Supporting Information for "Binuclear Palladium Complexes Supported By Bridged Pincer Ligands"

*David E. Herbert and Oleg V. Ozerov**

Department of Chemistry, Texas A&M University, College Station, Texas 77842

ozerov@mail.chem.tamu.edu

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Table SI-1. ^{1}H NMR data (ppm) for **5-Cl/OTf** and **6-Cl/OAc** in CD_2Cl_2.

	*H*C=N	Ar C*H*	CH_2	*i*Pr C*H*Me	CH*Me*	Ar *Me*
5a-Cl	8.38 (d, 4.8 Hz)	6.94 (m, 4H), 6.75 (dt, 7.4 1.3 Hz, 2H)	4.40	2.43 (m)	1.38 (dd, 19.3, 7.3 Hz), 1.28 (dd, 16.2, 7.0 Hz)	-
5b-Cl	8.26 (d, 5.0 Hz)	7.01 (m, 4H), 6.76 (br d, 7.2 Hz, 2H)	3.83, 1.96	2.42 (m)	1.39 (dd, 19.2, 7.2 Hz), 1.30 (dd, 16.1, 6.7 Hz)	-
5a-OTf	8.36 (d, 4.5 Hz)	7.08 (d, 8.0 Hz, 2H), 7.04 (dd, 7.5, 6.5 Hz, 2H), 6.8 (d, 8.0 Hz, 2H)	4.11	2.59 (m)	1.38 (dd, 20.5, 7.5 Hz), 1.28 (15.5, 7.0 Hz)	-
5b-OTf	8.13 (d, 5.0 Hz)	7.07 (m, 4H), 6.79 (d, 7.0 Hz, 2H)	3.71, 1.84	2.57 (m)	1.36 (dd, 20.0, 7.0 Hz), 1.28 (16.0, 7.0 Hz)	-
6a-Cl[a]	7.95 (d, 13.4 Hz)	7.09 (d, 8.7 Hz, 2H), 7.05 (d, 13.0 Hz, 2H), 6.71 (br t, 7.6 Hz, 4H), 6.37 (4H)	5.11, 4.02	2.75 (m, 2H), 2.31 (m, 2H)	1.58 (dd, 16.8, 6.6 Hz), 1.52 (dd, 16.5, 7.3 Hz), 1.29 (dd, 18.2, 7.0 Hz), 1.15 (dd, 15.6, 6.7 Hz)	2.27, 1.96
6b-Cl[a]	7.79 (d, 13.2 Hz)	7.29 (m, 2H), 7.15 (m, 4H), 6.95 (m, 4H), 6.85 (d, 13.2 Hz, 2H)	4.76, 3.35, 2.00	2.71 (m, 2H), 2.31 (m, 2H)	1.33 (dd, 18.1, 6.4 Hz), 1.18 (dd, 15.3, 6.8)	2.26, 2.18
6a-OAc[b]	7.95 (d, 12.4 Hz)	7.10 (d, 8.6 Hz, 2H), 6.96 (d, 8.6 Hz, 2H), 6.70 (pseudo t, 10.1 Hz, 4H), 6.42 (m, 2H), 6.36 (2H)	4.53, 3.90	2.59 (m, 2H), 2.43 (m, 2H)	1.45 (dd, 18.2, 7.0 Hz), 1.29 (dd, 15.9, 7.0 Hz), 1.24 (dd, 19.2, 7.0 Hz), 1.14 (dd, 13.6, 7.0 Hz)	2.25, 1.90
6b-OAc[b]	7.66 (d, 12.0 Hz)	7.32 (dd, 8.0, 3.5 Hz, 2H), 7.12 (m, 2H), 6.97 (d, 8.0 Hz, 2H), 6.91 (m, 4H), 6.86 (d, 8.5 Hz, 2H)	4.09, 3.27, 2.01, 1.80	2.62 (m, 2H), 2.36 (m, 2H)	1.32 (overlapped m's, 18H), 1.15 (dd, 14.0, 7.0 Hz, 6H)	2.25, 2.18

[a]resonances for minor isomer not included in table.

[b]resonances for acetate methyl groups not included in table.

Table SI-2. $^{13}C\{^1H\}$, $^{31}P\{^1H\}$ and ^{19}F NMR data (ppm) for **5-Cl/OTf** and **6-Cl/OAc** in CD_2Cl_2.

