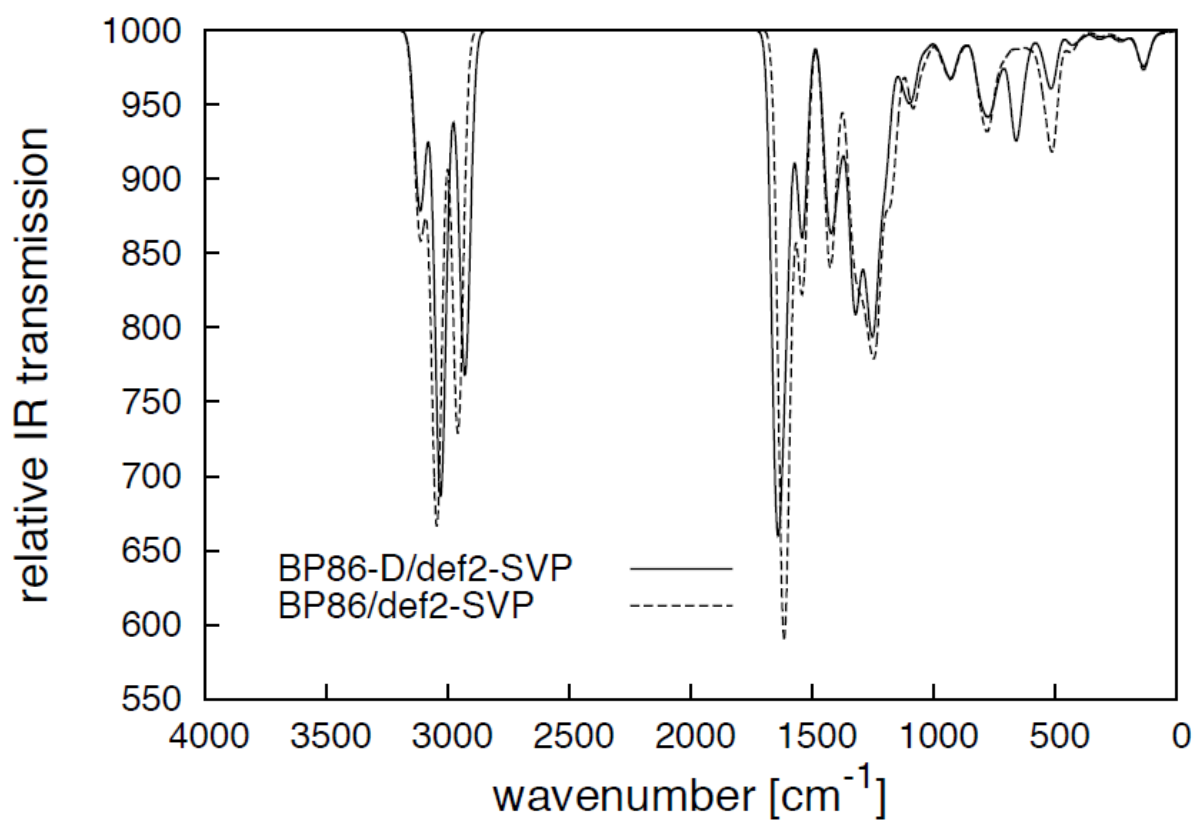


Fig. 2. Theoretical IR spectrum of compound 3

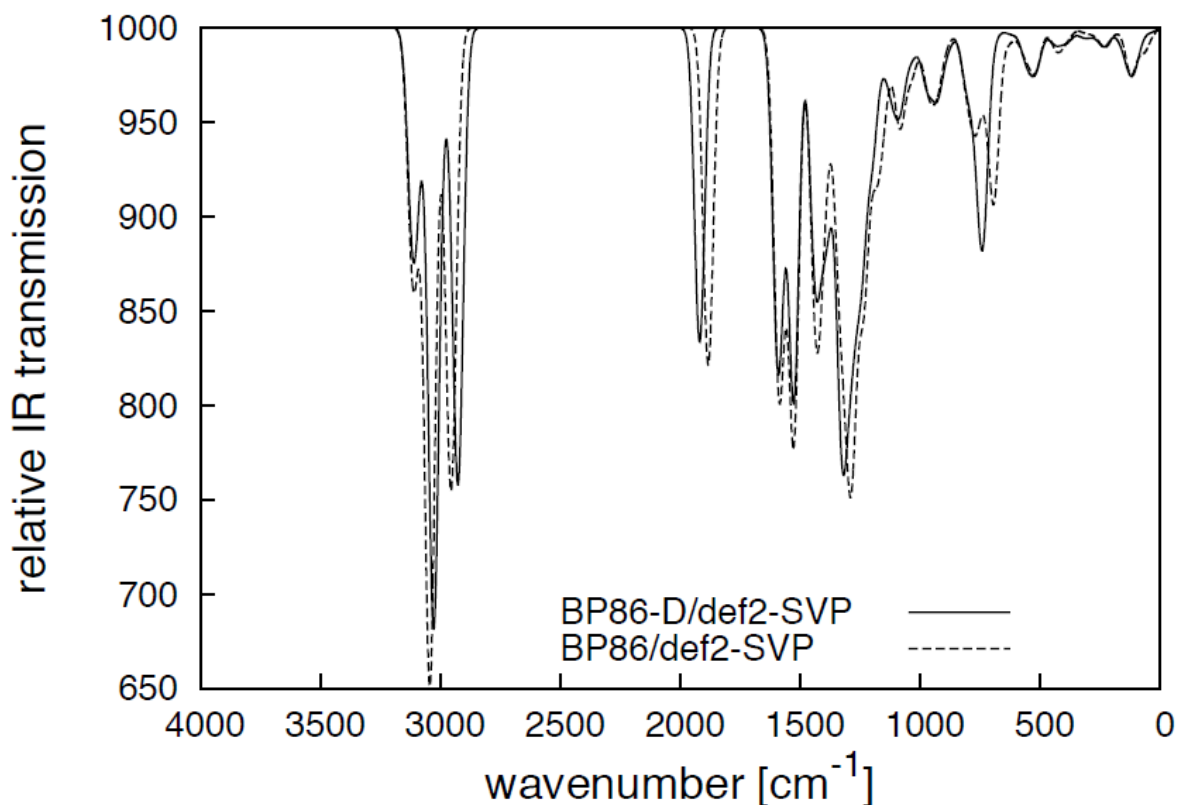


Fig. 3. Theoretical IR spectrum of compound **4**

S3. Crystallographic details

The shock cooled crystals were selected and mounted under nitrogen atmosphere using the X-TEMP2.^(S2) The data for **3** and **4** were collected on a rotating anode with mirror optics equipped with a Bruker Smart Apex II Ultra detector (Mo K α radiation, $\lambda = 0.71073$ Å, 100K). The integration was performed with SAINT V7.68A^(S3), followed by an empirical absorption correction with TWINABS 2008/4 (**3**) and SADABS 2008/1 (**4**).^(S4) The structures were solved by direct methods (SHELXS) and refined against F^2 using the full-matrix least-squares methods with SHELXL.^(S5) All non-hydrogen atoms were refined with anisotropic displacement parameters (ADPs). Disordered moieties were refined by using bond lengths similarity restraints and restraints on ADPs. The distance of the hydrogen atoms attached to the metal ions was restrained to the theoretically determined value (BP86-D) and the U_{iso} -value was set to 1.5 times the value of the metal ion.

