Contrasting Reductions of Group 14 Metal(II) Chloride Complexes: Synthesis of a β-Diketiminato Tin(I) Dimer

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SUPPLEMENTARY INFORMATION

Contents

1. Syntheses

General considerations. All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of high purity dinitrogen. Hexane, 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. Mass spectra were recorded at the EPSRC National Mass Spectrometric Service at Swansea University. Microanalyses were carried out the Science Centre, London Metropolitan University. IR spectra were recorded using a Nicolet 510 FT-IR spectrometer as Nujol mulls between NaCl plates. ^{1}H, ^{13}C{^{1}H} and ^{119}Sn{^{1}H} NMR spectra were recorded on either Bruker DXP300 or DRX400 spectrometers and were referenced to the residual solvent resonances (^{1}H and ^{13}C{^{1}H}), or external $SnMe_4$ (^{119}Sn{^{1}H}). ^{But}MesNacnacH,[1] ^{But}NacnacH,[1] [(^{But}MesNacnac)GeCl][2] and [{(^{Mes}Nacnac)Mg}$_2$][3] were prepared by variations of literature procedures. All other reagents were used as received.

Synthesis of [(^{But}MesNacnac)SnCl] 5: A 1.6 M solution of *n*-butyllithium in hexane (1.6 cm^3, 2.56 mmol) was added to a solution of ^{But}MesNacnacH (0.99 g, 2.36 mmol) in diethyl ether (15 cm^3) at -78 °C. The resultant solution was warmed to room temperature and was stirred for 1 hr before being cooled again to -78 °C. The solution was then treated with suspension of $SnCl_2$ (0.45g, 2.37 mmol) in diethyl ether (15 cm^3), whereupon the reaction solution was warmed to ambient temperature. Volatiles were then removed *in vacuo*, the residue extracted with hexane (20 cm^3), and the extract filtered. The filtrate was concentrated to *ca.* 10 cm^3 and stored at overnight at -30 °C yielding colourless needle-like crystals of **5** (yield 0.93g, 69%). M.p. 196 °C (sharp); ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 1.09 (s, 18H, C(C*H*$_3$)$_3$), 2.05 (s, 12H, *o*-C*H*$_3$), 2.63 (s, 6H, *p*-C*H*$_3$), 5.99 (s, 1H,

NCC*H*CN), 6.64 (s, 4H, Ar-*H*); $^{13}C\{^1H\}$ NMR (400 MHz, C_6D_6, 300K): δ 20.5 (*o*-*C*H_3), 21.0 (*p*-*C*H_3), 31.3 (C(*C*H_3)$_3$), 42.3 (*C*(CH$_3$)$_3$), 103.7 (NC*C*HCN), 128.9, 130.1, 134.4, 143.8 (Ar-*C*), 173.7 (N*C*CH); $^{119}Sn\{^1H\}$ NMR (149.2 MHz, C_6D_6, 300K): δ - 235.5; IR *v*/cm^{-1} (Nujol): 1377s, 1260s, 1093s, 859w, 722w; MS (EI 70eV), *m*/*z* (%): 572.2 (M$^+$, 21), 417.3 (^{But}MesNacnac$^+$, 36), 202.1 (MesNCBu$^{t\,+}$, 100); anal. calc. for $C_{29}H_{41}ClSnN_2$: C 60.91%, H 7.23%, N 4.90%; found: C 60.18%, H 7.14%, N 5.04%.

Synthesis of [(^{But}MesNacnac)PbCl] 6: $^{t\text{Bu}}$MesNacnacH (0.79 g, 1.88 mmol) was dissolved in THF (20 cm^3) and treated with a 1.6 M solution of *n*-butyllithium in hexane (1.25 cm^3, 2.00 mmol) at -80 °C. This mixture was subsequently warmed to ambient temperature and stirred for 2 hours, before being added to a suspension of $PbCl_2$ (0.523 g, 1.88 mmol) in THF (20 cm^3) at -80 °C. Upon warming to room temperature, the solution took on a bright yellow colour. All volatiles were subsequently removed *in vacuo*, and the residue was extracted into hexane (15 cm^3). The extract was filtered and the filtrate stored at -30 °C overnight to yield yellow crystals of **6** (yield 0.46 g, 42%). M.p. 209-212 °C (decomp.); ^1H NMR (300 MHz, C_6D_6, 298 K): δ 1.14 (s, 18H, C(C*H*$_3$)$_3$), 2.08 (s, 6H, *o*-C*H*$_3$), 2.12 (s, 6H, *o*-C*H*$_3$), 2.65 (s, 6H, *p*-C*H*$_3$), 5.71 (s, 1H, NCC*H*CN), 6.70 (s, 4H, Ar-*H*); $^{13}C\{^1H\}$ NMR (400 MHz, C_6D_6, 300K): δ 19.6 (*o*-*C*H$_3$), 20.6 (*o*-*C*H$_3$), 20.9 (*p*-*C*H$_3$), 31.8 (C(*C*H$_3$)$_3$), 43.6 (*C*(CH$_3$)$_3$), 107.7 (NC*C*H), 130.3, 132.2, 133.9, 145.1 (Ar-*C*), 173.0 (N*C*CH); IR *v*/cm^{-1} (Nujol): 1623w, 1376s, 1260s, 800s, 721m, 668w; MS (EI 70eV), *m*/*z* (%): 660.2 (M$^+$, 10), 625.3 (M$^+$-Cl, 8), 417.3 (^{But}MesNacnac$^+$, 90), 202.1 (MesNCBu$^{t\,+}$, 100); anal. calc. for $C_{29}H_{41}N_2PbCl$: C 52.75%, H 6.26%, N 4.24%; found: C 52.59%, H 6.18%, N 4.14%.

