Carborane-Based Pincers: Synthesis and Structure of SeBSe and SBS Pd(II) Complexes

Alexander M. Spokoyny, Matthew G. Reuter, Charlotte L. Stern, Mark A. Ratner, Tamar Seideman and Chad A. Mirkin*

Department of Chemistry and International Institute for Nanotechnology, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208

*To whom correspondence should be addressed:

E-mail chadnano@northwestern.edu

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1. Synthetic and characterization methods and procedures.

All reactions were carried out under an inert atmosphere of nitrogen using standard Schlenk techniques and dry solvents; work-up and all post-reaction manipulations were done at ambient conditions, unless specifically noted otherwise. Solvents were purified by standard procedures. Deuterated solvents were purchased from Cambridge Isotope Laboratories and used as received. All reagents were used as received from Aldrich Chemical Company. **2** and **3** were prepared according to previously published literature procedures.[*S1-2] All NMR spectra were recorded Bruker Advance 400MHz. ^{1}H and ^{13}C NMR were referenced to residual proton resonances in deuterated solvents. ^{11}B and ^{77}Se NMR were referenced to BF_3-etherate and Me_2Se standards respectively. Electrospray ionization (ESI) mass spectra were recorded on an Agilent ESI-MS MSD1100 mass spectrometer. Elemental analyses (C, H, Cl) were performed by Quantitative Technologies (Intertek), Whitehouse, NJ.

[*]NMR data for compound **3** (not reported in ref. 2): (^{1}H NMR (400.1 MHz, CD_2Cl_2, 25 °C, TMS): δ 4.2−1.1 (bm, 10 H, B-Hs), 3.72 (s, 4 H, CH_2−Br); $^{13}C\{^{1}H\}$ NMR (100.6 MHz, CD_2Cl_2, 25 °C, TMS): δ 73.7 (cage **C**), 32.4 (**C**H_2-Br); $^{11}B\{^{1}H\}$ (128.53 MHz, CD_2Cl_2, 25 ^{o}C, BF_3-ether): δ -6.2 (s, 2B), -10.9 (s, 6B), -13.3 (s, 2B).)

Compounds **4**: 0.64 g (2.05 mmols) of diphenyldiselenide was dissolved in 15 mL of anhydrous EtOH in a 50 mL Schlenk flask equipped with magnetic stir bar at room temperature. Approximately 175mg of $NaBH_4$ was added slowly to a reaction mixture kept under stream of nitrogen. After 5 minutes reduction of diselenide was complete (disappearance of yellow color). 660 mg (2 mmols) of **3** was dissolved in 5 mL of anhydrous EtOH, degassed, and subsequently added to the flask with selenide via syringe. The reaction mixture was refluxed for 18 hours, the solvent was evaporated *in vacuo*, and the residual oily substance was extracted with dichloromethane and brine. The organic

layer was dried with $MgSO_4$ and chromatographed on a silica column with petroleum ether/benzene (8/2) mixture to yield analytically pure **4** (0.7 g, 72%) as an off-white solid. ^{1}H NMR (400.1 MHz, CD_2Cl_2, 25 °C, TMS): δ 7.51 (m, 4H), δ 7.29 (m, 6H) δ 4.2−1.1 (bm, 10 H, B-Hs), 3.44 (s, 4 H, CH_2−Se); $^{13}C\{^{1}H\}$ NMR (100.6 MHz, CD_2Cl_2, 25 °C, TMS): δ 133.5 (aromatic **C**H), 130.6 (aromatic **C**Se), 129.9 (aromatic **C**H), 128.3 (aromatic **C**H), δ 75.9 (cage **C**), 33.5 (**C**H_2-Se); $^{11}B\{^{1}H\}$ (128.53 MHz, CD_2Cl_2, 25 ^{o}C, BF_3-ether): δ -6.7 (s, 2B), -10.9 (s, 6B), -13.2 (s, 2B); ^{77}Se NMR (76.34 MHz, CD_2Cl_2, 25 °C, Me_2Se): δ 354.1 (s). Anal. Calcd for $C_{16}H_{24}B_{10}Se_2$: C, 39.84; H, 5.01. Found: C, 39.93; H, 4.93.

Compound **5**: 335 mg (0.75 mmol) of $Pd(CH_3CN)_4[BF_4]_2$ was added to 360 mg (0.75 mmols) of **4** in 3 mL of CH_3CN; the mixture was refluxed under nitrogen for 24 hours. The resulting yellowish compound was cooled to room temperature and 2eq of $(^{n}Bu)_4NCl$ in 2mL of dry CH_3CN was added. After 10 mins, a precipitate was collected by filtration, washed with methanol, redissolved in dichloromethane, and filtered through a layer of celite. The organic filtrate was evaporated *in vacuo* to yield crude product. Further recrystallization from the dichloromethane/pentane mixture yielded analytically pure **5** as a tan yellow solid (355 mg, 76%). Single crystals of X-Ray quality were grown by slow evaporation from dichloromethane in a NMR tube. ESI-MS: m/z (positive mode) 1210 $[2M+Cl]^{+}$ and m/z (negative mode) 659 $[M+Cl]^{-}$. ^{1}H NMR (400.1 MHz, CD_2Cl_2, 25 °C, TMS): δ 8.03 (bs, 4H), δ 7.48 (bs, 6H) δ 4.2−1.1 (bm, 9H, B-Hs), 3.9 (b, 4 H, CH_2−Se); $^{13}C\{^{1}H\}$ NMR (74.49 MHz, DMF, 25 °C, TMS): δ 134.3 (aromatic **C**H), 130.8 (aromatic **C**H), 130.3(aromatic **C**H), 84 (b, **C**-cage), 45 (b, **C**H_2Se); $^{11}B\{^{1}H\}$ (128.53 MHz, CD_2Cl_2, 25 ^{o}C, BF_3-ether): δ -0.7 (s, 1B), -3 to -18 (bm, 9B). Anal. Calcd for $C_{16}H_{23}B_{10}ClPdSe_2$: C, 30.83; H, 3.72; Cl, 5.69. Found: C, 30.90; H, 3.72; Cl, 5.36.

Compund **6**: 1 g (7 mmols) of *m*-carborane **1** was dissolved in 30 mL of dry Et_2O in an oven-dried Schlenk flask. 9.4 mL of MeLi (1.6M in Et_2O, 15 mmoles) was added dropwise to the mixture stirring on ice under nitrogen. The lithiation proceeded overnight at room temperature and was followed by the addition of 2.5g (15 mmoles) α-chlorothioanisole dissolved in 5 mL of dry Et_2O to the reaction stirred on ice. Reaction was stirred at room temperature for 24 hours, then extracted with ethyl acetate and brine; the organic extract was dried with $MgSO_4$ and evaporated *in vacuo*. The crude product was chromatographed on a silica column eluted with petroleum ether to afford analytically pure **6**. (1.78g, 66%) ^{1}H NMR (400.13 MHz, CD_2Cl_2, 25 °C, TMS): δ 7.5-7.1 (m, 10H), δ 3.36 (s, 4H) δ 3.2−1.5 (bm, 10H, B-Hs); $^{13}C\{^1H\}$ NMR (100.62 MHz, CD_2Cl_2, 25 °C, TMS): δ 135.8 (aromatic **C**H), 130.5 (aromatic **C**H), 129.7 (aromatic **C**H), 127.6 (aromatic **C**H), 75.8 (s, C-cage), δ 40.8 (s, CH_2S); $^{11}B\{^1H\}$ (128.37 MHz, CD_2Cl_2, 25 ^oC, BF_3-ether): δ -6.7 (s, 2B), -11.1 (s, 6B), -13.8 (s, 2B). Anal. Calcd for $C_{16}H_{24}B_{10}S_2$: C, 49.45; H, 6.23. Found: C, 49.65; H. 6.17.

