Electronic Supplementary Information

Fluxional chloro-pyrrole-Pd(II) complex to cationic η^2-Pyrrole-Pd(II) complex: subtlety in structure-directed bonding mode

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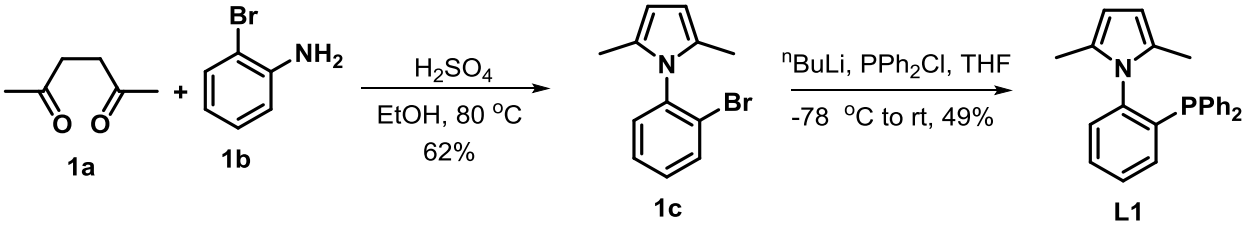
1.1 Experimental Section.

General Information. Unless otherwise noted all starting materials were obtained from commercial suppliers. Organic solvents were dried and distilled as described elsewhere. All reactions were carried out in an oven-dried flask under argon atmosphere. Column chromatography was performed with silica gel 230 - 400 mesh. All ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra were recorded in $CDCl_3$ solution and reported in ppm (δ). ^{1}H NMR spectra were referenced internally to the residual proton resonance in $CDCl_3$ (δ 7.26 ppm), or with tetramethylsilane (TMS, δ 0.00 ppm) as the internal standard. ^{13}C NMR spectra were referenced to $CDCl_3$ (δ 77.0 ppm, the middle peak). ^{31}P NMR spectra were referenced to PPh_3 (δ -4.8 ppm) externally. High resolution mass spectra (HRMS) were obtained on a FT-ICR mass spectrometer (ESIMS – Micromass Q-TOF micro). CHN analysis was performed with CHNS analyzer (2400 series II). X-ray single crystal data were collected using MoKα (λ = 0.7107 Å) radiation. Data collection, data reduction, structure solution/refinement were carried out using the software package of BRUKER APEX II. The single crystal structures of complex **2** and **3** were solved by direct and Patterson method respectively and refined in a routine manner.

Scheme 1. Synthesis of ligand L1.



1-(2-Bromophenyl)-2,5-dimethy-*1H*-pyrrole (1c). A solution of 2,5-hexanedione (**1a**) (456.5 mg, 4 mmol) and 2-bromo aniline (**1b**) (825.6 mg, 4.8 mmol) in ethanol (24 mL) was refluxed for 15 h in the presence of catalytic amount of conc. H_2SO_4. Solvent was removed under reduced pressure. It was then extracted with dichloromethane (2×25 mL). The combined organic layer was washed subsequently with water and brine and dried over anhydrous Na_2SO_4. Evaporation of solvent under reduced pressure gave the crude product. Purification by flash column chromatography (silica gel 230-400 mesh, 1% ethyl acetate/petroleum ether) afforded **1c** as yellow liquid (662 mg, 62%); R_f (2.5% ethyl acetate/petroleum ether) 0.41; IR λ_{max}

(neat, cm^{-1}) 3100, 3050, 2975, 2914, 2889, 1572, 1486, 1434, 1405, 1383, 1224, 1065, 1028; ^1H NMR ($CDCl_3$, 400 MHz, ppm). δ 7.76 (dd, J = 8.4 Hz, 1.2 Hz, 1H), 7.46 (t, J = 7.2 Hz, 1H), 7.36 – 7.32 (m, 2H), 5.98 (s, 2H), 1.9 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm). δ 138.6, 133.5, 130.6, 129.8, 128.5, 128.3, 124.6, 105.6, 12.6; HRMS (ESI) *m/z* calculated for $C_{12}H_{13}BrN$ $[M+H]^+$ 250.0231, found 250.0224.

1-(2-(Diphenylphosphino)phenyl)-2,5-dimethyl-*1H*-pyrrole (L1). To a stirred solution of 1-(2-bromophenyl)-2,5-dimethy-*1H*-pyrrole (**1c**) (250 mg, 1 mmol) in THF (4 mL) under argon atmosphere was added *n*-BuLi (0.8 mL, 1.2 mmol, 1.5 M in THF) drop wise at -78 °C. The mixture was slowly warmed to rt and then stirred for further ½ h at rt. After the mixture was cooled to -78°C, chloro diphenylphosphine (0.2 mL, 1.2 mmol) was added and stirring was continued for 10 h. It was then quenched with saturated NH_4Cl solution at 0 °C and extracted with diethyl ether (2×20 mL). The combined organic layer was washed with water and brine and dried over anhydrous Na_2SO_4. Evaporation of solvent under reduced pressure gave the crude product. Purification by flash column chromatography (Silica gel 230-400 mesh, 0.5% ethyl acetate /petroleum ether) afforded ligand (**L1**) as white solid (174 mg, 49 %). R_f (2.5% ethyl acetate/petroleum ether) 0.33; mp 83 °C – 85 °C; IR λ_{max} (KBr, cm^{-1}) 3053, 2980, 2915, 2888, 1587, 1566, 1525, 1495, 1474, 1436, 1397, 1317, 1212, 1095, 1035; ^1H NMR ($CDCl_3$, 500 MHz, ppm). δ 7.34 (t, J = 7.5 Hz, 1H), 7.27 (t, J = 7.5 Hz, 1H), 7.21 – 7.20 (m, 6H), 7.16 – 7.11 (m, 6H), 5.78 (s, 2H), 1.65 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm). δ 143.6 (d, J = 27.5 Hz), 139.3 (d, J = 13.8 Hz), 136.3 (d, J = 11.2 Hz), 134.8, 134.0 (d, J = 20 Hz), 130.0, 129.6, 129.1, 128.7, 128.5, 128.4 (d, J = 7.5 Hz), 105.5, 12.8; ^{31}P NMR ($CDCl_3$, 202.44 MHz, ppm). δ -16.70 (s); HRMS (ESI) *m/z* calculated for $C_{24}H_{23}NP$ $[M+H]^+$ 356.1568, found 356.1565.

Procedure for synthesis of complex 2. A solution of **L1** (355.4 mg, 1 mmol) and $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (365.9 mg, 1 mmol) in dichloromethane (5 mL) was stirred for 20 min at rt. The color of the solution was changed into red. The solvent was removed under reduced pressure. The residue was rinsed with hexane and dried in vacuo, affording **2** as red powder (515 mg, 96%), which was crystallized from acetone/ hexane; mp>200 °C; ^1H NMR ($CDCl_3$, 500 MHz, ppm). δ 7.59 (t, J = 8.7 Hz, 1H), 7.56 – 7.31 (m, 12H), 7.07 – 7.04 (m, 1H), 5.72 (s, 2H) 5.49-5.41 (m, 1H), 4.63 (br. s, 1H), 3.45 (br. s, 1H), 2.71 (br. s, 2H), 1.64 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz,

ppm). δ 144.2 (d, J = 20.0 Hz), 137.2 (d, J = 7.5 Hz), 133.9 (d, J = 20.0 Hz), 132.9, 132.4, 132.1, 131.8 (d, J = 8.7 Hz), 131.3, 130.9, 130.2, 128.5, 128.4, 128.2 (d, J = 16.25 Hz) 118.5 (d, J = 7.5 Hz) , 106.8, 14.0; ^{31}P NMR ($CDCl_3$, 202.44 MHz, ppm). δ 11.91; Anal. Calcd. For $C_{27}H_{27}NPClPd$: C, 60.24; H, 5.06; N, 2.60. Found: C, 59.94; H, 5.32; N, 2.65.