Synthesis of [{(^{But}MesNacnac)Sn}$_2$] 7: A solution of [{(^{Mes}Nacnac)Mg}$_2$] (0.13 g, 0.18 mmol) in toluene (20 cm^3) was added to a solution of [(^{But}MesNacnac)SnCl] (0.20 g, 0.35 mmol) in toluene (20 cm^3) at -78 °C over 5 mins. This led to an immediate colour change of the reaction solution to deep green. This solution was warmed to 0 °C over 4 hrs, and stirred at that temperature for a further 2 hrs, before all volatiles were removed *in vacuo*. The residue was extracted with cold hexane (10 cm^3) and the extract filtered. The filtrate was stored at -30 °C overnight, affording small dark green crystals of **7** (yield 0.11 g, 55 %). M.p. 43-45 °C (decomp.); ^1H NMR (300 MHz, C_6D_6, 298 K): δ 1.17 (s, 36H, C(C*H*$_3$)$_3$), 2.07 (s, 12H, *o*-C*H*$_3$), 2.35 (s, 12H, *o*-C*H*$_3$), 2.44 (s, 12H, *p*-C*H*$_3$), 5.91 (s, 2H, NCC*H*CN), 6.67 (s, 8H, Ar*H*); $^{13}C\{^1H\}$ NMR (400 MHz, C_6D_6, 300K): δ 21.9, 21.1 (*o*-*C*H$_3$ and *p*-*C*H$_3$), 32.0 (C(*C*H$_3$)$_3$), 42.7 (*C*(CH$_3$)$_3$), 105.0 (NC*C*HCN), 129.5, 129.6, 132.9, 143.0 (Ar-*C*), 177.6 (N*C*(Bu^t)CH); $^{119}Sn\{^1H\}$ NMR (149.2 MHz, C_6D_6, 300K): δ 502.1; IR *v*/cm^{-1} (Nujol): 1377s, 1260s, 866w, 722w, 683w, 666w; MS (EI 70eV), *m*/*z* (%): 1072.5 (M$^+$, 4), 537.2

((^{But}MesNacnac)Sn$^+$, 100), 202.1 (MesNCBu^t $^+$, 81); anal. calc. for $C_{58}H_{82}N_4Sn_2$ C 64.94%, H 7.70%, N 5.22%; found C 64.83%, H 7.72%, N 5.28%.

Synthesis of [{C(Bu^t)C(H)C(Bu^t)N(Mes)}Ge(μ-NMes)Mg(^{Mes}Nacnac)] 8: A solution of [{(^{Mes}Nacnac)Mg}$_2$] (0.34 g, 0.48 mmol) in toluene (20 cm^3) was added over 5 min to a solution of [(^{But}MesNacnac)GeCl] (0.25 g, 0.48 mmol) in toluene (20 cm^3) at -78 °C. Upon addition, the reaction solution immediately turned to a wine-red colour. The mixture was warmed slowly to 0 °C and stirred at that temperature for 2 hrs. All volatiles were subsequently removed *in vacuo*, the residue extracted with cold hexane (10 cm^3), and the extract filtered. Storage of the filtrate at -30 °C overnight yielded small red crystals of **8** (yield 0.26 g, 65 %). M.p. 135-140 °C (decomp.); ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 0.84 (s, 9H, C(C*H*$_3$)$_3$), 1.47 (s, 9H, C(C*H*$_3$)$_3$), 1.55 (s, 6H, NC(C*H*$_3$)), 1.58 (s, 6H, Ar-C*H*$_3$), 1.85 (s, 6H, Ar-C*H*$_3$), 2.06 (s, 12H, *o*-C*H*$_3$), 2.19 (s, 3H, *p*-C*H*$_3$), 2.22 (s, 6H, Ar-C*H*$_3$), 2.30 (s, 3H, *p*-C*H*$_3$), 4.85 (s, 1H, NCC*H*CN), 6.60 (s, 2H, Ar-*H*), 6.64 (s, 2H, Ar-*H*), 6.76 (s, 4H, Ar-*H*), 6.97 (s, 1H, NC(Bu^t)*H*C(Bu^t)); ^{13}C{^{1}H} NMR (400 MHz, C_6D_6, 300K): δ 18.8 (NC*C*H$_3$), 19.0, 21.0, 21.1, 21.7, 23.3, 28.9 (Ar-*C*H$_3$), 29.5, 33.3 (C(*C*H$_3$)$_3$), 38.8, 40.4 (*C*(CH$_3$)$_3$), 95.3 (NC*C*CN), 123.7 (NC*C*), 125.1, 128.5, 128.6, 129.0, 129.5, 130.3, 131.1, 132.5, 133.4, 134.2, 143.1, 144.9 (Ar-*C*), 154.3 (N*C*C), 169.5 (MgN(Mes)*C*), Ge*C*C not observed; IR *ν*/cm^{-1} (Nujol): 1377s, 1260s, 854w, 722w, 684w; MS (EI 70eV), *m*/*z* (%): 334.3 (^{Mes}NacnacH$^+$, 80), 286.2 (MesNC(Bu^t)C(H)C(Bu^t)$^+$, 100). Due to the extremely air sensitive nature of this compound, reproducible microanalyses could not be obtained.