Table 1. X-ray data for compound **3** and **4**

	3	4
Empirical formula	C ₃₄ H ₄₄ N ₂ Sn·2C ₇ H ₈	C ₃₄ H ₄₄ GeN ₂
<i>M</i> (g/mol)	783.67	553.30
Crystal system	Monoclinic	Monoclinic
Space group	<i>Pc</i>	<i>C2/c</i>
<i>a</i>	10.511(2)	15.509(2)
<i>b</i>	13.107(2)	8.506(2)
<i>c</i>	15.884(3)	24.339(3)
β	98.82°(2)	103.03°(2)
<i>V</i> [Å³]	2162.4(7)	3128.1(9)
<i>Z</i>	2	4
ρ [Mg/m³]	1.204	1.175
μ [mm⁻¹]	0.623	1.002
<i>F</i>(000)	824	1176
$\theta_{\text{min}/\text{max}}$	1.55°, 31.56°	1.72°, 30.55°
Index ranges	-15 ≤ <i>h</i> ≤ 15 -19 ≤ <i>k</i> ≤ 19 -23 ≤ <i>l</i> ≤ 23	-22 ≤ <i>h</i> ≤ 21 -11 ≤ <i>k</i> ≤ 12 -28 ≤ <i>l</i> ≤ 34
Collected reflections	14410	31743
Independent reflections	14410	4786 [<i>R</i> _{int} = 0.0253]
Completeness to θ_{max} [%]	99.6	99.6
Transmission (min., max.)	0.806692, 0.862275	0.9508, 1.0000
Restraints	426	1
Parameters	573	182
Goof	1.088	1.041
<i>R</i>₁ [<i>I</i> > 2σ(<i>I</i>)]	0.0354	0.0409
<i>R</i>₁ (all data)	0.0437	0.0516
<i>wR</i>₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0700	0.1038
<i>wR</i>₂ (all data)	0.0739	0.1098
Extinction coefficient		0.0007(2)
Largest diff peak/hole [eÅ⁻³]	0.691, -0.398	0.648 / -0.324

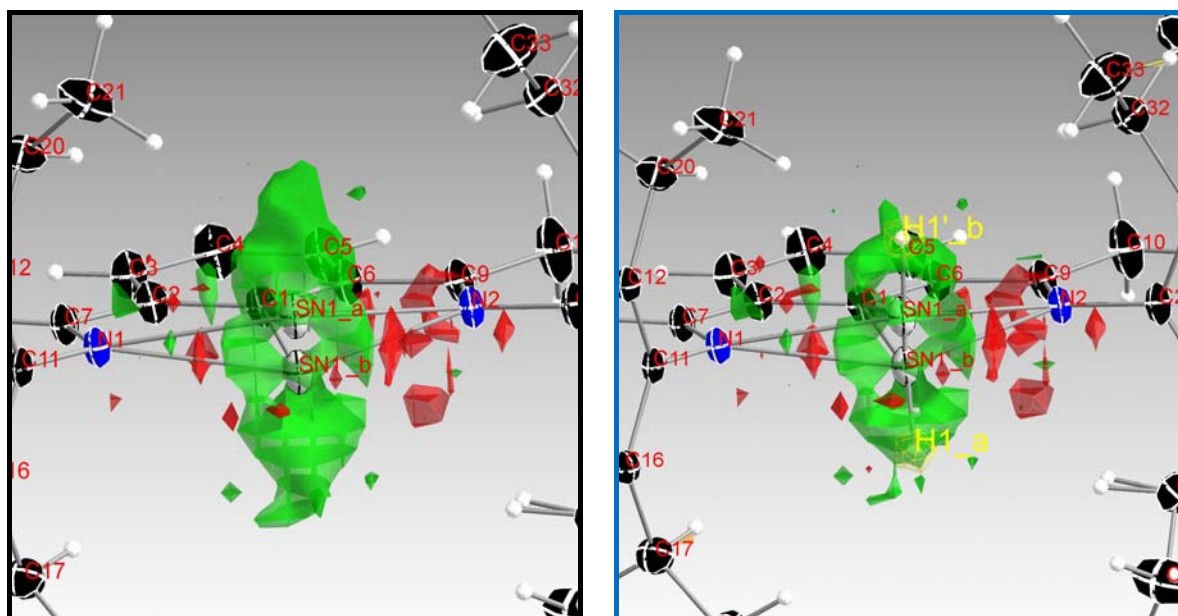


Figure 4: $F_{\text{obs}} - F_{\text{calc}}$ images of the Sn moiety before and after the refinement of the attached hydrogen atom (isosurface level at $0.15 \text{ e}/\text{\AA}^{-3}$).