Procedure for synthesis of complex 3. A solution of **L1** (355.4 mg, 1 mmol) and [Pd(η^3-C_3H_5)Cl]$_2$ (365.9 mg, 1 mmol) in dichloromethane (5 mL) was stirred for 20 min at rt. The color of the solution was changed into red. $AgSbF_6$ (343.6 mg, 1 mmol) was then added, and the solution became deep red. Filtration of AgCl on Celite followed by evaporation of the dichloromethane under reduced pressure affording **3** as a deep red solid (651.8 mg, 88%) which was crystallized from acetone/hexane; mp>200 °C; ^{1}H NMR ($CDCl_3$, 500 MHz, ppm). δ 7.71 (t, J = 12 Hz, 1H), 7.55 (t, J = 12 Hz, 1H), 7.50-7.29 (m, 9H), 7.19 – 7.10 (m, 4H), 6.64 (s, 1H), 6.15 (s, 1H), 5.72-5.58 (m, 1H), 5.25-5.18 (m, 1H), 5.25-5.18 (m, 1H), 3.71 (dd, J = 21 and 16 Hz, 2H), 3.48 (d, J = 9.5 Hz, 1H), 2.76 (d, J = 21 Hz, 1H), 1.91 (s, 3H), 1.34 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm). δ 143.2 (d, J = 23.7 Hz), 139.0, 134.5, 134.7, 133.6, 133.1 (d, J = 22.5 Hz), 132.3, 131.9, 130.8 (d, J = 10.0 Hz), 129.8 (d, J = 25.1 Hz), 129.8 (d, J = 3.7 Hz), 128.9, 126.2, 125.6, 120.3, 120.2, 102.4, 95.0, 80.6, 80.3, 67.8 14.8, 13.5, ^{31}P NMR ($CDCl_3$, 202.44 MHz, ppm). δ 18.23; Anal. Calcd. For $C_{27}H_{27}NF_6PPdSb$: C, 43.90; H, 3.68; N, 1.90. Found: C, 43.84; H, 3.51; N, 1.82.

1.2a X-ray crystal structure of Complex 2.

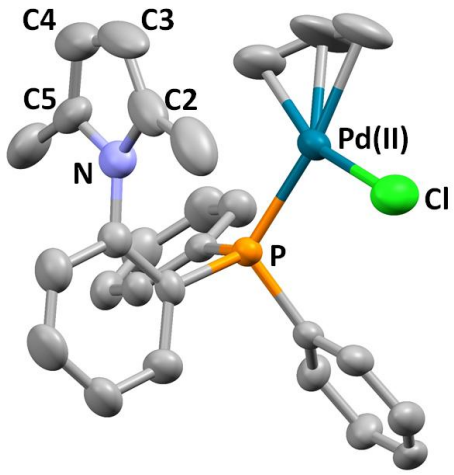


Figure S1. ORTEP diagram for the molecular complex **2** at 30% probability level. For clarity, hydrogen atoms are omitted.

Table 1. Crystal data of 2

Identification code	ds010214r2_0m
Empirical formula	$C_{29.5}H_{30.5}ClNPPd$
Formula weight	571.87
Temperature/K	293.15
Crystal system	monoclinic
Space group	C2/c
a/Å	25.378(3)
b/Å	10.2854(12)
c/Å	21.374(3)
α/°	90
β/°	110.1600(10)
γ/°	90
Volume/Å^3	5237.3(11)
Z	8
ρ_{calc}g/cm^3	1.451
μ/mm^{-1}	0.890
F(000)	2340.0
Crystal size/mm^3	0.28 × 0.2 × 0.14
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.42 to 54.832

Index ranges	$-32 \leq h \leq 32, -12 \leq k \leq 11, -27 \leq l \leq 26$
Reflections collected	20251
Independent reflections	5421 [R_{int} = 0.0418, R_{sigma} = 0.0399]
Data/restraints/parameters	5421/6/335
Goodness-of-fit on F^2	1.027
Final R indexes [I>=2σ (I)]	R_1 = 0.0358, wR_2 = 0.0862
Final R indexes [all data]	R_1 = 0.0531, wR_2 = 0.0960
Largest diff. peak/hole / e $Å^{-3}$	0.43/-0.57

Table 2 Bond Lengths Complex **2**.

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
Pd01	P002	2.3203(8)	C00B	C00G	1.376(4)
Pd01	Cl03	2.3952(10)	C00C	C00K	1.386(5)
Pd01	C00Q	2.140(12)	C00D	C00M	1.381(5)
Pd01	C00R	2.175(13)	C00E	C00F	1.366(5)
Pd01	C00X	2.163(5)	C00F	C00K	1.376(5)
Pd01	C1	2.20(2)	C00G	C00J	1.387(5)
Pd01	C2	2.150(10)	C00H	C00O	1.377(5)
Pd01	C3	2.10(2)	C00I	C00T	1.478(6)
P002	C005	1.849(3)	C00I	C00U	1.351(6)
P002	C006	1.842(3)	C00J	C00N	1.378(5)
P002	C007	1.827(3)	C00L	C00P	1.368(6)
N004	C008	1.438(4)	C00L	C00V	1.471(6)
N004	C00I	1.390(5)	C00M	C00O	1.381(5)
N004	C00L	1.389(5)	C00P	C00U	1.393(7)
C005	C008	1.394(4)	C00Q	C00X	1.407(14)
C005	C00D	1.396(4)	C00R	C00X	1.384(11)
C006	C009	1.391(4)	C00S	C5	1.207(10)
C006	C00C	1.390(4)	C4	C00Y	1.74(2)
C007	C00A	1.396(4)	C4	C00Y[1]	1.74(2)
C007	C00B	1.384(4)	C4	C5	1.98(3)
C008	C00H	1.400(5)	C00Y	C5	1.487(7)
C009	C00E	1.383(4)	C1	C2	1.387(15)
C00A	C00N	1.385(5)	C2	C3	1.406(19)

[1]1-X,+Y,1/2-Z

Table 3 Bond Angles for Complex **2**.

Atom	Atom	Atom	Angle/°
P002	Pd01	Cl03	102.07(3)
C00Q	Pd01	P002	97.6(3)
C00Q	Pd01	Cl03	159.4(4)
C00Q	Pd01	C00R	66.5(4)
C00Q	Pd01	C00X	38.2(4)
C00R	Pd01	P002	164.0(3)
C00R	Pd01	Cl03	93.6(3)
C00X	Pd01	P002	129.5(2)
C00X	Pd01	Cl03	126.0(2)
C00X	Pd01	C00R	37.2(3)
C1	Pd01	P002	165.9(6)
C1	Pd01	Cl03	89.5(6)
C2	Pd01	P002	135.8(4)
C2	Pd01	Cl03	120.0(5)
C2	Pd01	C1	37.2(5)
C3	Pd01	P002	101.4(6)
C3	Pd01	Cl03	156.4(6)
C3	Pd01	C1	67.0(7)
C3	Pd01	C2	38.6(6)
C005	P002	Pd01	118.99(10)
C006	P002	Pd01	112.83(10)
C006	P002	C005	103.54(13)
C007	P002	Pd01	116.90(10)
C007	P002	C005	102.22(13)
C007	P002	C006	99.81(13)
C00I	N004	C008	125.2(3)
C00L	N004	C008	122.8(3)
C00L	N004	C00I	109.4(3)
C008	C005	P002	122.3(2)
C008	C005	C00D	117.7(3)
C00D	C005	P002	119.9(2)
C009	C006	P002	122.2(2)
C00C	C006	P002	119.7(2)
C00C	C006	C009	118.0(3)
C00A	C007	P002	119.0(2)
C00B	C007	P002	122.3(2)
C00B	C007	C00A	118.3(3)
C005	C008	N004	123.0(3)
C00N	C00A	C007	120.1(3)
C00G	C00B	C007	121.5(3)
C00K	C00C	C006	120.6(3)
C00M	C00D	C005	122.0(3)
C00F	C00E	C009	120.3(3)
C00E	C00F	C00K	119.8(3)
C00B	C00G	C00J	119.8(3)
C00O	C00H	C008	121.0(3)
N004	C00I	C00T	123.7(3)
C00U	C00I	N004	106.7(4)
C00U	C00I	C00T	129.7(4)
C00N	C00J	C00G	119.4(3)
C00F	C00K	C00C	120.3(3)
N004	C00L	C00V	121.2(4)
C00P	C00L	N004	106.4(4)
C00P	C00L	C00V	132.4(4)
C00D	C00M	C00O	119.8(3)
C00J	C00N	C00A	120.8(3)
C00H	C00O	C00M	119.4(3)
C00L	C00P	C00U	108.4(4)
C00X	C00Q	Pd01	71.8(5)
C00X	C00R	Pd01	70.9(5)
C00I	C00U	C00P	109.1(4)
C00Y	C4	C00Y^{1}	93.2(15)
C00Y^{1}	C4	C5	46.6(7)
C00Y	C4	C5	46.6(7)
C00Q	C00X	Pd01	70.1(6)
C00R	C00X	Pd01	71.9(6)
C00R	C00X	C00Q	115.9(12)
C5	C00Y	C4	75.0(8)
C2	C1	Pd01	69.5(8)
C1	C2	Pd01	73.3(10)
C1	C2	C3	116.2(19)
C3	C2	Pd01	68.7(11)
C2	C3	Pd01	72.7(10)
C00S	C5	C4	180.0
C00S	C5	C00Y^{1}	121.6(4)
C00S	C5	C00Y	121.6(4)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C005	C008	C00H	120.0(3)	C00Y	C5	C4	58.4(4)
C00H	C008	N004	117.0(3)	C00Y[1]	C5	C4	58.4(4)
C00E	C009	C006	121.0(3)	C00Y	C5	C00Y[1]	116.8(8)

[1]1-X,+Y,1/2-Z

1.2b X-ray crystal structure of Complex 3.