Synthesis of [(^{But}MesNacnac)$_2$Pb] and [{(^{Mes}Nacnac)MgCl}$_2${(^{But}MesNacnac)PbCl}$_2$]: A solution of [{(^{Mes}Nacnac)Mg}$_2$] (0.163 g, 0.23 mmol) dissolved in 20 cm^3 of toluene was added to a solution of [(^{But}MesNacnac)PbCl] (0.300 g, 0.45 mmol) in toluene (20 cm^3) at -80 °C, yielding a dark green solution. This was subsequently warmed to 0 °C, with the deposition of lead metal at *ca.* -30 °C, to give a red-orange solution. Volatiles were then removed from the reaction solution *in vacuo*, the residue extracted with cold hexane, and the extract filtered. Placing the filtrate at -30 °C overnight afforded yellow crystals of [{(^{Mes}Nacnac)MgCl}$_2${(^{But}MesNacnac)PbCl}$_2$] (yield 0.057 g, 12 % based on [(^{But}MesNacnac)PbCl]). Placing the mother liquor at -80 °C for 2 weeks gave orange crystals of [(^{But}MesNacnac)$_2$Pb] (yield 0.032 g, 7% based on [(^{But}MesNacnac)PbCl]). Data for [(^{But}MesNacnac)$_2$Pb]: M.p. 116-118 °C (decomp); ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 1.08 (s, 36H, C(C*H*$_3$)$_3$), 2.20 (s, 12H, *p*-C*H*$_3$), 2.23 (s, 24H, *o*-C*H*$_3$), 5.52 (s, 2H, NCC*H*CN), 6.64 (s, 8H, Ar-*H*); ^{13}C{^{1}H} NMR (400 MHz, C_6D_6, 300K): δ 20.5, 20.7 (*o*-*C*H$_3$ and *p*-*C*H$_3$), 31.5 (C(*C*H$_3$)$_3$), 44.6 (*C*(CH$_3$)$_3$), 95.6 (NC*C*HCN), 128.9, 130.9, 132.1, 146.0 (Ar-*C*), 171.7 (N*C*CH); IR *ν*/cm^{-1} (Nujol): 1614m, 1376s, 1260s, 1113m, 852w, 800m; MS (EI 70eV), *m*/*z* (%): 1042.2 (M$^+$, 6), 625.3

(M^+-^{But}MesNacnac, 10), 417.3 (^{But}MesNacnac$^+$, 70), 202.1 (MesNCBu^{t+}, 100). Data for [{(^{Mes}Nacnac)MgCl}$_2${(^{But}MesNacnac)PbCl}$_2$]: M.p. 170-174 °C (decomp.); Solution NMR spectroscopic data for the compound could not be reliably assigned due the poor solubility of the crystalline compound in non-coordinating solvents and the broadness and complexity of the signals in its NMR spectra. IR ν/cm^{-1} (Nujol): 1376s, 1260s, 799s, 721w, 670w, 667w; MS (EI 70eV), *m*/*z* (%): 417.3 (^{But}MesNacnac$^+$, 25), 334.2 (^{Mes}NacnacH$^+$, 32).

Synthesis of [(^{But}Nacnac)PbCl]: A 1.6 M solution of *n*-butyllithium in hexane (1.6 cm^3, 2.60 mmol) was added to a solution of ^{But}NacnacH (1.19 g, 2.38 mmol) in THF (20 cm^3) at -80 °C, and the reaction mixture subsequently warmed to room temperature. This solution was then slowly added to a suspension of $PbCl_2$ (0.662 g, 2.38 mmol) in THF (20 cm^3) at -80 °C. The resultant mixture was warmed to room temperature slowly and stirred overnight. All volatiles were subsequently removed *in vacuo*, and the yellow residue was extracted into hexane (10 cm^3). The extract was filtered, and the filtrate left to stand at room temperature for 2 days to give yellow crystals of [(^{But}Nacnac)PbCl] (yield 0.52 g, 30%); M.p. 218-224 °C (decomp.); ^{1}H NMR (400 MHz, C_6D_6, 298 K) 0.98 (d, 6H, $^3J_{HH}$= 6.8 Hz, CH(C*H*$_3$)$_2$), 1.21 (s, 18H, C(C*H*$_3$)$_3$), 1.22 (d, 6H, $^3J_{HH}$= 6.8 Hz, CH(C*H*$_3$)$_2$), 1.32 (d, 6H, $^3J_{HH}$= 6.8 Hz, CH(C*H*$_3$)$_2$), 1.46 (d, 6H, $^3J_{HH}$= 6.8 Hz, CH(C*H*$_3$)$_2$), 3.13 (sept, 2H, $^3J_{HH}$= 6.8 Hz, C*H*(CH$_3$)$_2$), 4.07 (sept, 2H, $^3J_{HH}$= 6.8 Hz, C*H*(CH$_3$)$_2$), 5.89 (s, 1H, NCC*H*CN), 6.94-7.04 (m, 6H, Ar-*H*); ^{13}C NMR (400 MHz, C_6D_6, 300K): δ 23.8 (CH(*C*H$_3$)$_2$), 24.2 (CH(*C*H$_3$)$_2$), 26.8 (*C*H(CH$_3$)$_2$), 27.4 (CH(*C*H$_3$)$_2$), 27.8 (CH(*C*H$_3$)$_2$), 29.5 (*C*H(CH$_3$)$_2$), 32.4 (C(*C*H$_3$)$_3$), 43.8 (*C*(CH$_3$)$_3$), 108.3 (NC*C*HCN), 123.7 (Ar-*C*), 125.0 (Ar-*C*), 126.0 (Ar-*C*), 143.0 (Ar-*C*), 143.8 (Ar-*C*), 143.9 (Ar-*C*), 173.2 (N*C*CH); IR ν/cm^{-1} (Nujol): 1619w, 1376s, 1260s, 799s, 721m; MS (EI 70eV), *m*/*z* (%): 744.3 (M^+, 23), 244.1 (DipNCCBu^{t}H$^+$, 100); anal. calc. for $C_{35}H_{53}N_2PbCl$: C 56.47%, H 7.18%, N 3.76%; found: C 56.58%, H 7.23%, N 3.79%.

N.B. The reduction of [(^{But}Nacnac)PbCl] with half an equivalent of [{(^{Mes}Nacnac)Mg}$_2$] in toluene at -80 °C led to the deposition of lead metal upon warming to room temperature, and a complex mixture of unidentified products, as determined by an ^{1}H NMR spectroscopic analysis of the total reaction solution.

2. X-Ray Crystallography

Crystals of **7**·(hexane)$_{0.5}$, **8**, [(^{But}MesNacnac)$_2$Pb]·(hexane) **1S**·(hexane), [{(^{Mes}Nacnac)MgCl}$_2${(^{But}MesNacnac)PbCl}$_2$]·(hexane) **2S**·(hexane), and [(^{But}Nacnac)PbCl] **3S** suitable for X-ray structural determination were mounted in silicone oil. Crystallographic measurements for **7** and **8** were made using the MX1 beamline of the Australian Synchrotron (λ = 0.71069 Å). The software package Blu-Ice[4] was used for data acquisition, while the program XDS[5]

was employed for data reduction. Crystallographic measurements for **1S**, **2S** and **3S** were made using an Oxford Gemini Ultra diffractometer 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)[6] using all unique data. All non-hydrogen atoms are anisotropic with hydrogen atoms included in calculated positions (riding model). Crystal data, details of data collections and refinements for all structures can be found in their CIF files and are summarized in Table S1.