Compound **7**: **6** was palladated in a similar fashion as ligand **4** on a 0.5 mmol scale to afford **7** in 71% yield. Single crystals of **7** were obtained in a similar fashion to **5**. ESI-MS: m/z (positive mode) 1023 $[2M+Cl]^+$ and m/z (negative mode) 564 $[M+Cl]^-$. ^{1}H NMR (400.13 MHz, CD_2Cl_2, 25 °C, TMS): δ 7.86 (m, 4ArH), δ 7.45 (m, 6ArH) δ 3.84−3.65 (dd, 4H, CH_2), 3.1-1.0 (bm, 9H, cage-Hs); $^{13}C\{^1H\}$ NMR (100.62 MHz, CD_2Cl_2, 25 °C, TMS): δ 133.5 (aromatic **C**H), 132.0 (aromatic **C**H), 131.2 (aromatic **C**H), 130.4 (aromatic CH) 80.0 (s, C-cage), δ 54.1 (s, CH_2S); $^{11}B\{^1H\}$ (128.53 MHz, CD_2Cl_2, 25 ^oC, BF_3-ether): δ 0.8 (s, 1B), -6.5 to -15 (bm, 9B). Anal. Calcd for $C_{16}H_{23}B_{10}S_2PdCl$: C, 36.30; H, 4.38; Cl, 6.70. Found: C, 36.28; H, 4.17; Cl, 7.07.

2. Crystallographic structure determination details of 5 and 7.[S3]

(a) **5**: $C_{16}H_{23}B_{10}ClPdSe_2$, M_r = 623.21, monoclinic, space group $P2_1/n$, a = 12.4086(3) Å, b = 11.5587(2) Å, c = 16.2997(3) Å, α = γ = 90°, β = 109.1730(10)°, V = 2208.15 $Å^3$, Z = 4, ρ_{calcd} = 1.875 g/cm^3, F(000) = 1200, R(int) = 0.0383, goodness-of-fit on F^2 = 1.143; the R values are R_1 = 0.0253 and wR^2 = 0.0642 (I > 2σ(I)); max/min Fourier map electron density = 0.786/−0.596 e $Å^{-3}$.

(b) **7**: $C_{16}H_{23}B_{10}ClPdS_2$, M_r = 623.21, orthorhombic, space group Pbca, a = 10.4063(4) Å, b = 15.4367(5) Å, c = 27.9230(10) Å, α = β= γ = 90°, V = 4485.5 (3) $Å^3$, Z = 8, ρ_{calcd} = 1.568 g/cm^3, F(000) = 2112, R(int) = 0.1009, goodness-of-fit on F^2 = 1.239; the R values are R_1 = 0.0495 and wR^2 = 0.1073 (I > 2σ(I)); max/min Fourier map electron density = 1.167/−3.066 e^- $Å^{-3}$.

3. Computational details.

DFT calculations on **5** were performed using the B3LYP and BP86 functionals with various basis sets. The presence of heavy atoms necessitated the use of effective core potentials (ECPs); calculations without ECPs were inconsistent. Table SI-1 shows the calculated HOMO-LUMO gap and Mulliken partial charges of the Pd, the boron bonded to the Pd, and the boron on the opposite side of the cage. As can be seen, the HOMO-LUMO energy gaps appear to be well-converged; however, we note the pernicious theoretical concern about the physical interpretation of such HOMO-LUMO gaps in DFT calculations. Firstly, DFT is a ground-state formulation, and, secondly, such a gap between non-interacting particles in DFT may not correspond to the physical gap. Additionally, the Mulliken partial charges on the various atoms are wildly variable. In all calculations, we see that the palladium is negatively charged, and the boron bonded to the palladium is relatively positively charged (compared to the other borons in the cage). The magnitudes of these Mulliken partial charges are not converged. Upgrading to Löwdin partial charges maintains these trends, improving consistency with respect to choice of basis set and ECP. Table SI-2 shows the

Löwdin partial charges for the same atoms under two basis set/ECP combinations. We thus recommend caution in the choice of functional and ECP and in the (quantitative) interpretation of the results.

Functional	ECP	HOMO-LUMO Gap (eV)	Pd Charge (au)	B(Pd) Charge (au)	B(cage) Charge (au)
B3LYP	CRENBL	4.16	-0.46	1.21	0.05
B3LYP	LANL2DZ	4.14	-0.49	0.59	-0.27
B3LYP	SBKJC	4.16	-0.26	0.57	-0.44
BP86	CRENBL	4.19	-0.40	1.20	0.06
BP86	LANL2DZ	4.14	-0.36	0.26	0.06
BP86	SBKJC	4.19	-0.55	0.93	-0.24

Table SI-1.

Functional	ECP	Pd Charge (au)	B(Pd) Charge (au)	B(cage) Charge (au)
B3LYP	LANL2DZ	-1.11	-0.04	-0.15
B3LYP	SBKJC	-1.20	0.08	-0.13

Table SI-2.

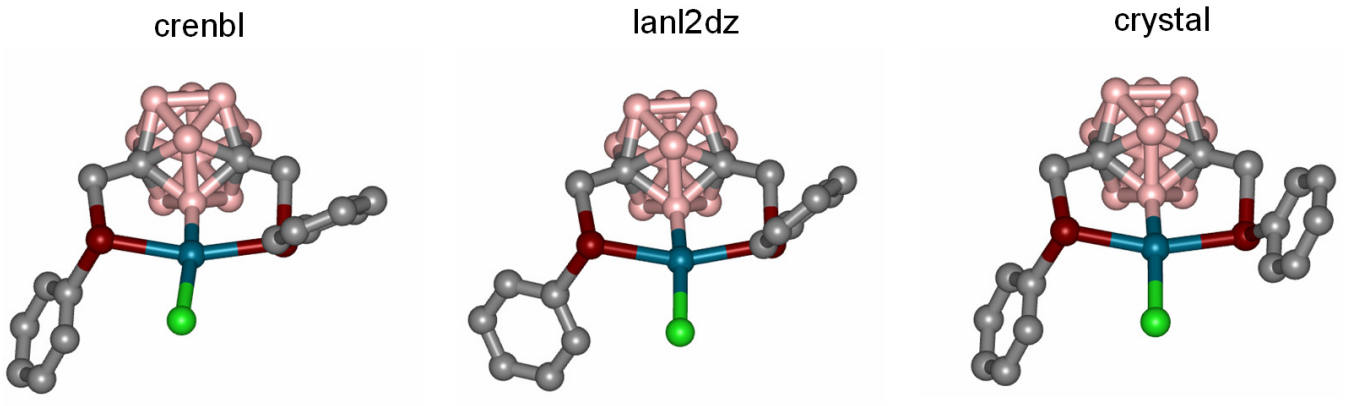

Figure SI-1. Visual comparison between different geometry optimizations of **5**.

