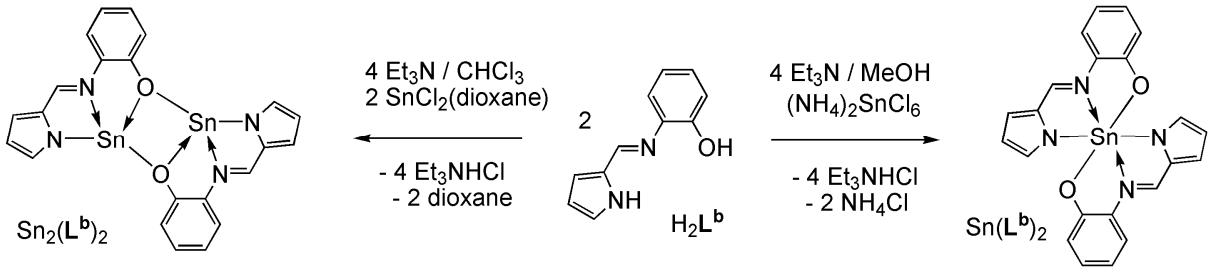
Supporting information material for

Group 10 – group 14 metal complexes [E–TM]^{IV}: The role of the group 14 site as an L, X and Z-type ligand

Erik Wächtler, Robert Gericke, Erica Brendler, Birgit Gerke, Thorsten Langer, Rainer Pöttgen, Lyuben Zhechkov, Thomas Heine and Jörg Wagler*

Table of content:

Synthesis and characterisation of the complexes $Sn_2(\mathbf{L^b})_2$, $Sn(\mathbf{L^b})_2$ and $[Cl_2Sn(\mu\text{-bztzS})_2Ni–PPh_3]$:



Scheme SI1 Synthesis of $Sn_2(\mathbf{L^b})_2$ and $Sn(\mathbf{L^b})_2$.

$Sn_2(\mathbf{L^b})_2$. $SnCl_2$(dioxane) (0.30 g, 1.08 mmol) was layered with chloroform (3 mL) followed by a layer of a chloroform solution (5 mL) of $H_2\mathbf{L^b}$ (0.20 g, 1.08 mmol) and triethylamine (0.30 g, 2.94 mmol). Crystals (suitable for X-ray crystallography) formed upon storage at room temperature, and after 10 d the product was isolated by decantation, washed with chloroform (3 mL) and dried *in vacuo*. Yield: 0.24 g (0.39 mmol, 74%). The compound is basically insoluble in most common organic solvents (such as toluene, THF, chloroform, acetonitrile, DMSO).

MP: not observed (stable up to 250°C).

^{119}Sn MAS NMR (149.17 MHz, ν_{rot}: 14 and 15 kHz): δ = -399 ppm;

^{119}Sn Mössbauer ($Ca^{119m}SnO_3$, 78 K): δ = 2.94(1) mm s^{-1}, Δ = 1.97(1) mm s^{-1}.

Anal. calcd. for $C_{22}H_{16}N_4O_2Sn_2$ (605.81 g mol^{-1}): C 43.62, H 2.66, N 9.25; found: C 43.54, H 2.58, N 9.19%.

$Sn(\mathbf{L^b})_2$. $(NH_4)_2SnCl_6$ (0.49 g, 1.34 mmol), $H_2\mathbf{L^b}$ (0.50 g, 2.69 mmol) and triethylamine (0.56 g, 5.50 mmol) were stirred in methanol (25 mL) at room temperature for 4 h whereby an orange precipitate formed. This was filtered off, washed with methanol (4 mL) and dried *in vacuo*. Yield: 0.39 g (0.75 mmol, 56%). Crystals for X-ray structure determination were obtained by recrystallisation from hot methanol (in this case the product crystallised as methanol solvate with one molecule of methanol per complex molecule).

MP: not observed (stable up to 300°C).

^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 6.31 (m, 1H), 6.77 (m, 1H), 6.83 (m, 1H), 6.90 (m, 1H), 6.98 (m, 1H), 7.10 (m, 1H), 7.40 (m, 1H) (Aryl), 8.68 ppm (s, 1H, *H*C=N, satellites $^3J_{1H\text{-}(117/119)Sn}$ = 108 Hz);

^{13}C{^{1}H} NMR (100.63 MHz, $CDCl_3$): δ = 113.7, 116.6, 117.6, 118.4, 122.3, 127.7, 128.9, 133.0, 136.3 (Aryl), 143.2 (*C*=N), 155.1 ppm (*C*-O);

^{119}Sn{^{1}H} NMR (149.21 MHz, $CDCl_3$): δ = -504.5 ppm;

^{119}Sn Mössbauer ($Ca^{119m}SnO_3$, 78 K): δ = 0.29(1) mm s^{-1}, Δ = 0.43(1) mm s^{-1}.

Anal. calcd. for $C_{22}H_{16}N_4O_2Sn$ (487.10 g mol^{-1}): C 54.25, H 3.31, N 11.50. found: C 54.11, H 3.20, N 11.47%.

$[Ni_2(bztzS)_4]$ was prepared according to a method reported by Ballester et al..[1]

$[Cl_2Sn(\mu\text{-}bztzS)_2NiPPh_3]$. $[Ni_2(bztzS)_4]$ (200 mg, 510 μmol) was layered with THF (3 mL) and thereafter with a THF solution (5 mL) of PPh_3 (140 mg, 550 μmol) and $SnCl_2$(dioxane) (140 mg, 510 μmol). The product formed as a crystalline material (containing X-ray quality crystals) within several days. After 10 d, the supernatant was decanted off and the crystals washed with THF (3 mL) and dried under vacuum. Yield: 240 mg (0.28 mmol, 56%). The compound is insoluble in common organic solvents.

MP: not observed (decomposition > 200°C).

^{31}P MAS NMR (162.02 MHz, ν_{rot}: 10 kHz): δ = 26.0 ppm (satellites: $^2J_{31P\text{-}119Sn}$ = 2842 Hz, $^2J_{31P\text{-}117Sn}$ = 2709 Hz);

^{119}Sn MAS NMR (149.17 MHz, ν_{rot}: 14 and 15 kHz): δ = -470.3 ppm (d);

^{119}Sn Mössbauer ($Ca^{119m}SnO_3$, 78 K): δ = 1.70(1) mm s^{-1}, Δ = 1.67(1) mm s^{-1}.

Anal. calcd. for $C_{32}H_{23}Cl_2N_2NiPS_4Sn$ (843.08 g mol^{-1}): C 45.59, H 2.75, N 3.32; found: C 45.78, H 2.97, N 3.29%.

Molecular structures of the complexes $Sn_2(\mathbf{L}^b)_2$, $Sn(\mathbf{L}^b)_2$, $[Ni_2(bztzS)_4]$, $[Cl_2Sn(\mu\text{-}bztzS)_2NiPPh_3]$ and $O[ClGe(\mu\text{-}pyS)_2PdPPh_3]_2$ in the crystal:

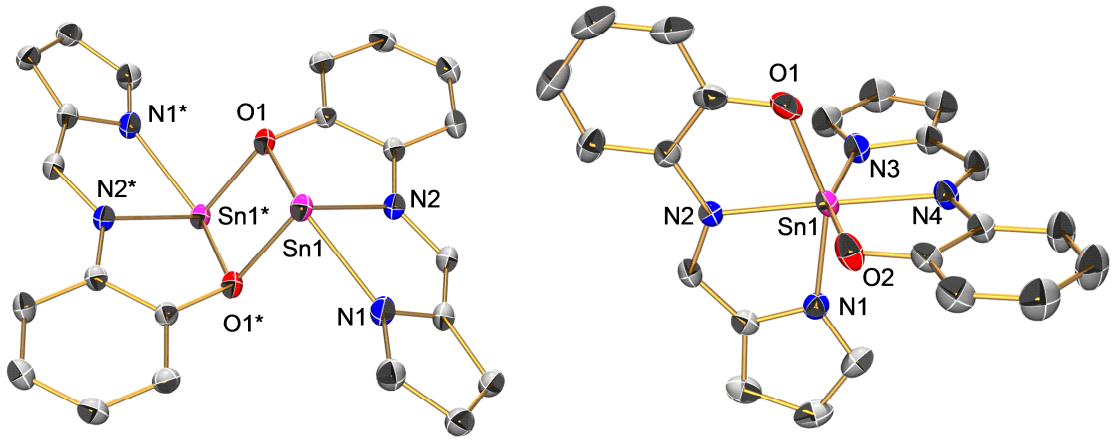


Fig. SI1 Molecular structures of complexes $Sn_2(\mathbf{L}^b)_2$ (left) and $Sn(\mathbf{L}^b)_2$ (right) in the crystal (ellipsoids set at 50% probability, hydrogen atoms are omitted). Selected bond lengths [Å] for $Sn_2(\mathbf{L}^b)_2$: Sn1-O1 2.510(1), Sn1-N1 2.240(1), Sn1-N2 2.234(1), Sn1-O1* 2.153(1), symmetry operation *: -x, 2-y, 1-z; $Sn(\mathbf{L}^b)_2$: Sn1-O1 2.064(1), Sn1-N1 2.142(1), Sn1-N2 2.135(1), Sn1-O2 2.058(1), Sn1-N3 2.124(1), Sn1-N4 2.136(1).

