Supporting Information:

Coordination Chemistry of Stannylene-Based Lewis pairs – Insertion into M–Cl and M–C bonds. From base stabilized stannylenes to bidentate ligands.

Kilian M. Krebs, Sarah Freitag, Jakob J. Maudrich, Hartmut Schubert, Peter Sirsch, Lars Wesemann*

Institute of Inorganic Chemistry, University of Tübingen, Auf der Morgenstelle 18, 72076 Tübingen, Germany

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1 Crystallographic Details

1.1 Crystal Structure Refinement Tables

Table S1. Crystal structure refinement table of compounds **1** - **5**.

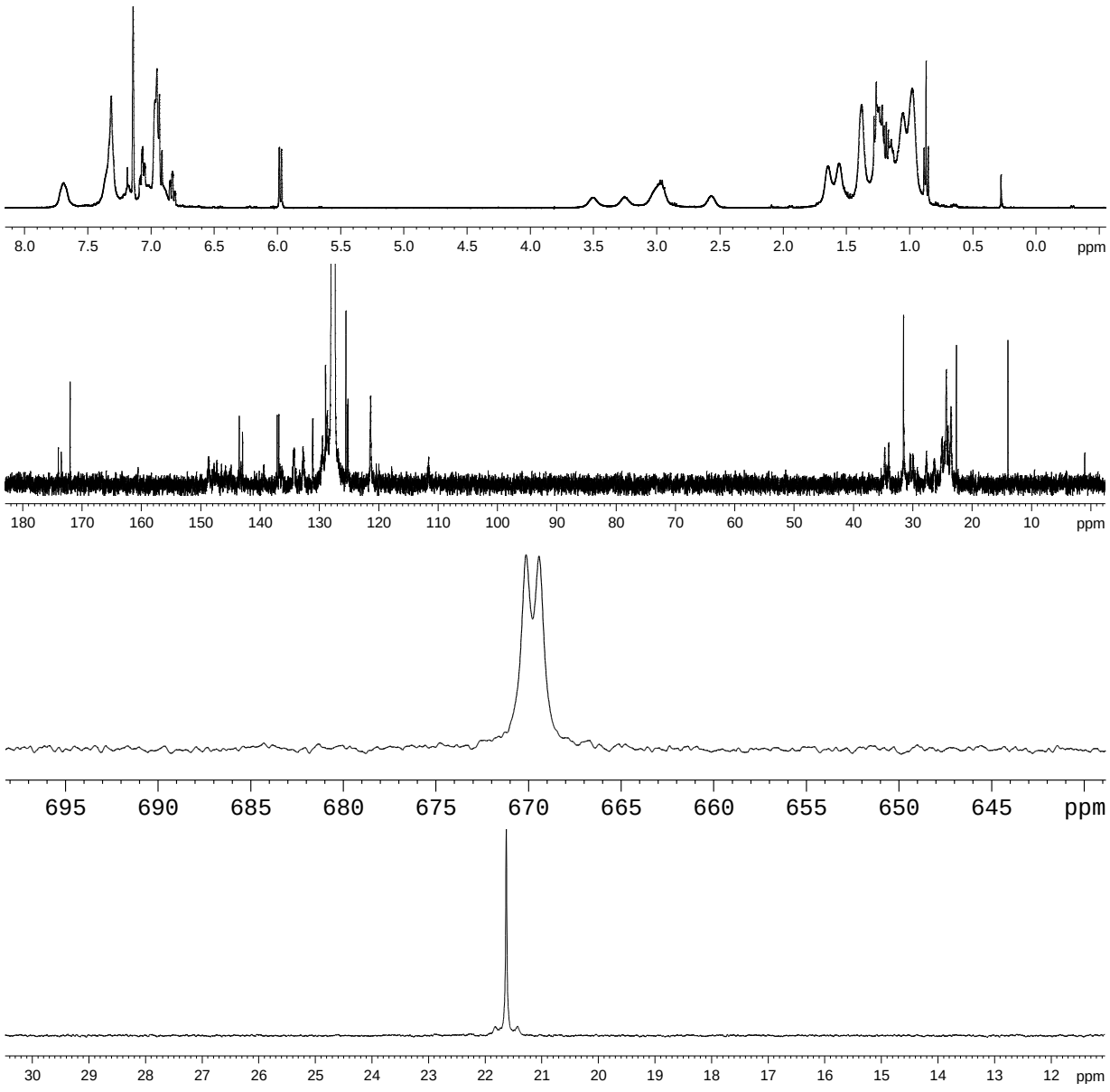
	E	2 × (**1** · 0.5 C_5H_{12} · 0.75 C_6H_6)	**2**	**3** · Et_2O	**4** · C_5H_{12}
Empirical formula	$C_{54}H_{63}PPdSn$	$C_{228.50}H_{271}P_4Pd_2Sn_4$	$C_{62}H_{75}ClIrPSn$	$C_{66}H_{96.68}ClIrOPSn$	$C_{58.63}H_{74.13}ClPRhSn$
M_r / g mol^{-1}	968.10	3828.88	1195.72	1283.42	1066.82
λ / Å	0.71073	0.71073	0.71073	0.71073	0.71073
T / K	100(2)	100(2)	100(2)	100(2)	100(2)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	*P* $2_1/n$	P $2_1/c$	P $2_1/c$	P$2_1/c$	P $2_1/n$
Z	4	4	4	4	4
a / Å	11.8542(3)	30.3699(12)	15.7017(4)	14.6015(3)	13.1474(2)
b / Å	29.1032(7)	23.0190(9)	15.4093(4)	24.6948(6)	16.9062(3)
c / Å	13.0527(3)	31.7092(12)	22.9954(5)	17.6646(4)	24.3248(4)
α / °	90	90	90	90	90
β / °	96.1220(10)	118.378(2)	108.6070(10)	110.0670(10)	103.3070(10)
γ / °	90	90	90	90	90
V / Å^3	4477.44(19)	19503.6(14)	5273.0(2)	5982.8(2)	5261.57(15)
D_c / g cm^{-3}	1.436	1.304	1.506	1.425	1.347
μ / mm^{-1}	1.031	0.771	3.114	2.751	0.905
F(000)	1992	7976	2420	2639	2212
Crystal size / mm	0.08 × 0.14 × 0.22	0.28 × 0.33 × 0.45	0.10 × 0.23 × 0.34	0.07 × 0.14 × 0.37	0.23 × 0.26 × 0.44
θ range / °	2.72 - 27.08	2.72 - 27.12	2.30 - 28.41	2.45 - 28.27	2.96 - 28.29
Limiting indices	–15 ≤ *h* ≤ 15 –31 ≤ *k* ≤ 37 –16 ≤ *l* ≤ 16	–38 ≤ *h* ≤ 38 –29 ≤ *k* ≤ 29 –40 ≤ *l* ≤ 40	–20 ≤ *h* ≤ 20 –20 ≤ *k* ≤ 20 –30 ≤ *l* ≤ 30	–18 ≤ *h* ≤ 19 –32 ≤ *k* ≤ 24 –23 ≤ *l* ≤ 23	–17 ≤ *h* ≤ 17 –22 ≤ *k* ≤ 14 –30 ≤ *l* ≤ 31
Reflects. collect.	39321	316738	82748	56658	49922
Indepdnt Reflects	9866	43063	13226	14729	12968
R_{int}	0.0368	0.0480	0.0266	0.0324	0.0203
Completeness	99.8	99.5	99.6	98.8	99.0
Absorp. Corr.	numerical	multi-scan	numerical	numerical	numerical
Trans.(max., min.)	0.8663, 1.0000	0.6644, 0.7455	0.5142, 0.7676	0.4529, 0.8907	0.7567, 0.9048
Parameters/restraints	526/0	2209/189	656/0	689/210	601/82
R_1, ωR_2 [$I > 2\sigma(I)$]	0.0292, 0.0574	0.0721, 0.0977	0.0236, 0.0496	0.0318, 0.0638	0.0282, 0.0632
R_1, ωR_2 (all data)	0.0469, 0.0625	0.0488, 0.1157	0.0290, 0.0517	0.0517, 0.0710	0.0350, 0.0664
GooF on F^2	1.043	1.087	1.051	1.038	1.047
$\Delta\rho_{max,min}$ / e·Å^{-3}	0.73, –0.90	2.659, –1.223	2.103, –1.744	1.454, –1.160	1.020, –0.635
CCDC	1575456	1575450	1575455	1575452	1575454