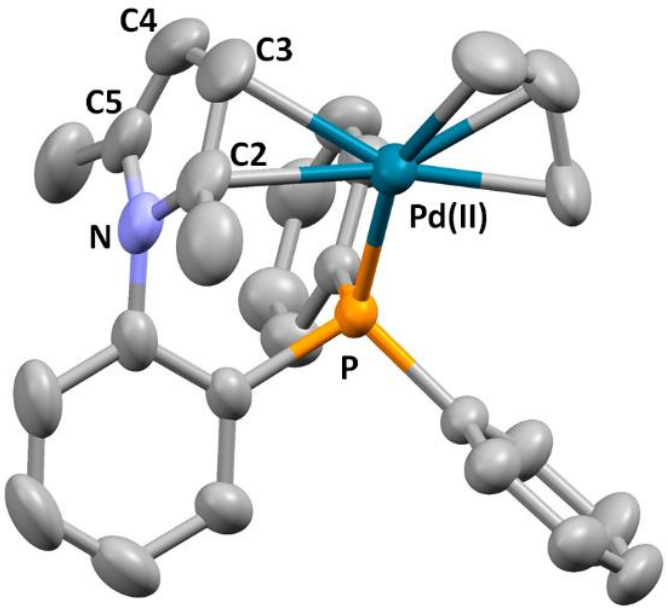


Figure S2. ORTEP diagram for the molecular complex **3** at 30% probability level. For clarity, hydrogen atoms are omitted.

Table 4. Crystal data of 3

Identification code	DS250113_0m
Empirical formula	$C_{27}H_{27}F_{6.17}NPPdSb$
Formula weight	741.94
Temperature/K	293.15
Crystal system	triclinic
Space group	P-1
a/Å	8.9132(8)
b/Å	11.1285(10)
c/Å	14.9029(14)

α/°	89.114(2)
β/°	75.267(2)
γ/°	81.910(2)
Volume/Å^3	1415.1(2)
Z	2
ρ_{calc}g/cm^3	1.741
μ/mm^{-1}	1.704
F(000)	727.0
Crystal size/mm^3	0.3 × 0.24 × 0.16
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.698 to 62.67
Index ranges	-11 ≤ h ≤ 12, -14 ≤ k ≤ 16, -19 ≤ l ≤ 19
Reflections collected	16266
Independent reflections	7064 [R_{int} = 0.0227, R_{sigma} = 0.0283]
Data/restraints/parameters	7064/0/404
Goodness-of-fit on F^2	1.040
Final R indexes [I>=2σ (I)]	R_1 = 0.0294, wR_2 = 0.0731
Final R indexes [all data]	R_1 = 0.0381, wR_2 = 0.0777
Largest diff. peak/hole / e Å^{-3}	0.35/-0.75

Table 5 Bond Lengths for Complex **3**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pd01	P003	2.3099(6)	C00G	C00V	1.489(4)
Pd01	C00G	2.386(3)	C00I	C00S	1.397(4)
Pd01	C00I	2.110(3)	C00J	C00W	1.360(5)
Pd01	C00K	2.371(3)	C00K	C00P	1.434(5)
Pd01	C00S	2.166(3)	C00L	C00U	1.376(5)
Pd01	C00T	2.215(3)	C00M	C00P	1.343(5)
P003	C005	1.819(2)	C00M	C00X	1.499(5)
P003	C007	1.837(2)	C00N	C00Y	1.354(4)
P003	C008	1.813(2)	C00O	C00U	1.374(5)
N004	C00C	1.430(3)	C00Q	C00Y	1.373(4)
N004	C00G	1.392(3)	C00S	C00T	1.357(5)
N004	C00M	1.392(3)	F1	Sb6	1.790(3)
C005	C009	1.379(3)	F1	Sb6A	1.966(4)
C005	C00D	1.382(3)	F0AA	Sb6	1.829(5)
C007	C00A	1.387(3)	F2	Sb6	1.721(16)
C007	C00C	1.396(3)	F2	F6	1.41(4)
C008	C00B	1.383(3)	F4	Sb6	1.857(5)
C008	C00E	1.396(3)	F5	Sb6	1.978(13)

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C009	C00F	1.385(4)	Sb6	F6	1.871(8)
C00A	C00O	1.389(4)	Sb6A	F6A	1.671(13)
C00B	C00Q	1.386(4)	Sb6A	F0AB	1.98(2)
C00C	C00L	1.386(4)	Sb6A	F4A	1.762(12)
C00D	C00W	1.391(4)	Sb6A	F2A	1.618(14)
C00E	C00N	1.384(4)	Sb6A	F5A	1.571(8)
C00F	C00J	1.384(4)	Sb6A	F7	1.985(16)
C00G	C00K	1.378(4)	F6A	F2A	0.87(3)

Table 6 Bond Angles for Complex **3**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
P003	Pd01	C00G	87.72(7)	N004	C00M	C00X	120.4(3)
P003	Pd01	C00K	108.98(9)	C00P	C00M	N004	108.4(3)
C00I	Pd01	P003	93.04(8)	C00P	C00M	C00X	131.2(3)
C00I	Pd01	C00G	162.54(13)	C00Y	C00N	C00E	120.7(3)
C00I	Pd01	C00K	156.23(12)	C00U	C00O	C00A	120.1(3)
C00I	Pd01	C00S	38.12(12)	C00M	C00P	C00K	108.2(3)
C00I	Pd01	C00T	66.50(12)	C00Y	C00Q	C00B	119.7(3)
C00K	Pd01	C00G	33.69(10)	C00I	C00S	Pd01	68.78(15)
C00S	Pd01	P003	127.76(9)	C00T	C00S	Pd01	73.95(18)
C00S	Pd01	C00G	144.52(11)	C00T	C00S	C00I	119.0(3)
C00S	Pd01	C00K	118.11(12)	C00S	C00T	Pd01	69.98(16)
C00S	Pd01	C00T	36.07(13)	C00O	C00U	C00L	120.6(3)
C00T	Pd01	P003	158.47(10)	C00J	C00W	C00D	120.6(3)
C00T	Pd01	C00G	109.74(12)	C00N	C00Y	C00Q	120.6(3)
C00T	Pd01	C00K	92.33(13)	F6	F2	Sb6	72.6(15)
C005	P003	Pd01	112.62(7)	F1	Sb6	F0AA	90.3(2)
C005	P003	C007	103.20(10)	F1	Sb6	F4	178.6(4)
C007	P003	Pd01	116.01(8)	F1	Sb6	F5	86.0(4)
C008	P003	Pd01	113.61(7)	F1	Sb6	F6	81.2(5)
C008	P003	C005	107.25(10)	F0AA	Sb6	F4	90.8(3)
C008	P003	C007	103.08(10)	F0AA	Sb6	F5	72.2(6)
C00G	N004	C00C	121.7(2)	F0AA	Sb6	F6	90.1(4)
C00M	N004	C00C	124.6(2)	F2	Sb6	F1	100.8(7)
C00M	N004	C00G	108.8(2)	F2	Sb6	F0AA	130.9(18)
C009	C005	P003	117.24(17)	F2	Sb6	F4	79.3(7)
C009	C005	C00D	119.5(2)	F2	Sb6	F5	155.3(16)
C00D	C005	P003	123.19(19)	F2	Sb6	F6	46.0(14)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C00A	C007	P003	121.39(18)	F4	Sb6	F5	93.3(6)
C00A	C007	C00C	119.0(2)	F4	Sb6	F6	99.8(6)
C00C	C007	P003	119.65(18)	F6	Sb6	F5	158.1(6)
C00B	C008	P003	121.87(17)	F2	F6	Sb6	61.4(5)
C00B	C008	C00E	118.7(2)	F1	Sb6A	F0AB	89.0(17)
C00E	C008	P003	119.39(18)	F1	Sb6A	F7	86.8(7)
C005	C009	C00F	120.6(2)	F6A	Sb6A	F1	88.5(4)
C007	C00A	C00O	120.2(3)	F6A	Sb6A	F0AB	79.3(12)
C008	C00B	C00Q	120.5(2)	F6A	Sb6A	F4A	93.6(9)
C007	C00C	N004	119.1(2)	F6A	Sb6A	F7	142.7(8)
C00L	C00C	N004	120.4(2)	F0AB	Sb6A	F7	63.7(12)
C00L	C00C	C007	120.5(3)	F4A	Sb6A	F1	168.3(9)
C005	C00D	C00W	119.7(3)	F4A	Sb6A	F0AB	102.7(17)
C00N	C00E	C008	119.8(3)	F4A	Sb6A	F7	98.3(11)
C00J	C00F	C009	119.4(3)	F2A	Sb6A	F1	88.6(5)
N004	C00G	Pd01	108.35(16)	F2A	Sb6A	F6A	30.5(11)
N004	C00G	C00V	119.9(3)	F2A	Sb6A	F0AB	109.8(17)
C00K	C00G	Pd01	72.54(16)	F2A	Sb6A	F4A	87.4(12)
C00K	C00G	N004	107.2(3)	F2A	Sb6A	F7	172.1(10)
C00K	C00G	C00V	130.4(3)	F5A	Sb6A	F1	94.9(4)
C00V	C00G	Pd01	104.14(18)	F5A	Sb6A	F6A	121.9(9)
C00S	C00I	Pd01	73.11(17)	F5A	Sb6A	F0AB	158.5(11)
C00W	C00J	C00F	120.3(2)	F5A	Sb6A	F4A	74.2(8)
C00G	C00K	Pd01	73.78(15)	F5A	Sb6A	F2A	91.4(14)
C00G	C00K	C00P	107.3(3)	F5A	Sb6A	F7	95.4(7)
C00P	C00K	Pd01	106.46(19)	F2A	F6A	Sb6A	71.3(14)
C00U	C00L	C00C	119.7(3)	F6A	F2A	Sb6A	78.1(17)