	Crenbl (Cartesian xyz [Å])			Lanl2dz (Cartesian xyz [Å])			Crystal (Cartesian xyz [Å])		
Pd	0.096245	-0.6778	-0.26307	0.155272	-0.74727	-0.42394	0.1735	0.096	1.0315
Se	-1.86521	-0.8875	1.244459	-1.72827	-0.9598	1.242085	-2.1415	0.064	0.3085
Se	2.237797	0.073928	-1.31861	2.359329	-0.00467	-1.44628	2.5545	0.582	1.1555
Cl	0.372681	-3.14617	-0.19375	0.406368	-3.23463	-0.59839	-0.3345	-0.173	3.4005
C	-2.2983	1.053803	1.652662	-2.15997	1.013772	1.602665	-2.0345	0.335	-1.6455
C	-1.44752	2.024577	0.847964	-1.34136	1.957076	0.748164	-0.6055	0.251	-2.1395
C	0.932367	2.51286	-0.27449	0.9883	2.450394	-0.47679	1.9325	0.766	-1.6185
C	2.328255	1.969958	-0.54078	2.381753	1.950189	-0.79231	2.8765	1.376	-0.6215
C	-3.40264	-1.47404	0.141519	-3.35196	-1.46655	0.214458	-2.7335	-1.767	0.4945
C	-4.44854	-0.64044	-0.27409	-4.61776	-1.10183	0.68718	-2.8535	-2.684	-0.5395
C	-5.50894	-1.17981	-1.02407	-5.75653	-1.51155	-0.01679	-3.2435	-3.981	-0.2445
C	-5.51631	-2.54064	-1.3628	-5.62544	-2.29713	-1.16766	-3.5455	-4.352	1.0515
C	-4.45491	-3.36513	-0.9542	-4.3544	-2.68026	-1.61094	-3.4615	-3.421	2.0715
C	-3.39474	-2.83837	-0.20092	-3.20603	-2.26692	-0.92315	-3.0535	-2.129	1.8015
C	3.732792	-0.6932	-0.27217	3.724241	-0.70399	-0.17688	2.7525	2.168	2.2445
C	3.530037	-1.7587	0.616497	3.473975	-1.8745	0.545209	2.4075	2.033	3.5815
C	4.632516	-2.29118	1.308528	4.460179	-2.35502	1.41802	2.5755	3.1	4.4335
C	5.91787	-1.76132	1.118934	5.673171	-1.67427	1.565551	3.0655	4.301	3.9745
C	6.112138	-0.69977	0.219129	5.915899	-0.51184	0.824005	3.4275	4.423	2.6505
C	5.020307	-0.1682	-0.48563	4.944865	-0.02602	-0.05985	3.2755	3.356	1.7755
B	-0.32199	1.305073	-0.27648	-0.25338	1.237312	-0.40274	0.5615	0.008	-0.9095
B	-1.7722	2.188097	-0.85107	-1.73163	2.08547	-0.9399	0.1595	-1.279	-2.0665
B	-2.13512	3.528932	0.308736	-2.06085	3.443224	0.19791	-0.2455	-0.516	-3.6265
B	-0.88837	3.499175	1.61073	-0.77123	3.452133	1.446655	-0.0765	1.241	-3.4495
B	0.219107	2.145457	1.241958	0.335897	2.108999	1.069743	0.4315	1.554	-1.7935
B	-0.19619	2.521932	-1.59608	-0.19368	2.419078	-1.74765	1.8395	-0.929	-1.7175
B	-1.31814	3.8829	-1.24667	-1.31128	3.767892	-1.38692	1.3395	-1.267	-3.3895
B	-0.76686	4.696271	0.275019	-0.71397	4.613939	0.088012	1.2025	0.293	-4.2555
B	0.698828	3.830159	0.858283	0.773943	3.782214	0.631639	1.6305	1.583	-3.0965
B	0.432096	4.071612	-0.90706	0.439168	3.98263	-1.11992	2.4995	0.035	-3.0595
H	-3.36338	1.20541	1.486553	-3.22682	1.136345	1.414761	-2.5795	-0.353	-2.1015
H	-2.10285	1.143749	2.721549	-1.96331	1.160726	2.665492	-2.4075	1.223	-1.8735
H	2.917101	1.87496	0.370187	3.027244	1.953772	0.086041	2.7335	2.355	-0.5825
H	2.862399	2.570204	-1.27607	2.840033	2.530184	-1.59362	3.8115	1.21	-0.8995
H	-4.4606	0.41672	-0.0406	-4.73072	-0.52045	1.596707	-2.6725	-2.428	-1.4355
H	-6.31763	-0.52984	-1.34389	-6.73973	-1.22464	0.341654	-3.3035	-4.623	-0.9425
H	-6.337	-2.9527	-1.94114	-6.50945	-2.61623	-1.70943	-3.8115	-5.245	1.2405
H	-4.44425	-4.41726	-1.22007	-4.24797	-3.30066	-2.49445	-3.6845	-3.67	2.9605
H	-2.56576	-3.47445	0.093804	-2.22037	-2.581	-1.25204	-2.9925	-1.49	2.5035
H	2.543903	-2.19428	0.741033	2.53594	-2.40866	0.423647	2.0565	1.211	3.9055
H	4.477076	-3.12201	1.989579	4.268788	-3.26216	1.981497	2.3505	3.006	5.3515
H	6.763166	-2.1766	1.658652	6.428592	-2.04855	2.248625	3.1525	5.039	4.5665
H	7.10577	-0.29425	0.05576	6.860767	0.012747	0.92263	3.7835	5.245	2.3335
H	5.179466	0.633227	-1.20104	5.149782	0.863531	-0.6473	3.5295	3.442	0.8635
H	-2.65373	1.574064	-1.33531	-2.62726	1.453774	-1.37618	-0.3365	-2.223	-1.7265
H	-3.25992	3.758394	0.585664	-3.17632	3.671966	0.510294	-1.0145	-0.955	-4.3125
H	-1.17867	3.696289	2.737907	-1.01994	3.680945	2.577507	-0.7275	1.96	-4.0095
H	0.739667	1.480931	2.063667	0.898332	1.474398	1.886915	0.1285	2.491	-1.2615
H	0.162467	2.167355	-2.66544	0.12085	2.044817	-2.82367	2.4855	-1.634	-1.1345
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H	1.641206	4.287666	1.403539	1.727126	4.270268	1.129556	2.1325	2.531	-3.4175
H	1.215022	4.699736	-1.52976	1.186945	4.608276	-1.78611	3.5755	-0.035	-3.3595

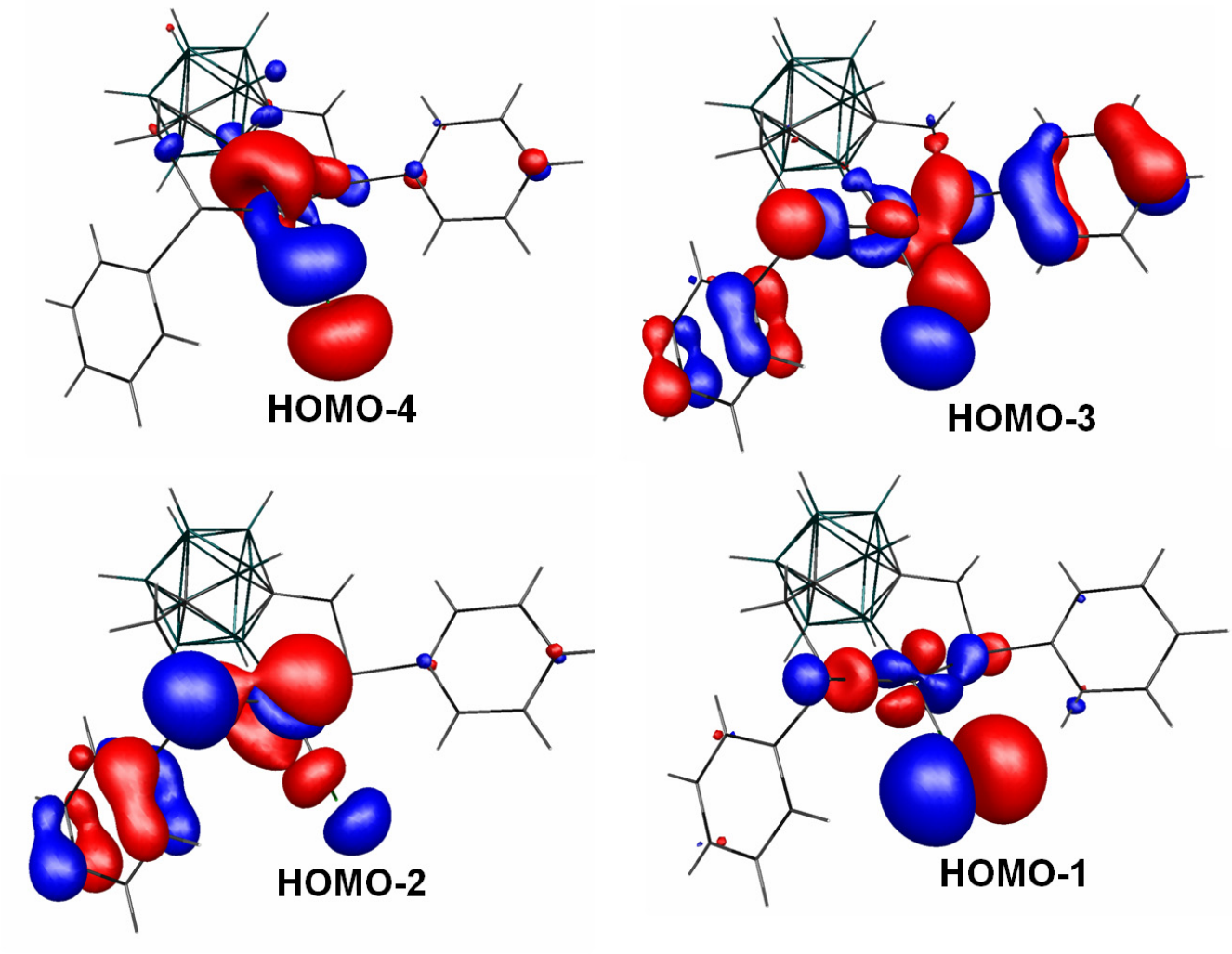


Figure SI-2. Calculated bonding orbitals of **5**, based on a B3LYP/LANL2DZ DFT calculation.

