Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

Dimeric platinum-stannylene complexes by twofold ligand transfer from a NHC adduct to an organotin(II) hydride

Christian P. Sindlinger and Lars Wesemann*
Institut für Anorganische Chemie, Auf der Morgenstelle 18, 72076 Tübingen, Germany

Table of Contents

Experimental Details

General Information

All manipulations were carried out under argon atmosphere using standard Schlenk techniques or an MBraun Glovebox. Benzene was distilled from sodium/benzophenone, toluene from sodium. Hexane and pentane were obtained from an MBRAUN solvent purification system and degassed. Toluene-d_8 and Methylcyclohexane-d_{14} were distilled from sodium. Terphenyl- iodide (Ar*I)[1], -lithium-etherate (Ar*Li(OEt_2))[1], -Sn(II) chloride (Ar*SnCl)[2] and trihydride (Ar*SnH_3)[3] were prepared according to literature procedures or slight modifications thereof. Pt(cod)$_2$ was prepared according to a literature procedure.[4]

Elemental analysis was performed by the Institut für Anorganische Chemie, Universität Tübingen using a Vario MICRO EL analyzer. IR spectra were recorded as KBr pellets prepared in a glovebox and measured with a Bruker VERTEX 70 IR spectrometer. UV/Vis spectra were measured with a PerkinElmer Lambda35 spectrometer in dilute solutions in pentane at room temperature within 5 minutes after sample preparation.

NMR spectroscopy

NMR spectra were recorded with a Bruker AVII+ 500 NMR spectrometer with a variable temperature set up and a 5 mm ATM probe head or a 5 mm TBO probe head and operating at 500.13 (^{1}H), 125.76 (^{13}C), 186.55 MHz (^{119}Sn) and 106.97 MHz (^{195}Pt). Chemical shifts are reported in δ values in ppm relative to external TMS(^{1}H, ^{13}C), $SnMe_4$ (^{119}Sn), or $[PtCl_6]^{2-}$ (^{195}Pt) and referenced on the solvent ^{2}H resonance frequency (Ξ(^{13}C) = 25.145020 %, Ξ(^{119}Sn) = 37.290632 %, Ξ(^{195}Pt) = 21.496784 %).[5] Solutions in d_{14}-MeCy were locked and referenced by setting the solvent ^{2}H chemical shift to that of cyclohexane-d_{12} leading to possible systematic deviations in the reported shifts. The proton and carbon signals were assigned where possible via a detailed analysis of ^{1}H, ^{13}C or ^{13}C-UDEFT, ^{1}H-^{1}H COSY, ^{1}H-^{13}C HSQC, ^{1}H-^{13}C HMBC NMR spectra. Due to the thermal sensitivity of compound **2** no prolonged 1D-^{13}C NMR resolving all signals could have been taken at lower temperatures. Missing signal were located by means of ^{1}H-^{13}C HMBC NMR spectra. Selected 1D-NMR spectra of the compounds and mixtures can be found in the Supporting Information.

Synthetic Details

Synthesis of Ar*SnH(NHC) (1)

Analogous to our recent procedure[6], to a solution of Ar*SnH_3 (200 mg, 0.331 mmol, 1 eq) in benzene (3 mL) a solution of 1,3,4,5-tetramethylimidazol-2-ylidine (82.3 mg, 0.663 mmol) in benzene (2 mL) was quickly added via syringe at room temperature and the mixture was stirred for 20 min before all volatiles were thoroughly removed under reduced pressure to give Ar*SnH(NHC) **1** in almost quantitative yield (237 mg, 0.327 mmol, 98%) as a white to off-white powder.

Analytical data: **^{1}H**-NMR (C_6D_6, 299.2 K, 500.13 MHz): 7.26 (d, 2H, $^4J_{H-H}$ = 1.75 Hz, *m*-CH_{Trip}), 7.21-2.14 (m, 3H, *o*/*p*-CH_{Ph}), 7.01 (d, 2H, $^4J_{H-H}$ = 1.75 Hz, *m*-CH_{Trip}), 6.90 (s, 1H, $^1J_{117/119Sn-H}$ = 218/228 Hz, Sn-*H*), 3.53 (sept., 2H, $^3J_{H-H}$ = 6.85 Hz, *o*-C*H*Me$_2$), 3.05 (s, 6H, N-CH_3), 2.96 (sept, 2H, $^3J_{H-H}$ = 6.83 Hz, *o*-C*H*Me$_2$), 2.86 (sept, 2H, $^3J_{H-H}$ = 6.88 Hz, *p*-C*H*Me$_2$), 1.71 (d, 6H, $^3J_{H-H}$ = 6.88 Hz, *o*-CH*Me*$_2$), 1.271 (d, 6H, $^3J_{H-H}$ = 6.78 Hz, *o*-CH*Me*$_2$), 1.266 (d, 6H, $^3J_{H-H}$ = 6.84 Hz, *o*-CH*Me*$_2$), 1.25 (d, 6H, $^3J_{H-H}$ = 6.91 Hz, *p*-CH*Me*$_2$), 1.22 (s, 6H, NHC-CH_3), 1.17 (d, 6H, $^3J_{H-H}$ = 6.76 Hz, *o*-CH*Me*$_2$), 1.10 (d, 6H, $^3J_{H-H}$ = 6.88 Hz, *o*-CH*Me*$_2$); **^{13}C{^{1}H}-udeft** (C_6D_6, 298 K, 125.77 MHz): δ = 173.1 (NHC-*C*-Sn, $^1J_{Sn-C}$ = 570±10 Hz), 161.8 (*ipso*-C_{Ph}), 148.8 (*o*-C_{Ph}), 147.1 (*p*-C_{trip}), 147.0 (*o*-C_{trip}), 146.9 (*o*-C_{trip}) 142.6 (*ipso*-C_{trip}), 128.5 (*m*-C_{Ph}), 124.5 (NHC-*C*-CH$_3$), 124.3 (*p*-C_{Ph}), 121.0 (*m*-C_{trip}), 120.2 (*m*-C_{trip}), 36.2 (N-*C*H$_3$), 34.7 (*p*-*C*HMe$_2$), 31.2 (*o*-*C*HMe$_2$), 30.7 (*o*-*C*HMe$_2$), 26.9 (*o*-CH*Me*$_2$), 26.4 (*o*-CH*Me*$_2$), 24.7 (*p*-CH*Me*$_2$), 24.4 (*p*-

CH*Me*$_2$), 24.0 (*o*-CH*Me*$_2$), 23.2 (*o*-CH*Me*$_2$), 8.4 (NHC-C-*C*H$_3$); **^{119}Sn**{^{1}H} (C_6D_6, 299 K, 186.46 MHz) δ = –329.5 (d, $^1J_{Sn-H}$ = 228Hz); **IR** (KBr pellet) 1605 cm^{-1} (s, Sn-H stretch).

Synthesis of {Ar*Sn[(NHC)Pt(μ-H)]$_2$SnAr*} (2)

To a cool (–40°C) solution of Pt(cod)$_2$ (70.0 mg, 0.170 mmol, 1 eq) in toluene (1 mL) a solution of Ar*SnH(NHC) **1** (123.4 mg, 0.170 mmol, 1 eq) in cool (–40°C) toluene (1.5 mL) was rapidly added *via* syringe and the immediately deep dark green mixture was stirred for 10 min at –40°C. All volatiles where thoroughly removed under constant maintenance of a temperature below 0°C under reduced pressure. The crude dark green residue was extracted with cool (–40°C) pentane (2 × 1 mL) and the extracts were filtered through a precooled syringe filter. A minimum amount of a red-brown residue is observed after pentane extraction. The deep green extracts were carefully reduced in volume under reduced pressure to approx. 1 mL and the concentrated solution was usually kept for 5-10 days at –40°C to yield {Ar*Sn[(NHC)Pt(μ-H)]$_2$SnAr*} co-crystallized with one molecule of lattice pentane as dark blue-green plate shape crystals after drying under reduced pressure (74 mg, 0.040 mmol, 47%).