1.3 Details of computations.

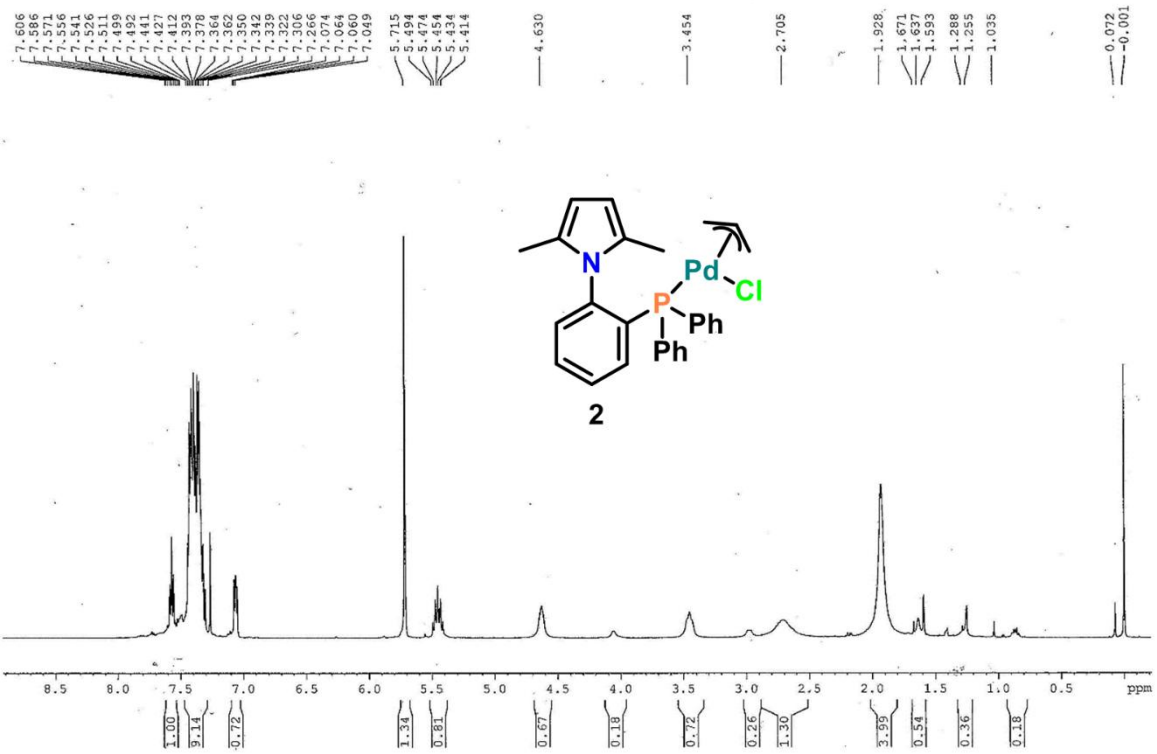
Geometry optimization for intermediates and transition states was performed at the density functional level of theory (DFT) using the B3LYP hybrid functional, with effective core potential LANL2 along with LANL2DZ on the Palladium center and 6-31+G** basis function on all the other atoms in gas phase with Gaussian09 quantum chemistry suite.[i] Single point calculations were done on this optimized geometry with 6-311++G** basis set to generate wave function for AIM computation. The electron density, ρ, and its associated Laplacian, $\nabla^2\rho$ were calculated based on AIM theory as implemented in AIM 2000 program package.[ii]

To obtain the correct barrier, we have done single point solvent phase calculation on gas phase optimized geometries for dichloromethane solvent using CPCM model with effective core potential LANL2 along with LANL2DZ on the Pd atom and 6-311++G(d, p) basis function on all other atom by B3LYP functional. For obtaining solvent phase free energy, entropies are obtained by scaling of gas phase entropies calculated in ideal gas phase model to account suppression of entropies in solution phase.

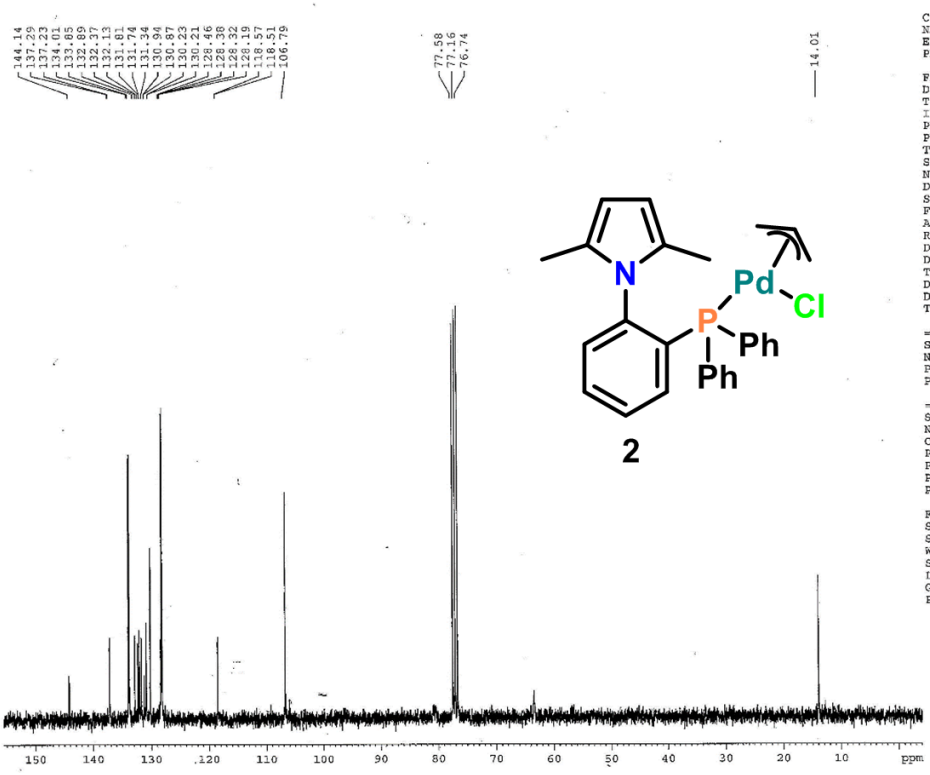
i) *Gaussian*-09, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, 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. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. 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, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.

ii) Bader, R.F.W.; *Atoms in Molecules: A Quantum Theory*; Clarendon Press, Oxford, 1990; b) Biegler-König, F; Schönbohm, J.; Bayles, D. *J. Comp. Chem.* **2001**, *22*, 545.

1.4a ^{1}H Spectra of complex 2 at room temperature.



1.4b ^{13}C Spectra of complex 2 at room temperature.