Table S1. Crystal structure refinement table of compounds **1** - **5**.

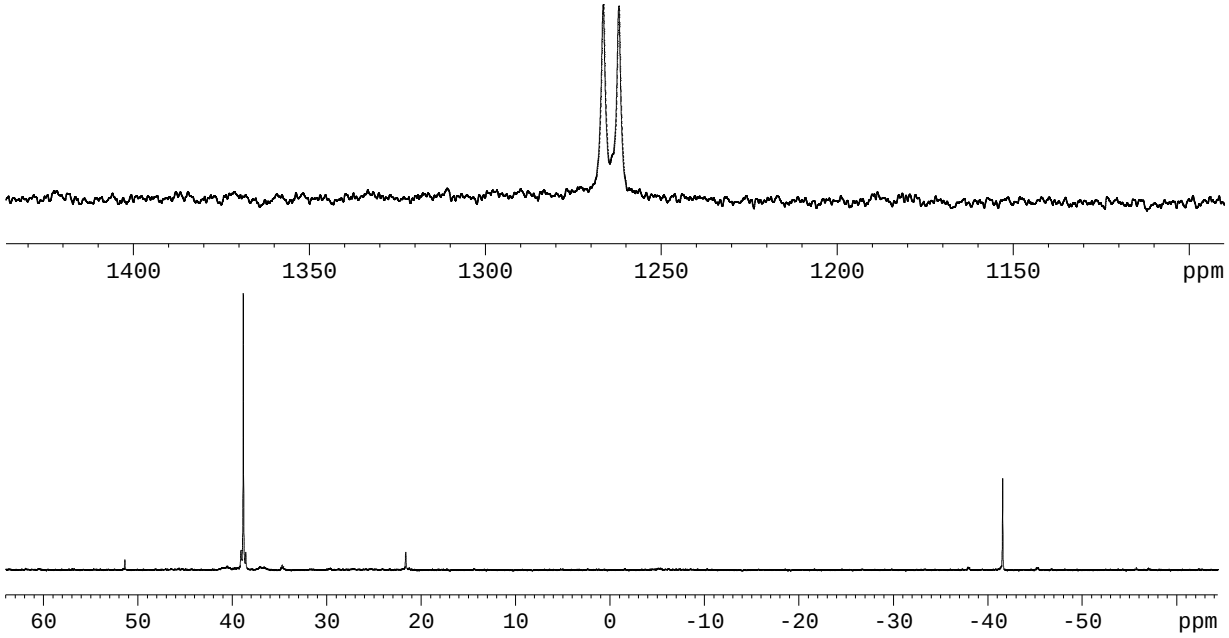
	2 × **5**	**6** · 3 C_6H_{14}	**7** · 2.5 C_6H_6
Empirical formula	$C_{54}H_{75}ClPRhSn$	$C_{126}H_{168}Au_2Cl_2P_2Sn_2$	$C_{127}H_{151}P_2PtSn_2$
M_r / g mol^{-1}	1012.16	2446.75	2171.89
λ / Å	0.71073	0.71073	0.71073
T / K	100(2)	100(2)	100(2)
Crystal system	triclinic	triclinic	monoclinic
Space group	P -1	*P* -1	$P\,2_1/c$
Z	4	2	4
a / Å	10.7739(3)	16.4035(16)	28.0389(11)
b / Å	21.1752(7)	19.1262(19)	17.6143(7)
c / Å	21.9700(7)	21.0975(19)	23.7299(10)
α / °	102.270(2)	115.474(5)	90
β / °	95.204(2)	95.227(5)	113.2410(10)
γ / °	95.573(2)	94.065(5)	90
V / Å^3	4842.5(3)	5905.9(10)	10768.8(8)
D_c / g cm^{-3}	1.388	1.376	1.340
μ / mm^{-1}	0.979	3.012	1.835
F(000)	2104	2492	4484
Crystal size / mm	0.06 × 0.08 × 0.13	0.10 × 0.17 × 0.21	0.17 × 0.15 × 0.12
θ range / °	2.26 - 26.39	2.35 - 27.08	1.40 – 27.52
Limiting indices	–12 ≤ *h* ≤ 12 –24 ≤ *k* ≤ 25 –26 ≤ *l* ≤ 26	–21 ≤ *h* ≤ 20 –24 ≤ *k* ≤ 24 –27 ≤ *l* ≤ 27	–36 ≤ *h* ≤ 35 –22 ≤ *k* ≤ 22 –26 ≤ *l* ≤ 30
Reflects. collect.	74568	97945	24382
Indepdnt Reflects	17674	25901	17843
R_{int}	0.0481	0.0533	0.0732
Completeness	99.6	99.0	98.4
Absorp. Corr.	numerical	numerical	numerical
Trans.(max., min.)	0.8757, 1.0000	0.6223, 0.8785	0.75, 0.84
Parameters/restraints	1058/0	1245/337	1216/84
R_1, ωR_2 [$I > 2\sigma(I)$]	0.0323, 0.0665	0.0388, 0.0746	0.0436, 0.0609
R_1, ωR_2 (all data)	0.0590, 0.0740	0.0629, 0.0809	0.0843, 0.0699
GooF on F^2	0.989	1.021	1.035
$\Delta\rho_{max,min}$ / e·Å^{-3}	1.213, –0.624	2.710, –1.511	2.220, –2.713
CCDC	1575451	1575453	1575457