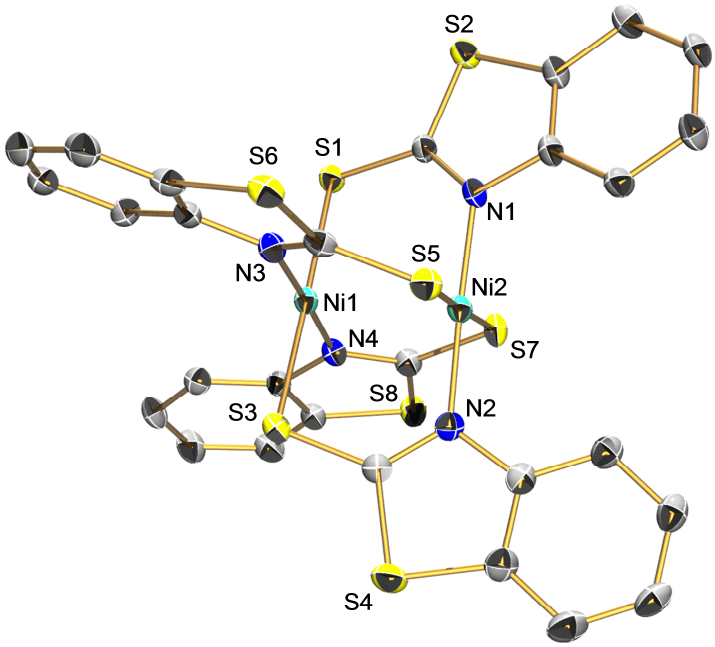


Fig. SI2 Molecular structure of $[Ni_2(bztzS)_4]$ in the crystal (ellipsoids set at 50% probability, hydrogen atoms are omitted). Selected bond lengths [Å]: Ni1-S1 2.227(1), Ni1-S3 2.234(1), Ni1-N3 1.881(3), Ni1-N4 1.879(3), Ni2-S5 2.247(1), Ni2-S7 2.239(1), Ni2-N1 1.900(3), Ni2-N2 1.893(3), Ni1···Ni2 2.5681(6).

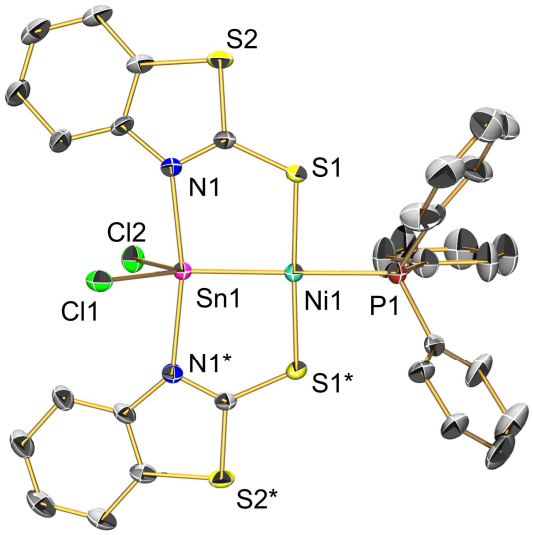


Fig. SI3 Molecular structure of $[Cl_2Sn(\mu\text{-bztzS})_2NiPPh_3]$ in the crystal (ellipsoids set at 50% probability, hydrogen atoms are omitted). Selected bond lengths [Å]: Ni1-Sn1 2.4494(7), Ni1-S1 2.1623(9), Ni1-P1 2.2362(14), Sn1-N1 2.290(3), Sn1-Cl1 2.3814(12), Sn1-Cl2 2.3881(12), symmetry operation *: x, 1-y, z.

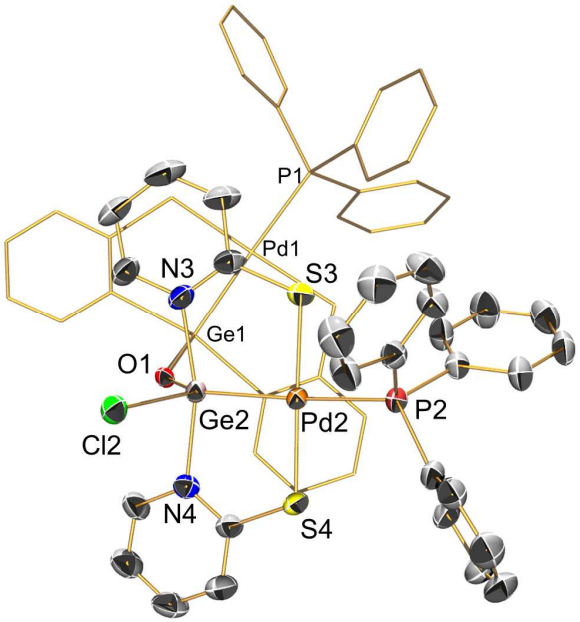


Fig. SI4 Molecular structure of $O[ClGe(\mu\text{-pyS})_2PdPPh_3]_2$ in the crystal (ellipsoids set at 50% probability, hydrogen atoms are omitted). For clarity one part of the molecule is displayed as stick model. Selected bond lengths [Å]: Pd1-Ge1 2.381(2), Pd1-S1 2.302(2), Pd1-S2 2.298(2), Pd1-P1 2.381(2), Ge1-N1 2.192(3), Ge1-N2 2.168(3), Ge1-Cl1 2.286(3), Ge1-O1 1.761(3), Pd2-Ge2 2.3758(4), Pd2-S3 2.298(1), Pd2-S4 2.301(1), Pd2-P2 2.356(1), Ge2-N3 2.154(3), Ge2-N4 2.182(3), Ge2-Cl2 2.230(1), Ge2-O1 1.793(2). (Note: These labels for Pd, Ge, Cl, S, P and O correspond to the labels with disorder group index A in the CIF, e.g., Pd1 = Pd1A, for clarity this index has been omitted in the graphic).

Parameters of data collection and structure refinement for the structures of **2**, **3**, **4**, **9**, **10** · 2 THF, **11** · DCM, **12**, **13** · 2 EtOH · DCM, $Sn_2(\mathbf{L^b})_2$, $Sn(\mathbf{L^b})_2$ · MeOH, $[Ni_2(bztzS)_4]$, $[Cl_2Sn(\mu\text{-}bztzS)_2NiPPh_3]$ and $O[ClGe(\mu\text{-}pyS)_2PdPPh_3]_2$:

Table SI1 Parameters of data collection and structure refinement for the structures of **2**, **3**, **4** and $O[ClGe(\mu\text{-}pyS)_2PdPPh_3]$.