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PROCNO                        1

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TD0                           1

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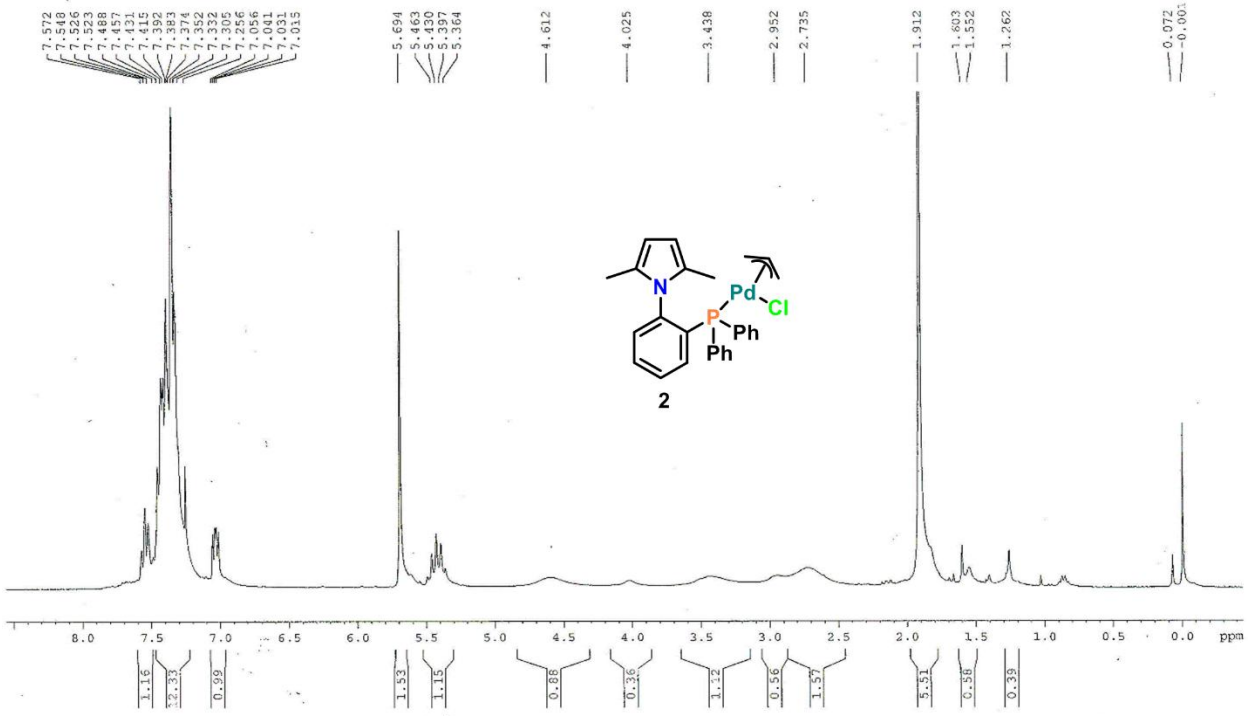
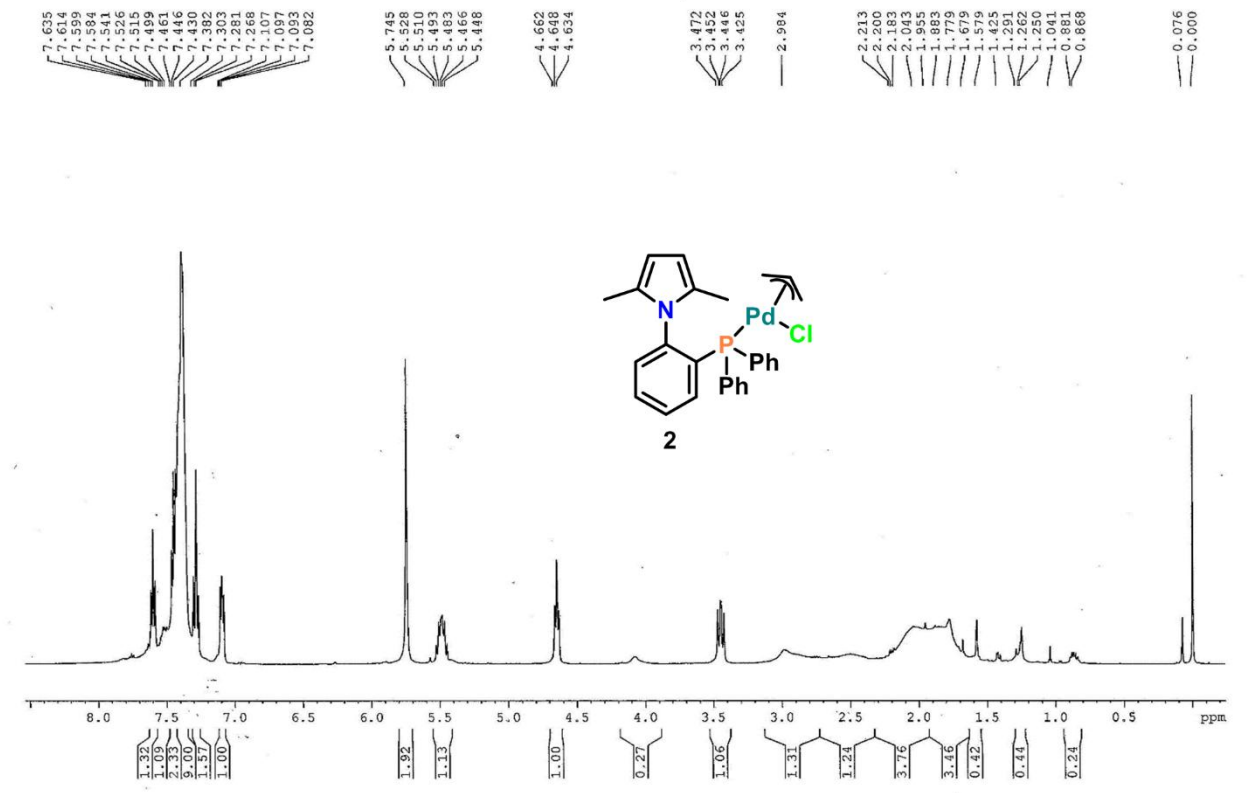
1.4c ^{1}H Spectra of complex 2 at 50 °C.



1.4d ^{1}H Spectra of complex 2 at 0 °C.



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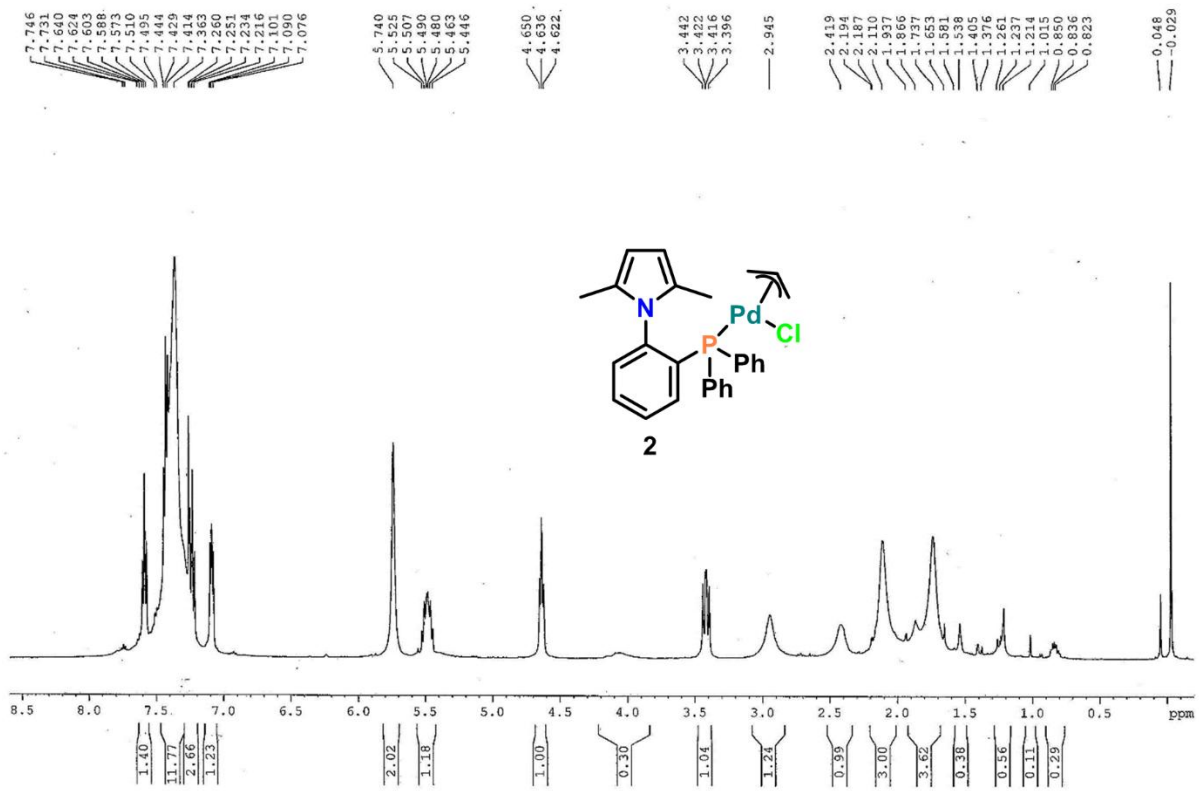