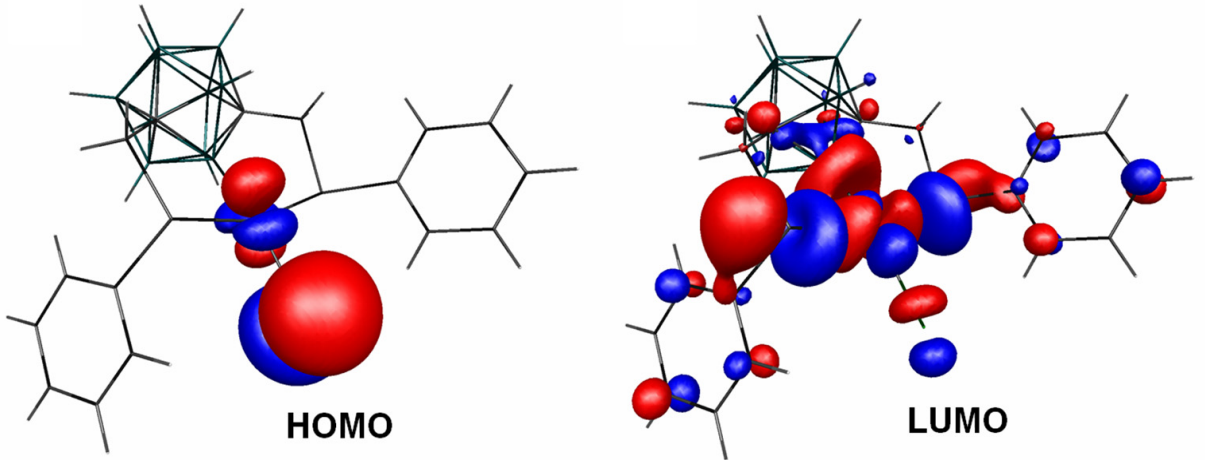
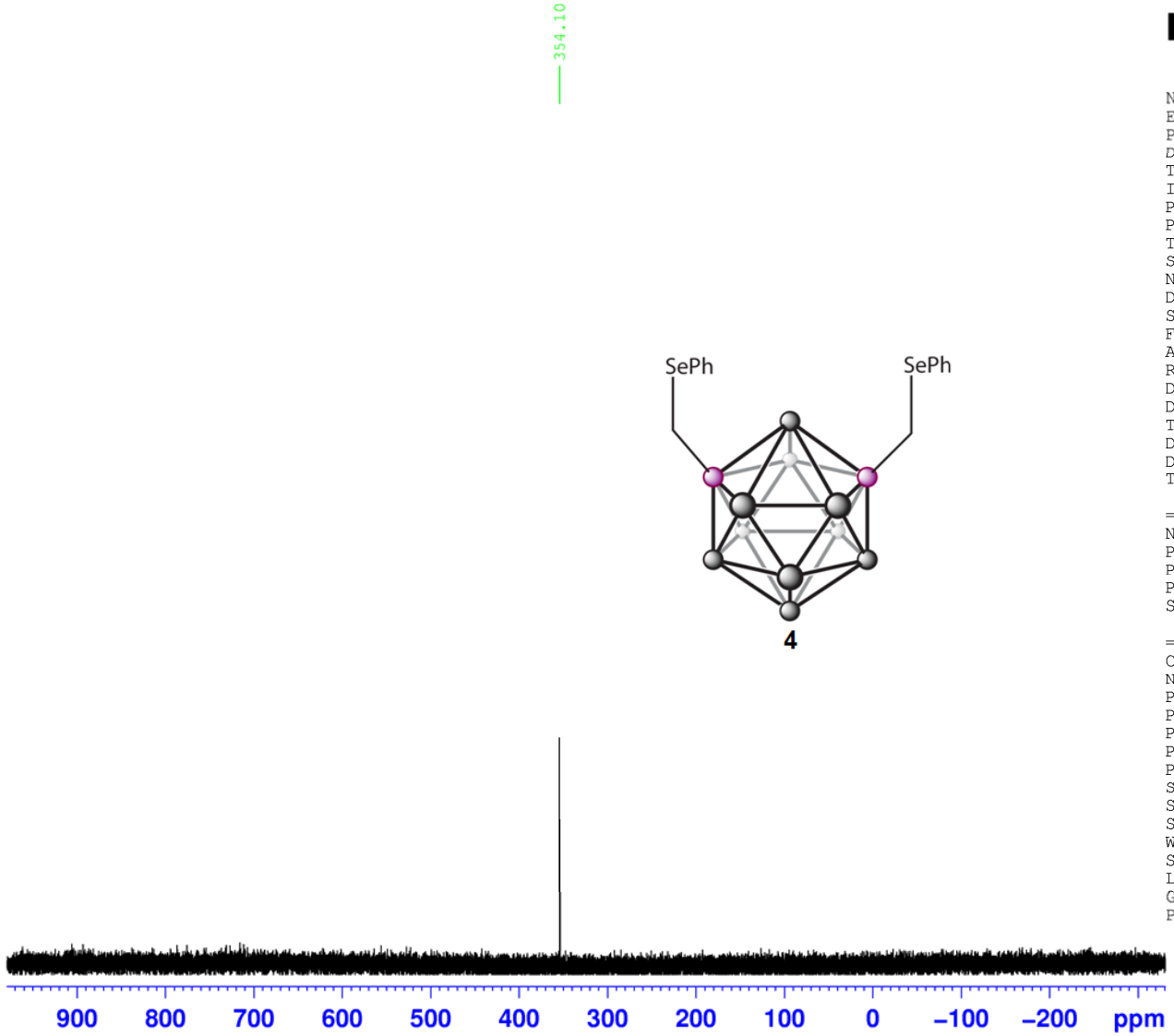


Figure SI-3. Molecular orbital plots of the **5** HOMO and LUMO, based on a B3LYP/LANL2DZ DFT calculation.

pincer_se_ligand



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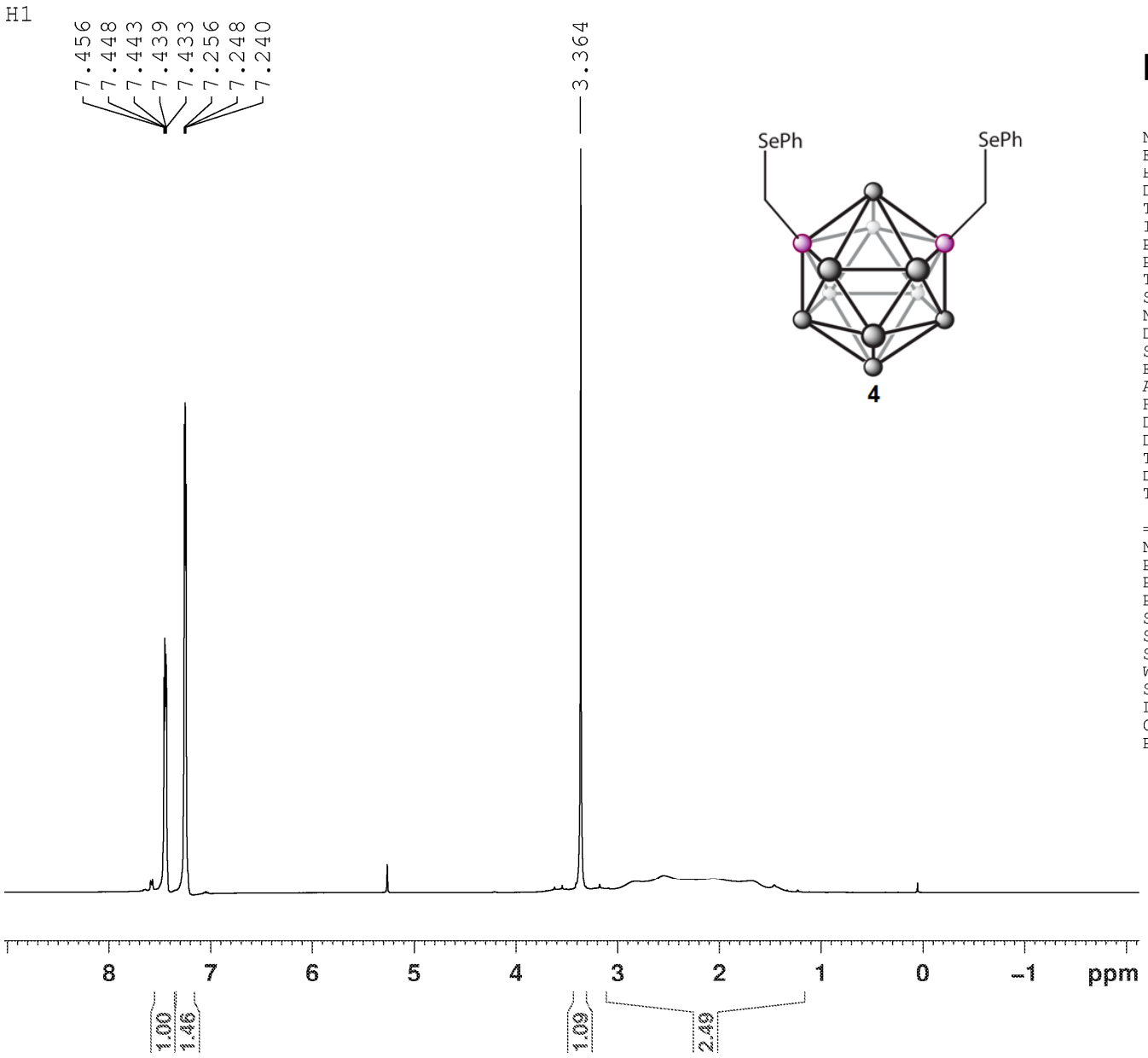