Analytical data: **^{1}H**-NMR (*d$_8$*-tol, 273 K K, 500.13 MHz): 7.28 (t, 2H, $^3J_{H-H}$ = 7.41 Hz, *p*-C*H*$_{Ph}$), 7.20 (d, 4H, $^3J_{H-H}$ = 7.39 Hz, *m*-C*H*$_{Ph}$), 7.03 (s, 8H, *m*-C*H*$_{Trip}$), 3.37 (sept., 8H, $^3J_{H-H}$ = 6.78 Hz, *o*-C*H*Me$_2$), 2.88 (s, 12H, NC*H$_3$*), 2.85 (sept, 4H, $^3J_{H-H}$ = 6.89 Hz, *p*-C*H*Me$_2$), 1.83 (s, 12H, NHC-C*H$_3$*), 1.29 (d, 24H, $^3J_{H-H}$ = 6.89 Hz, *p*-CH*Me$_2$*), 1.23 (d, 24H, $^3J_{H-H}$ = 6.68 Hz, *o*-CH*Me$_2$*), 1.06 (d, 24H, $^3J_{H-H}$ = 6.71 Hz, *o*-CH*Me$_2$*), –6.54 (s+satellites, 2H, $^1J_{Pt-H}$=565 Hz, PtH); (*d$_{14}$*-MeCy, 253 K, 500.13 MHz): 7.74 (t, 2H, $^3J_{H-H}$ = 7.49 Hz, *p*-C*H*$_{Ph}$), 7.52 (d, 4H, $^3J_{H-H}$ = 7.49 Hz, *m*-C*H*$_{Ph}$), 7.27 (s, 8H, *m*-C*H*$_{Trip}$), 3.54 (sept., 8H, $^3J_{H-H}$ = 6.67 Hz, *o*-C*H*Me$_2$), 3.30 (sept, 4H, $^3J_{H-H}$ = 6.93 Hz, *p*-C*H*Me$_2$), 3.27 (s, 12H, NC*H$_3$*), 2.60 (s, 12H, NHC-C*H$_3$*), 1.74 (d, 24H, $^3J_{H-H}$ = 6.93 Hz, *p*-CH*Me$_2$*), 1.51 (d, 24H, $^3J_{H-H}$ = 6.67 Hz, *o*-CH*Me$_2$*), 1.32 (d, 24H, $^3J_{H-H}$ = 6.67 Hz, *o*-CH*Me$_2$*), –6.18 (s, 2H, satellites broadened due to coalescence, PtH); **^{13}C{^{1}H}** (*d$_{14}$*-MeCy, 253 K, 125.77 MHz): δ = 181.4 (Pt–*C*$_{NHC}$), 177.0 (*ipso-C$_{Ph}$*), 146.5 (*o-C$_{trip}$*), 146.3 (*p-C$_{trip}$*), 140.8 (*ipso-C$_{trip}$*), 129.2 (*m-C$_{Ph}$*), 126.1 (*o-C$_{Ph}$*), 122.6 (C=C$_{NHC}$), 120.4 (*m-C$_{trip}$*), 36.7 (N*C*H$_3$), 34.6 (overlayed by strong solvent signals, *p*-*C*HMe$_2$), 30.5 (*o*-*C*HMe$_2$), 25.7 (overlayed by strong solvent signals, *o*-CH*Me$_2$*), 24.4 (*p*-CH*Me$_2$*), 23.6 (*o*-CH*Me$_2$*), 9.5 (NHC-*C*H$_3$); **^{119}Sn** (*d$_{14}$*-MeCy, 233 K, 186.62 MHz) δ = 2487 (s + Pt-satellites, $\omega_{1/2}$ ≈ 1760 Hz, $^1J_{195Pt-119Sn}$ ≈ 9900 Hz, Ar*SnPt$_2$), 692 (s, $\omega_{1/2}$ ≈ 2650 Hz, Ar*Sn(μ-H)$_2$Pt$_2$), **^{195}Pt** (tol-*d$_8$*, 233 K, 106.97 MHz) δ = –4945 (d, $^1J_{195Pt-H}$ ≈ 1135 Hz, $\omega_{1/2}$ ≈ 250 Hz); IR(KBr): 1757 cm^{-1} (Pt–H); UV/Vis(pentane, RT) ε_{max} at λ = 624 nm; Anal. Calcd for [**2×pentane**] $C_{86}H_{124}N_4Pt_2Sn_2$×(C_5H_{12}): C 57.11, H 7.16, N 2.93 Found: C 56.76, H 7.16, N 2.97.

Crystallographic Details

Refinement Details

X-ray data for **2** was collected with a Bruker Smart APEX IIduo diffractometer with graphite- monochromated Mo Kα radiation and a fine-focussed microsource. The programs used were Bruker's APEX2 v2011.8-0 including SADABS for absorption correction and SAINT for structure solution, as well as the ShelXLE graphical user interface for shelxl for structure refinement.[7] For further refinement details see the attached .cif-files.

For **2** one molecule of pentane was found occupying two positions within the asymmetric unit. The pentane molecules were disordered and treated with DFIX, DANG, SIMU, DELU, ISOR and EADP commands. The Pt-bound hydrides were located within the difference Fourier map and refined freely without constraints after their possible positions were indicated by accompanying computational studies. The reported Pt-H distance is therefore likely underestimated.

Table 1. Selected crystallographic data for compound 2

Compound	**2·× (C_5H_{12})**
CCDC number	1061351
Empirical formula	$C_{91}H_{136}N_4Pt_2Sn_2$
Formula weight	1913.60
T [K]	100(2)
Λ [Å]	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
a [Å]	15.6296(3)
b [Å]	19.9002(3)
c [Å]	30.4007(5)
α [°]	90
β [°]	100.5000(10)
γ [°]	90
V [Å^3]	9297.3(3)
Z	4
ρ [Mg m^{-3}]	1.367
μ [mm^{-1}]	3.572
F(000)	3864
Crystal size [mm^3]	0.092 × 0.133 × 0.379
Theta range [°]	1.72 – 29.28
Index ranges	$-21 \leq h \leq 21$
	$-27 \leq h \leq 27$
	$-41 \leq h \leq 41$
Refl. collected	144045
Indep. refl. / [R(int)]	25189 (0.0444)
Completeness to theta max	99.3 %
Data/restraints/parameter	25189 / 136 / 969
GooF	1.042
Final *R* indices [*I* >2sigma(*I*)] *R*1 / *wR*2	0.0283 / 0.0661
R indices (all data) *R*1 / *wR*2	0.0429 / 0.0721
Largest diff. peak and hole [eA^{-3}]	1.620 and -1.203

Computational Details

General Methodology

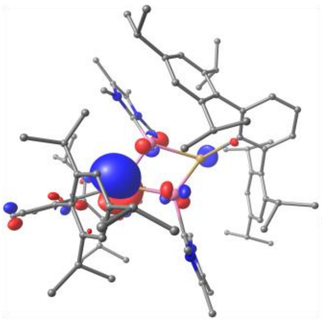
DFT calculations have been performed using the Gaussian09 Revision D.01 program.[8] The structure of complex **2** has been optimized using the BP86[9,10] functional with def2svp basis set on C, H and N as well as def2QZVP basis set on Sn and Pt along with w06 density fitting[11, 12] as well as Stuttgart-Dresden effective core potentials on tin (MWB46) and Pt (MWB60) as implemented in Gaussian. Grimme dispersion correction with Becke-Johnson damping has been taken into account using the GD3BJ option implemented in Gaussian.[13] The starting geometry for geometry optimizations applying C_1-symmetry were taken from the X-ray data of complex **2** and two hydrides were intuitively attached to the platinum atoms. Pictures have been created with the ChemCraft progamm. The optimized gasphase structure of platinum complex **2** reproduces the experimentally determined geometry (see Table 2SI). A frequency calculation for the optimized structure of **2** revealed no imaginary frequencies. Cartesian coordinates of the optimized structure of complex **2** are attached at the end of the file.

Table 2. Selected computational vs. experimental structural details

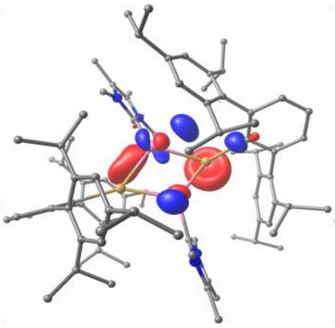
	Pt complex **(2)**	
	Experimental	**Computational**
Sn1-Pt1/Pt2 [Å]	2.5082 / 2.5235	2.558 / 2.566
Sn2-Pt1/2 [Å]	2.5813 / 2.6121	2.645 / 2.664
Pt1-Pt2 [Å]	2.8275	2.9034
Pt-Carbene [Å]	2.005 / 2.006	2.001 / 2.003
Pt2-H1	1.42	1.64
Pt1-H2	1.49	1.66
Sn2-H1	2.17	2.27
Sn2-H2	2.24	2.28
Pt-Sn1/2-Pt [°]	68.4 / 66.0	69.0 / 66.3

Selected CMOs of complex 2

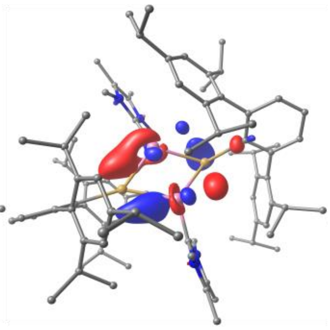
Hydrogen atoms have been omitted for the sake of clarity. The left Sn-moiety corresponds to Sn1, with the LUMO indicating the presence of an empty p-orbital perpendicular to the Pt-Pt-Sn1 plane. The right Sn-moiety corresponds to Sn2 with the HOMO indicating the presence of a tin-centered lone-pair.