	2	**3**	**4**	$O[ClGe(\mu\text{-}pyS)_2Pd–PPh_3]_2$
Empirical formula	$C_{28}H_{23}Cl_2N_2NiPS_2Sn$	$C_{28}H_{23}Cl_2N_2PPtS_2Sn$	$C_{28}H_{23}Cl_2GeN_2PPdS_2$	$C_{56}H_{46}Cl_2Ge_2N_2OP_2PdS_4$
Formula weight	730.87	867.25	732.46	1410.03
T (K)	200(2)	200(2)	200(2)	200(2)
λ (Å)	0.71073			
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	P-1	P-1	$P2_1/n$
Unit cell dimensions.				
a (Å)	15.6578(4)	8.7609(3)	11.7504(6)	9.5367(2)
b (Å)	16.2539(5)	11.8010(4)	11.9994(6)	22.0550(4)
c (Å)	23.8975(7)	15.1557(6)	12.0861(6)	26.8568(6)
α (°)	90	96.445(3)	60.360(4)	90
β (°)	106.036(2)	93.501(3)	81.827(4)	96.955(2)
γ (°)	90	107.876(3)	75.635(4)	90
V (Å^3)	5845.3(3)	1474.26(9)	1434.44(12)	5607.3(2)
Z / D_c (g cm^{-3})	8 / 1.66	2 / 1.95	2 / 1.70	4 / 1.67
μ (mm^{-1})	1.9	6.0	2.1	2.0
F(000)	2912	828	728	2808
Crystal size (mm)	0.30×0.30×0.05	0.30×0.25×0.20	0.45×0.35×0.20	0.30×0.25×0.20
θ range for data collection	2.5-27.0	1.8-32.0	2.7-32.0	2.4-27.0
Reflections collected	61845	42811	29868	130137
Independent reflections / R(int)	12752 / 0.0460	10237 / 0.0353	9947 / 0.0228	12231 / 0.0670
Completeness to θ_{max}	99.9%	99.9%	99.9%	99.9%
Refinement	Full-matrix least-squares on F^2			
Data / restraints / parameters	12752 / 0 / 667	10237 / 0 / 335	9947 / 0 / 334	12231 / 1 / 712
Goodness-of-fit on F^2	1.025	1.101	1.043	1.042
$R1$ / $wR2$ [$I > 2\sigma(I)$]	0.0255 / 0.0523	0.0262 / 0.0646	0.0212 / 0.0504	0.0373 / 0.0857
$R1$ / $wR2$ (all data)	0.0411 / 0.0568	0.0294 / 0.0661	0.0261 / 0.0522	0.0542 / 0.0916
Largest diff. peak / hole [e Å^{-3}]	0.43 / -0.38	1.26 / -2.02	0.42 / -0.48	0.64 / -0.90

Table SI2 Parameters of data collection and structure refinement for the structures of $[Cl_2Sn(\mu\text{-}bztzS)_2NiPPh_3]$, **9**, **10** · 2 THF, **11** · DCM.

	$[Cl_2Sn(\mu\text{-}bztzS)_2Ni–PPh_3]$[1]	**9**	**10** · 2 THF [2]	**11** · DCM
Empirical formula	$C_{32}H_{23}Cl_2N_2NiPS_4Sn$	$C_{28}H_{41}Cl_2N_2PPdS_2Sn$	$C_{48}H_{48}Cl_8N_8O_2Pd_4S_8Sn_4$	$C_{40}H_{34}Cl_2N_5O_2PPdS_2Sn$
Formula weight	843.03	796.71	2209.38	1007.80
T (K)	150(2)	150(2)	150(2)	150(2)
λ (Å)	0.71073			
Crystal system	Monoclinic	Monoclinic	Tetragonal	Triclinic
Space group	Cm	$P2_1/m$	I-4	P-1
Unit cell dimensions.				
a (Å)	7.8975(3)	8.2710(6)	11.8143(3)	11.5645(4)
b (Å)	17.3839(6)	16.4657(8)	11.8143(3)	12.0423(4)
c (Å)	12.3904(5)	12.0613(8)	24.1508(8)	15.0296(4)
α (°)	90	90	90	80.499(3)
β (°)	107.098(3)	109.724(5)	90	73.274(2)
γ (°)	90	90	90	84.786(3)
V (Å^3)	1625.89(11)	1546.23(17)	3370.9(2)	1974.93(11)
Z / D_c (g cm^{-3})	2 / 1.72	2 / 1.71	2 / 2.18	2 / 1.66
μ (mm^{-1})	1.8	1.8	3.1	1.4
F(000)	840	800	2112	1004
Crystal size (mm)	0.26×0.12×0.11	0.17×0.09×0.04	0.28×0.22×0.18	0.30×0.22×0.18
θ range for data collection	2.3-32.0	2.5-27.0	2.4-30.0	2.4-30.0
Reflections collected	15598	14914	40152	46100
Independent reflections / R(int)	5578 / 0.0335	3492 / 0.0617	4938 / 0.0286	11510 / 0.0252
Completeness to θ_{max}	99.7%	99.9%	99.9%	99.9%
Refinement	Full-matrix least-squares on F^2			
Data / restraints / parameters	5578 / 99 / 235	3492 / 0 / 178	4938 / 28 / 206	11510 / 0 / 448
Goodness-of-fit on F^2	1.066	1.021	1.176	1.022
$R1$ / $wR2$ [$I > 2\sigma(I)$]	0.0271 / 0.0694	0.0303 / 0.0613	0.0183 / 0.0394	0.0217 / 0.0482
$R1$ / $wR2$ (all data)	0.0290 / 0.0705	0.0507 / 0.0665	0.0196 / 0.0400	0.0289 / 0.0501
Largest diff. peak / hole [e Å^{-3}]	0.66 / -1.00	0.71 / -0.60	0.38 / -0.49	0.63 / -0.86

[1] Absolute structure parameter: -0.014(12)
[2] Structure refined as a racemic twin (73% / 27%)

Table SI3 Parameters of data collection and structure refinement for the structures of **12**, **13** · 2 EtOH · DCM, $Sn_2(\mathbf{L^b})_2$, $Sn(\mathbf{L^b})_2$ · MeOH and $[Ni_2(bztzS)_4]$.

	12	**13** · 2 EtOH · DCM	$Sn_2(\mathbf{L^b})_2$	$Sn(\mathbf{L^b})_2$ · MeOH [1]	$[Ni_2(bztzS)_4]$ [2]
Empirical formula	$C_{39}H_{31}N_4OPPdS_2Sn$	$C_{61}H_{62}Cl_4N_4O_4P_2Pd_2S_4Sn_2$	$C_{22}H_{16}N_4O_2Sn_2$	$C_{23}H_{20}N_4O_3Sn$	$C_{28}H_{16}N_4Ni_2S_8$
Formula weight	891.86	1697.31	605.81	519.12	782.35
T (K)	200(2)	150(2)	150(2)	200(2)	100(2)
λ (Å)	0.71073				
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Monoclinic	Orthorhombic
Space group	*Pbca*	*Pbca*	*Pbcn*	$P2_1/c$	*Pbca*
Unit cell dimensions.					
a (Å)	13.2982(3)	16.4638(4)	12.0878(2)	9.3183(2)	14.8803(4)
b (Å)	16.9219(4)	22.8991(5)	10.4438(2)	23.7683(5)	16.4815(4)
c (Å)	32.2817(7)	17.3745(6)	15.6612(3)	10.2246(3)	24.0587(7)
α (°)	90	90	90	90	90
β (°)	90	90	90	106.442(2)	90
γ (°)	90	90	90	90	90
V (Å^3)	7264.4(3)	6550.3(3)	1977.11(6)	2171.94(9)	5900.4(3)
Z / D_c (g cm^{-3})	8 / 1.63	4 / 1.72	4 / 2.04	4 / 1.56	8 / 1.76
μ (mm^{-1})	1.4	1.7	2.6	1.2	1.9
F(000)	3552	3368	1168	1040	3168
Crystal size (mm)	0.25×0.18×0.10	0.35×0.18×0.08	0.35×0.25×0.18	0.25×0.15×0.12	0.25×0.20×0.04
θ range for data collection	2.4-30.0	2.5-28.0	2.6-37.0	1.7-32.0	2.0-25.0
Reflections collected	91301	53202	25040	45224	40361
Independent reflections / R(int)	10588 / 0.0439	7894 / 0.0498	4990 / 0.0279	7517 / 0.0362	5195 / 0.0774
Completeness to θ_{max}	99.9%	99.9%	99.2%	99.7%	100%
Refinement	Full-matrix least-squares on F^2				
Data / restraints / parameters	10588 / 0 / 442	7894 / 1 / 381	4990 / 0 / 136	7517/1 / 301	5195 / 0 / 380
Goodness-of-fit on F^2	1.050	1.050	1.042	1.149	1.011
$R1$ / $wR2$ [$I > 2\sigma(I)$]	0.0237 / 0.0476	0.0344 / 0.0724	0.0222 / 0.0544	0.0278 / 0.0702	0.0364 / 0.0820
$R1$ / $wR2$ (all data)	0.0334 / 0.0502	0.0527 / 0.0779	0.0364 / 0.0579	0.0312 / 0.0719	0.0604 / 0.0883
Largest diff. peak / hole [e Å^{-3}]	0.42 / -0.56	0.97 / -0.94	0.65 / -0.50	0.62 / -0.77	0.65 / -0.48