Table S1. Summary of Crystallographic Data for Compounds **7**·(hexane)$_{0.5}$, **8**, **1S**·(hexane), **2S**·(hexane) and **3S**.

	7·(hexane)$_{0.5}$	**8**	**1S**·(hexane)	**2S**·(hexane)	**3S**
empirical formula	$C_{61}H_{89}N_4Sn_2$	$C_{52}H_{70}GeMgN_4$	$C_{64}H_{96}N_4Pb$	$C_{110}H_{154}Cl_4Mg_2N_8Pb_2$	$C_{35}H_{53}ClN_2Pb$
formula weight	1115.74	848.02	1128.64	2193.21	744.43
crystal system	triclinic	monoclinic	triclinic	monoclinic	monoclinic
space group	*P*-1	$P2_1/c$	*P*-1	$P2_1/c$	$P2_1/c$
a (Å)	11.094(2)	20.546(4)	11.6557(4)	14.0924(5)	16.5359(4)
b (Å)	11.584(2)	12.171(2)	12.1595(4)	28.9325(9)	10.6225(2)
c (Å)	22.708(5)	19.870(4)	22.2271(8)	27.2581(13)	19.5757(5)
α (deg.)	94.78(3)	90	74.160(3)	90	90
β (deg)	98.11(3)	105.60(3)	76.098(3)	95.860(4)	100.726(2)
γ (deg.)	101.14(3)	90	86.034(2)	90	90
vol (Å^3)	2816.2(10)	4785.8(17)	2941.78(18)	11055.8(7)	3378.45(13)
Z	2	4	2	4	4
ρ (calcd) (g.cm^{-3})	1.316	1.177	1.274	1.318	1.464
μ (mm^{-1})	0.927	0.691	2.908	3.197	5.097
F(000)	1166	1816	1180	4504	1504
T (K)	100(2)	100(2)	123(2)	123(2)	123(2)
reflections collected	48811	82740	19383	65659	22710
unique reflections	12819	12014	10856	19435	7372
R_{int}	0.0178	0.0382	0.0432	0.1289	0.0277
R1 indices [$I>2\sigma(I)$]	0.0330	0.0414	0.0403	0.0585	0.0228
*w*R2 indices (all data)	0.0905	0.1078	0.0842	0.1102	0.0487
CCDC No.	859478	859474	859475	859477	859476

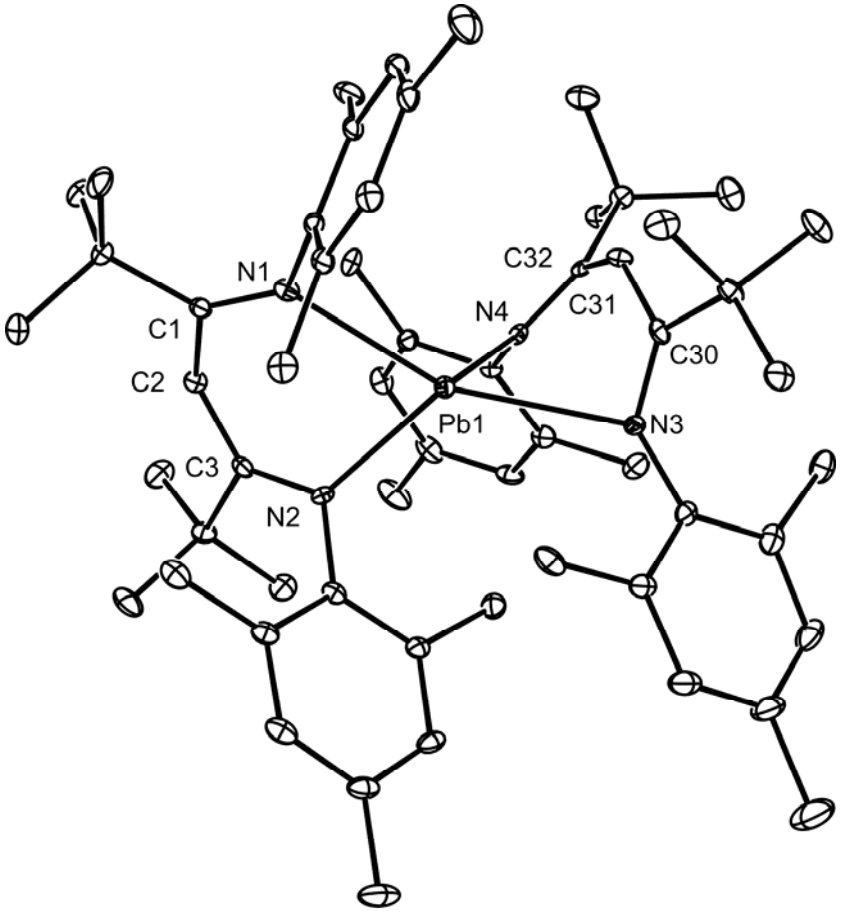

Fig. S1 Molecular structure of [(^{But}MesNacnac)$_2$Pb] **1S** (25% thermal ellipsoids; hydrogen atoms omitted). Selected bond lengths (Å) and angles (º): Pb(1)-N(2) 2.367(3), Pb(1)-N(4) 2.428(4), Pb(1)-N(1) 2.511(4), Pb(1)-N(3) 2.619(4), N(1)-C(1) 1.312(5), N(2)-C(3) 1.372(6), N(3)-C(30) 1.317(6), N(4)-C(32) 1.315(5), C(1)-C(2) 1.444(6), C(2)-C(3) 1.370(6), C(30)-C(31) 1.415(6), C(31)-C(32) 1.428(6), N(2)-Pb(1)-N(1) 76.77(12), N(4)-Pb(1)-N(3) 73.90(11).