2 Additional NMR Data

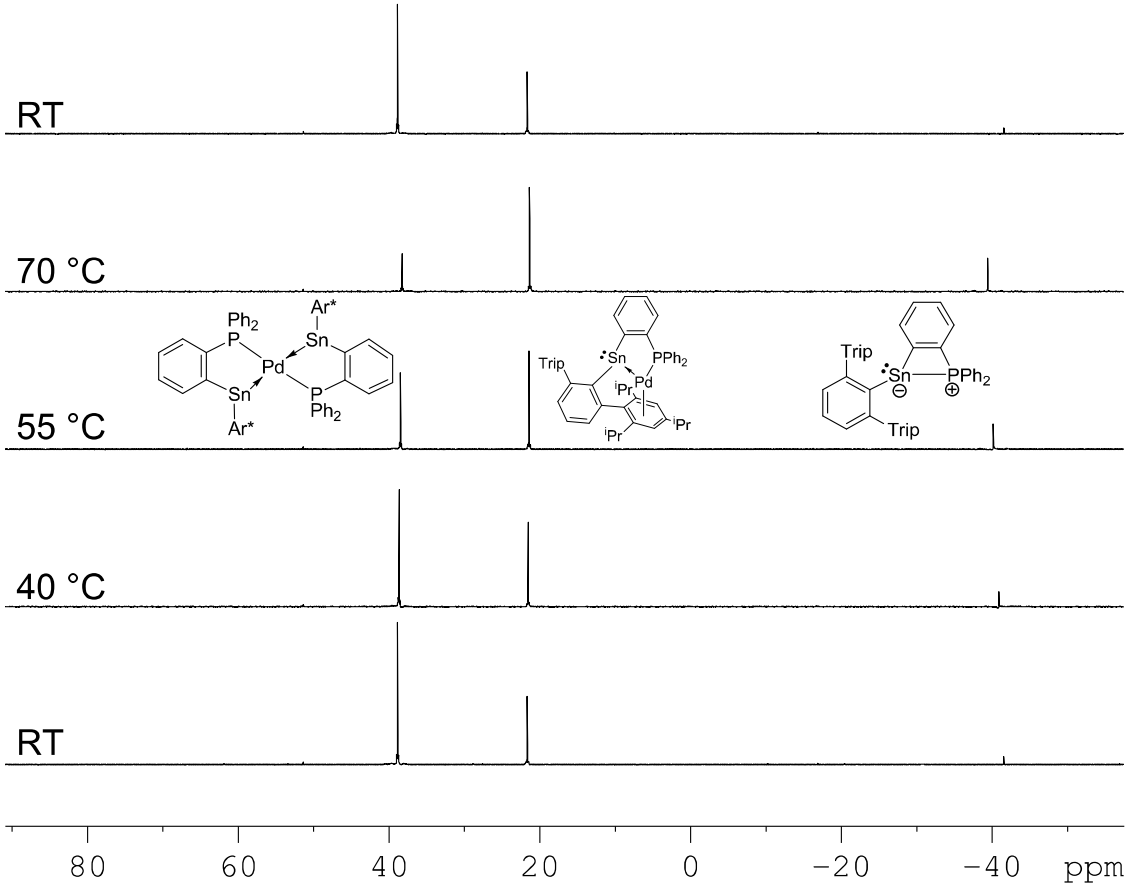
2.1 ^{1}H, ^{13}C, ^{119}Sn and ^{31}P NMR spectra for compound **E** (C_6D_6)



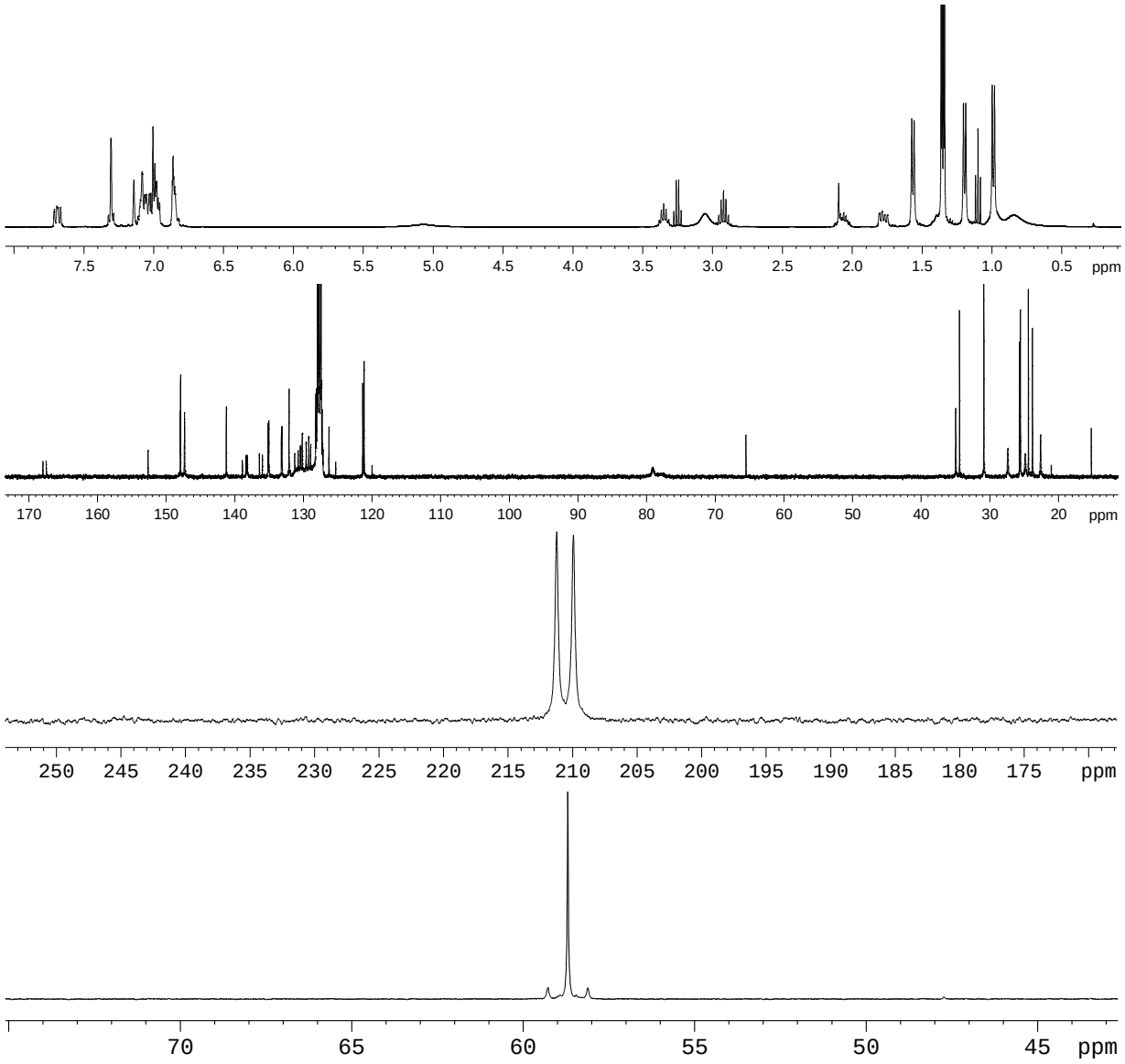
2.2 ^{119}Sn and ^{31}P NMR spectra for compound **1** (C_6D_6) and dT $^{31}P\{^1H\}$ NMR spectra for the equilibrium of **A**, **E** and **1**.