[1] extinction coefficient: 0.0082(6)
[2] extinction coefficient: 0.0011(1)

^{119}Sn Mössbauer spectra of compounds **2**, **3**, [$Cl_2Sn(\mu$-bztzS)$_2$NiPPh$_3$], **9**, **10**, **11**, **12**, **13**, Sn_2(**L^b**)$_2$ and Sn(**L^b**)$_2$ and parameters of the fitting procedure:

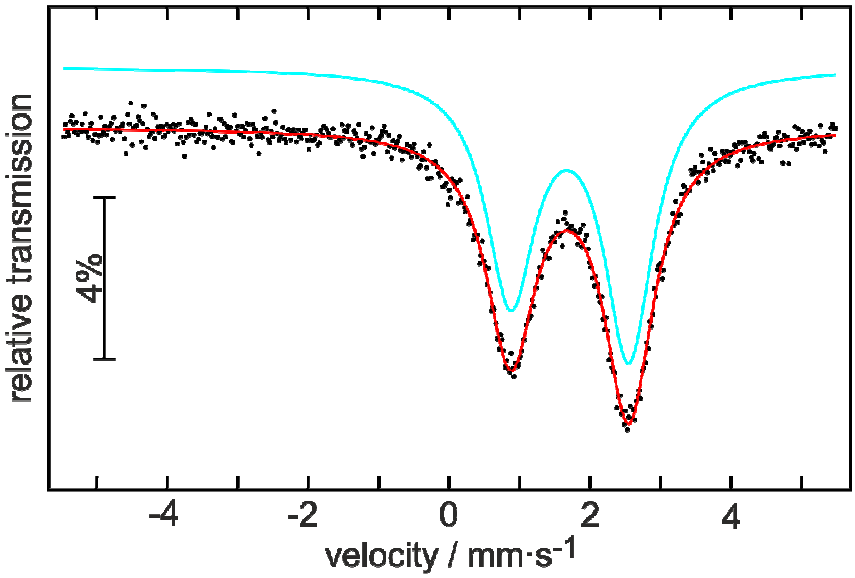


Fig. SI5 ^{119}Sn Mössbauer spectrum of **2** at 78 K.

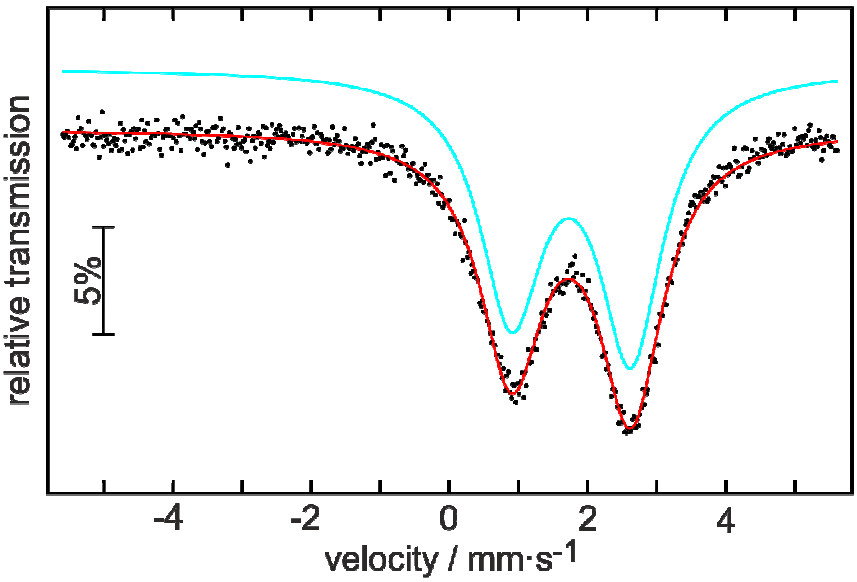


Fig. SI6 ^{119}Sn Mössbauer spectrum of **2** at 5 K.

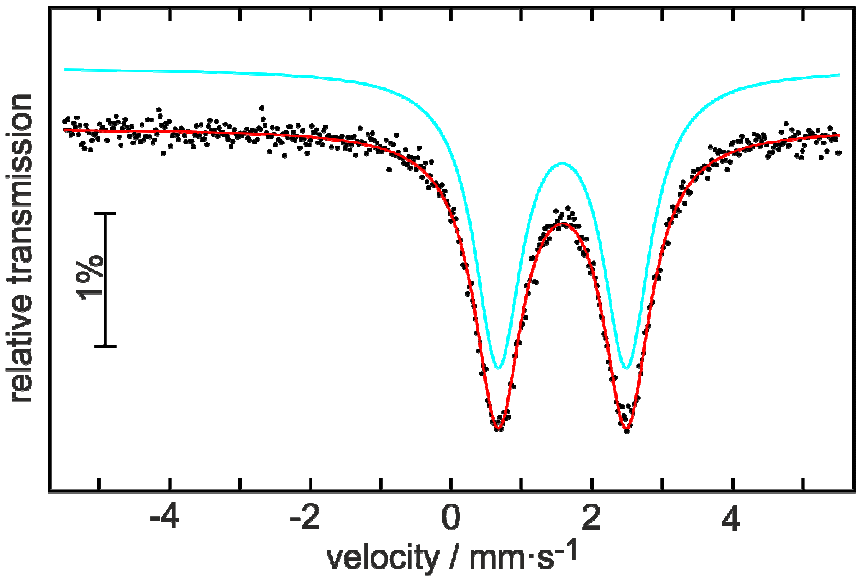


Fig. SI7 ^{119}Sn Mössbauer spectrum of **3** at 78 K.

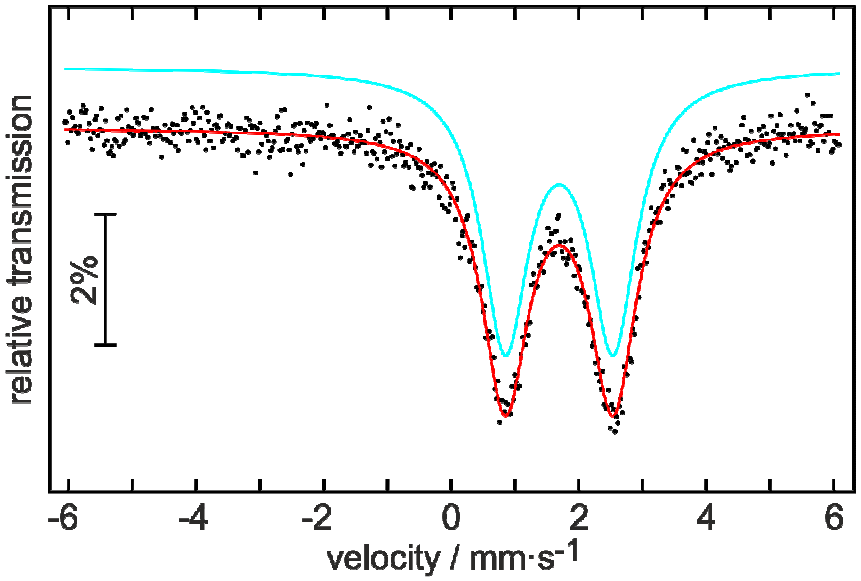


Fig. SI8 ^{119}Sn Mössbauer spectrum of $[Cl_2Sn(\mu\text{-bztzS})_2NiPPh_3]$ at 78 K.

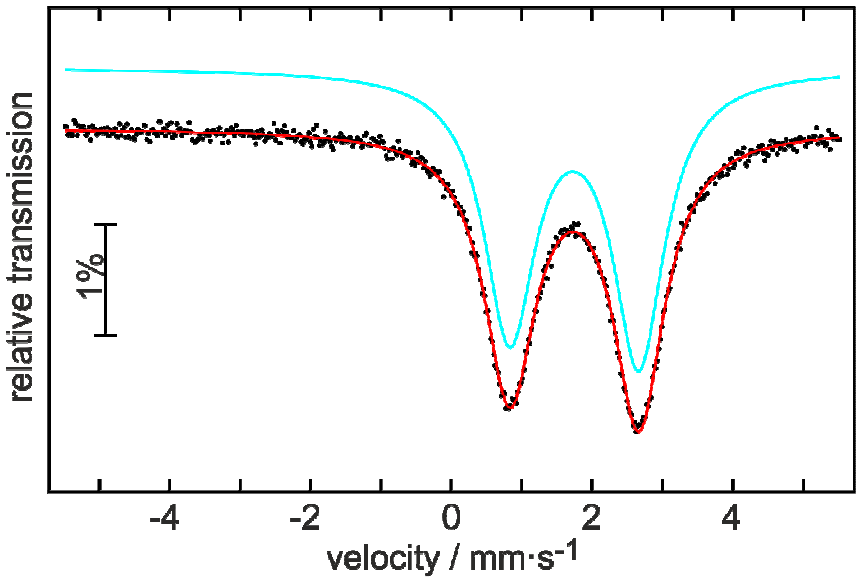


Fig. SI9 ^{119}Sn Mössbauer spectrum of **9** at 78 K.