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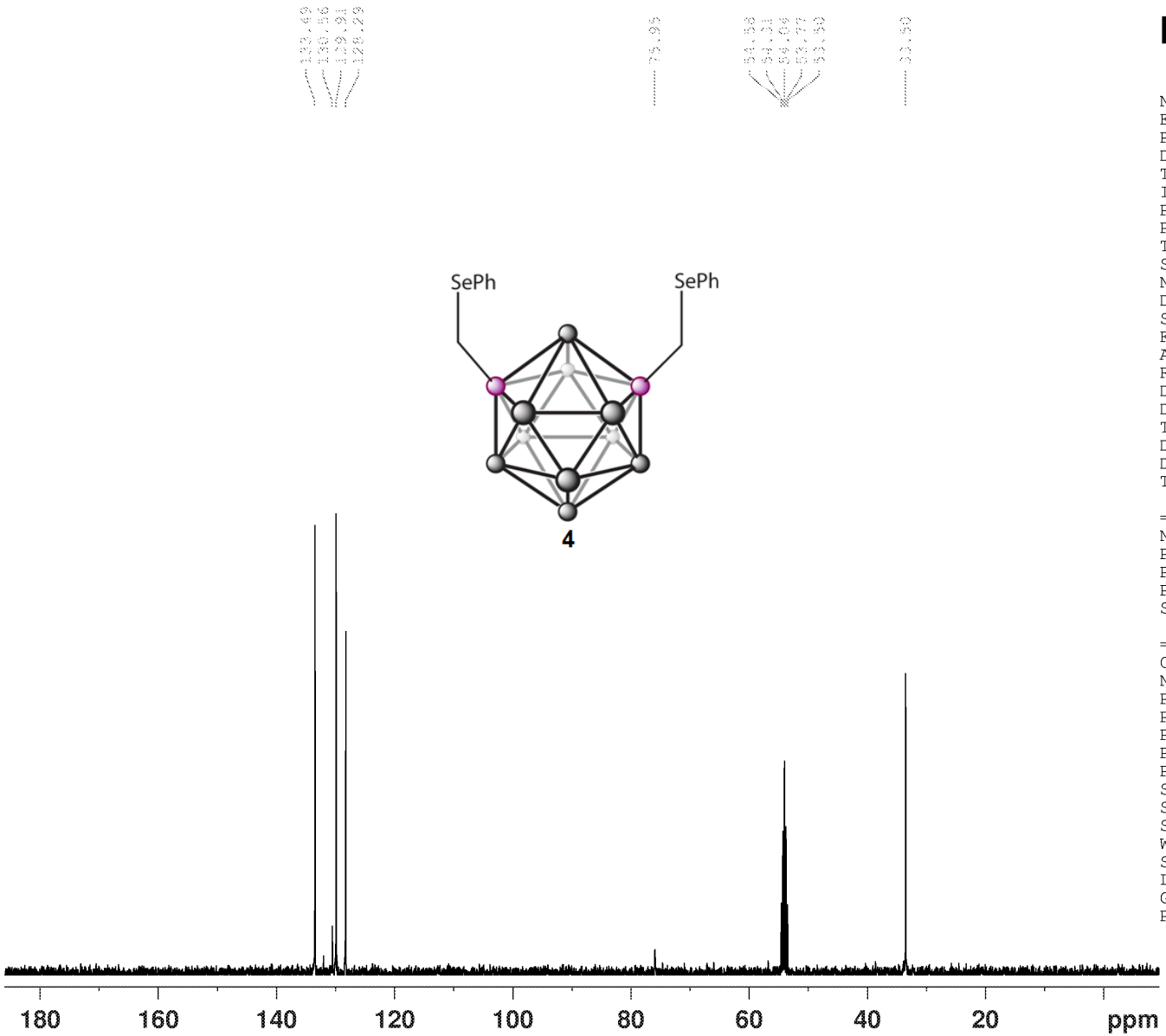


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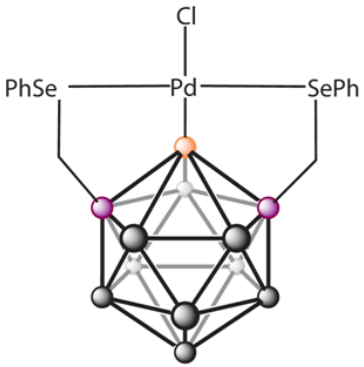
PL1                  -2.50 dB
PL1W           68.78927612 W
SFO1          100.6228298 MHz