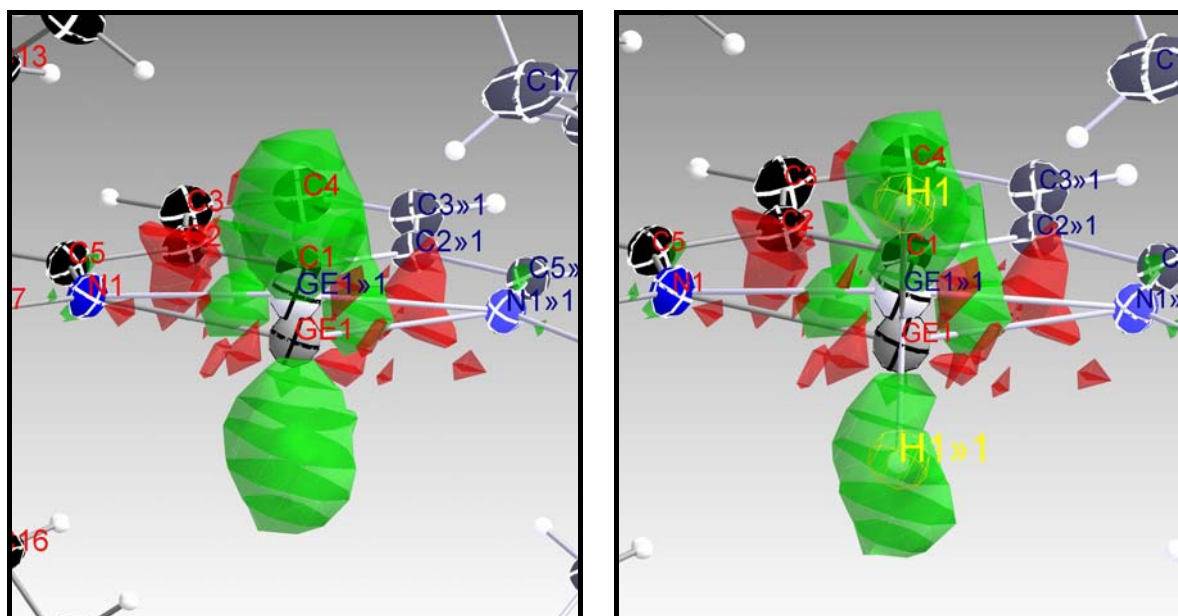
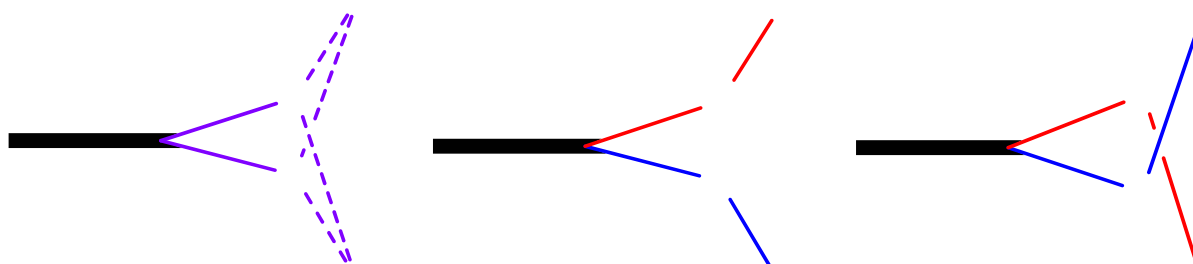


Figure 5: $F_{\text{obs}} - F_{\text{calc}}$ images of the Ge moiety before and after the refinement of the attached hydrogen atom (isosurface level at $0.08 \text{ e}/\text{\AA}^{-3}$).

Hydrogen treatment at Sn (3) and Ge (4) Figure 4 (left) and Figure 5 (left) show the residual density around Sn and Ge before hydrogen refinement. The metal ions are disordered above and below the ligand plane and the residual density distribution on both sides is similar (Sn, positional disorder about 52 : 48) or the same (Ge, symmetry induced disorder). The high

residual density and its spatial distribution can be explained by the presence of a hydrogen atom in addition to the lone pair of the metal ion. In general, the accurate determination of hydrogen atom positions, especially those of hydrogen atoms that are attached to heavy atoms, is not possible by means of X-ray diffraction. The disorder in the present case further obstructs the determination of the hydrogen atom positions. They have a high uncertainty and can be easily modified by using restraints. The distances of the hydrogen atoms to the metal ions were therefore restrained to their theoretical value (BP86-D). The theoretical data also gave necessary information about the ligand–M–H geometry (M = Sn, Ge). The metal ion and the hydrogen atom are located below and above the ligand plane, respectively. It was not possible to distinguish between the cases where the metal atom and the hydrogen atom were both situated at the same or each on opposite sides with respect to the ligand plane (see scheme 1).