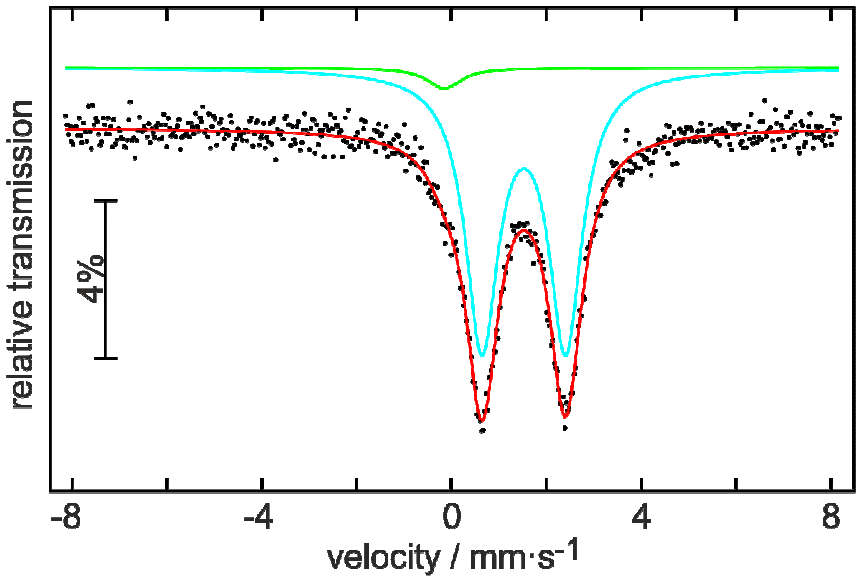


Fig. SI10 ^{119}Sn Mössbauer spectrum of **10** at 78 K.

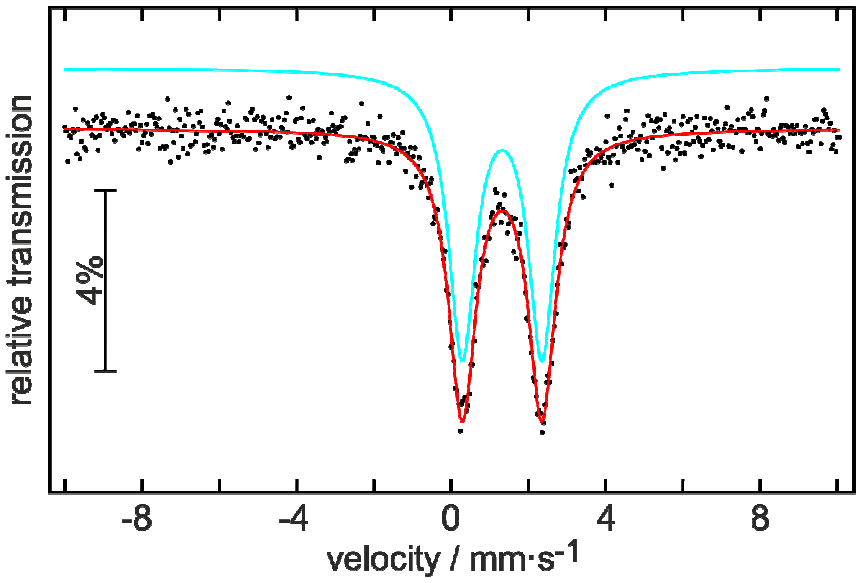


Fig. SI11 ^{119}Sn Mössbauer spectrum of **11** at 78 K.

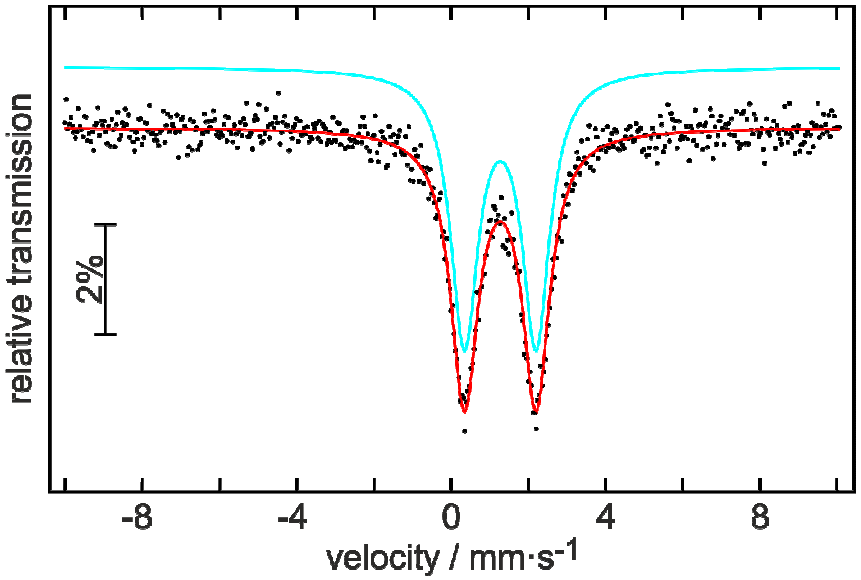


Fig. SI12 ^{119}Sn Mössbauer spectrum of **12** at 78 K.

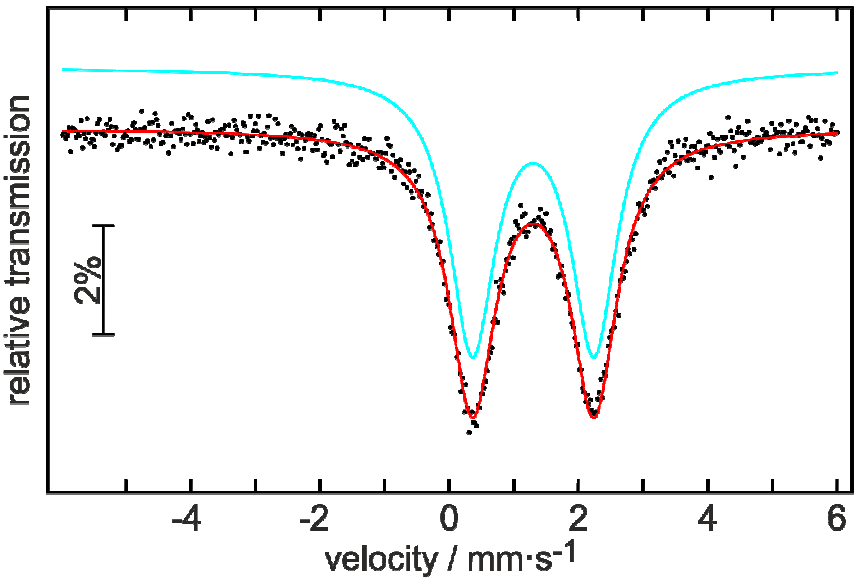


Fig. SI13 ^{119}Sn Mössbauer spectrum of **13** at 78 K.