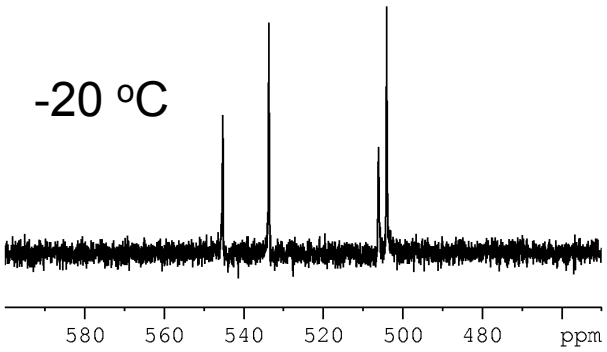
======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                80.00 usec
PL2                  -0.50 dB
PL12                 14.20 dB
PL2W           14.48648834 W
PL12W           0.49086621 W
SFO2          400.1316005 MHz
SI                    32768
SF            100.6127095 MHz
WDW                      EM
SSB                       0
LB                    2.00 Hz
GB                        0
PC                    1.40
```

^{77}Se

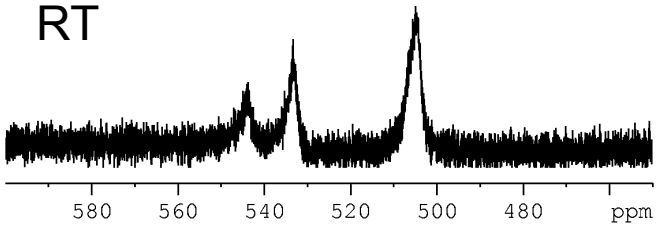


5

-20 °C

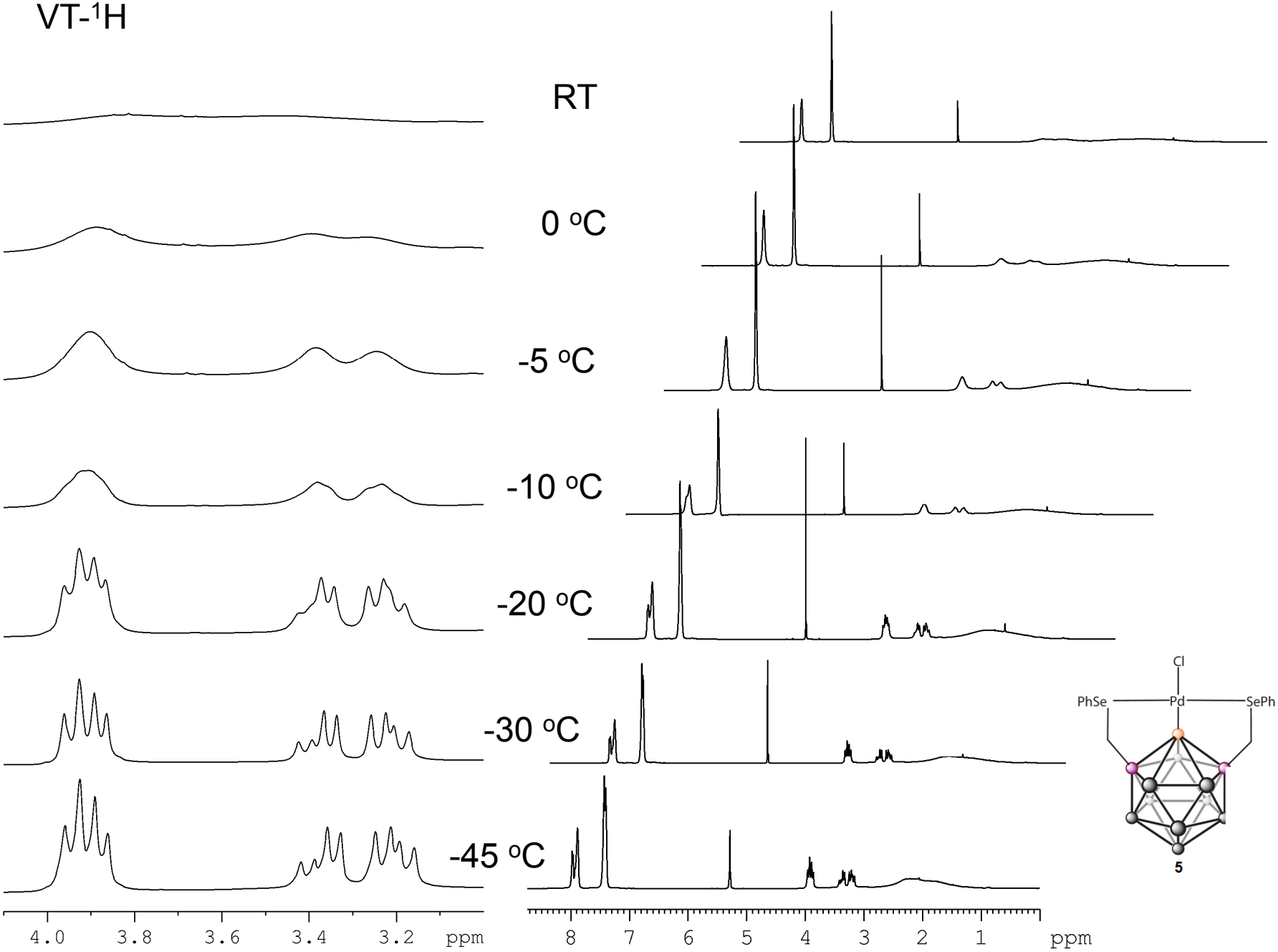


RT



-20 °C

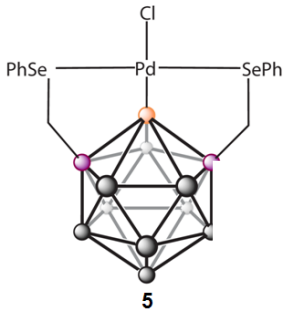
VT-^{1}H


RT
0 ºC
-5 ºC
-10 ºC
-20 ºC
-30 ºC
-45 ºC
4.0
3.8
3.6
3.4
3.2
ppm
8
7
6
5
4
3
2
1
ppm

Cl
PhSe
Pd
SePh

5

VT-^{13}C



5

RT

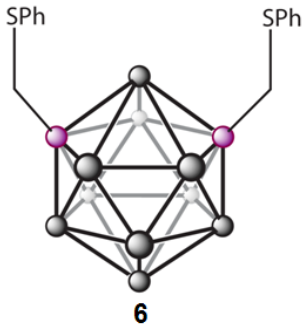
0 °C

-20 °C

-45 °C

180 160 140 120 100 80 60 40 20 ppm

H1



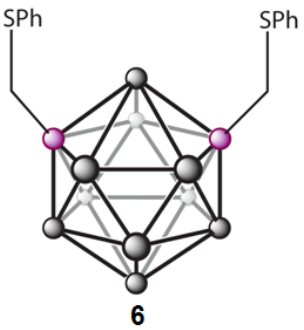
6

BRUKER

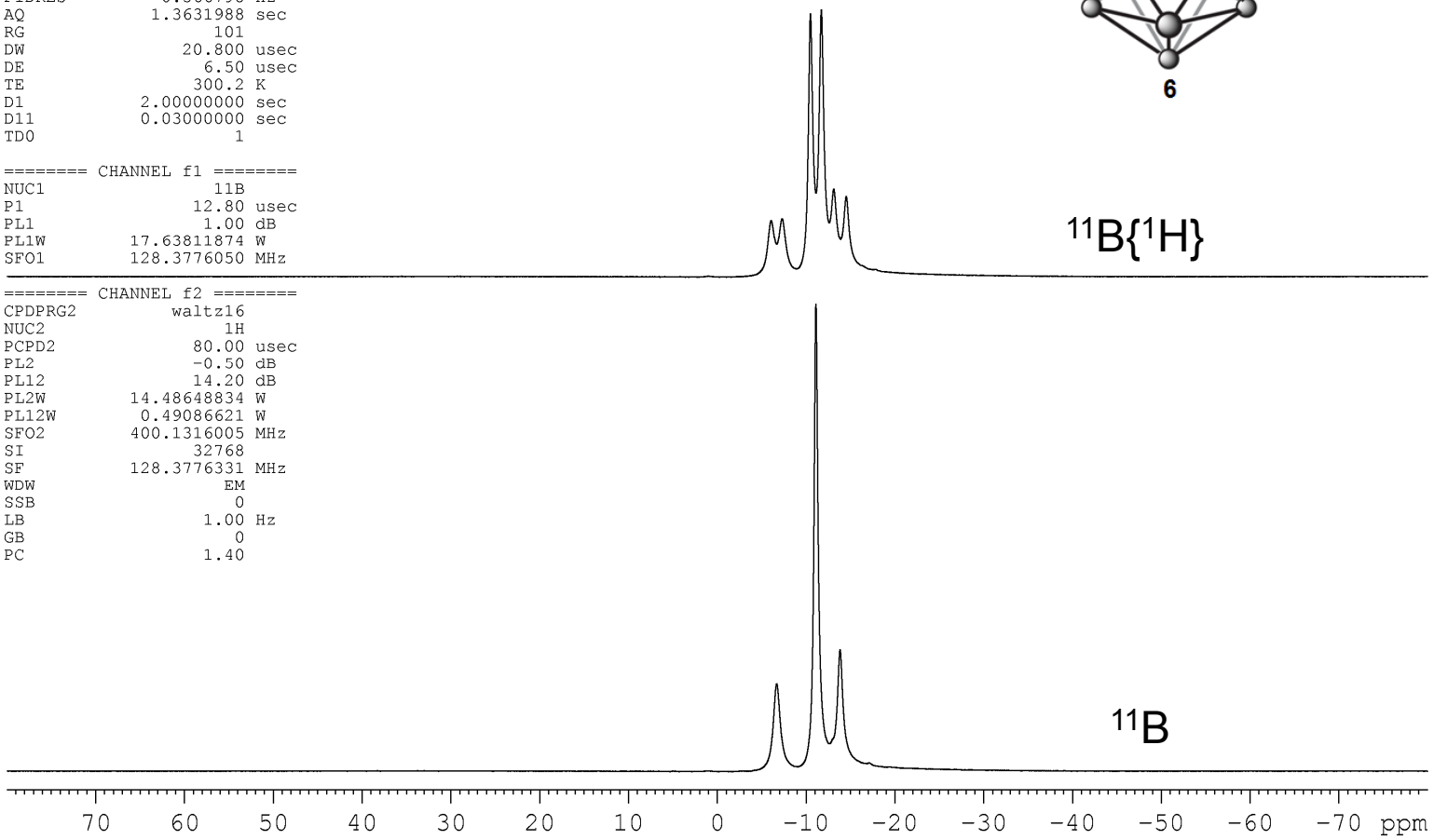
NAME	pincer_sph_ligand
EXPNO	1
PROCNO	1
Date_	20090211
Time	14.36
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg
TD	65536
SOLVENT	CD2C12
NS	4
DS	0
SWH	12019.230 Hz
FIDRES	0.183399 Hz
AQ	2.7263477 sec
RG	18
DW	41.600 usec
DE	6.50 usec
TE	300.2 K
D1	8.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	14.45 usec
PL1	-0.50 dB
PL1W	14.48648834 W
SFO1	400.1324710 MHz
SI	32768
SF	400.1300372 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