Scheme 1: Disorder of the ligand–M–H geometry (M = Sn, Ge) (left); possible configuration of the MH moieties: both M and H below/above the ligand plane (middle), M and H below and above the ligand plane (right).

TWIN-Refinement of (3) The crystal of **3** is a non-merohedral twin with twin fractions of 96 % and 4 %. The large domain also shows racemic twinning. TWINABS 2008/4 was used to create an HKLF 5 dataset constructed from all observations involving the large domain.

14410 corrected reflections were written to the file twin5.hkl and the reflections were merged according to point-group *m*. Single reflections that also occur in composites were omitted and

racemic twinning was included for all components. The twin refinement requires three batch scale factors (BASF) to refine the ratio of racemic twinning of both domains, respectively (see table 2). BASF 1 is zero within the standard deviation and BASF 3 at 0.04(1), meaning that domain 2 (4 % of the crystal) is virtually totally inverted, factoring in the high standard deviation. BASF 2 is 0.25(1), meaning 25 % of the crystal is the inverted part of domain 1. The information about the absolute structure is reflected in the batch scale factors, therefore the FLACK X parameter in the CIF-file is meaningless.

Table 2: Values of the three batch scale factors after 100 refinement cycles with XL in SHELXTL Version 2008/4. (') indicates the second domain, (-) the racemic component.

value	esd	shift/esd	parameter	
0.71141	—	—	$1-\sum(\text{BASF } 1-3)$	h,k,l,
-0.00113	0.01062	-0.002	BASF 1	h',k',l'
0.24823	0.01055	0.001	BASF 2	-h,-k,-l
0.04149	0.01064	0.002	BASF 3	-h',-k',-l'

esd = estimated standard deviation

S4. Solid state NMR

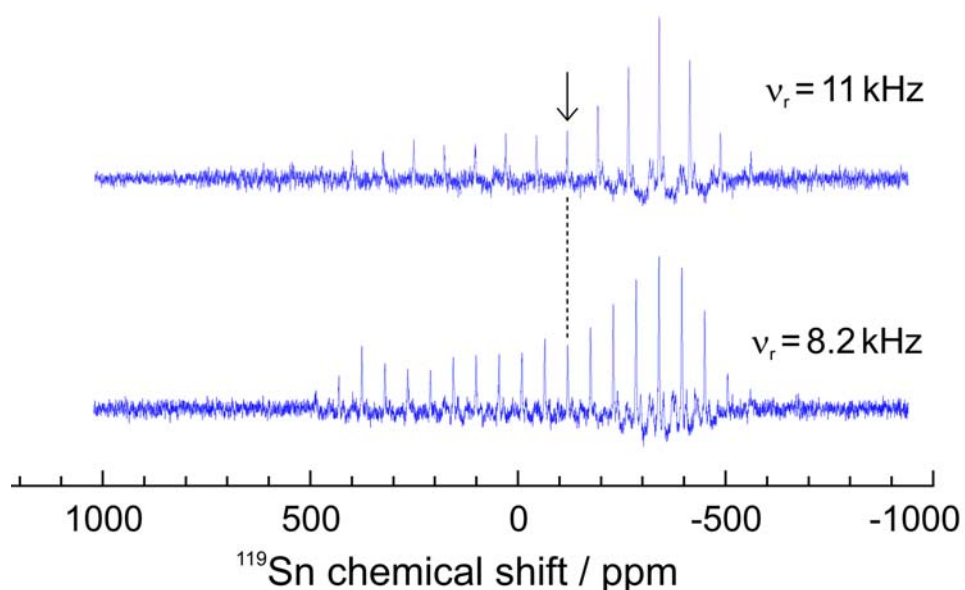


Fig. 6. ^{119}Sn solid-state NMR cross-polarization spectra of **3**. The spectra were recorded at 8.2 kHz and 11 kHz MAS on a 9.4 T spectrometer (Bruker Biospin, Germany). The isotropic chemical shift (-119.4 ppm) is indicated by an arrow. The ^{119}Sn chemical shift is given in reference to Me_4Sn and was externally calibrated using the sharp resonance of tetracyclohexyltin.

S5. References

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