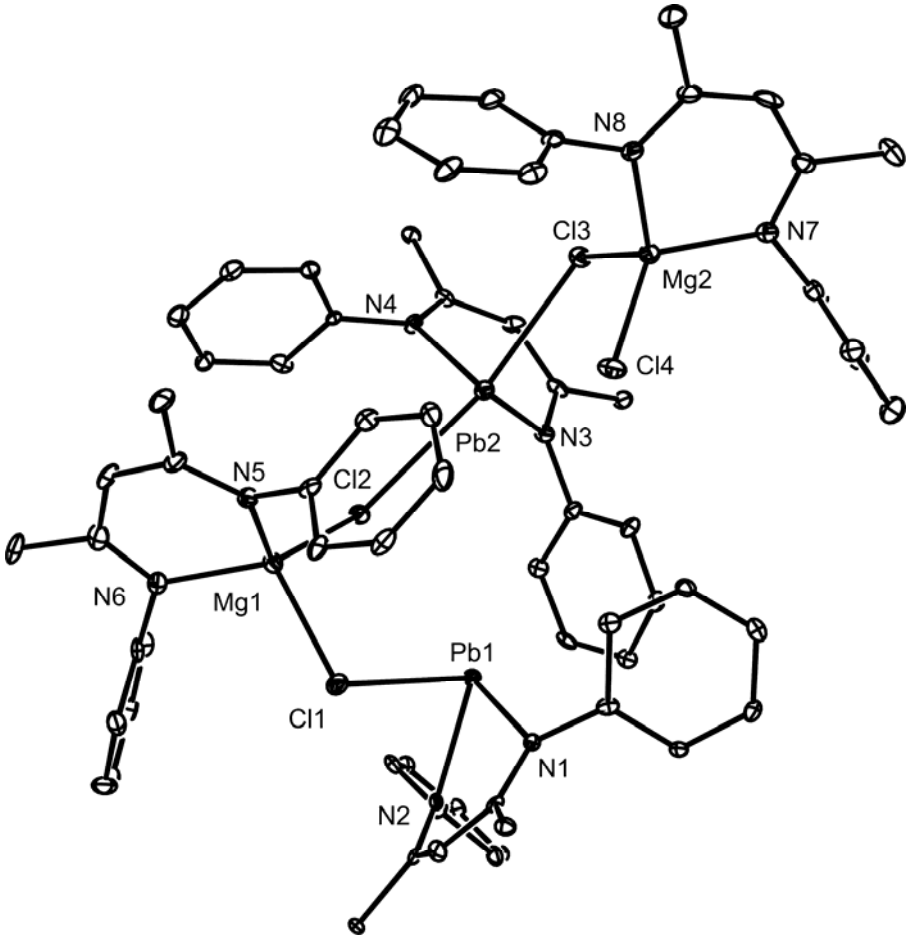

Fig. S2 Molecular structure of [{(^{Mes}Nacnac)MgCl}$_2${(^{But}MesNacnac)PbCl}$_2$] **2S** (25% thermal ellipsoids; hydrogen atoms, mesityl methyl groups, and *tert*-butyl methyl groups omitted). Selected bond lengths (Å) and angles (º): Pb(1)-N(1) 2.277(6), Pb(1)-N(2) 2.287(6), Pb(1)-Cl(1) 2.739(2), Cl(1)-Mg(1) 2.339(3), Mg(1)-N(6) 2.016(7), Mg(1)-N(5) 2.022(7), Mg(1)-Cl(2) 2.331(3), Pb(2)-N(3) 2.258(6), Pb(2)-N(4) 2.306(6), Pb(2)-Cl(3) 2.825(2), Pb(2)-Cl(2) 3.023(2), Mg(2)-N(8) 2.018(7), Mg(2)-N(7) 2.020(8), Mg(2)-Cl(4) 2.288(3), Mg(2)-Cl(3) 2.359(3), N(1)-Pb(1)-N(2) 82.2(2), Mg(1)-Cl(1)-Pb(1) 105.35(10), N(6)-Mg(1)-N(5) 94.2(3), N(3)-Pb(2)-N(4) 82.9(2), Cl(3)-Pb(2)-Cl(2) 170.41(6), Mg(1)-Cl(2)-Pb(2) 130.97(10), N(8)-Mg(2)-N(7) 4.7(3), Mg(2)-Cl(3)-Pb(2) 104.66(9).