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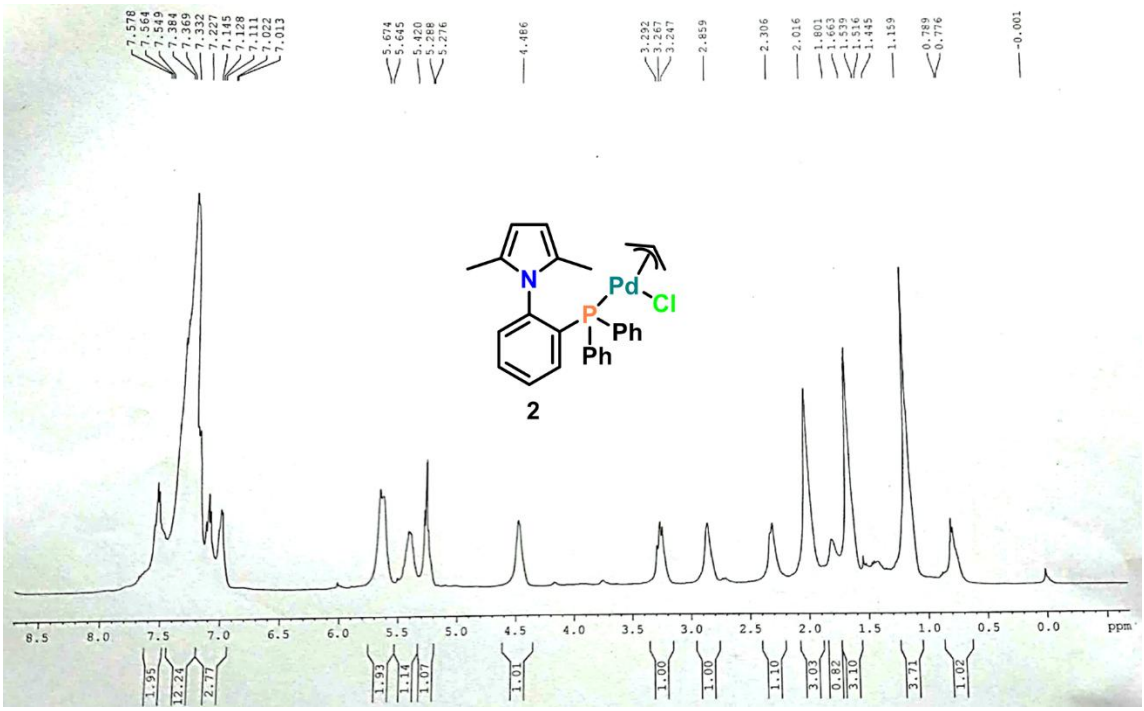
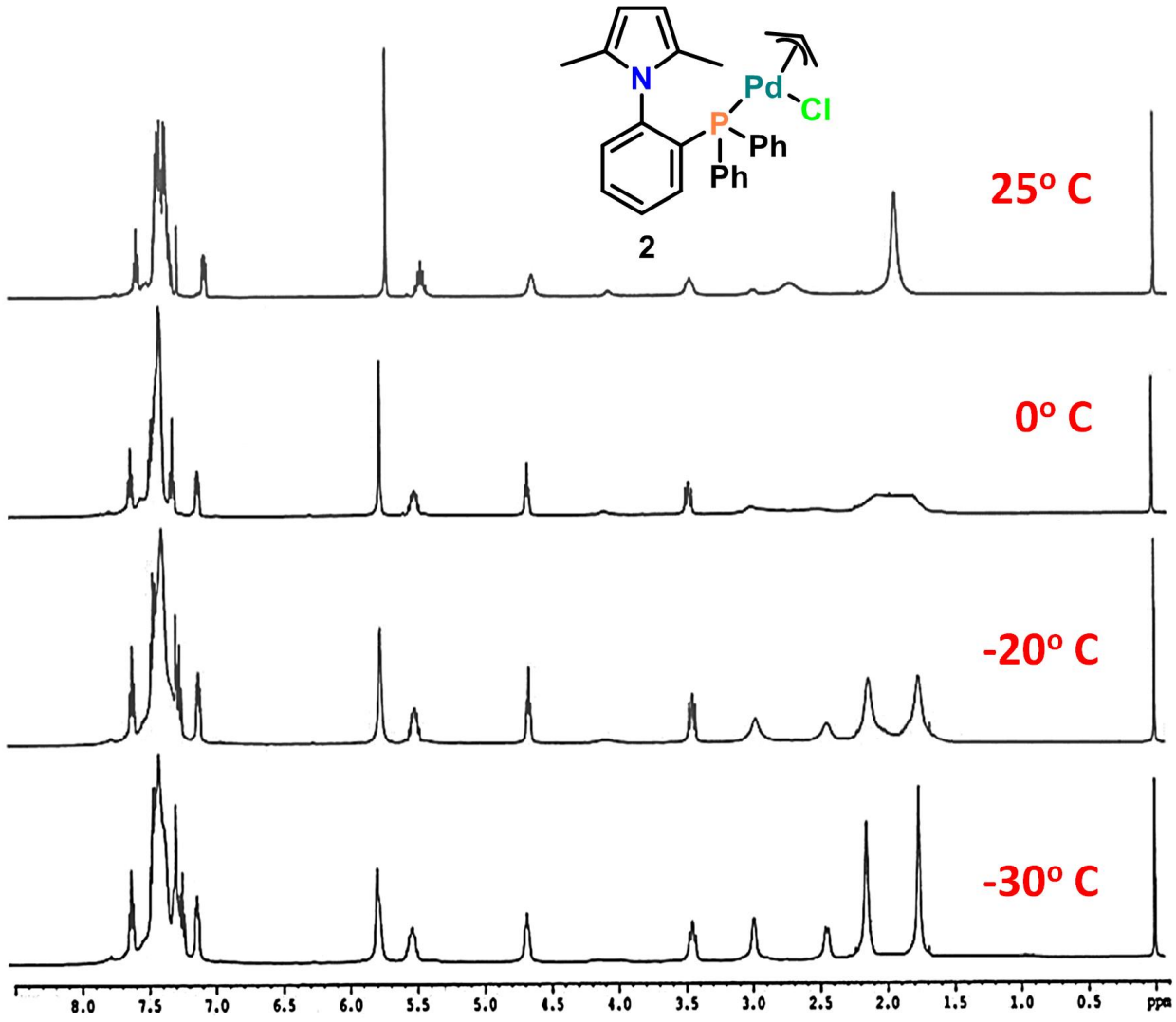
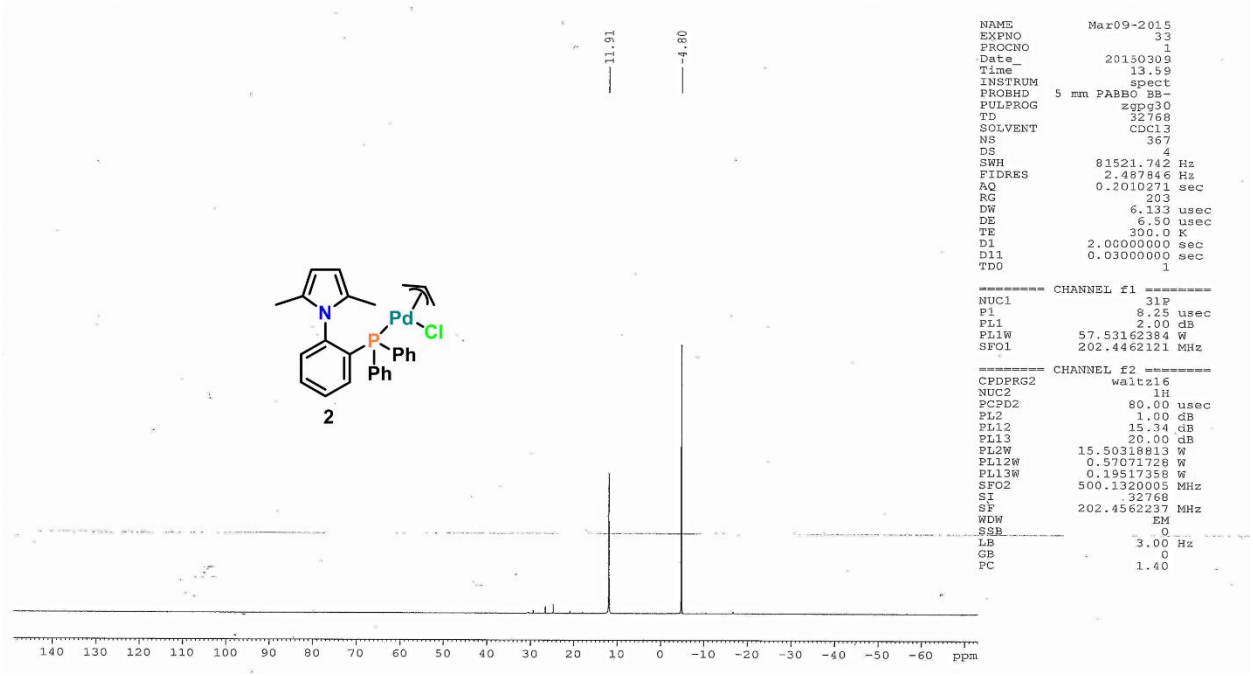