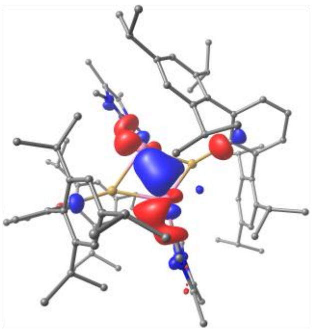
LUMO



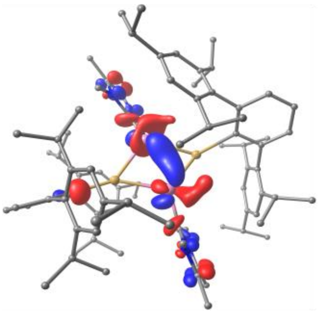
HOMO



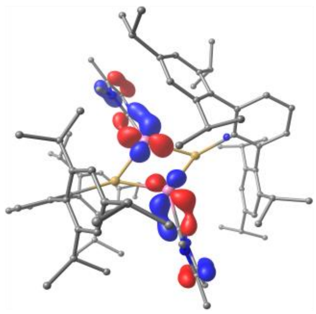
HOMO-1



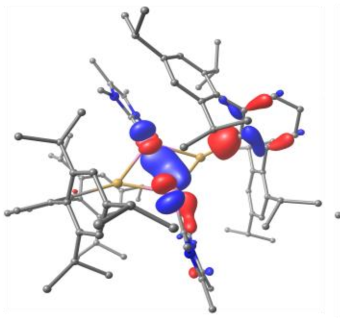
HOMO-2



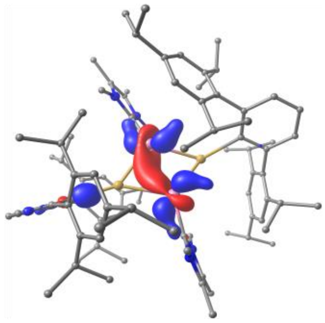
HOMO-3



HOMO-23



HOMO-24

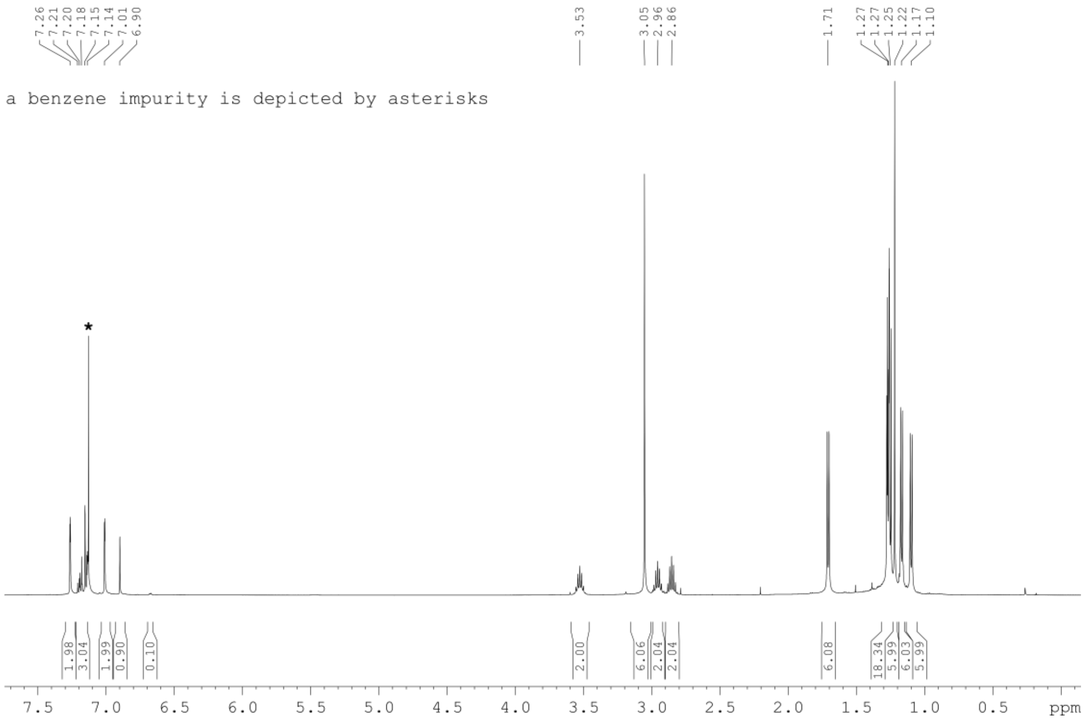


HOMO-28

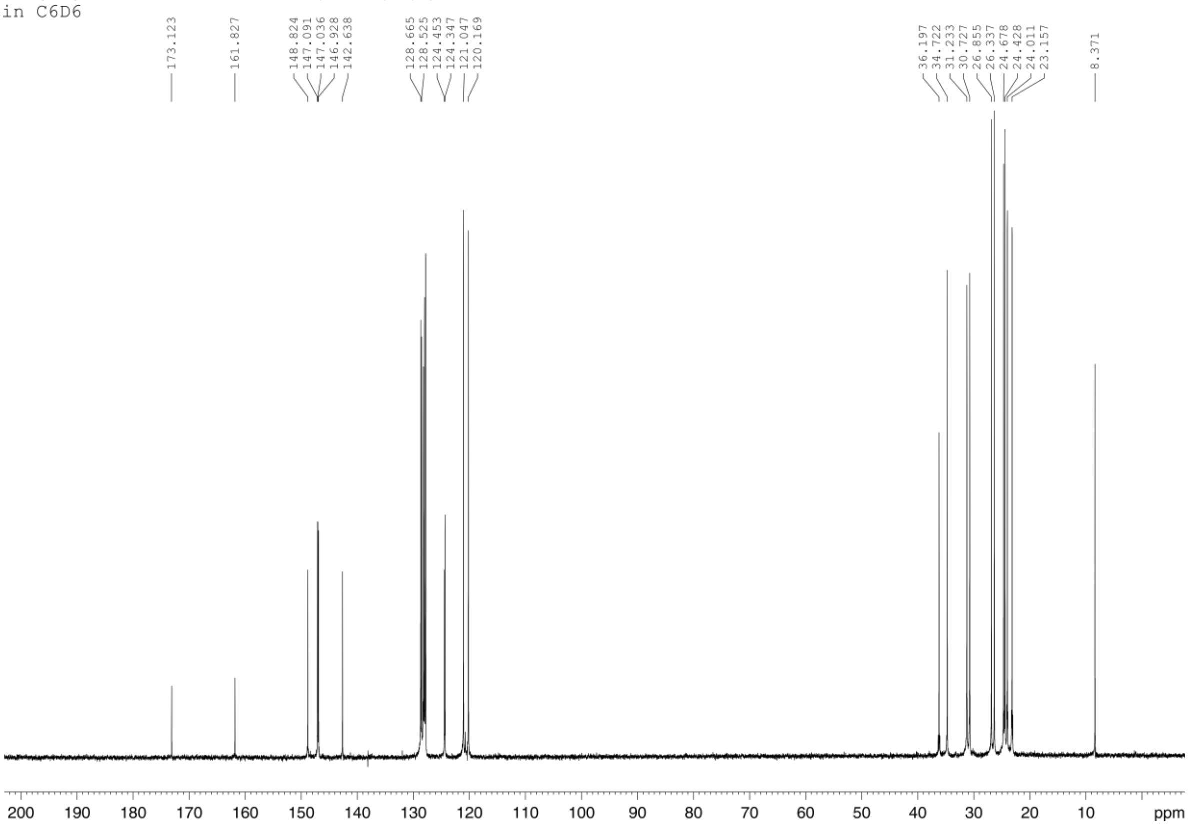
NMR Spectra

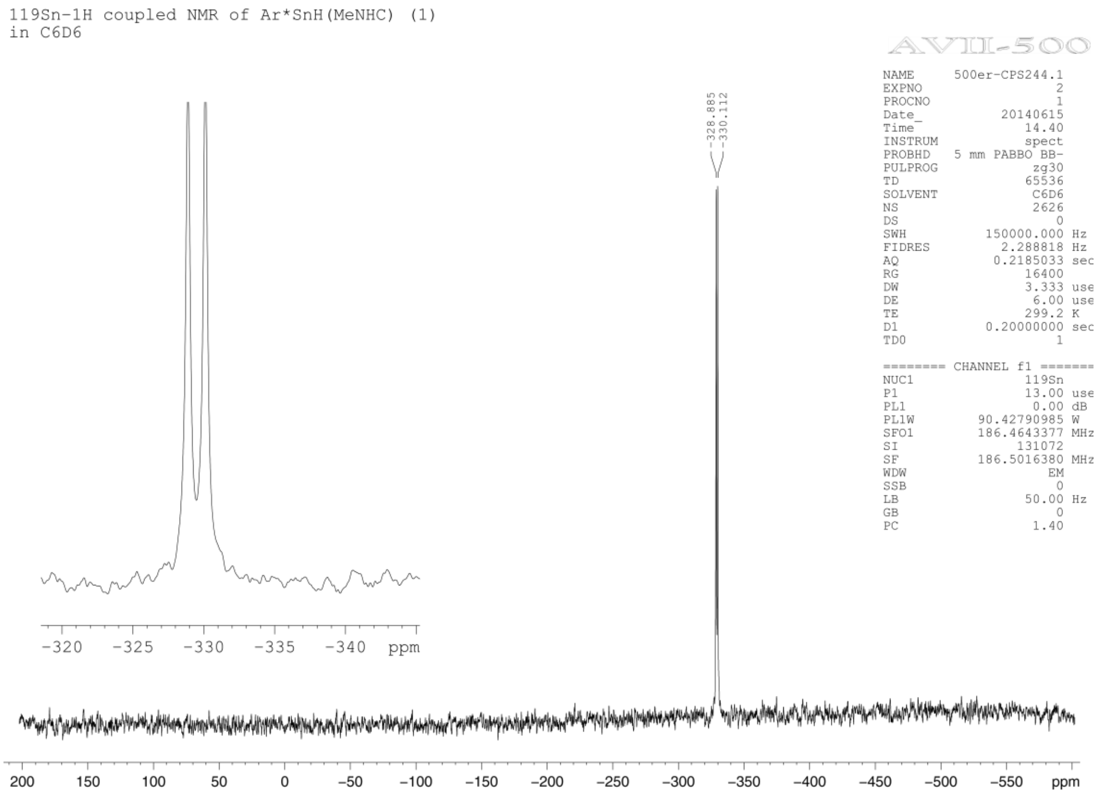
Compound 1 Ar*SnH(^{Me}NHC)