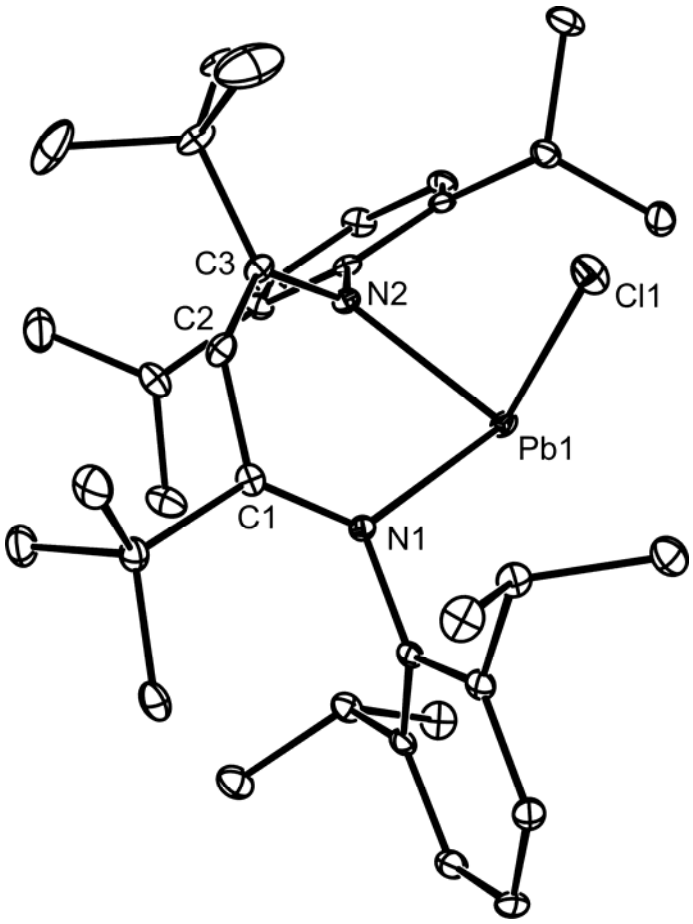

Fig. S3 Molecular structure of [(^{But}Nacnac)PbCl] **3S** (25% thermal ellipsoids; hydrogen atoms omitted). Selected bond lengths (Å) and angles (º): Pb(1)-N(2) 2.241(2), Pb(1)-N(1) 2.309(2), Pb(1)-Cl(1) 2.5637(9), N(1)-C(1) 1.316(4), N(2)-C(3) 1.353(4), C(1)-C(2) 1.424(4), C(2)-C(3) 1.395(4), N(2)-Pb(1)-N(1) 85.52(8), N(2)-Pb(1)-Cl(1) 93.34(6), N(1)-Pb(1)-Cl(1) 94.18(6).

3. Computational Studies

For quantum-chemical calculations the Turbomole[7] (version 5.9) program package was used, employing the Becke-Perdew 86-functional[8] at RI-DFT[9] level with the def2-SVP basis set[10] for non-metal atoms and the def2-TZVPP basis set[11] for Ge and Sn atoms. The molecular orbitals of the global minimum energy structure of **7** (showing zero imaginary frequencies) in the main text were visualized with the aid of molden.[12] NBO orbital analyses were performed using the program package Gaussian09[13] and NBO 3.0[14] at the very same combination of functional and basis sets as above.

Table S2. Cartesian coordinates for the calculated structure of **7**.

Sn	0.40700	-1.35000	-0.65900
N	0.49300	-2.66500	1.27700
N	-1.82700	-1.96300	-0.60100
H	3.08500	-1.18600	0.40300
C	-0.51100	-2.53900	2.17300
C	1.54300	-3.62600	1.30400
C	-2.50000	-2.13700	0.54400
C	-2.26200	-2.14800	-1.95500
C	3.24700	-1.71900	1.37100
C	-0.30800	-2.76900	3.72300
C	-1.82100	-2.12400	1.80800
C	1.27100	-5.02400	1.24400
C	2.90200	-3.18600	1.27400
C	-4.05300	-2.40900	0.58100
C	-2.08400	-3.41700	-2.58800
C	-2.66600	-1.03000	-2.73800
H	4.32000	-1.58100	1.62500
H	2.63900	-1.19000	2.14000
C	-1.34600	-3.76400	4.30200
C	1.09400	-3.26500	4.13900
C	-0.50500	-1.38300	4.40400
H	-2.48200	-1.99700	2.66800
C	2.34800	-5.93000	1.15100
C	-0.13000	-5.59400	1.29100
C	3.93700	-4.13100	1.18800
C	-4.64400	-2.32200	2.01100
C	-4.33900	-3.84200	0.06400
C	-4.84700	-1.39400	-0.27900
C	-2.43900	-3.56200	-3.94000
C	-1.44800	-4.57200	-1.85500
C	-3.00300	-1.23200	-4.09300
C	-2.74500	0.37000	-2.17400
H	-1.25800	-4.76400	3.82500
H	-2.39300	-3.41800	4.17300
H	-1.17100	-3.89300	5.39400
H	1.15100	-3.26400	5.25100
H	1.90100	-2.60200	3.76600
H	1.31000	-4.29500	3.79300
H	-1.53200	-0.98300	4.26700
H	0.21100	-0.63100	4.00000
H	-0.32400	-1.47500	5.49900
H	2.11900	-7.01000	1.09900
C	3.68900	-5.51700	1.11900
H	-0.25500	-6.39500	0.52900

H	-0.90700	-4.82600	1.11400
H	-0.34000	-6.06200	2.28100
H	4.98000	-3.76900	1.18500
H	-5.74300	-2.48000	1.95000
H	-4.48100	-1.32400	2.47400
H	-4.24000	-3.10000	2.69200
H	-3.77500	-4.60200	0.65000
H	-4.08400	-3.95600	-1.01000
H	-5.42400	-4.06500	0.17500
H	-4.63600	-1.50400	-1.36000
H	-4.62200	-0.34800	0.02200
H	-5.93700	-1.56800	-0.13400
H	-2.30700	-4.55100	-4.41300
C	-2.92200	-2.48800	-4.71500
H	-2.00600	-4.86100	-0.94000
H	-0.41600	-4.30400	-1.52600
H	-1.37800	-5.46600	-2.51000
H	-3.33400	-0.35900	-4.68500
H	-3.79700	0.70700	-2.04200
H	-2.26500	1.09500	-2.86600
H	-2.25200	0.45900	-1.18400
C	4.82600	-6.50800	0.99600
C	-3.32200	-2.68800	-6.16000
H	4.48000	-7.55000	1.16600
H	5.63600	-6.29400	1.72900
H	5.29000	-6.47300	-0.01700
H	-2.57600	-3.30300	-6.71100
H	-3.42700	-1.71900	-6.69300
H	-4.29900	-3.21900	-6.24100
Sn	0.73100	1.29300	1.16100
N	-0.72300	3.08800	0.85100
N	2.03300	2.47900	-0.42800
H	-1.87100	0.60000	2.36400
C	-0.07500	4.26800	1.06000
C	-2.10800	2.98000	0.56900
C	2.11200	3.79800	-0.27400
C	2.80400	1.63400	-1.27900
C	-2.42200	1.53100	2.64500
C	-0.69800	5.45400	1.90000
C	1.26100	4.48400	0.66500
C	-2.96800	2.22800	1.42300
C	-2.65100	3.59000	-0.60000
C	3.08300	4.76100	-1.05800
C	4.03600	1.09900	-0.80400
C	2.29100	1.22500	-2.54000
H	-3.24100	1.22300	3.33100
H	-1.71200	2.17000	3.21500
C	-2.19000	5.30800	2.27300
C	0.09500	5.47600	3.24100
C	-0.53900	6.82600	1.19700
H	1.64600	5.46900	0.94900
C	-4.34400	2.17400	1.13900
C	-4.03600	3.50200	-0.84200
C	-1.76400	4.31700	-1.58500
C	2.22400	5.83200	-1.78600
C	4.02700	5.46600	-0.04400
C	3.98300	4.11500	-2.13600
C	4.74800	0.20700	-1.62800
C	4.60400	1.50800	0.53800
C	3.04300	0.32800	-3.32300
C	0.96800	1.75300	-3.03600
H	-2.39500	4.37000	2.82600
H	-2.86100	5.34200	1.39200