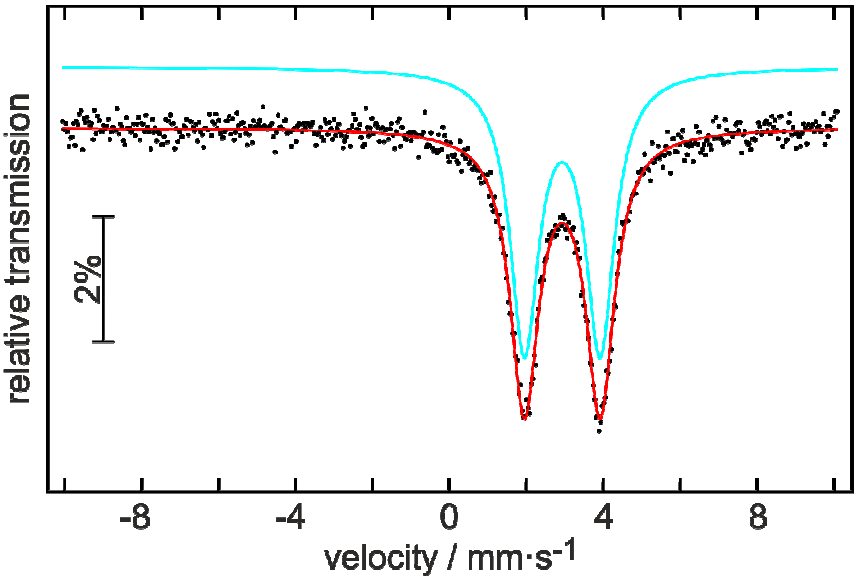


Fig. SI14 ^{119}Sn Mössbauer spectrum of $Sn_2(\mathbf{L^b})_2$ at 78 K.

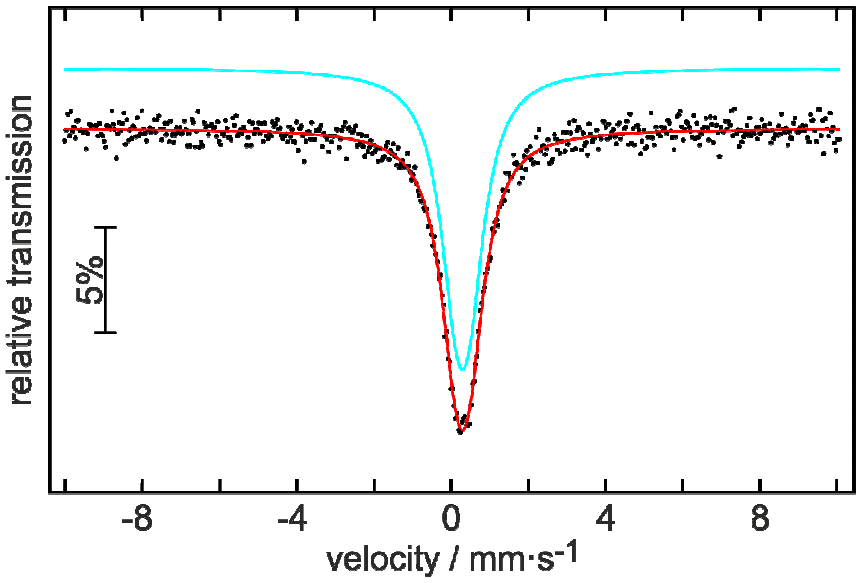


Fig. SI15 ^{119}Sn Mössbauer spectrum of Sn(**L^{b}**)$_2$ at 78 K.

Table SI4 Fitting parameters of the ^{119}Sn Mössbauer spectroscopic investigations. δ: isomer shift, Δ: electric quadrupole splitting, Γ: experimental line width [mm s^{-1}] at 78 K. a) Asymmetry (A_{21}) [mm s^{-1}] = 1.25(1); b) A_{21} = 1.16(1); c) A_{21} = 1.10 (1); * parameter kept fixed during fitting procedure.

Compound	δ	Δ	Γ
2 [a]	1.71(1)	1.68(1)	0.85(1)
2 (5K) [b]	1.76(1)	1.73(1)	1.11(1)
3	1.58(1)	1.83(1)	0.82(1)
[Cl_2Sn(μ-bztzS)$_2$NiPPh_3]			
	1.69(1)	1.69(1)	0.89(1)
9 [c]	1.75(1)	1.83(1)	0.88(1)
10	1.53(1)	1.77(1)	0.84(1)
impurity (4%)	-0.15(1)	0*	0.85*
11	1.32(1)	2.06(1)	0.85(1)
12	1.27(1)	1.86(1)	0.85(1)
13	1.30(1)	1.88(1)	0.86(1)
Sn_2(**L^{b}**)$_2$	2.94(1)	1.97(1)	0.91(2)
Sn(**L^{b}**)$_2$	0.29(1)	0.43(1)	0.9*

Quantum chemical calculations:

Optimizations of the molecular structures have been carried out using DFT methodology as implemented in the adf2012.01a and adf2013.01a software packages.[2] The X-ray structure of the Ge/Pd heterobimetallic complex **4** was used as starting point for the full optimisation for the Si/Pd complex **5**. For all other calculations, the non-H atomic coordinates obtained from the crystal structures (after exclusion of solvent molecules) have been kept constant while the hydrogen atoms have been relaxed. The optimizations have been carried out using scalar relativistic corrections,[3] applying a Triple-Zeta polarised (TZP) basis set for the elements of the first and second row of the periodic table, and a Triple-Zeta double polarised (TZ2P) basis set for the heavier elements.[4] NBO/NLMO analyses have been carried out with adf2013.01a[2] using NBO version 6.0.[5] The calculations have been carried out using hybrid PBE[6] functional and all electron ZORA TZ2P basis set[4] and scalar relativistics[3] for the optimised molecular structures.

For the optimization of Sn(II) and Sn(IV) benchmark compounds the atomic coordinates from the crystal structures of $SnCl_4$ [7], $SnCl_5^-$ [8], $SnCl_6^{2-}$ [9], $SnCl_3^-$ [10] and $SnCl_4^{2-}$ [9] were used. In the case of $SnCl_4^{2-}$ the axial Cl-Sn-Cl bond angle of the see-saw shaped anion was constrained in order to retain this relative molecular arrangement. The other chlorotin compounds were optimized without any constraints.

Optimization of the structure of **5**

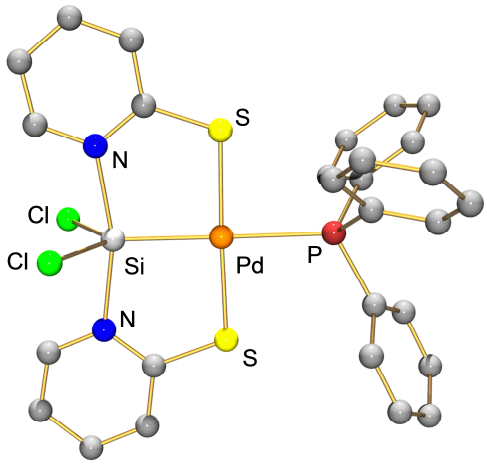


Fig. SI16 Molecular structure (gas phase) of **5** (H atoms are not depicted) after full optimization. Selected bond lengths [Å]: Pd-Si 2.352, Pd-S 2.312, Pd-S 2.299, Pd-P 2.429, Si-N 2.095, Si-N 2.073, Si-Cl 2.142, Si-Cl 2.142.

Table SI5 Atomic coordinates of **5** after full optimisation.