1H NMR of Ar*SnH(MeNHC) (1)
in C6D6



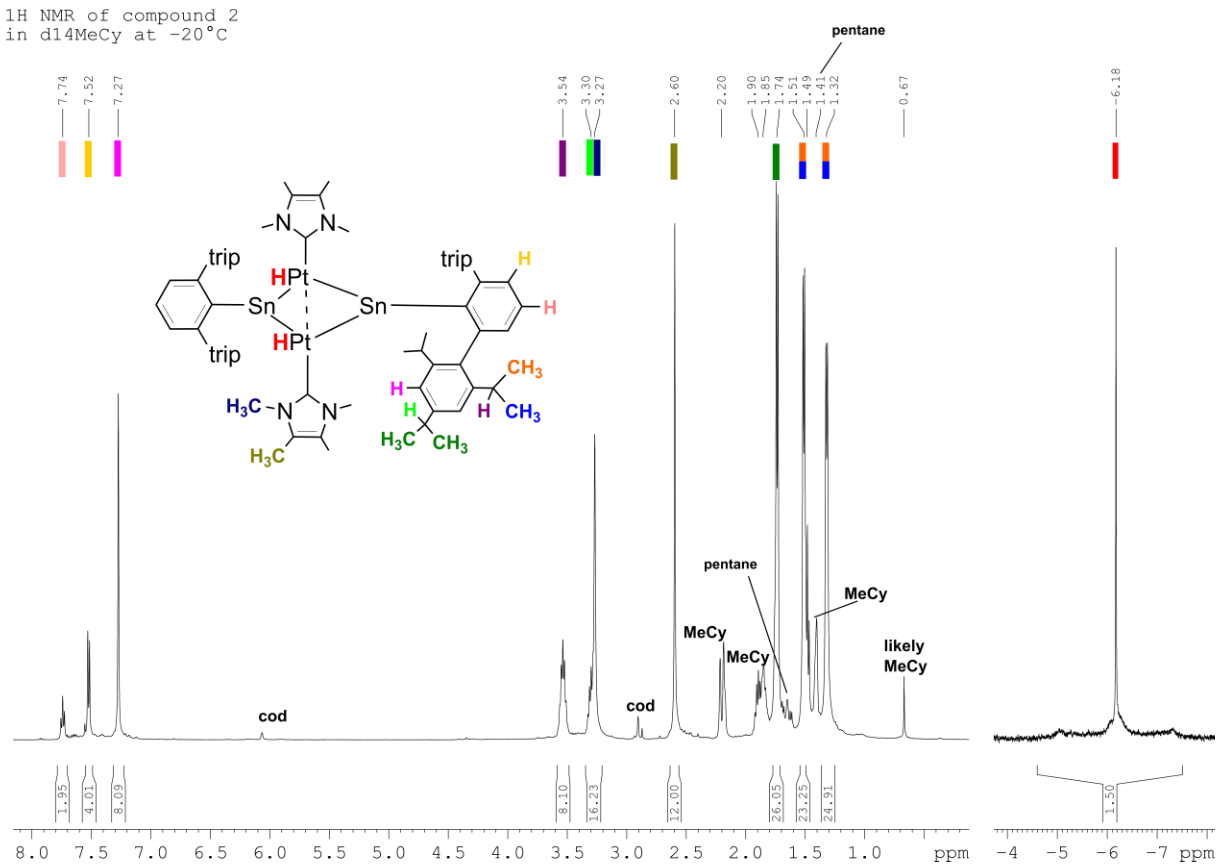
13C{1H}-udeft NMR of Ar*SnH(MeNHC) (1)
in C6D6