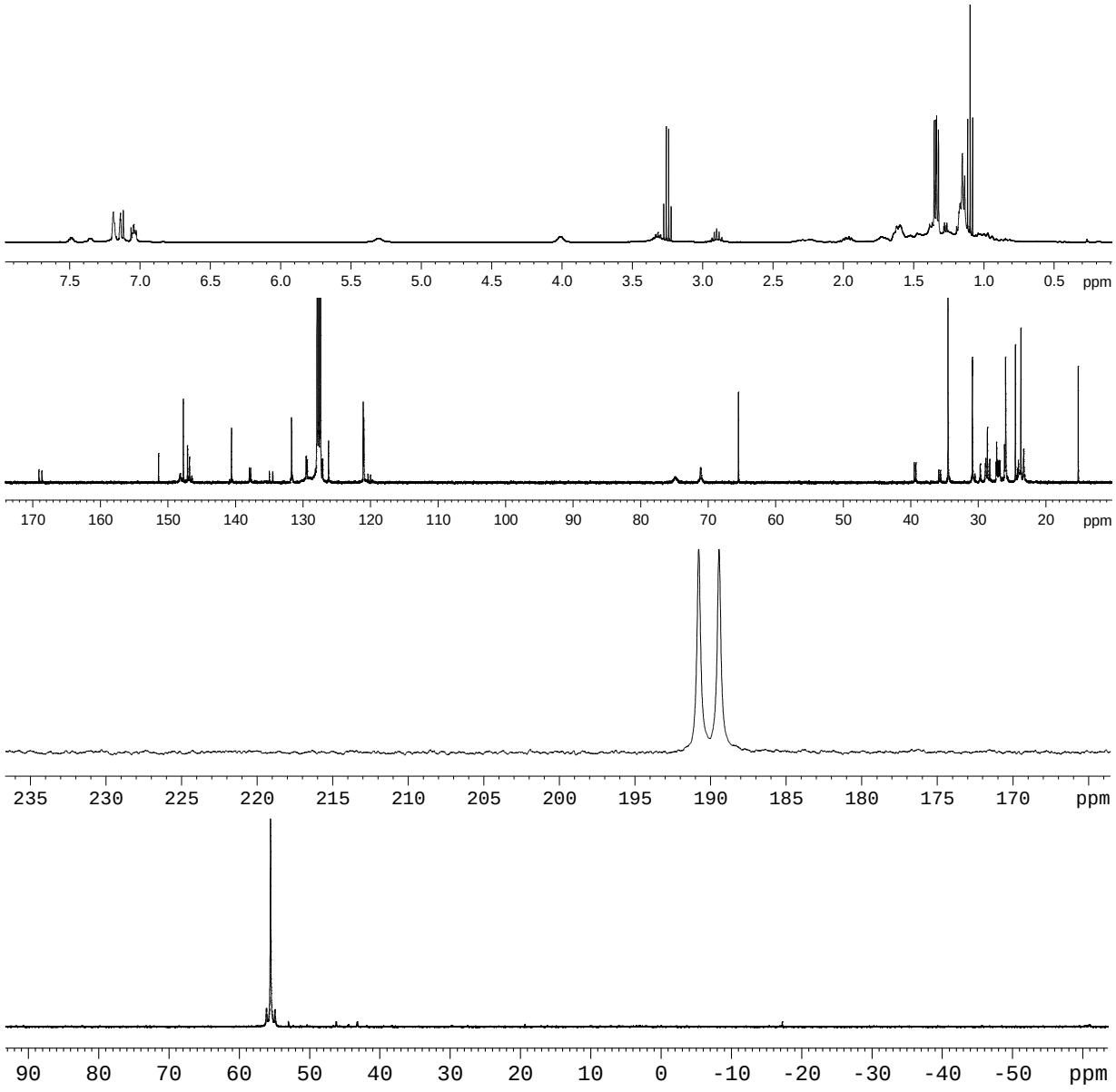
The room temperature spectrum at the top was obtained after the heating process.



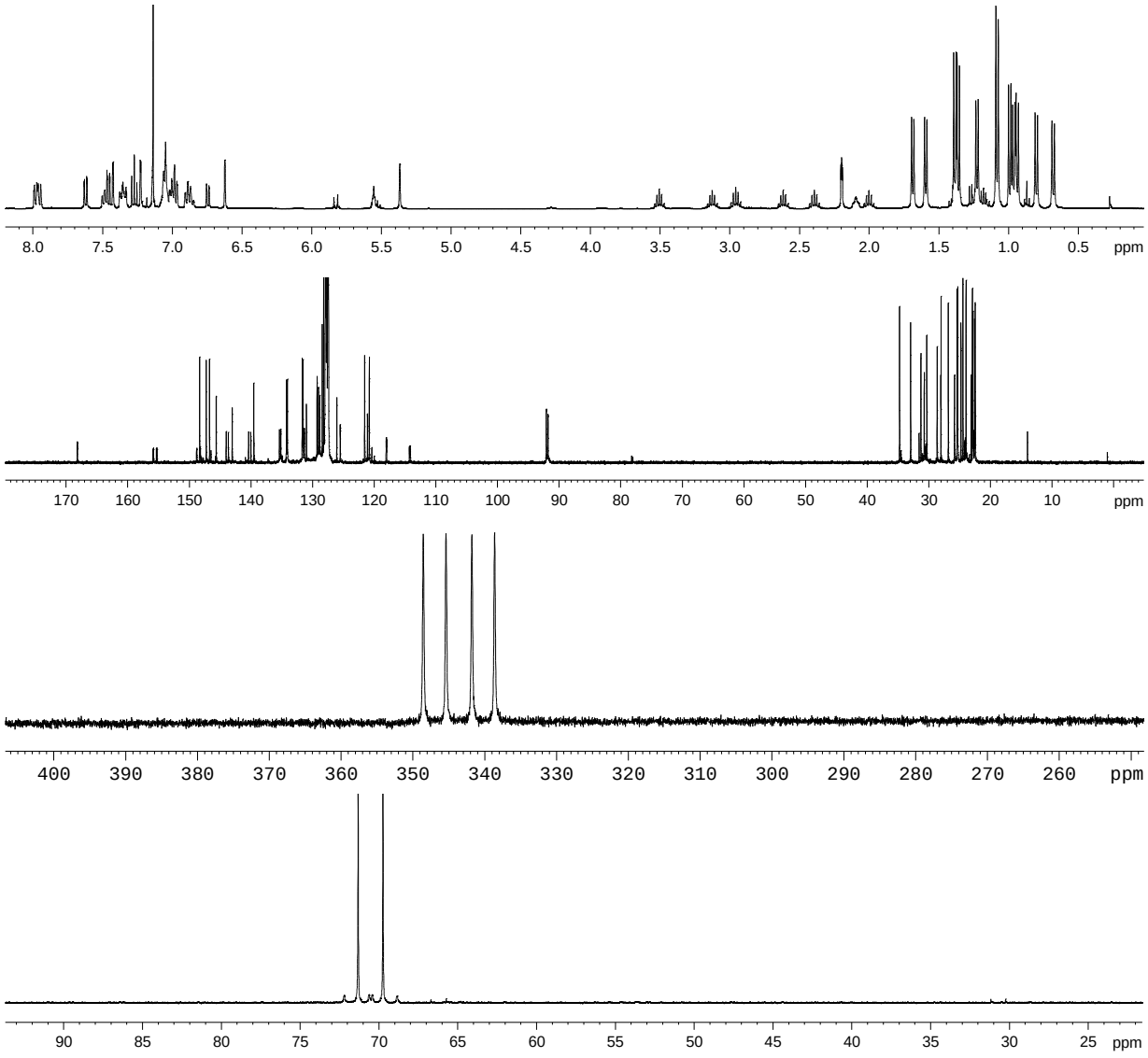
2.3 ^{1}H, ^{13}C, ^{119}Sn and ^{31}P NMR spectra for compound **2** (C_6D_6)