H	-2.46600	6.15300	2.94200
H	-0.31300	6.27000	3.90800
H	1.17600	5.67600	3.08900
H	0.00400	4.50000	3.76800
H	-1.05400	6.84000	0.21200
H	0.52100	7.11200	1.03200
H	-0.99700	7.62300	1.82500
H	-5.00300	1.62700	1.83700
C	-4.91000	2.81400	0.01800
H	-4.44500	3.98900	-1.74600
H	-1.48300	5.33700	-1.23700
H	-2.27500	4.43300	-2.56500
H	-0.81200	3.76900	-1.74100
H	2.88700	6.53200	-2.34300
H	1.60400	6.42900	-1.08600
H	1.53800	5.35700	-2.52200
H	4.63400	4.72900	0.52500
H	3.48400	6.09700	0.69000
H	4.73000	6.13000	-0.59600
H	4.56700	4.92600	-2.62800
H	3.40200	3.60000	-2.92700
H	4.70900	3.38900	-1.72200
H	5.70700	-0.19800	-1.25700
C	4.28000	-0.19000	-2.89600
H	5.39300	0.80000	0.86800
H	3.82200	1.55600	1.32900
H	5.06900	2.52100	0.49600
H	2.63800	0.01700	-4.30200
H	0.16200	1.57500	-2.28800
H	0.67300	1.26700	-3.99000
H	0.99900	2.85400	-3.20900
C	-6.39600	2.73000	-0.26000
C	5.08200	-1.13400	-3.76400
H	-6.68600	1.72100	-0.63600
H	-6.71100	3.47200	-1.02400
H	-6.99500	2.91300	0.66000
H	5.92300	-0.60600	-4.27200
H	4.45300	-1.59400	-4.55600
H	5.53100	-1.95800	-3.16600

Table S3. Cartesian coordinates for the calculated structure of **8**.

Ge	-1.13900	-0.44900	-0.74800
N	-0.46500	-1.25300	-2.53200
C	-2.55000	-1.85500	-0.93100
N	0.25300	-0.51700	0.51400
C	-1.39800	-2.03500	-3.09000
C	0.79300	-0.85000	-3.08000
C	-2.51800	-2.33900	-2.22600
C	-3.81700	-1.98800	-0.07100
Mg	0.19400	1.24900	1.42900
C	1.26100	-1.48200	0.70300
C	-1.48300	-2.52500	-4.56200
C	0.94500	0.44900	-3.63400
C	1.90300	-1.73300	-2.98800
H	-3.36700	-2.89500	-2.66100
C	-5.04300	-1.39100	-0.81400
C	-4.08700	-3.49000	0.21300
C	-3.66100	-1.24400	1.27300
N	0.12400	3.29300	1.12000
N	0.23500	1.35600	3.48700

H	2.78200	1.04100	0.77200
H	2.35700	0.55700	-0.90700
C	2.62700	-1.12400	0.45600
C	1.00300	-2.80000	1.20600
C	-1.66400	-4.06700	-4.55800
C	-2.73600	-1.86600	-5.21100
C	-0.27800	-2.19400	-5.46900
C	2.21600	0.83400	-4.10400
C	-0.22500	1.39800	-3.75400
C	3.15100	-1.29400	-3.47000
C	1.75500	-3.12300	-2.41700
H	-5.95500	-1.45900	-0.17800
H	-5.25300	-1.92900	-1.76500
H	-4.87100	-0.32000	-1.06100
H	-3.24500	-3.95400	0.77000
H	-4.22800	-4.06300	-0.73000
H	-5.01000	-3.60500	0.82500
H	-2.77500	-1.60100	1.83800
H	-4.56200	-1.38900	1.91100
H	-3.54100	-0.15000	1.10400
C	0.24900	4.15800	2.15100
C	-0.13200	3.84300	-0.18300
C	0.39300	2.51900	4.14000
C	0.04400	0.15100	4.24200
C	2.96400	0.26800	-0.02100
C	3.65900	-2.05900	0.66500
C	2.06600	-3.70200	1.39300
C	-0.39800	-3.20100	1.58000
H	-0.77900	-4.57300	-4.11300
H	-1.77700	-4.43300	-5.60300
H	-2.56100	-4.39100	-3.98900
H	-3.67800	-2.13600	-4.68900
H	-2.82700	-2.19800	-6.27000
H	-2.65000	-0.75700	-5.20800
H	-0.10600	-1.10300	-5.56900
H	-0.48600	-2.59600	-6.48600
H	0.66600	-2.65300	-5.11300
H	2.32900	1.84000	-4.54500
C	3.33500	-0.01800	-4.03500
H	-0.52800	1.81000	-2.76600
H	-1.12600	0.89500	-4.17000
H	0.02900	2.25500	-4.41200
H	4.01200	-1.98100	-3.39400
H	1.20700	-3.79900	-3.11400
H	1.19000	-3.11600	-1.46100
H	2.74800	-3.57600	-2.22100
C	0.15000	5.65300	1.87700
C	0.44000	3.79000	3.50700
C	-1.47300	3.97400	-0.63600
C	0.94500	4.25200	-1.01800
C	0.51300	2.50900	5.65600
C	-1.27200	-0.21500	4.63800
C	1.14400	-0.69100	4.55000
H	4.03900	0.35500	-0.28800
H	4.70100	-1.75400	0.45600
C	3.40700	-3.36500	1.12400
H	1.83300	-4.71100	1.78100
H	-1.09400	-3.11000	0.71500
H	-0.79700	-2.53400	2.37800
H	-0.43300	-4.24800	1.95200
C	4.68100	0.41000	-4.57800
H	0.89300	5.98400	1.12000
H	0.30100	6.24300	2.80300