```
NAME      pincer_sph_ligand
EXPNO                    3
PROCNO                   1
Date_             20090211
Time                 15.08
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG               zgig
TD                   65536
SOLVENT             CD2Cl2
NS                       10
DS                        0
SWH              24038.461 Hz
FIDRES            0.366798 Hz
AQ                1.3631988 sec
RG                      101
DW                   20.800 usec
DE                    6.50 usec
TE                   300.2 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    11B
P1                   12.80 usec
PL1                   1.00 dB
PL1W           17.63811874 W
SFO1           128.3776050 MHz
======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                  -0.50 dB
PL12                 14.20 dB
PL2W           14.48648834 W
PL12W           0.49086621 W
SFO2           400.1316005 MHz
SI                   32768
SF             128.3776331 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

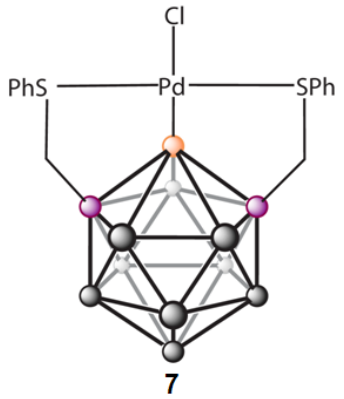


6



```
NAME      pincer_sph_complex
EXPNO                      3
PROCNO                     3
Date_               20090212
Time                   11.29
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG                   zg
TD                     65536
SOLVENT             CD2Cl2
NS                         17
DS                          0
SWH               24038.461 Hz
FIDRES             0.366798 Hz
AQ                1.3631988 sec
RG                       101
DW                  20.800 usec
DE                   6.50 usec
TE                   300.0 K
D1                4.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                     11B
P1                     12.80 usec
PL1                     1.00 dB
PL1W            17.63811874 W
SFO1            128.3776050 MHz
SI                       32768
SF              128.3776331 MHz
WDW                        EM
SSB                         0
LB                      1.00 Hz
GB                          0
PC                      1.40
```