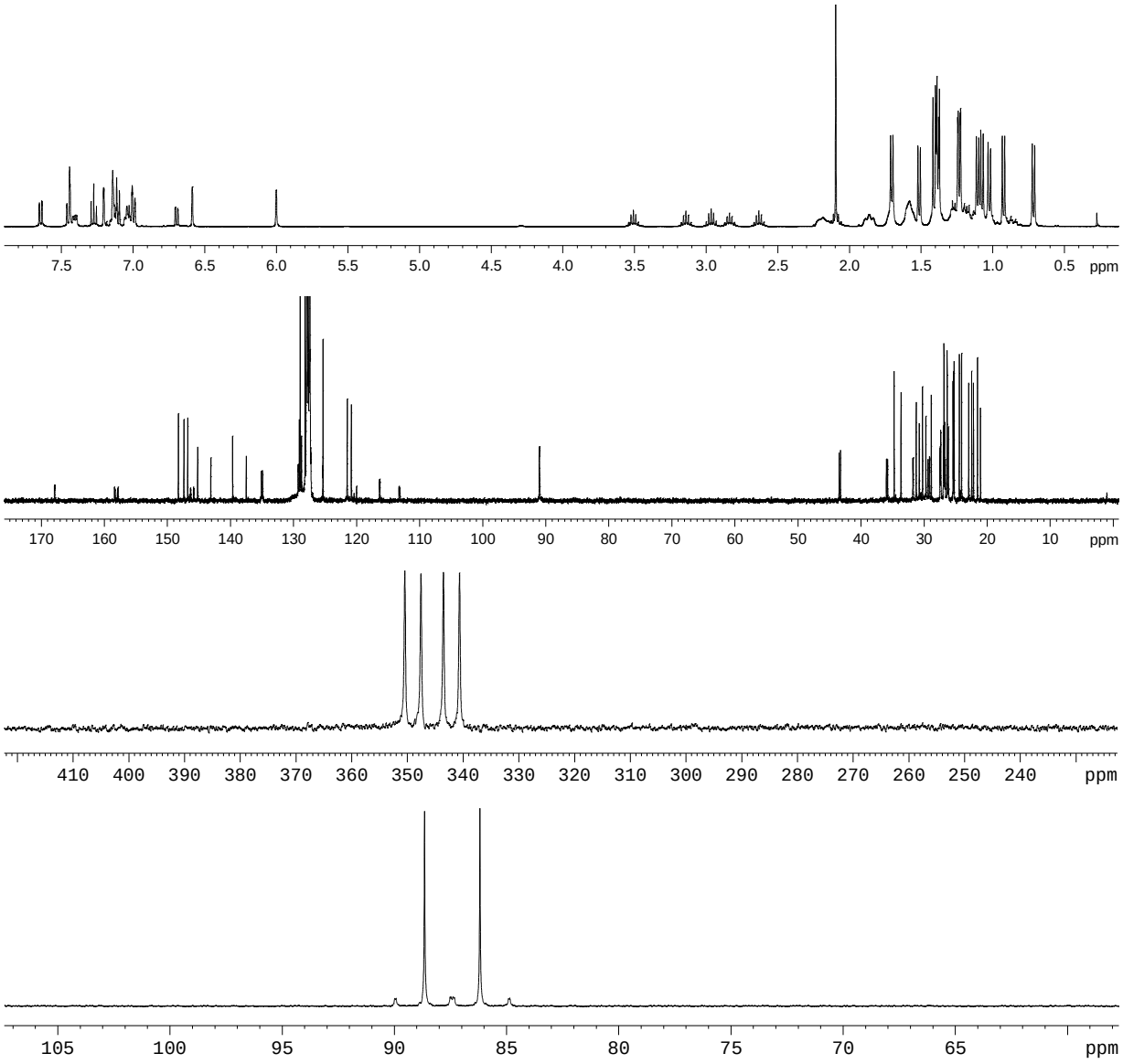
2.4 ^{1}H, ^{13}C, ^{119}Sn and ^{31}P NMR spectra for compound **3** (C_6D_6)