1.4f ^{1}H spectra of the complex 2 at variable temperature



1.4f ^{31}P spectra of the complex 2 Room temperature



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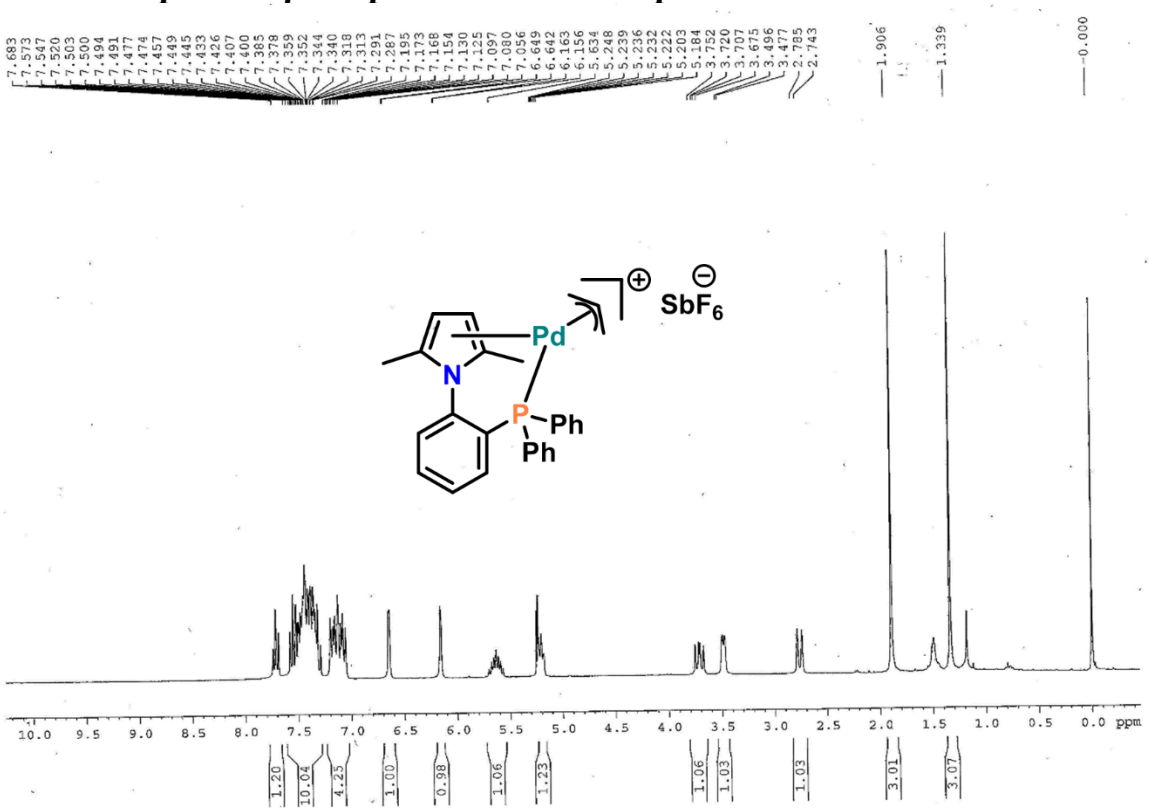

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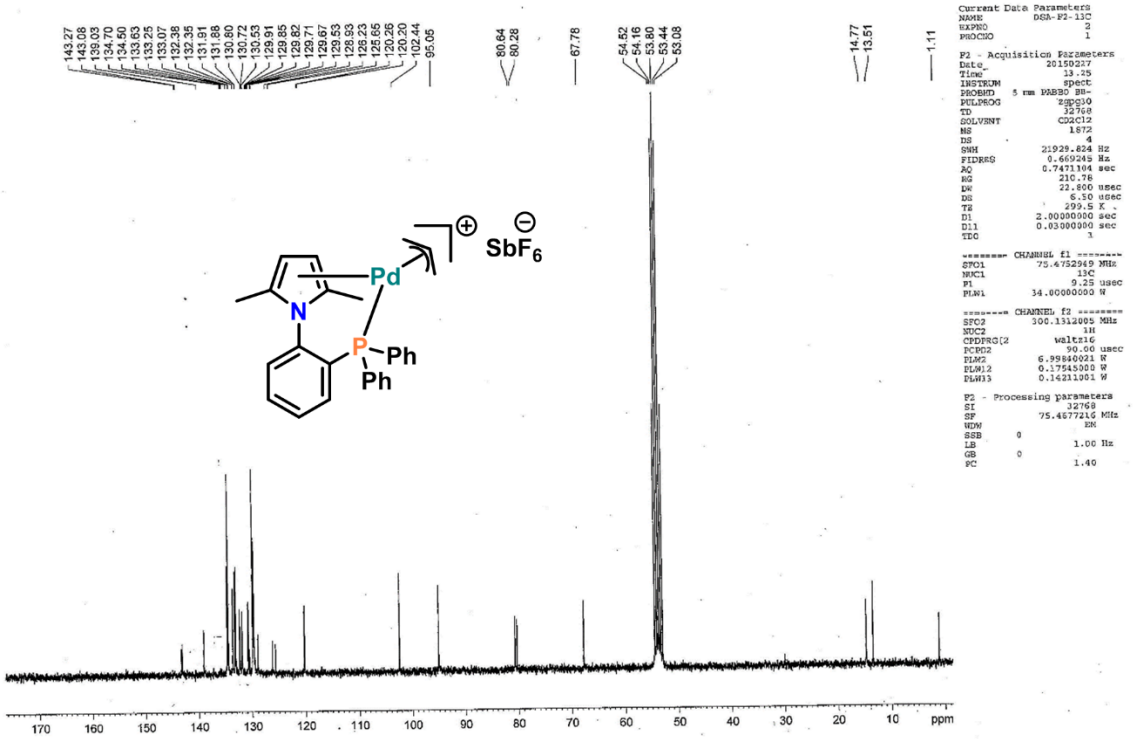

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DW 22.800 usec
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D11 0.03000000 sec
TD0 1

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NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
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PLW12 0.17545000 W
PLW13 0.14211001 W

F2 - Processing parameters
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LB 1.00 Hz
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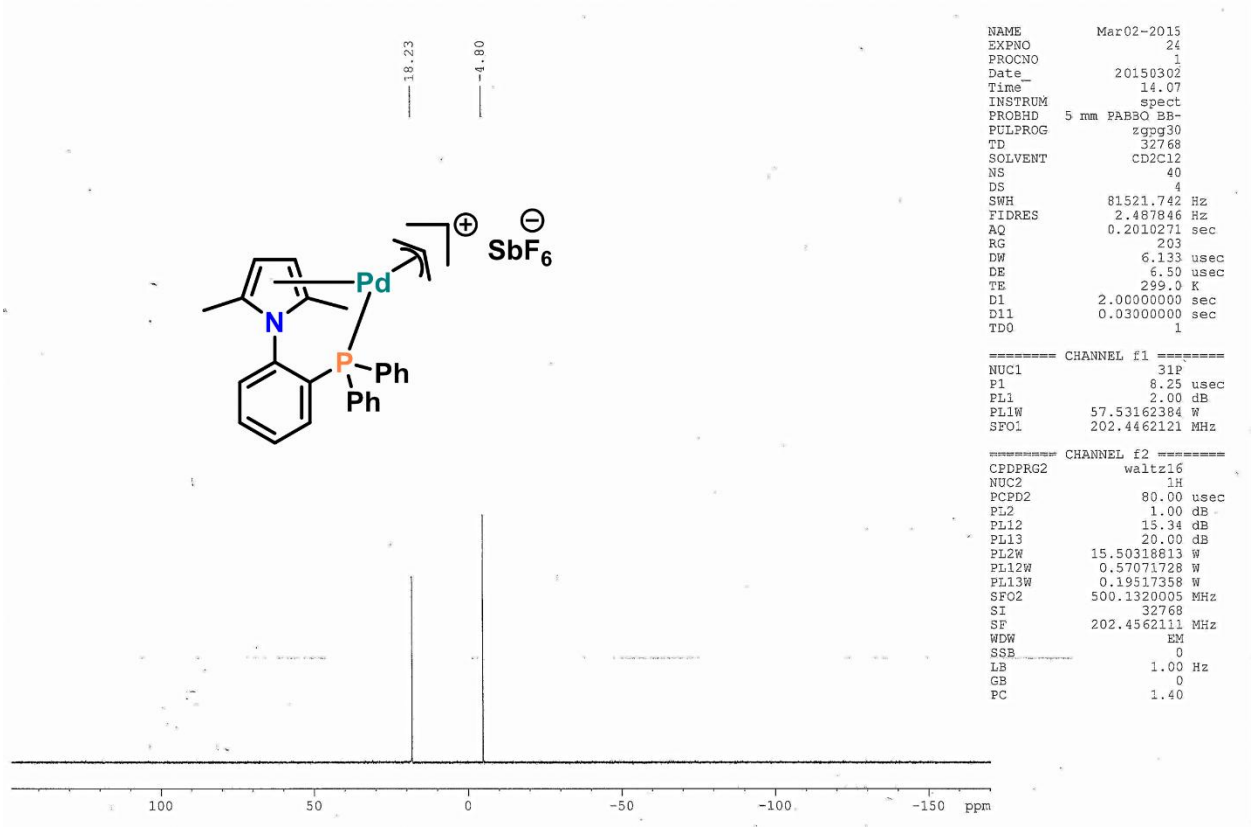