H	-1.35564128	-1.47628643	-4.73659684
H	-3.35503656	-2.96984389	-4.70318289
C	-1.94617042	-1.58308586	-3.82556245
C	-3.06583692	-2.42095820	-3.80432532
H	-4.67050407	-3.23164624	-2.59870834
C	-3.80422412	-2.56730082	-2.62559053
H	-0.67195292	-0.26865842	-2.67645832
C	-1.56541358	-0.89628083	-2.67083898
H	-4.44998932	3.50130062	-2.26643950
H	-3.34995773	1.28358820	-2.17616771
Cl	4.28502077	0.01840815	-1.65469657
C	-3.93189372	3.19426736	-1.35594069
C	-3.30953249	1.94220502	-1.30707919
C	-3.43410058	-1.87073256	-1.47156486
C	-2.31524098	-1.02492350	-1.48832022
H	-4.38152270	5.02051601	-0.28636196
H	-4.00951118	-2.00061301	-0.55412602
C	-3.89335614	4.04406354	-0.24677809
C	-2.64348479	1.53116174	-0.14357159
H	5.32848644	2.03209710	-0.06897907
H	5.96238593	-4.06193682	0.62351436
H	5.40019282	-1.63540616	0.52838713
H	5.73843868	4.48780684	-0.20614150
C	4.50367473	2.74061005	-0.10175073
C	4.93287151	-3.74087410	0.46953229
C	4.62995947	-2.39610324	0.42044430
C	4.72114542	4.09993490	-0.17777583
N	3.26310205	2.18973843	-0.06876063
P	-1.74448875	-0.06846938	-0.02687937
Si	3.03000132	0.13545465	0.07656763
N	3.36893048	-1.92469375	0.24619505
H	4.07042503	-5.73767208	0.35063554
C	3.87843429	-4.66316237	0.31904364
C	2.17010198	2.99050842	-0.09531371
C	3.59733176	4.94972359	-0.21932973
S	0.56918375	2.34955802	-0.03096280
Pd	0.68085197	0.05317971	-0.00177959
C	2.34290743	-2.79682619	0.09581703
H	3.72153513	6.03254414	-0.28363069
C	2.59447018	-4.19430178	0.12997035
C	2.33314218	4.39934376	-0.17667795
S	0.72170203	-2.25396483	-0.15031385
H	1.75149247	-4.87238282	0.00575994
H	1.43792586	5.01976048	-0.20257573
C	-3.22182089	3.64159223	0.91352962
C	-2.59428029	2.39682350	0.96433095
H	-4.51505219	-0.04997781	1.04314053
H	-3.17969972	4.30212423	1.78121514
C	-2.53412208	-0.83901025	1.44598382
H	-2.06574583	2.09404346	1.86931063
C	-3.90440592	-0.65881637	1.71194179
Cl	4.09893013	0.30877882	1.92486772
H	-0.68876378	-1.72189327	2.14241683
C	-1.75333263	-1.58831505	2.34000177
C	-4.48331319	-1.23542849	2.84439045
H	-5.54640890	-1.08704065	3.04226268
C	-2.33618018	-2.16049959	3.47485796
C	-3.69991022	-1.98753467	3.72796656
H	-1.71668007	-2.73594357	4.16530543
H	-4.15209964	-2.43015997	4.61797209

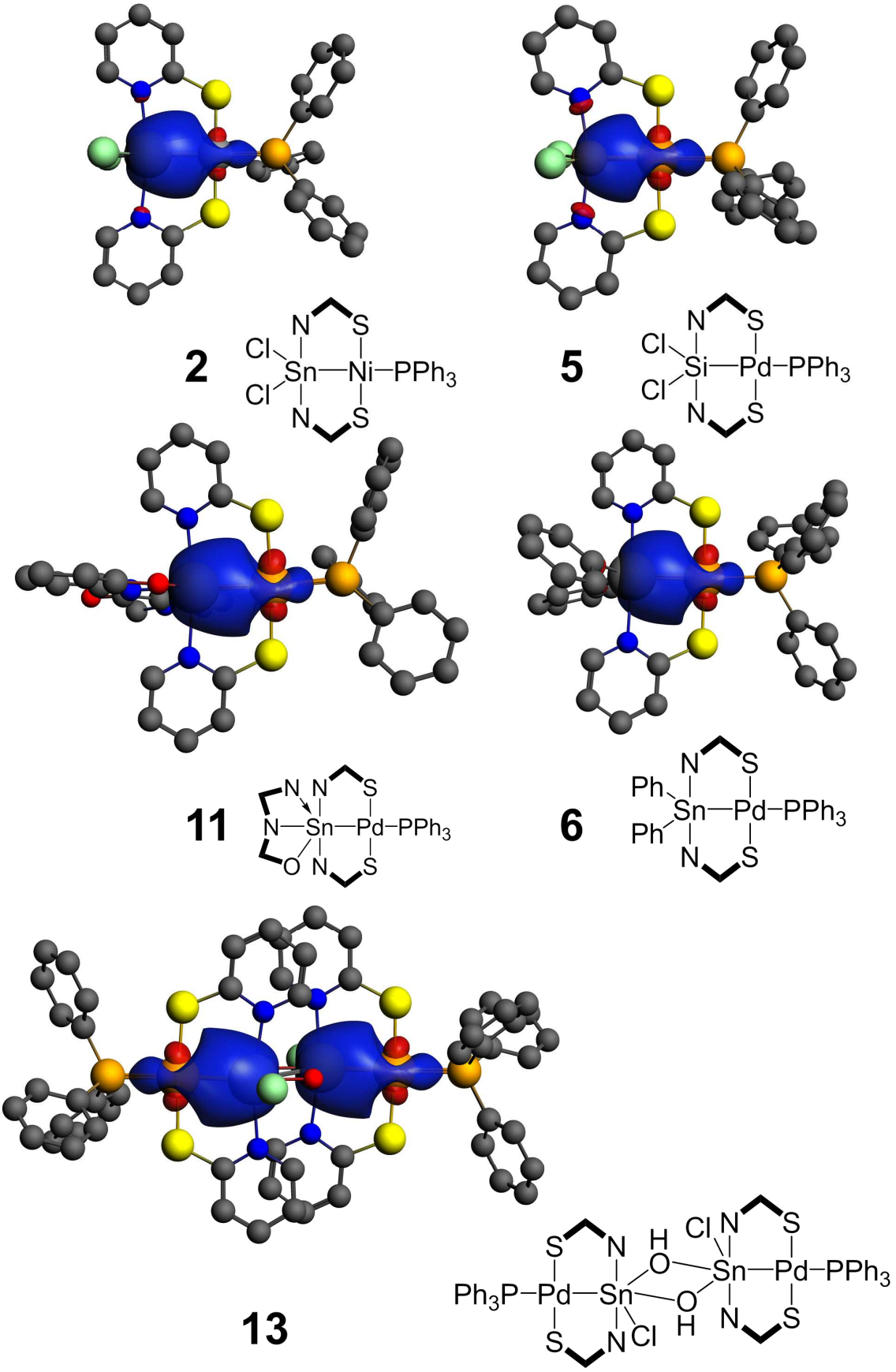


Fig. SI17 NLMOs of the E–TM bonds in **2**, **5**, **6**, **11** and **13** (plotted at an isosurface value of 0.03 e).

.