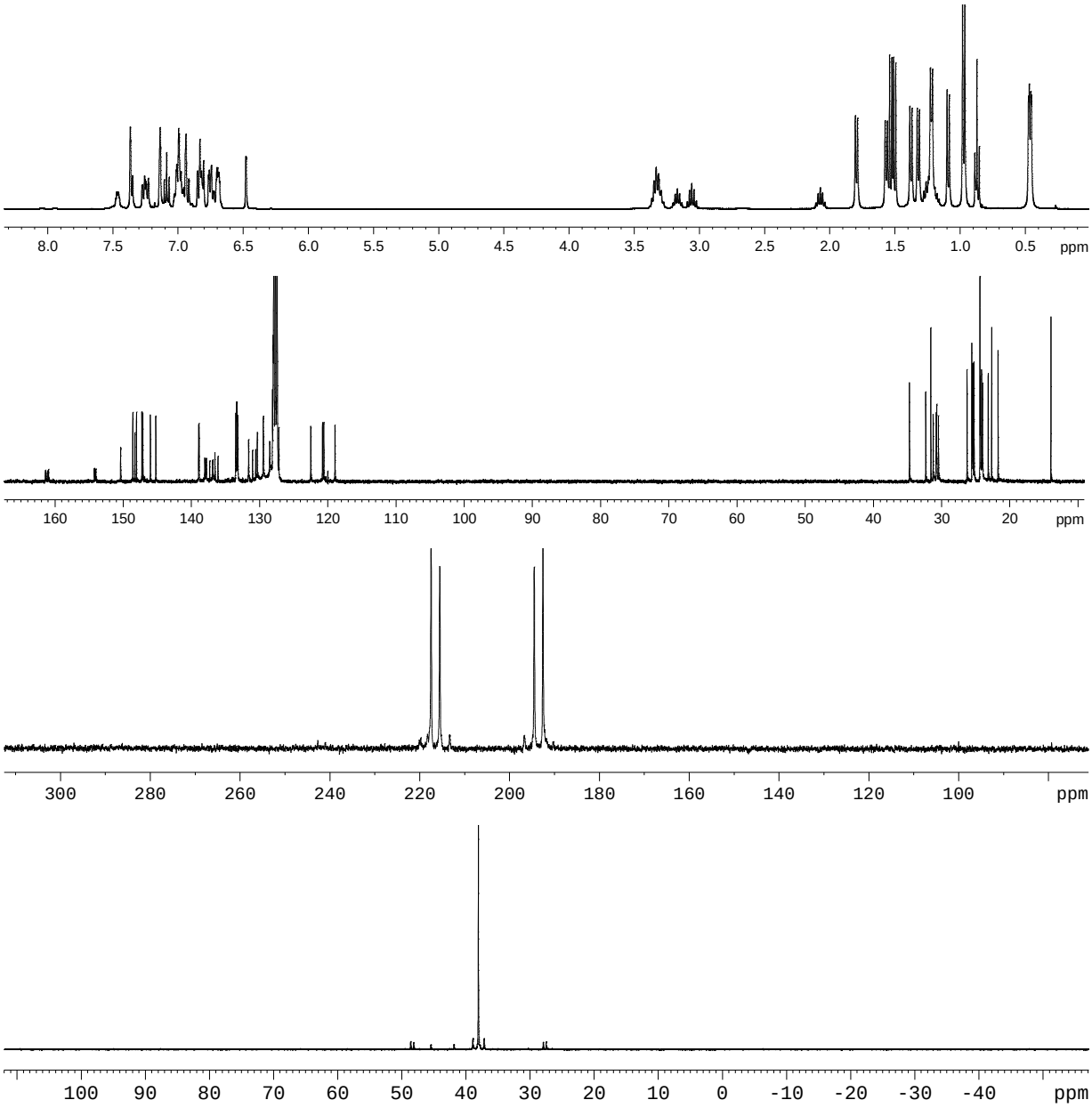
2.5 ^{1}H, ^{13}C, ^{119}Sn and ^{31}P NMR spectra for compound **4** (C_6D_6)



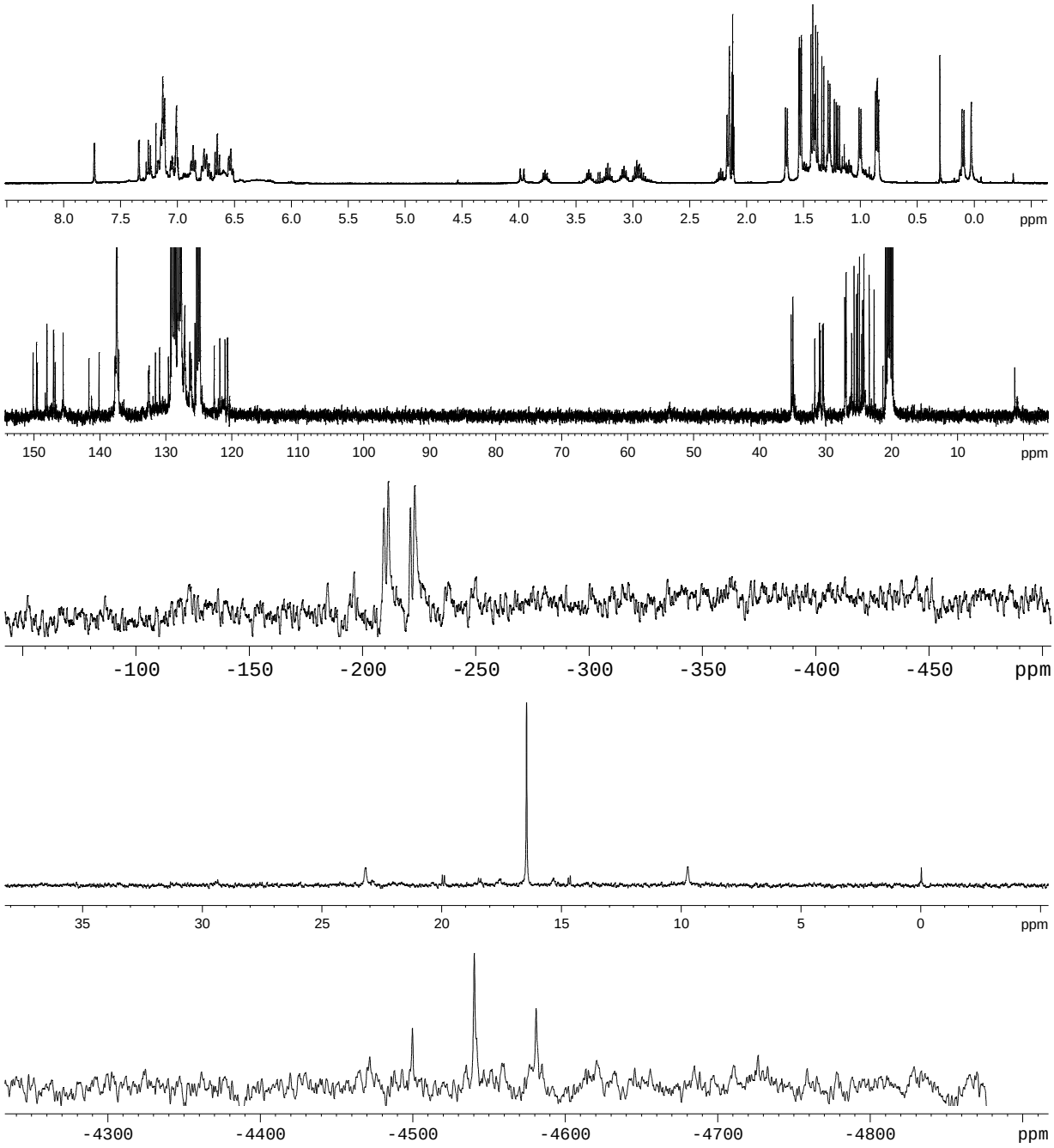
2.6 ^{1}H, ^{13}C, ^{119}Sn and ^{31}P NMR spectra for compound **5** (C_6D_6)



2.7 ^{1}H, ^{13}C, ^{119}Sn and ^{31}P NMR spectra for compound **6** (C_6D_6)



2.8 ^{1}H, ^{13}C, ^{119}Sn, ^{31}P and ^{195}Pt NMR spectra for compound **7** (Tol-d_8)