H	-0.84900	5.90800	1.45800
H	0.57400	4.63700	4.19500
C	-1.71200	4.53700	-1.90500
C	-2.62500	3.50700	0.22400
C	0.65200	4.81400	-2.27500
C	2.38200	4.08500	-0.57600
H	-0.41400	2.11600	6.12700
H	0.70600	3.52500	6.05500
H	1.33400	1.83500	5.98400
C	-1.46000	-1.42100	5.34100
C	-2.44900	0.67500	4.30800
C	0.90400	-1.88400	5.25900
C	2.54600	-0.33400	4.11100
C	4.52300	-4.36900	1.32700
H	5.51800	-0.01900	-3.98400
H	4.79100	1.51600	-4.57800
H	4.82200	0.06700	-5.63100
H	-2.75600	4.63800	-2.24900
C	-0.66800	4.97800	-2.73800
H	-3.60000	3.78800	-0.22800
H	-2.58500	3.92900	1.25200
H	-2.61700	2.39500	0.32600
H	1.49200	5.13800	-2.91500
H	3.07600	4.57400	-1.29200
H	2.66500	3.01000	-0.51900
H	2.57300	4.51400	0.43200
H	-2.48400	-1.70000	5.64700
C	-0.38700	-2.27300	5.66300
H	-3.40700	0.19800	4.60500
H	-2.50200	0.89500	3.21800
H	-2.38900	1.66300	4.82000
H	1.76300	-2.53400	5.50200
H	3.30000	-0.93200	4.66600
H	2.77700	0.74300	4.26300
H	2.69200	-0.55700	3.02700
H	5.52000	-3.91200	1.14800
H	4.42800	-5.23900	0.63600
H	4.52300	-4.78300	2.36100
C	-0.95000	5.62800	-4.07600
C	-0.61600	-3.58200	6.38900
H	-0.91200	6.74000	-4.00300
H	-1.95800	5.35800	-4.45700
H	-0.20200	5.32900	-4.84400
H	-0.72200	-4.42900	5.67200
H	-1.54400	-3.55400	7.00100
H	0.23200	-3.83100	7.06300

Table S4. Cartesian coordinates for the calculated structure of [(^{But}MesNacnac)Sn]·

Sn	-0.00300	-1.32100	0.18400
N	-1.56800	0.37900	0.04700
N	1.56600	0.37600	0.04100
H	-1.82000	-0.52700	2.63000
C	-1.31900	1.69400	0.02100
C	-2.80300	-0.33200	-0.02000
C	1.32100	1.69000	0.01500
C	2.80100	-0.33700	-0.02100
C	-2.91100	-0.32600	2.53200
C	-2.43900	2.80800	-0.02400
C	0.00200	2.23100	0.04000

C	-3.43400	-0.76400	1.18200
C	-3.29500	-0.76700	-1.28300
C	2.44300	2.80200	-0.03800
C	3.43000	-0.76300	1.18400
C	3.29200	-0.78500	-1.28100
H	-3.43800	-0.85500	3.35400
H	-3.04500	0.76900	2.69300
C	-3.90300	2.31200	-0.06400
C	-2.30800	3.69400	1.24600
C	-2.23600	3.68300	-1.29100
H	0.00300	3.32300	0.03700
C	-4.57500	-1.58300	1.08900
C	-4.44000	-1.58600	-1.31700
C	-2.61500	-0.34300	-2.56300
C	2.23400	3.67400	-1.30800
C	2.32100	3.69300	1.22900
C	3.90600	2.30300	-0.08700
C	4.56900	-1.58600	1.09800
C	2.90300	-0.32100	2.53000
C	4.43400	-1.60700	-1.30800
C	2.60900	-0.37300	-2.56400
H	-4.18300	1.71500	0.82600
H	-4.13000	1.70700	-0.96500
H	-4.56800	3.20400	-0.08700
H	-3.09700	4.47900	1.24000
H	-1.32600	4.20600	1.31700
H	-2.43900	3.08800	2.17000
H	-2.30400	3.06800	-2.21600
H	-1.25700	4.20600	-1.30600
H	-3.03300	4.46000	-1.34200
H	-5.06900	-1.90400	2.02300
C	-5.10000	-2.00700	-0.14700
H	-4.82500	-1.91100	-2.30000
H	-2.70300	0.75500	-2.73900
H	-3.05600	-0.86100	-3.44100
H	-1.52500	-0.57100	-2.53500
H	3.03300	4.44800	-1.36700
H	1.25700	4.19900	-1.31700
H	2.29300	3.05500	-2.23000
H	2.45800	3.09000	2.15400
H	1.34000	4.20700	1.30400
H	3.11200	4.47700	1.21500
H	4.57300	3.19400	-0.11700
H	4.12600	1.69500	-0.98700
H	4.19100	1.70900	0.80400
H	5.05700	-1.90800	2.03400
C	5.09700	-2.01600	-0.13500
H	3.43200	-0.84300	3.35600
H	1.81200	-0.52800	2.62900
H	3.03000	0.77500	2.68700
H	4.81400	-1.94700	-2.28800
H	1.51800	-0.60200	-2.53200
H	3.04900	-0.90000	-3.43700
H	2.69600	0.72200	-2.75000
C	-6.30400	-2.92200	-0.21100
C	6.34000	-2.87600	-0.19700
H	-6.00800	-3.99000	-0.08500
H	-6.82900	-2.84000	-1.18700
H	-7.03700	-2.69200	0.59300
H	7.26500	-2.25300	-0.21500
H	6.35600	-3.50900	-1.11000
H	6.41900	-3.54700	0.68700

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