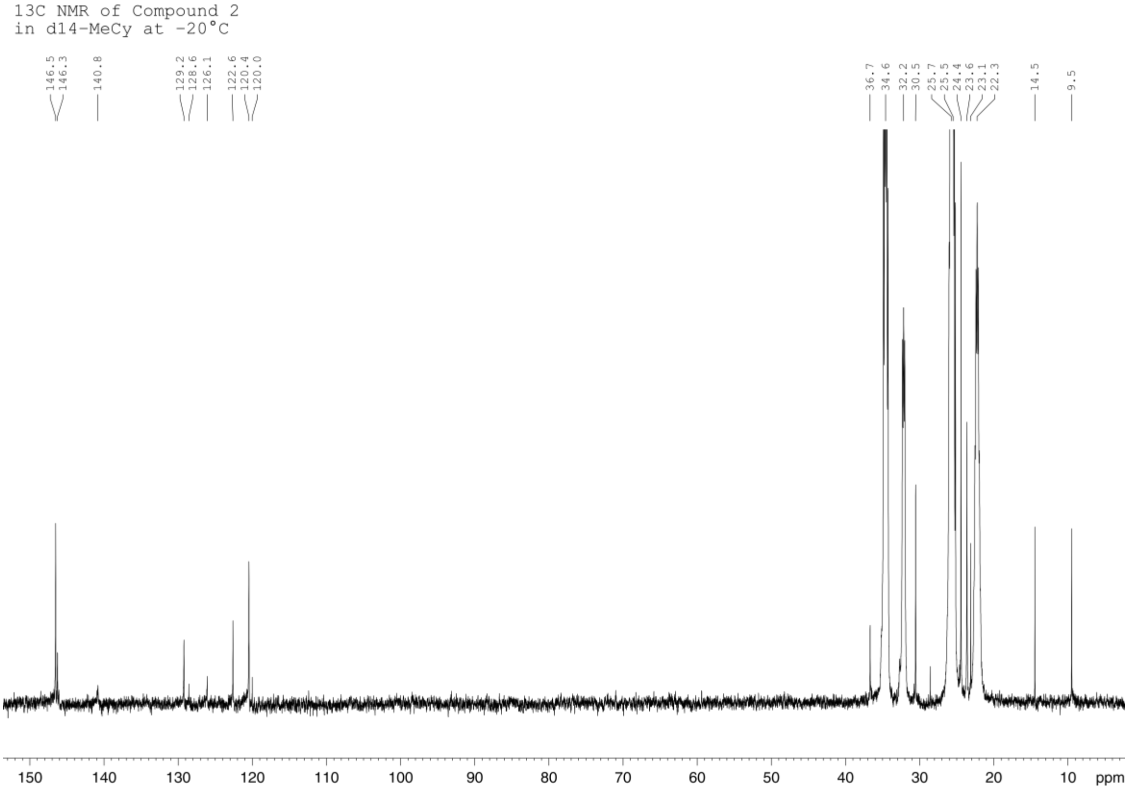


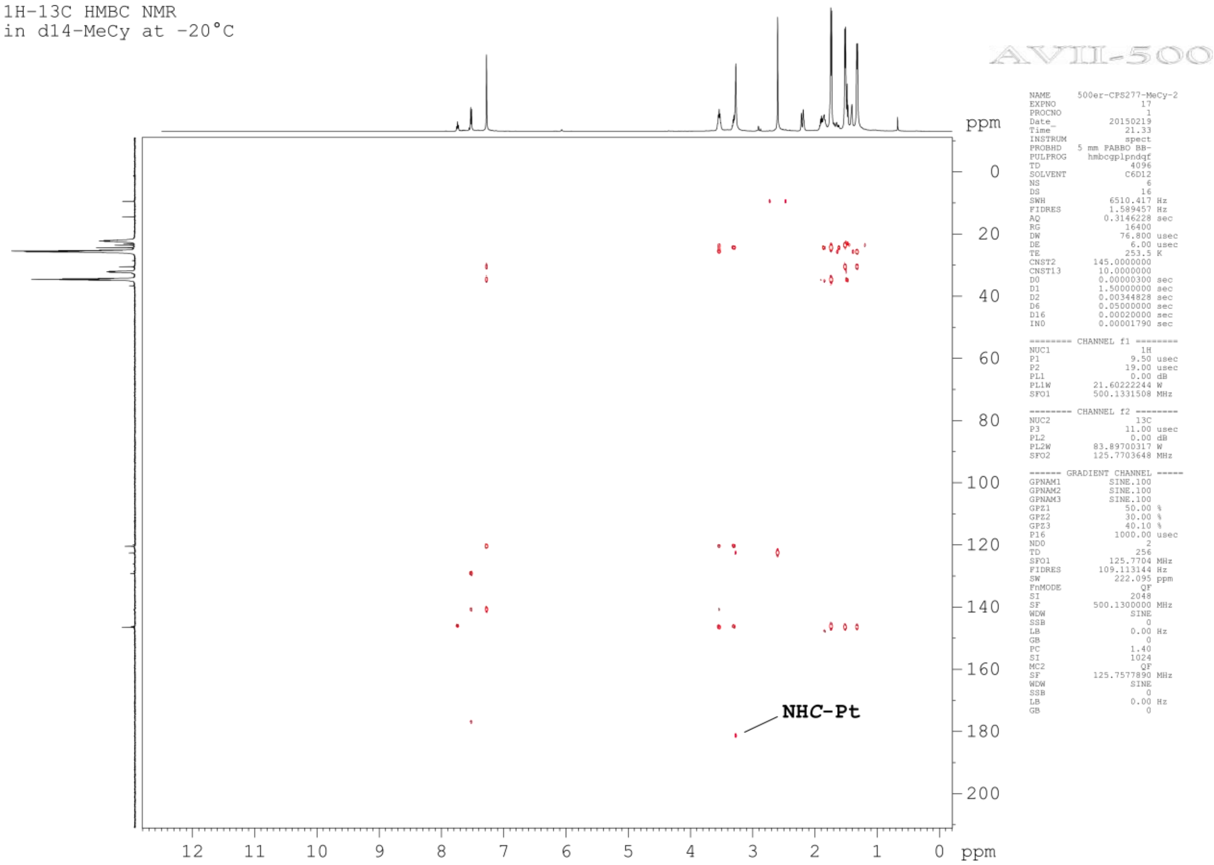
119Sn-1H coupled NMR of Ar*SnH(MeNHC) (1)
in C6D6
-328.885
-330.112
NAME 500er-CPS244.1
EXPNO 2
PROCNO 1
Date_ 20140615
Time 14.40
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT C6D6
NS 2626
DS 0
SWH 150000.000 Hz
FIDRES 2.288818 Hz
AQ 0.2185033 sec
RG 16400
DW 3.333 use
DE 6.00 use
TE 299.2 K
D1 0.20000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 119Sn
P1 13.00 use
PL1 0.00 dB
PL1W 90.42790985 W
SFO1 186.4643377 MHz
SI 131072
SF 186.5016380 MHz
WDW EM
SSB 0
LB 50.00 Hz
GB 0
PC 1.40
ppm

Compound 2

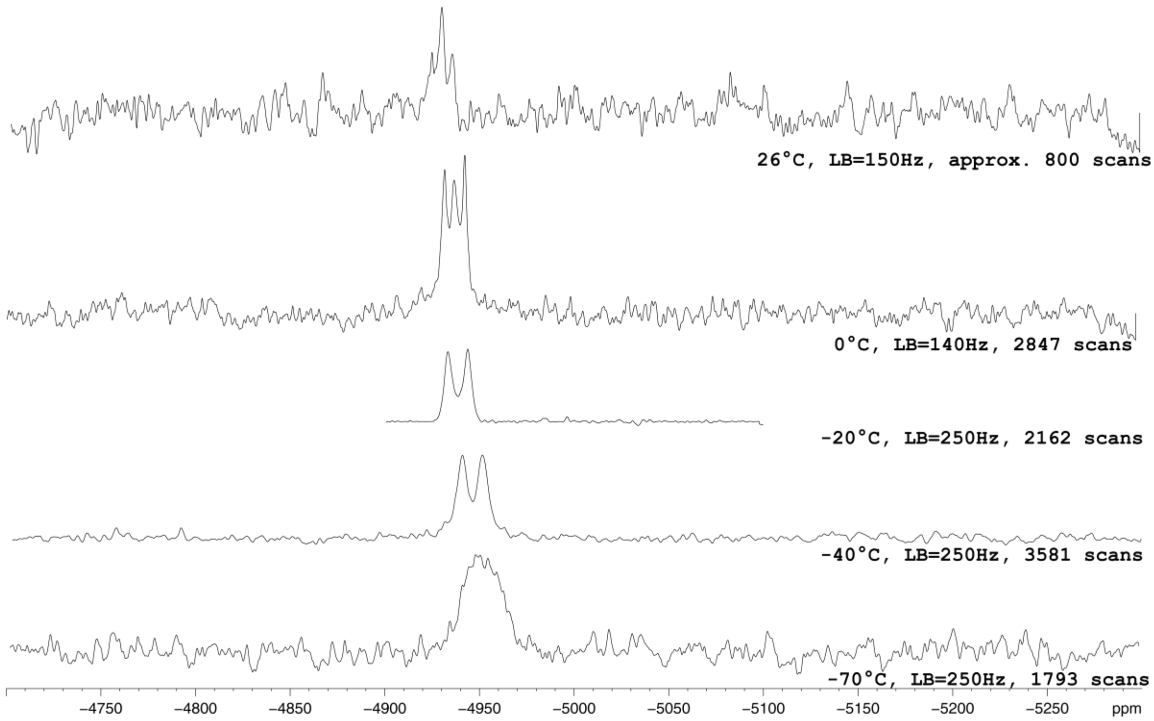


1H NMR of compound 2
in d14MeCy at -20°C
pentane
7.74
7.52
7.27
3.54
3.30
3.27
2.60
2.20
1.90
1.85
1.74
1.51
1.49
1.41
1.32
0.67
-6.18
trip
trip
trip
Sn
Sn
HPt
HPt
N
N
H3C
H3C
CH3
CH3
H3C
CH3
H
H
H
H
H
cod
cod
MeCy
MeCy
MeCy
likely MeCy
pentane
1.95
4.01
8.09
8.10
16.23
12.00
26.05
23.25
24.91
1.50
ppm

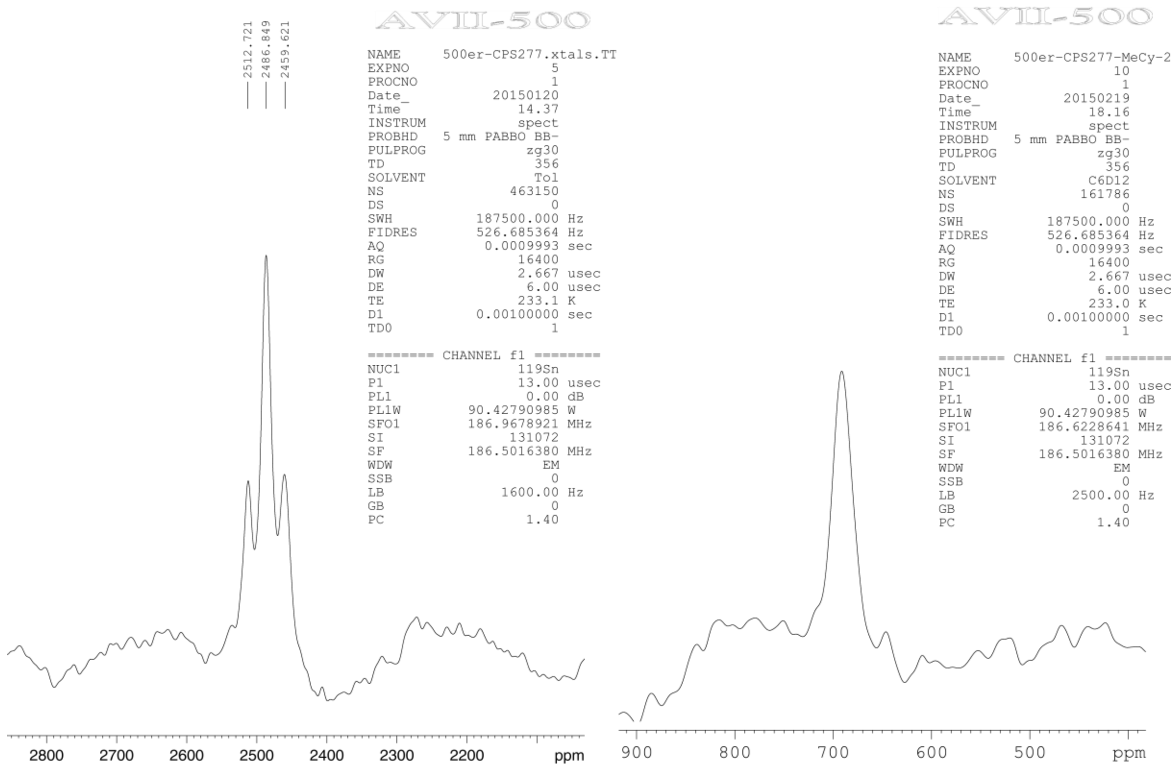

13C NMR of Compound 2
in d14-MeCy at -20°C
146.5
146.3
140.8
129.2
128.6
126.1
122.6
120.4
120.0
36.7
34.6
32.2
30.5
25.7
25.5
24.4
23.6
23.1
22.3
14.5
9.5
ppm