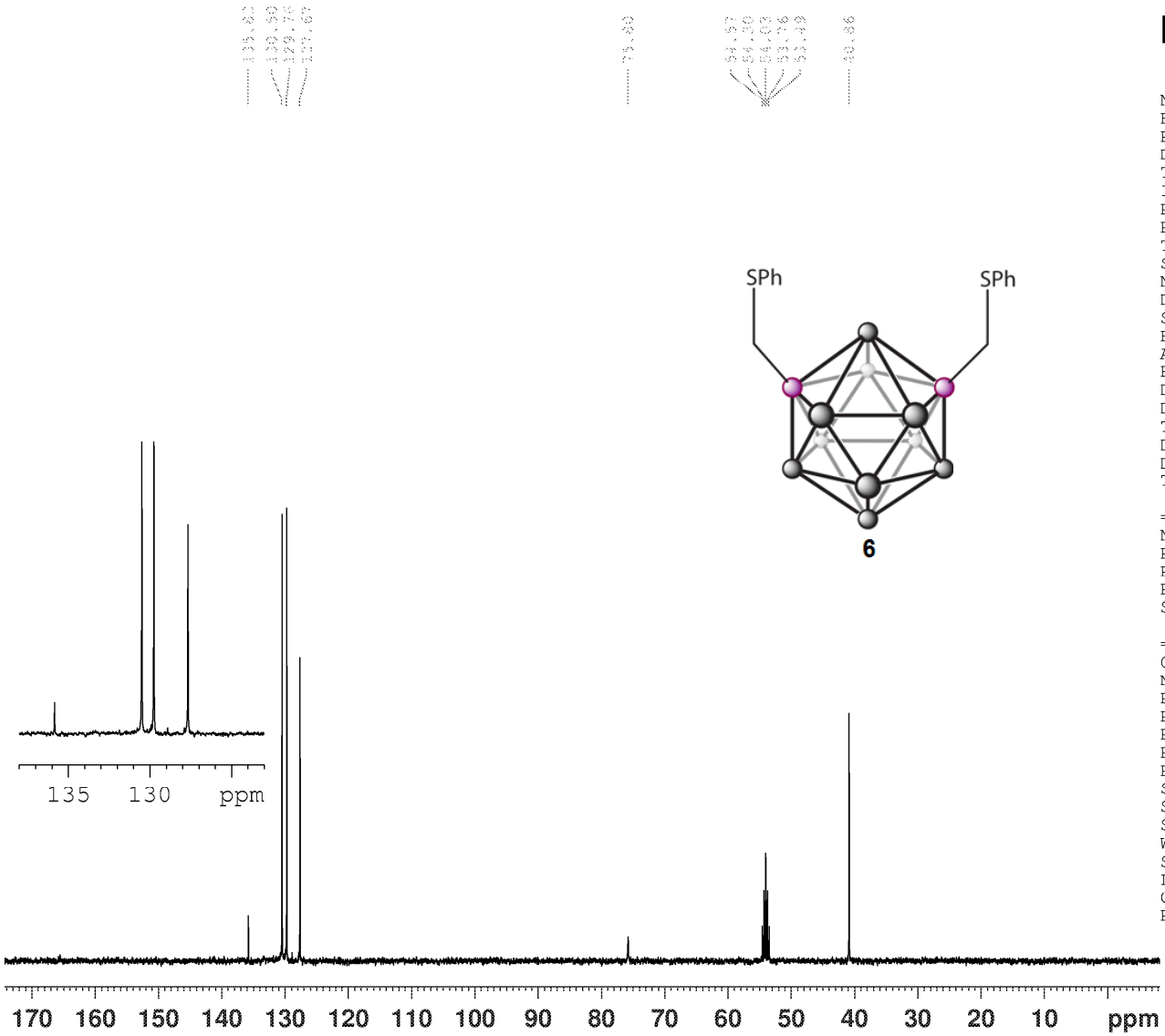
7

$^{11}B\{^{1}H\}$

^{11}B

70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 ppm

c13

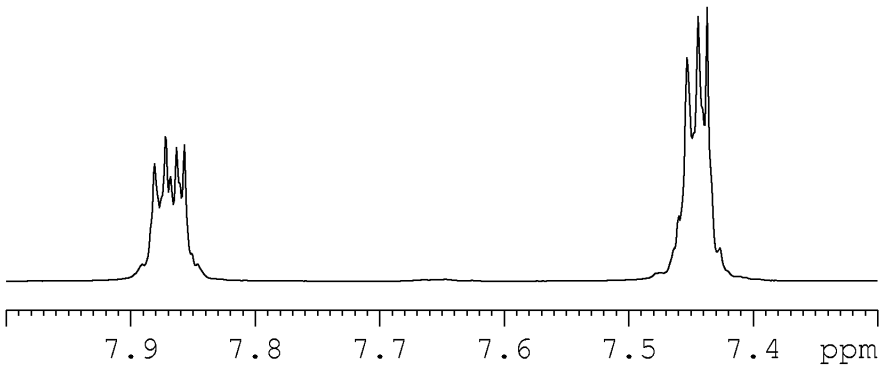


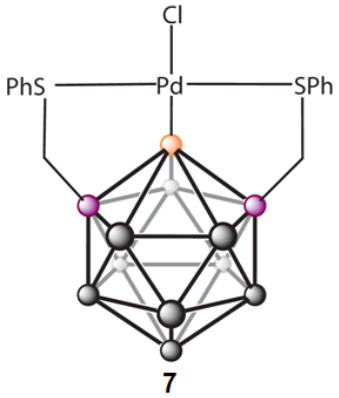

```
NAME          pincer_sph_ligand
EXPNO                        2
PROCNO                       1
Date_             20090211
Time                   14.42
INSTRUM                spect
PROBHD     5 mm PABBO BB-
PULPROG                 zgig
TD                     65536
SOLVENT            CD2Cl2
NS                       35
DS                        0
SWH               24038.461 Hz
FIDRES             0.366798 Hz
AQ                 1.3631988 sec
RG                       228
DW                    20.800 usec
DE                     6.50 usec
TE                    300.2 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                       13C
P1                        9.34 usec
PL1                      -2.50 dB
PL1W             68.78927612 W
SFO1            100.6228298 MHz

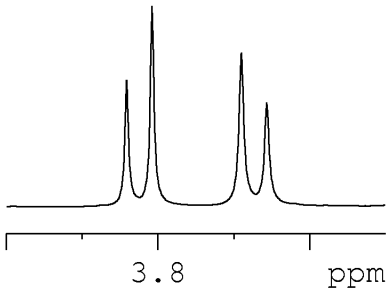
======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                       1H
PCPD2                  80.00 usec
PL2                    -0.50 dB
PL12                   14.20 dB
PL2W             14.48648834 W
PL12W             0.49086621 W
SFO2            400.1316005 MHz
SI                       32768
SF              100.6127095 MHz
WDW                        EM
SSB                         0
LB                     2.00 Hz
GB                          0
PC                      1.40
```

H1



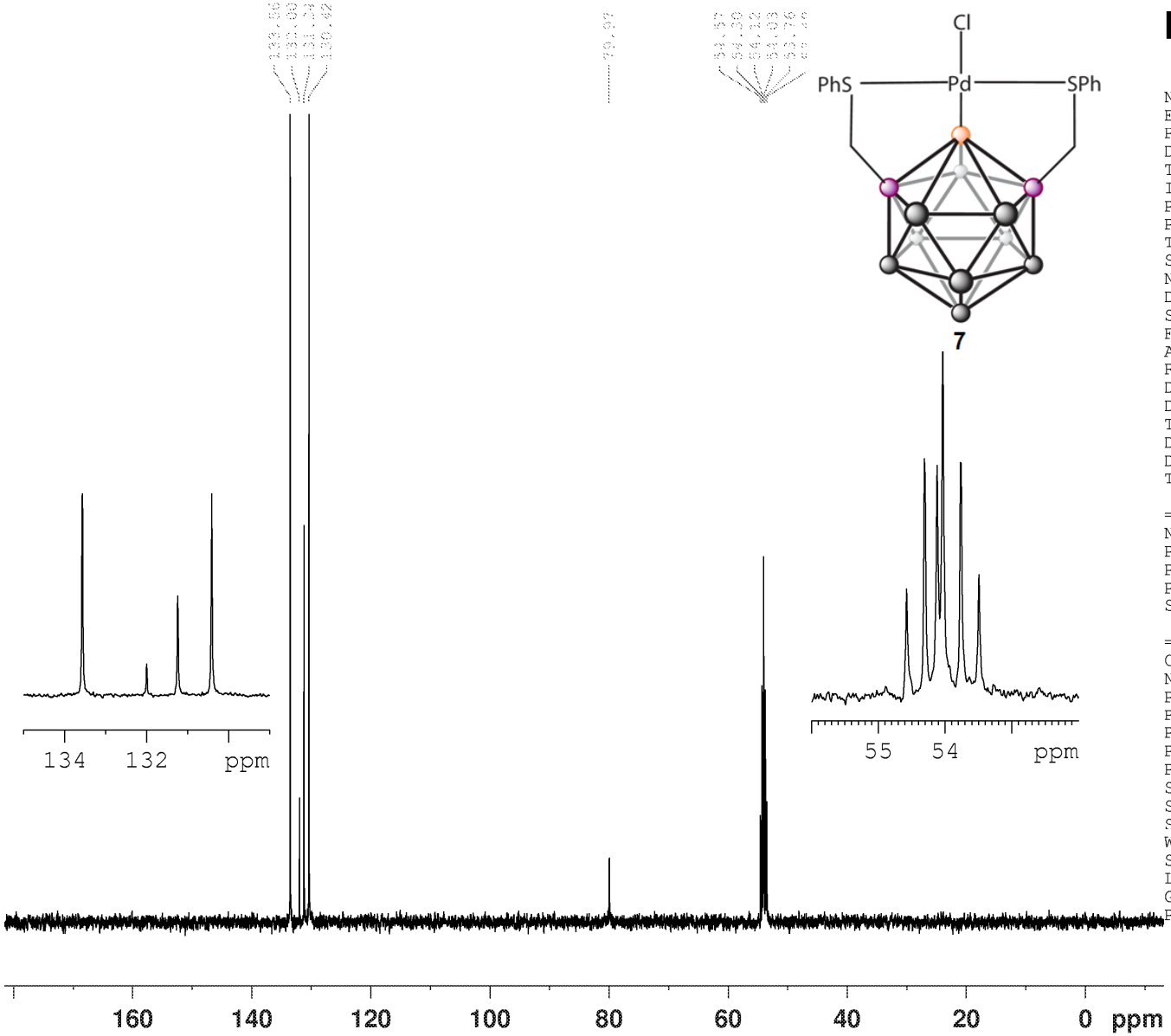


7



NAME	pincer_sph_complex
EXPNO	2
PROCNO	3
Date_	20090215
Time	18.14
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg
TD	65536
SOLVENT	CD2Cl2
NS	3
DS	0
SWH	12019.230 Hz
FIDRES	0.183399 Hz
AQ	2.7263477 sec
RG	18
DW	41.600 usec
DE	6.50 usec
TE	262.4 K
D1	8.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	14.45 usec
PL1	-0.50 dB
PL1W	14.48648834 W
SFO1	400.1324710 MHz
SI	32768
SF	400.1300372 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

c13



7

NAME	pincer_sph_complex
EXPNO	1
PROCNO	3
Date_	20090212
Time	11.18
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgig
TD	65536
SOLVENT	CD2Cl2
NS	146
DS	0
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	228
DW	20.800 usec
DE	6.50 usec
TE	300.1 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.34 usec
PL1	-2.50 dB
PL1W	68.78927612 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	-0.50 dB
PL12	14.20 dB
PL2W	14.48648834 W
PL12W	0.49086621 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127095 MHz
WDW	EM
SSB	0
LB	2.00 Hz
GB	0
PC	1.40

5. References.

S1. Grafstein, D.; Dvorak, J. *Inorg. Chem.* **1963**, *2*, 1128-1122.

S2. Zakharkin, L. I.; Kovredov, A. I.; Kazantsev, A. V.; Meiramov, M. G. *Zh. Obshch. Khim.* (*Russian Journal of General Chemistry*) **1981**, *51*, 357-361.

S3. Sheldrick, G.M. SHELXTL Version 6.14; Bruker Analytical X-ray Instruments, Inc.: Madison, WI, 2003.

S4. We performed a search in CCDC (ConQuest, vers. 5.29) for Pd-B bond, and obtained 61 hits. Out of these hits, only iminoboryl-Pd (Braunschweig, H.; Radacki, K.; Rais, D.; Uttinger, K. *Angew. Chem.* **2006**, *118*, 169-172) system (B-Pd – 1.958 Å) is significantly shorter.

S5. Search in CCDC (ConQuest, vers. 5.29) has given no structures with PhSe-Pd-SePh pincer motif. A number of PhS-Pd-SPh structures, allowed for indirect comparison: Gerhardt et al. *Org. Chem.*, **2006**, *71*, 6333–6341 (Pd-Cl distance – 2.40 Å) and Van Koten et al. *Angew. Chem. Int. Ed.* **1999**, 2186-2188 (Pd-Cl distance – 2.36 Å).