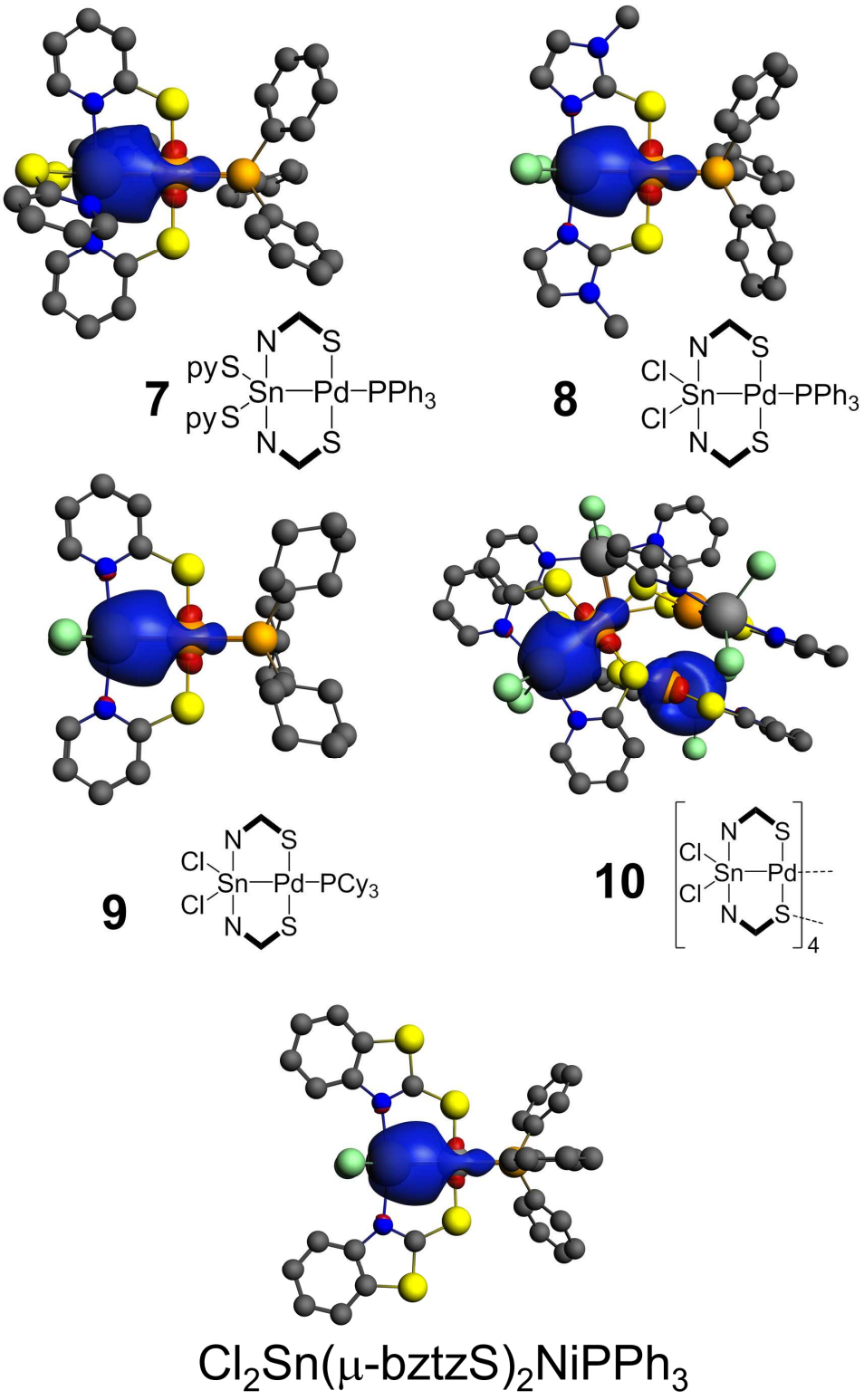


Fig. SI18 NLMOs of the E–TM bonds in **7**, **8**, **9**, **10** and [$Cl_2Sn(\mu$-bztzS)$_2$NiPPh$_3$] (plotted at an isosurface value of 0.03 e). For clarity, only two of the four equivalent NLMOs of compound **10** are shown.

Table SI6 Atomic coordinates of $SnCl_4$ after full optimisation.

Sn	-0.000035	0.000760	-0.000053
Cl	0.095376	1.865674	-1.376428
Cl	0.752514	-1.860393	-1.165775
Cl	-2.190293	-0.351026	0.681144
Cl	1.342428	0.344985	1.861103

Table SI7 Atomic coordinates of $SnCl_5^-$ after full optimisation.

Cl	-0.153435	1.790039	-1.610294
Cl	1.583451	-1.158604	-1.465750
Cl	-1.517980	-1.857508	-0.130717
Cl	-1.562373	1.196727	1.450853
Cl	1.648622	0.025569	1.756456
Sn	0.001704	0.003777	-0.000559

Table SI8 Atomic coordinates of $SnCl_6^{2-}$ after full optimisation.

Sn	0.000000	0.000000	0.000000
Cl	-1.780986	1.780986	0.000000
Cl	-1.780986	-1.780986	0.000000
Cl	0.000000	0.000000	2.512960
Cl	0.000000	0.000000	-2.512960
Cl	1.780986	1.780986	0.000000
Cl	1.780986	-1.780986	0.000000

Table SI9 Atomic coordinates of $SnCl_3^-$ after full optimisation.

Sn	-0.000035	0.000760	-0.000053
Cl	0.095376	1.865674	-1.376428
Cl	0.752514	-1.860393	-1.165775
Cl	-2.190293	-0.351026	0.681144
Cl	1.342428	0.344985	1.861103

Table SI10 Atomic coordinates of $SnCl_4^{2-}$ after partial optimisation (axial Cl-Sn-Cl angle constrained).

Cl	0.000000	2.028952	0.920525
Cl	2.805881	0.000000	-0.600003
Cl	-2.805881	0.000000	-0.600003
Cl	0.000000	-2.028952	0.920525
Sn	0.000000	0.000000	-0.688356

References:

1 L. Ballester, A. Gutierrez, M. F. Perpiñan, T. Rico, *Polyhedron*, 1994, 13, 2277–2283.

2 a) ADF2012.01: J. Autschbach, D. Bashford, A. Brces, F. M. Bickelhaupt, C. Bo, P. M. Boerrigter, L. Cavallo, D. P. Chong, L. Deng, R. M. Dickson, D. E. Ellis, M. van Faassen, L. Fan, T. H. Fischer, C. Fonseca Guerra, A. Ghysels, A. Giammona, S. J. A. van Gisbergen, A. W. Götz, J. A. Groeneveld, O. V. Gritsenko, M. Grüning, S. Gusarov, F. E. Harris, P. van den Hoek, C. R. Jacob, H. Jacobsen, L. Jensen, J. W. Kaminski, G. van Kessel, F. Kootstra, A. Kovalenko, M. V. Krykunov, E. van Lenthe, D. A. McCormack, A. Michalak, M. Mitoraj, J. Neugebauer, V. P. Nicu, L. Noodleman, V. P. Osinga, S. Patchkovskii, P. H. T. Philipsen, D. Post, C. C. Pye, W. Ravenek, J. I. Rodrguez, P. Ros, P. R. T. Schipper, G. Schreckenbach, J. S. Seldenthuis, M. Seth, J. G. Snijders, M. Sol, M. Swart, D. Swerhone, G. te Velde, P. Vernooijs, L. Versluis, L. Visscher, O. Visser, F. Wang, T. A. Wesolowski, E. M. van Wezenbeek, G. Wiesenekker, S. K. Wolff, T. K. Woo, A. L. Yakovlev, E. J. Baerends, T. Ziegler. Adf2012, scm, theoretical chemistry, Vrije Universiteit, Amsterdam, the Netherlands, http://www.scm.com. ADF2012, SCM;
b) J. Autschbach, D. Bashford, A. Brces, F.M. Bickelhaupt, C. Bo, P.M. Boerrigter, L. Cavallo, D.P. Chong, L. Deng, R.M. Dickson, D.E. Ellis, M. van Faassen, L. Fan, T.H. Fischer, C. Fonseca Guerra, A. Ghysels, A. Giammona, S.J.A. van Gisbergen, A.W. Götz, J.A. Groeneveld, O.V. Gritsenko, M. Grüning, S. Gusarov, F.E. Harris, P. van den Hoek, C.R. Jacob, H. Jacobsen, L. Jensen, J.W. Kaminski, G. van Kessel, F. Kootstra, A. Kovalenko, M.V. Krykunov, E. van Lenthe, D.A. McCormack, A. Michalak, M. Mitoraj, J. Neugebauer, V.P. Nicu, L. Noodleman, V.P. Osinga, S. Patchkovskii, P.H.T. Philipsen, D. Post, C.C. Pye, W. Ravenek, J.I. Rodrguez, P. Ros, P.R.T. Schipper, G. Schreckenbach, J.S. Seldenthuis, M. Seth, J.G. Snijders, M. Sol, M. Swart, D. Swerhone, G. te Velde, P. Vernooijs, L. Versluis, L. Visscher, O. Visser, F. Wang, T.A. Wesolowski, E.M. van Wezenbeek, G. Wiesenekker, S.K. Wol, T.K. Woo, A.L. Yakovlev, E.J. Baerends, T. Ziegler. ADF2013, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, http://www.scm.com.
c) ADF2010.01: C. Fonseca Guerra, J. G. Snijders, G. te Velde, E. J. Baerends, *Theor. Chem. Acc.,* 1998, **99**, 391–403; G. te Velde, F. M. Bickelhaupt, E. J. Baerends, C. Fonseca Guerra, S. J. A. van Gisbergen, J. G. Snijders, T. Ziegler, *J. Comput. Chem.,* 2001, **22**, 931–967; http://scm.com.

3 E. van Lenthe, E.J. Baerends, J.G. Snijders, *J. Chem. Phys.,* 1993, **99**, 4597–4610.

4 E. van Lenthe, E. J. Baerends, *J. Comput. Chem,* 2003, **24**, 1142–1156.

5 E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, A. F. Weinhold. NBO version 6.0. Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, 2013, http://nbo6.chem.wisc.edu/.

6 C. Adamo, V. Barone, *J. Chem. Phys.* 1999, **110(13)**, 6158–6170.

7 H. Reuter, R. Pawlak, *Z. Anorg. Allg. Chem.* 2000, **626**, 925–929.

8 Anion from crystal structure CCDC-626261 reported in: A. J. Boyall, K. B. Dillon, J. A. K. Howard, P. K. Monks, A. L. Thompson, *Dalton Trans.* 2007, 1374–1376.

9 Anion from crystal structure CCDC-265895 reported in: S. Rabe, W. Bubenheim, U. Mueller, *Z. Kristallogr.* 2004, **219**, 101–105.

10 Anion from crystal structure CCDC-1111797 reported in: U. Mueller, N. Mronga, C. Schumacher, K. Denicke, *Z. Naturforsch.* 1982, **37B**, 1122–1126.