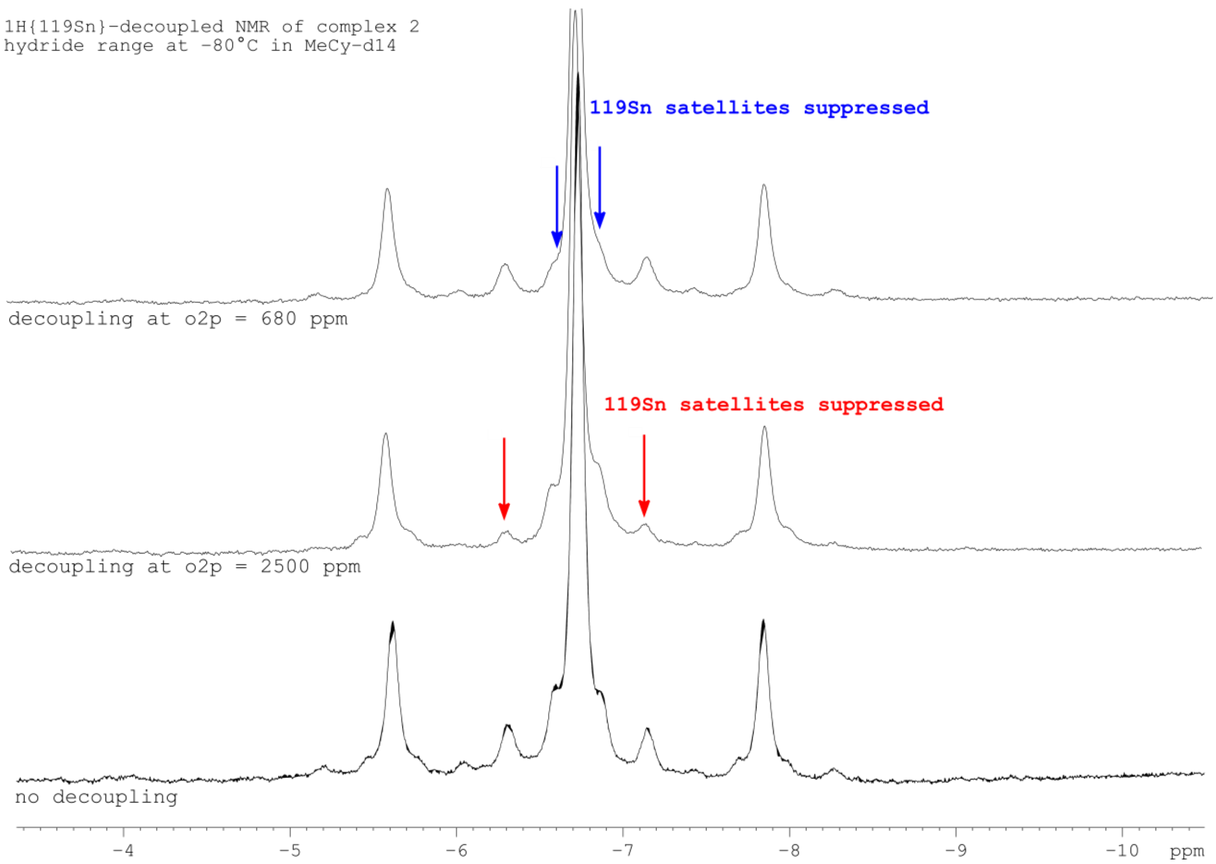

1H-13C HMBC NMR
in d14-MeCy at -20°C
AVII-500
NHC-Pt
ppm

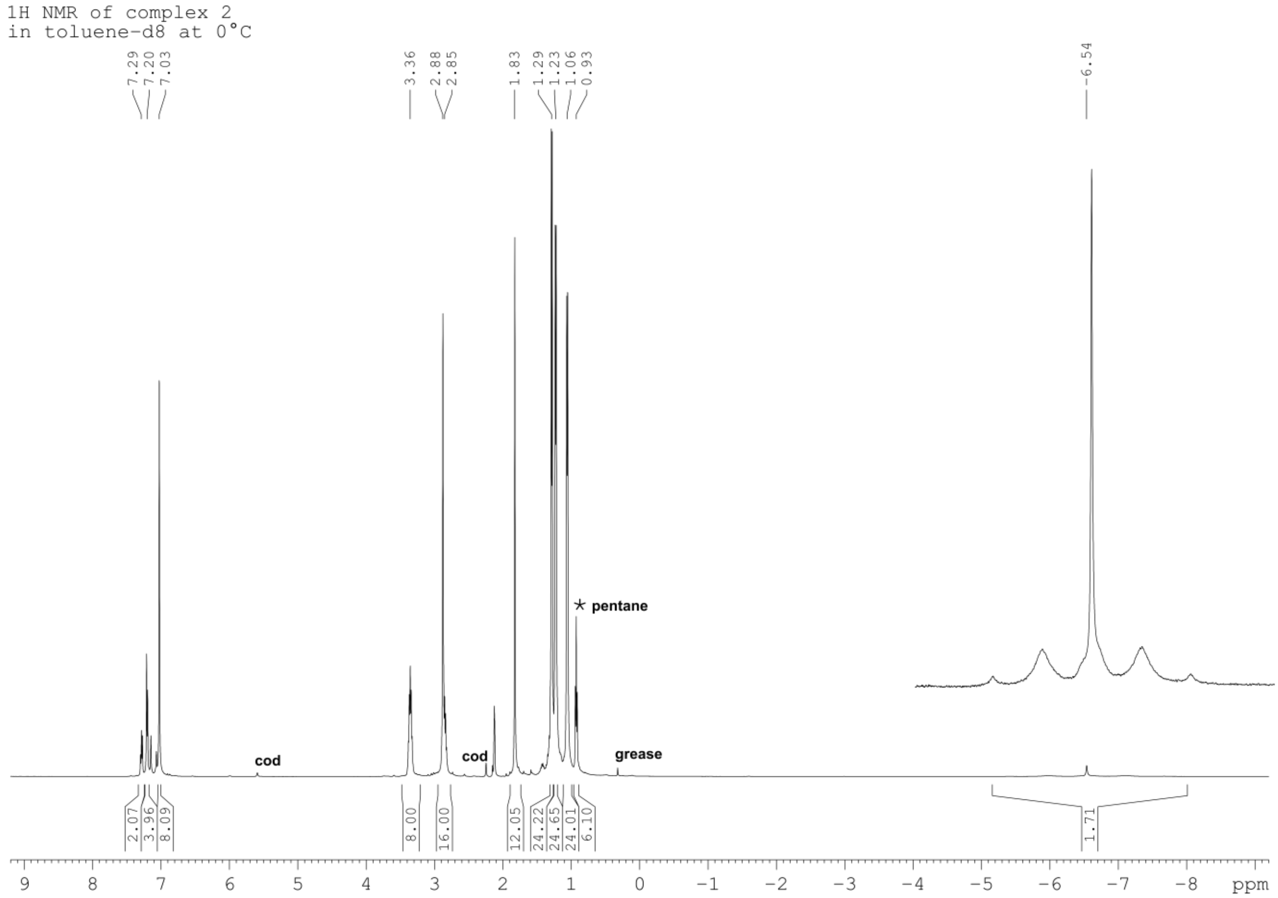
195Pt-1H coupled NMR of complex 2
in toluende-d8