3 Quantum chemical calculations

3.1 Computational Details: Structure Optimisation and NBO analysis

DFT calculations were carried out with Gaussian09.[1] The molecular structure of complex **E** was optimised using the BP86 functional, along with the implemented def2-TZVP basis set for all atoms, except Sn and Pd.[2-7] For these atoms, Stuttgart Dresden effective core potentials were employed, in combination with optimised valence basis sets as implemented in Gaussian 09.[2-7] Dispersion corrections were included by adding the D3 version of Grimme´s dispersion with Becke-Johnson damping.[8] The geometry optimization was performed without imposing any symmetry constraints, and the structure obtained was confirmed as a true minimum by calculating analytical frequencies, which gave two spurious imaginary frequencies. Natural bond orbitals were obtained using the NBO 6.0 software.[9-11] Plots were generated with the software Chemcraft.[12]

Table S2. Optimised geometry

Atom	X	Y	Z (Å)
C	-1.565497000000	-2.812048000000	-3.254853000000
C	3.915569000000	-1.224201000000	-3.506570000000
C	-1.100042000000	-4.891097000000	-1.877103000000
C	4.959792000000	-3.005743000000	-2.039026000000
C	-1.055485000000	-3.352756000000	-1.915629000000
C	-3.245474000000	2.438579000000	-3.907288000000
C	-3.264806000000	3.831743000000	-4.009185000000
C	3.955221000000	-1.840718000000	-2.103059000000
C	-6.191243000000	-2.821046000000	-0.750548000000
C	-2.801549000000	1.832102000000	-2.729098000000
C	-3.215478000000	-2.655968000000	-0.752365000000
C	-1.805623000000	-2.806865000000	-0.710059000000
C	-2.839850000000	4.617815000000	-2.931155000000
C	4.261180000000	-0.829848000000	-1.006289000000
C	-5.442767000000	-2.042746000000	0.337237000000
C	-5.650117000000	-0.523685000000	0.170093000000

C	5.226998000000	0.166515000000	-1.206923000000
C	-3.955693000000	-2.335345000000	0.393222000000
C	-2.378408000000	2.613948000000	-1.645889000000
C	-1.121660000000	-2.586930000000	0.529632000000
C	1.276678000000	-1.786513000000	0.252943000000
C	0.358816000000	-2.789226000000	0.638569000000
C	-2.398070000000	4.012956000000	-1.754320000000
C	0.802020000000	-3.989470000000	1.219371000000
C	2.642097000000	-2.005797000000	0.538582000000
C	2.159719000000	-4.202760000000	1.458098000000
C	3.074380000000	-3.198077000000	1.138930000000
C	3.645104000000	-0.932111000000	0.261192000000
C	0.958725000000	1.801210000000	-0.234776000000
C	2.202685000000	2.449382000000	-0.165330000000
C	5.610568000000	1.042823000000	-0.187836000000
C	-3.269365000000	-2.190038000000	1.615436000000
C	-1.876638000000	-2.295362000000	1.714270000000
C	6.678228000000	2.093435000000	-0.437476000000
C	-0.171244000000	2.513748000000	0.218254000000
C	6.110938000000	3.517312000000	-0.318538000000
C	3.992514000000	-0.033981000000	1.296245000000
C	2.330481000000	3.724965000000	0.390923000000
C	7.888307000000	1.900784000000	0.491762000000
C	4.980176000000	0.927255000000	1.056314000000
C	-4.272072000000	2.689901000000	0.847223000000
C	-0.050895000000	3.794392000000	0.785429000000
C	-2.935688000000	2.393905000000	1.161037000000
C	1.205553000000	4.393544000000	0.885232000000
C	-1.157208000000	-2.048083000000	3.031652000000
C	3.331975000000	-0.115705000000	2.665730000000
C	-0.577991000000	-0.621436000000	3.056501000000
C	-5.166192000000	3.064081000000	1.851967000000
C	-2.025500000000	-2.302538000000	4.268432000000
C	-2.509766000000	2.484626000000	2.497072000000
C	2.695831000000	1.215866000000	3.091610000000
C	4.332219000000	-0.620338000000	3.719245000000
C	-4.738398000000	3.144680000000	3.180690000000

C	-3.406650000000	2.857878000000	3.499066000000
H	-0.919616000000	-3.165868000000	-4.071315000000
H	-2.588835000000	-3.153061000000	-3.475098000000
H	3.577292000000	-1.972578000000	-4.238687000000
H	-0.529778000000	-5.313615000000	-2.717865000000
H	-1.551536000000	-1.712473000000	-3.262131000000
H	4.728543000000	-3.762477000000	-2.804700000000
H	-3.569992000000	1.821749000000	-4.747442000000
H	-2.138225000000	-5.251482000000	-1.950055000000
H	4.908406000000	-0.874471000000	-3.829414000000
H	-3.606320000000	4.308514000000	-4.929962000000
H	3.219586000000	-0.373284000000	-3.544787000000
H	5.984979000000	-2.642637000000	-2.212524000000
H	-5.890435000000	-2.494070000000	-1.757867000000
H	-0.002312000000	-3.046994000000	-1.810404000000
H	-3.728158000000	-2.807465000000	-1.701629000000
H	-0.667447000000	-5.275445000000	-0.942697000000
H	2.956146000000	-2.256540000000	-1.892683000000
H	4.933262000000	-3.494442000000	-1.054978000000
H	-2.764478000000	0.743385000000	-2.627332000000
H	-6.008584000000	-3.902832000000	-0.673445000000
H	-7.273874000000	-2.647957000000	-0.664300000000
H	-5.209977000000	-0.186791000000	-0.781743000000
H	5.711192000000	0.256840000000	-2.182364000000
H	-2.849248000000	5.706532000000	-3.011303000000
H	-6.720832000000	-0.267259000000	0.170868000000
H	0.069748000000	-4.749968000000	1.504547000000
H	2.499487000000	-5.137691000000	1.907473000000
H	7.025137000000	1.956201000000	-1.476334000000
H	-5.862736000000	-2.332742000000	1.316771000000
H	4.136305000000	-3.330013000000	1.360947000000
H	-5.158144000000	0.037878000000	0.975900000000
H	3.098424000000	1.942745000000	-0.531569000000
H	-2.060935000000	4.629502000000	-0.919640000000
H	5.266099000000	3.664913000000	-1.006710000000
H	-4.611221000000	2.627476000000	-0.188061000000
H	8.306489000000	0.888802000000	0.391600000000