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DE	6.50 usec
TE	299.0 K
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D11	0.03000000 sec
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PL2	1.00 dB
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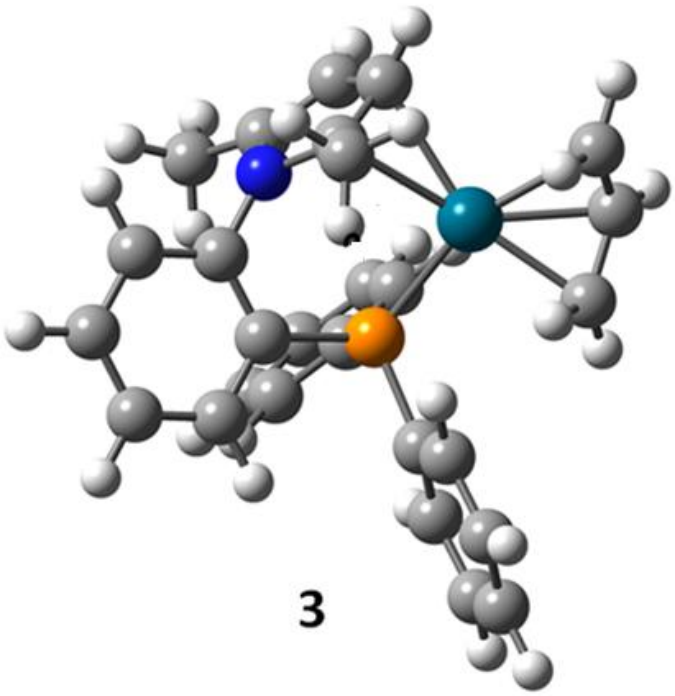
1.6 DFT

a) xyz coordinates:

Complex 3



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No. of imaginary frequency: 0

0, 2

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4	C	0	-0.799503	-2.563528	1.558761
5	H	0	-1.227309	-3.021068	0.654915
6	C	0	0.086652	-0.624352	2.705897
7	H	0	0.362840	0.439936	2.723420
8	C	0	-0.071551	-2.743668	3.854304
9	H	0	0.089227	-3.357349	4.752547
10	C	0	0.264985	-1.389712	3.858673
11	H	0	0.669913	-0.940625	4.777178
12	C	0	-0.615091	-3.327407	2.709627

13	H	0	-0.899883	-4.389563	2.713683
14	C	0	-2.351250	0.008113	-0.292179
15	C	0	-3.359930	-0.491851	0.531878
16	H	0	-3.099386	-1.095651	1.413263
17	C	0	-2.671004	0.767945	-1.417739
18	H	0	-1.882454	1.171391	-2.069441
19	C	0	-3.993841	1.023086	-1.718005
20	H	0	-4.260625	1.615203	-2.605428
21	C	0	-5.013615	0.533864	-0.901186
22	H	0	-6.070408	0.731277	-1.132517
23	C	0	-4.694323	-0.220494	0.228181
24	H	0	-5.486496	-0.606296	0.886143
25	C	0	-0.022796	-1.343081	-1.273605
26	C	0	-0.930017	-2.163055	-1.945218
27	H	0	-1.998951	-2.128574	-1.689314
28	C	0	1.331279	-1.380340	-1.607619
29	C	0	1.783045	-2.236814	-2.604571
30	H	0	2.848463	-2.270531	-2.874836
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32	H	0	-1.186912	-3.674819	-3.468131
33	N	0	2.247821	-0.536204	-0.945865
34	C	0	2.819030	-0.807667	0.293979
35	C	0	2.899852	1.407687	-0.063033
36	H	0	3.513206	2.161872	-0.184713
37	C	0	2.257493	0.836227	-1.159560
38	C	0	3.203345	0.363909	0.845869
39	H	0	3.615168	0.467291	1.671879
40	C	0	1.996800	1.375803	-2.515342
41	H	0	2.051491	2.444130	-2.491114
42	H	0	1.022030	1.075731	-2.838887
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49	H	0	1.228015	-3.748377	-4.063503
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52	H	0	-1.903148	2.530856	1.535116
53	C	0	-0.058213	3.603851	1.242111
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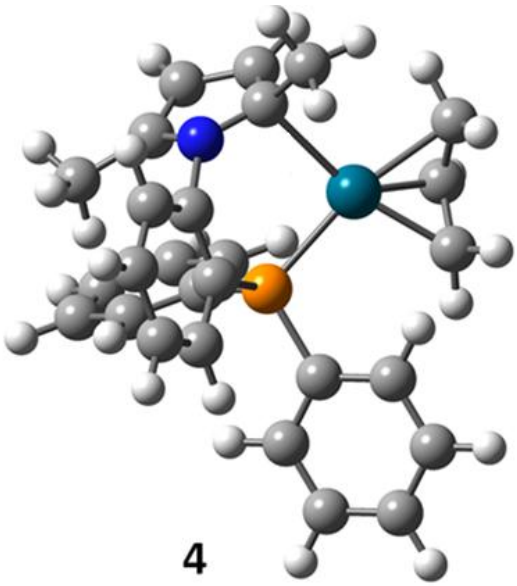
b) a) xyz coordinates:

Complex 4



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11	H	0	0.410730	-0.882279	4.785402
12	C	0	0.525583	-3.402882	2.511939
13	H	0	0.731965	-4.450509	2.442763
14	C	0	-2.377876	-0.400261	-0.234027
15	C	0	-3.118252	-1.495412	0.231031
16	H	0	-2.620185	-2.315928	0.703840
17	C	0	-3.030194	0.674414	-0.853333

18	H	0	-2.464859	1.510621	-1.208411
19	C	0	-4.422920	0.653914	-1.007560
20	H	0	-4.920961	1.474398	-1.480498
21	C	0	-5.163341	-0.441205	-0.542369
22	H	0	-6.226746	-0.456824	-0.659995
23	C	0	-4.510998	-1.515875	0.076897
24	H	0	-5.076321	-2.352037	0.432034
25	C	0	0.167734	-1.123327	-1.474643
26	C	0	-0.613738	-1.985844	-2.258694
27	H	0	-1.628655	-2.183298	-1.983229
28	C	0	1.484911	-0.875793	-1.801161
29	C	0	2.027644	-1.478710	-2.949575
30	H	0	3.046375	-1.287996	-3.215443
31	C	0	-0.073194	-2.586005	-3.398267
32	H	0	-0.671251	-3.239298	-3.998600
33	N	0	2.397622	-0.043025	-0.996895
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35	C	0	2.312096	1.267315	-0.620338
36	C	0	2.606142	2.226383	-1.788753
37	H	0	2.461005	3.236277	-1.466387
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39	H	0	3.618310	2.096677	-2.110597
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41	H	0	3.577522	-2.475053	1.179691
42	H	0	2.938770	-2.746765	-0.423808
43	H	0	1.849751	-2.504360	0.920923
44	C	0	1.251992	-2.326979	-3.747913
45	H	0	1.674337	-2.776195	-4.622418
46	C	0	-1.716432	2.825228	0.460740
47	H	0	-2.080743	3.431471	-0.342155
48	H	0	-2.603790	2.393590	0.874439
49	C	0	-0.646868	3.305353	1.309114
50	H	0	-0.704342	3.523186	2.355171
51	C	0	0.232795	4.022744	0.382235
52	H	0	-0.109135	4.276299	-0.599432
53	H	0	1.284621	4.091187	0.566181
54	C	0	3.234684	0.271127	1.115128
55	H	0	3.780056	0.103616	2.020322
56	C	0	2.819435	1.512125	0.630194
57	H	0	3.051305	2.452586	1.084731