119Sn-NMR of complex 2
at -40°C in tol-d8/MeCy-d14

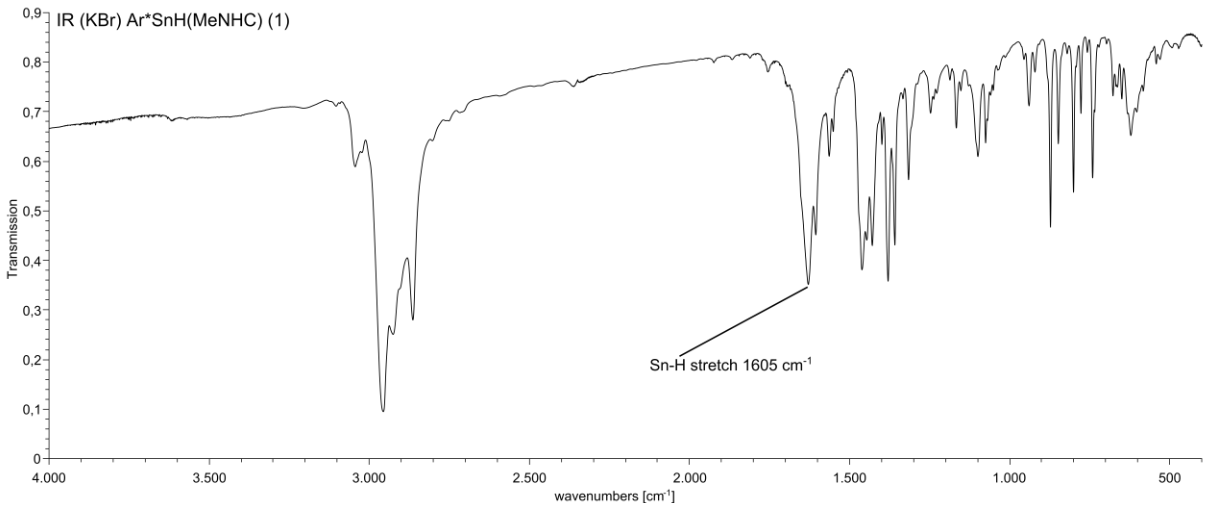



1H{119Sn}-decoupled NMR of complex 2
hydride range at -80°C in MeCy-d14
119Sn satellites suppressed
decoupling at o2p = 680 ppm
119Sn satellites suppressed
decoupling at o2p = 2500 ppm
no decoupling
ppm

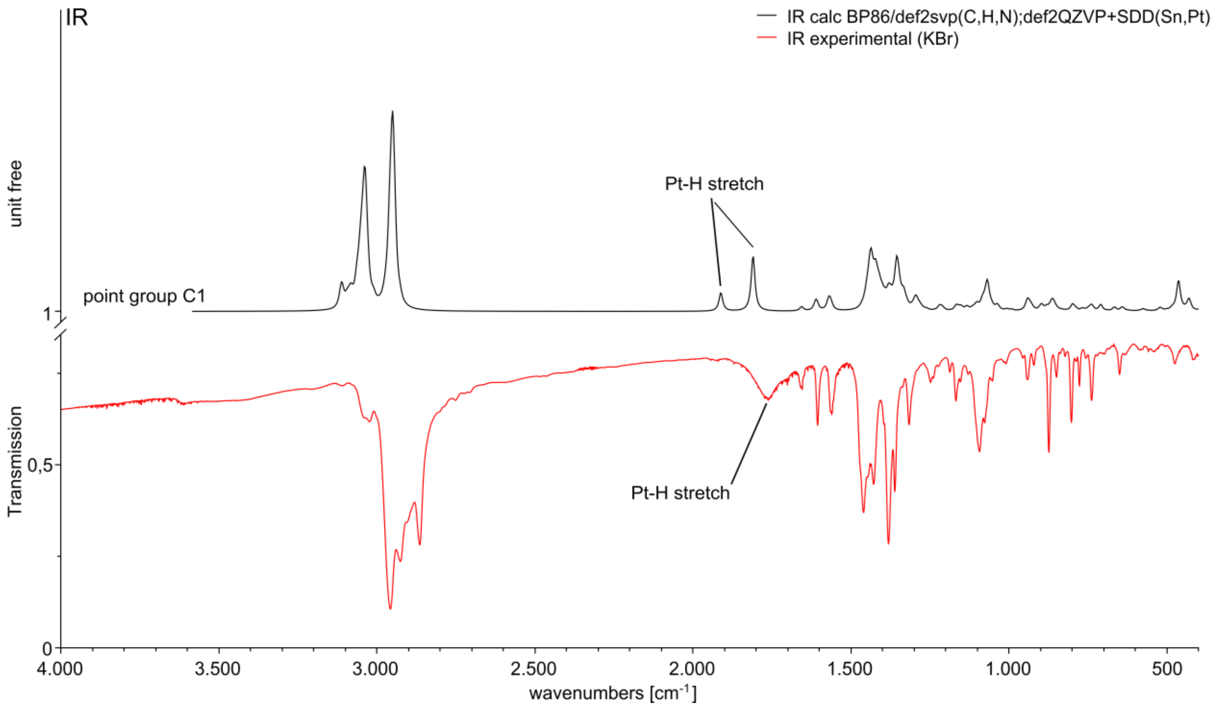

1H NMR of complex 2
in toluene-d8 at 0°C
7.29
7.20
7.03
3.36
2.88
2.85
1.83
1.29
1.23
1.06
0.93
-6.54
★ pentane
cod
cod
grease
2.07
3.96
8.09
8.00
16.00
12.05
24.22
24.65
24.01
6.10
1.71
ppm

IR Spectroscopy

Compound 1 Ar*SnH(^{Me}NHC)



Complex 2



Optimized Geometry of Complex 2

Pt	0.198018000	1.460899000	0.502566000
N	1.227068000	4.197540000	1.396773000
Pt	-0.198718000	-1.219061000	-0.542562000
N	-0.147209000	3.358428000	2.842432000
Sn	1.962116000	-0.390950000	0.565502000
Sn	-2.195382000	0.370487000	0.220621000
C	4.106036000	-0.751021000	0.944879000
C	5.070567000	-0.850890000	-0.081827000
C	4.589615000	-0.925649000	-1.500120000
C	0.488021000	3.072146000	1.655882000
C	2.121170000	4.258304000	0.259082000
H	2.441885000	5.299457000	0.078690000
H	1.582923000	3.870656000	-0.625038000
H	3.011971000	3.621535000	0.435351000
C	1.067619000	5.170306000	2.392273000
C	0.181637000	4.640117000	3.308017000
C	-1.075738000	2.449110000	3.485363000
H	-2.128213000	2.700394000	3.238282000
H	-0.941647000	2.475156000	4.584053000
H	-0.862142000	1.433976000	3.101987000
C	3.225706000	-1.250164000	-5.632124000
H	2.895260000	-0.231909000	-5.935700000
C	4.448478000	-1.623207000	-6.496012000
H	4.189454000	-1.628277000	-7.576044000
H	4.823936000	-2.634653000	-6.230877000
H	5.281540000	-0.907487000	-6.341667000
C	2.051571000	-2.208764000	-5.887869000
H	1.156724000	-1.905546000	-5.309769000
H	2.307533000	-3.252659000	-5.608613000
H	1.777039000	-2.214483000	-6.963240000
N	-0.931854000	-4.052343000	0.144896000
N	-0.005112000	-4.007090000	-1.813506000
C	1.778989000	6.481190000	2.373962000
H	1.540679000	7.073390000	1.463830000
H	2.883098000	6.356281000	2.407179000
H	1.485880000	7.089076000	3.251403000
C	-0.385321000	5.209570000	4.564760000
H	-0.016926000	6.241724000	4.720572000
H	-0.099774000	4.616041000	5.460814000
H	-1.495650000	5.249712000	4.537229000
C	4.277507000	0.244624000	-2.244898000
C	3.801414000	0.099389000	-3.560937000
H	3.562819000	0.995419000	-4.152257000
C	3.629313000	-1.158160000	-4.164726000
C	3.909910000	-2.301924000	-3.396791000
H	3.767614000	-3.300452000	-3.841324000
C	4.371138000	-2.210599000	-2.069932000
C	4.625866000	-3.485621000	-1.268702000
H	4.879960000	-3.179118000	-0.233918000
C	3.365813000	-4.363368000	-1.177685000
H	2.506422000	-3.785401000	-0.782822000
H	3.540300000	-5.229429000	-0.505967000
H	3.078042000	-4.770282000	-2.169917000
C	5.832136000	-4.265257000	-1.823468000
H	5.651881000	-4.597603000	-2.868272000
H	6.035592000	-5.169261000	-1.211309000
H	6.746901000	-3.637822000	-1.825191000
C	4.521941000	1.632593000	-1.654830000
H	4.281126000	1.576015000	-0.569000000