H	-3.850892000000	-1.951264000000	2.507755000000
H	6.881563000000	4.268054000000	-0.551981000000
H	3.314471000000	4.194347000000	0.453515000000
H	8.680516000000	2.628933000000	0.259001000000
H	-0.305193000000	-2.744349000000	3.069814000000
H	0.074359000000	-0.442999000000	2.191133000000
H	2.523580000000	-0.857793000000	2.593996000000
H	-0.933654000000	4.319557000000	1.157516000000
H	5.753083000000	3.710662000000	0.704791000000
H	7.601827000000	2.042253000000	1.545356000000
H	5.252927000000	1.616217000000	1.860241000000
H	-2.481299000000	-3.303701000000	4.248771000000
H	1.304016000000	5.383176000000	1.335756000000
H	-6.202053000000	3.293550000000	1.594902000000
H	1.927790000000	1.534694000000	2.374882000000
H	4.742755000000	-1.600414000000	3.435681000000
H	-1.397332000000	0.110558000000	3.018713000000
H	-2.833256000000	-1.559890000000	4.362699000000
H	-1.468646000000	2.275420000000	2.745246000000
H	0.000574000000	-0.453760000000	3.977778000000
H	5.176195000000	0.078583000000	3.828344000000
H	3.443807000000	2.020957000000	3.158530000000
H	-1.408869000000	-2.226289000000	5.175817000000
H	2.227499000000	1.111884000000	4.082473000000
H	3.845475000000	-0.721222000000	4.701717000000
H	-5.438290000000	3.437663000000	3.965260000000
H	-3.062329000000	2.929085000000	4.532597000000
P	-1.804893000000	1.761193000000	-0.127399000000
Pd	-1.822250000000	-0.448848000000	-0.280991000000
Sn	0.687628000000	-0.185505000000	-1.300533000000

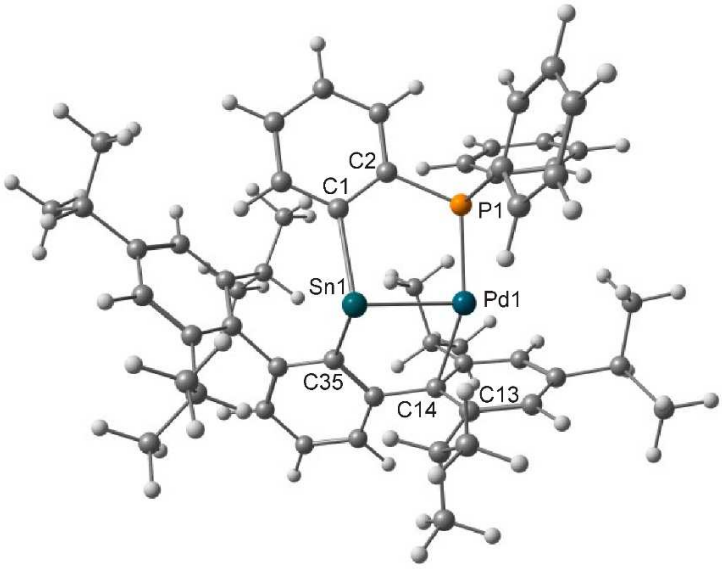


Fig. S1 Optimised molecular structure of compound **E**.

Table S3. Selected distances and angles of **E**, measured (molecular structure in the solid state) and calculated values

distance/angle	measured Å / °	calculated Å / °
Sn1–Pd1	2.6279(3)	2.722
Sn1–C1	2.221(2)	2.271
Sn1–C35	2.255(2)	2.307
Pd1–P1	2.2226(6)	2.215
Pd1–C13	2.418(2)	2.397
Pd1–C14	2.342(2)	2.392
P1–C2	1.831(3)	1.832
Pd1–Sn1–C1	94.3(1),	91.1
Pd1–Sn1–C35	87.2(1)	85.2
P1–Pd1–Sn1	85.2(1)	85.5
Sn1–C1–C2	118.4(2)	119.8
P1–C2–C1	116.7(2)	116.5
C1–Sn1–C35	105.6(1)	105.1

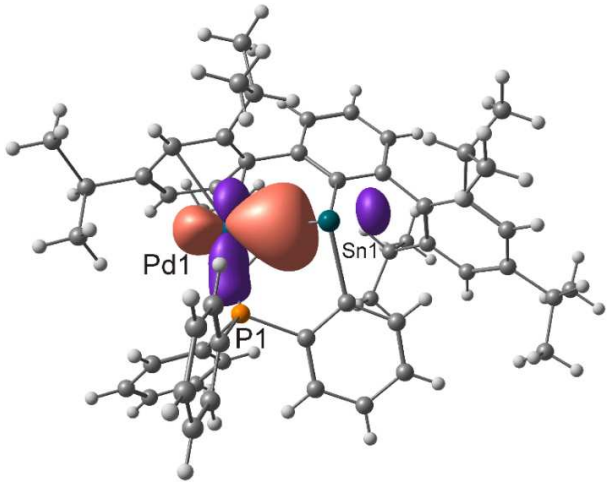


Fig. S2 NLMO 69 of compound **E**: donor acceptor interaction Pd-Sn

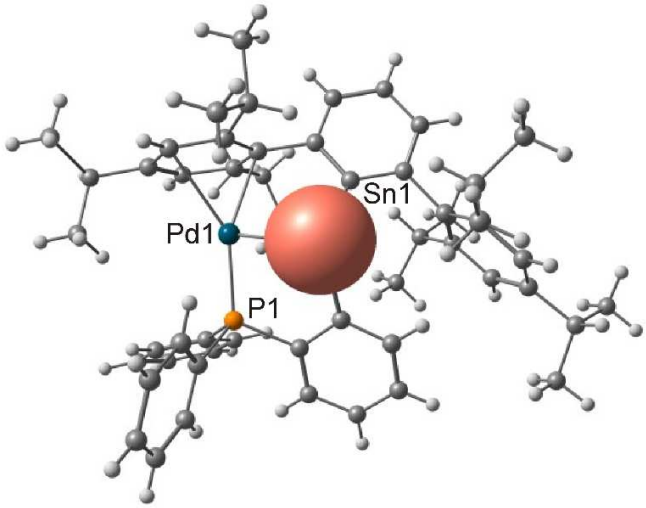


Fig. S3 NLMO 70 of compound **E**: lone pair at Sn.

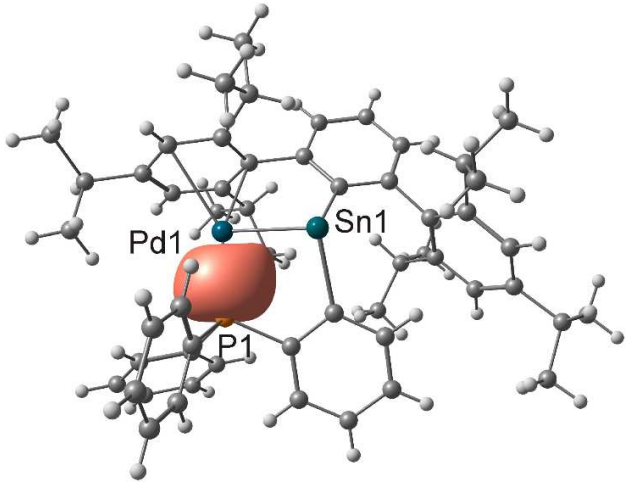


Fig. S4 NLMO 212 of compound **E**: P-Pd donor interaction.

The summary of the natural population analysis results with natural charges of 0.11 for Pd, 0.80 for Sn and 0.99 for P.

4 References

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