C	6.012392000	2.012321000	-1.775377000
H	6.316491000	2.060258000	-2.842618000
H	6.660632000	1.271035000	-1.268098000
H	6.205036000	3.005419000	-1.316890000
C	3.627267000	2.714808000	-2.272707000
H	3.816306000	3.690924000	-1.783518000
H	2.553187000	2.465210000	-2.156251000
H	3.836677000	2.859692000	-3.352897000
C	6.429574000	-1.017138000	0.263480000
H	7.184327000	-1.103798000	-0.534915000
C	6.814277000	-1.111673000	1.612433000
H	7.876647000	-1.244820000	1.870506000
C	5.845092000	-1.076542000	2.633245000
H	6.143091000	-1.198959000	3.687212000
C	4.487775000	-0.901134000	2.305677000
C	3.342629000	-0.933825000	3.277729000
C	2.486211000	-2.082063000	3.260607000
C	2.975804000	-3.391264000	2.639402000
H	3.593143000	-3.124999000	1.755878000
C	1.854343000	-4.310463000	2.144852000
H	1.217775000	-3.787069000	1.406494000
H	1.211376000	-4.673536000	2.974675000
H	2.281377000	-5.205267000	1.649415000
C	1.236149000	-2.003107000	3.899750000
H	0.567915000	-2.875755000	3.870102000
C	0.808304000	-0.833256000	4.557252000
C	1.702452000	0.247792000	4.634431000
H	1.387117000	1.159982000	5.167437000
C	2.969107000	0.219139000	4.015468000
C	3.891657000	1.431777000	4.091936000
H	4.856653000	1.132983000	3.633655000
C	4.174525000	1.841313000	5.548541000
H	4.905380000	2.676410000	5.584277000
H	4.587503000	0.995265000	6.135704000
H	3.251966000	2.187821000	6.061291000
C	3.339810000	2.605163000	3.266603000
H	4.070525000	3.440295000	3.224227000
H	2.399148000	2.996800000	3.705356000
H	3.104187000	2.276288000	2.235224000
C	-1.478660000	-3.580177000	1.405231000
H	-0.863442000	-2.723582000	1.740721000
H	-1.454984000	-4.388168000	2.160561000
H	-2.516540000	-3.214535000	1.269941000
C	-0.311016000	-3.206932000	-0.741864000
C	0.561333000	-3.471872000	-3.035959000
H	-0.239049000	-3.214799000	-3.761026000
H	1.250788000	-4.202341000	-3.497775000
H	1.115472000	-2.548502000	-2.777908000
C	-0.439233000	-5.324974000	-1.614054000
C	-1.029935000	-5.353141000	-0.366107000
C	-1.658504000	-6.471884000	0.393569000
H	-2.709894000	-6.240385000	0.671555000
H	-1.111991000	-6.697258000	1.335329000
H	-1.668107000	-7.395819000	-0.215760000
C	-0.236930000	-6.400197000	-2.627437000
H	-0.715045000	-6.148418000	-3.598532000
H	-0.677711000	-7.352060000	-2.273835000
H	0.840968000	-6.585751000	-2.827747000
C	-0.574158000	-0.760855000	5.193915000
H	-0.748039000	0.304793000	5.460102000
C	-1.688873000	-1.194202000	4.223006000
H	-1.621666000	-0.675547000	3.243275000
H	-2.691363000	-0.990255000	4.652300000
H	-1.638896000	-2.284210000	4.020402000

C	-0.623069000	-1.577616000	6.501061000
H	0.149278000	-1.235556000	7.220035000
H	-0.438960000	-2.654164000	6.298234000
H	-1.616946000	-1.490444000	6.988886000
C	3.901614000	-4.114935000	3.639808000
H	4.754287000	-3.471455000	3.935690000
H	4.311663000	-5.045673000	3.194055000
H	3.346000000	-4.388612000	4.561927000
C	-3.627383000	1.108491000	-1.361280000
C	-4.854592000	0.387338000	-1.400525000
C	-5.920248000	0.802947000	-2.222429000
H	-6.863725000	0.233176000	-2.220252000
C	-5.776504000	1.937122000	-3.038209000
H	-6.605474000	2.264957000	-3.685347000
C	-4.568802000	2.648577000	-3.024077000
H	-4.442966000	3.538783000	-3.662068000
C	-3.496130000	2.252246000	-2.188111000
C	-2.256265000	3.095291000	-2.227653000
C	-1.122103000	2.669334000	-2.975469000
C	-0.029217000	3.540928000	-3.099572000
H	0.841008000	3.221497000	-3.693641000
C	-0.013025000	4.818565000	-2.502397000
C	1.151947000	5.765249000	-2.788423000
H	2.089998000	5.202757000	-2.575253000
C	1.155785000	7.033518000	-1.924476000
H	2.074639000	7.628178000	-2.106368000
H	1.107094000	6.800195000	-0.841438000
H	0.287303000	7.683928000	-2.161086000
C	1.182138000	6.142919000	-4.285310000
H	2.059465000	6.783025000	-4.518725000
H	0.263112000	6.701794000	-4.562176000
H	1.232231000	5.243502000	-4.931017000
C	-1.107882000	5.181192000	-1.701149000
H	-1.103454000	6.150105000	-1.182563000
C	-2.231828000	4.343286000	-1.554259000
C	-3.359288000	4.738213000	-0.601489000
H	-4.268324000	4.188165000	-0.922115000
C	-3.028192000	4.266012000	0.830115000
H	-2.094193000	4.740964000	1.198667000
H	-2.864325000	3.169847000	0.858092000
H	-3.852696000	4.513947000	1.532099000
C	-3.693298000	6.238424000	-0.627012000
H	-2.868001000	6.854956000	-0.210964000
H	-4.593570000	6.445952000	-0.011552000
H	-3.892295000	6.592766000	-1.659463000
C	-1.103448000	1.293426000	-3.634034000
H	-1.710196000	0.625779000	-2.986349000
C	0.297623000	0.674532000	-3.700712000
H	0.969179000	1.212889000	-4.403095000
H	0.230221000	-0.375449000	-4.050395000
H	0.766700000	0.651583000	-2.695434000
C	-1.775122000	1.333198000	-5.020852000
H	-2.816557000	1.707627000	-4.954150000
H	-1.805201000	0.317909000	-5.471140000
H	-1.215819000	1.999149000	-5.712811000
C	-4.986466000	-0.837897000	-0.542316000
C	-5.326498000	-0.707489000	0.833077000
C	-5.353869000	-1.858142000	1.643910000
H	-5.612012000	-1.752047000	2.707725000
C	-5.037208000	-3.129461000	1.133388000
C	-4.695008000	-3.234399000	-0.228577000
H	-4.427744000	-4.224999000	-0.631752000
C	-4.661668000	-2.113834000	-1.078864000
C	-4.303803000	-2.263873000	-2.555240000

H	-3.927202000	-1.275266000	-2.894431000
C	-3.188095000	-3.287491000	-2.806961000
H	-2.892634000	-3.276617000	-3.877079000
H	-3.499640000	-4.325718000	-2.564856000
H	-2.299807000	-3.038062000	-2.198210000
C	-5.562857000	-2.594703000	-3.382192000
H	-6.344165000	-1.819114000	-3.257953000
H	-5.996691000	-3.567005000	-3.064087000
H	-5.318394000	-2.664448000	-4.463358000
C	-5.091749000	-4.383467000	1.999934000
H	-4.374324000	-5.108850000	1.550475000
C	-4.661327000	-4.144890000	3.456137000
H	-3.679710000	-3.632233000	3.514137000
H	-4.586184000	-5.105860000	4.006161000
H	-5.396657000	-3.515693000	4.000246000
C	-6.494103000	-5.023283000	1.931667000
H	-7.255624000	-4.331648000	2.350333000
H	-6.534386000	-5.970535000	2.510632000
H	-6.783561000	-5.242778000	0.883883000
C	-5.679542000	0.659878000	1.415784000
H	-5.204532000	1.421019000	0.760875000
C	-5.131653000	0.876203000	2.835829000
H	-4.041890000	0.665401000	2.867242000
H	-5.632340000	0.227003000	3.585221000
H	-5.291344000	1.927480000	3.154088000
C	-7.202304000	0.891319000	1.349214000
H	-7.468213000	1.900355000	1.729786000
H	-7.743756000	0.138344000	1.960891000
H	-7.570565000	0.809721000	0.306637000
H	-0.984032000	2.191038000	-0.371656000
H	-1.535746000	-0.981643000	-1.489719000

Literature

1. B. Schiemenz and P. P. Power, *Organometallics*, 1996, 15, 958-964.
2. B. E. Eichler, L. Pu, M. Stender and P. P. Power, *Polyhedron*, 2001, 20, 551-556.
3. M. Saito, H. Hashimoto, T. Tajima and M. Ikeda, *J. Organomet. Chem.*, 2007, 692, 2729-2735.
4. M. Green, J. A. K. Howard, J. L. Spencer and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1977, DOI: 10.1039/DT9770000271, 271-277.
5. R. K. Harris, E. D. Becker, S. M. Cabral de Menezes, R. Goodfellow and P. Granger, *Pure Appl. Chem.*, 2001, 73, 1795-1818.
6. C. P. Sindlinger and L. Wesemann, *Chem. Sci.*, 2014, 5, 2739-2746.
7. , SAINT, APEX2, Bruker AXS Inc.: Madison, WI.
8. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford, CT, USA, 2009.
9. A. D. Becke Phys. Rev. A, 1988, 38, 3098

10. J. P. Perdew, Phys. Rev. B, 1986, 33, 8822-24.

11. F. Weigend and R. Ahlrichs, Phy*s. Chem. Chem. Phys., 2*005, 7, 3297-3305.
12. F. Weigend, Phy*s. Chem. Chem. Phys., 2*006, 8, 1057-1065.
13. S. Grimme, S. Ehrlich and L. Goerigk, J. *Comput. Chem., 2*011, 32, 1456-1465.
5. SAINT, APEX2; Bruker AXS Inc.: Madison, WI, 2007.
6. G. M. Sheldrick, SADABS; University of Göttingen, Göttingen, Germany, 2008.
7. L. J .Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837 − 838.
8. G. M. Sheldrick, SHELXS 97; University of Göttingen, Göttingen, Germany, 1997.