	H*C*=N	Ar *C*	*C*H_2	*i*Pr *C*HMe	CH*Me*	Ar *Me*	$^{31}P\{^1H\}$	^{19}F
5a-Cl	176.8 (d, 3.8 Hz)	163.6 (d, 6.2 Hz), 153.0, 145.8, 126.7, 122.2, 114.3 (d, 15.6 Hz)	58.4	29.5 (d, 25.5 Hz)	17.5 (d, 5.8 Hz), 16.9	-	202.5	-
5b-Cl	174.4 (d, 4.3 Hz)	163.7 (d, 6.3 Hz), 153.1, 146.6, 126.6, 122.2, 114.0 (d, 15.6 Hz)	58.5, 27.6	29.6 (d, 25.3 Hz)	17.5 (d, 5.8 Hz), 16.9	-	202.6	-
5a-OTf	177.0 (d, 3.9 Hz)	164.3 (d, 6.2 Hz), 146.2 (d, 3.1 Hz), 145.9, 127.9, 123.6, 115.4 (d, 14.6 Hz)	58.0	29.5 (d, 25.2 Hz)	17.7 (d, 6.0 Hz), 16.8 (d, 2.3 Hz)	-	203.2	-78.8
5b-OTf	173.7 (d, 3.8 Hz)	164.3 (d, 5.4 Hz), 146.3, 146.1 (d, 3.1 Hz), 127.7, 123.1, 114.9 (d, 15.3 Hz)	59.1, 27.2	29.5 (d, 24.5 Hz)	17.7 (d, 6.2 Hz), 16.8 (d, 2.3 Hz)	-	202.7	-79.0
6a-Cl[a]	162.4	162.2 (d, 19.9 Hz), 149.6, 134.5 (d, 2.8 Hz), 133.5, 132.8, 131.0, 128.7 (d, 6.9 Hz), 125.8 (d, 7.4 Hz), 121.2 (d, 14.3 Hz), 120.1, 119.7, 118.2	60.4	27.0 (d, 24.1 Hz), 23.5 (d, 30.4 Hz)	19.0 (d, 3.9 Hz), 18.6, 17.9, 17.6	20.5, 20.1	71.3 (71.9)	-
6b-Cl[a,b]	161.7	162.6 (d, 19.8), 149.7, 134.5, 133.9, 132.9, 131.5, 129.2, 126.0, 125.9, 120.9 (d, 13.9 Hz), 120.5, 118.5	59.6, 29.2	27.0 (d, 25.5 Hz), 23.8 (d, 30.4 Hz)	18.9 (d, 3.2 Hz), 18.1, 18.0, 17.7	20.5, 20.1	70.8 (70.9)	-
6a-OAc[a]	162.5	162.4, 149.5, 134.6, 133.6, 132.7, 131.3, 128.2 (d, 7.0 Hz), 125.6 (d, 3.7 Hz), 120.8 (d, 13.0 Hz), 119.6, 119.3, 118.8	59.7	26.9 (d, 23.2 Hz), 21.7 (d, 29.1 Hz)	19.2 (d, 4.8 Hz), 19.0 (d, 3.7 Hz), 16.4 (d, 2.5 Hz), 16.3 (d, 6.1 Hz)	20.5, 20.2	66.2 (66.8)	-
6b-OAc[b,c]	161.4 (161.3)	162.8 (162.7), 149.6, 134.4, 134.0, 132.8, 131.7, 129.4 (128.9), 128.8 (128.5), 126.0 (125.6), 120.5 (120.4), 119.9 (119.5), 119.3	59.6 (59.5), 29.6	26.9 (d, 23.0 Hz), 21.8 (d, 28.0 Hz)	19.1 (d, 3.8 Hz), 18.5 (d, 3.3 Hz), 16.5, 16.4	20.5, 20.1	65.3	-

[a] when observed, resonance for minor isomer shown in brackets.

[b] resonances for acetate groups not included in table.

[c] peak heights for two isomers are nearly identical and so when observed, the second of each pair of peaks is reported in brackets.

Table SI-3. Selected ^{1}H NMR data for bridging hydrides **5-H** and **6a-H** (CD_2Cl_2).

	*H*C=N	Ar C*H*	CH_2	*i*Pr CHMe	CH*Me*	Ar *Me*	Pd-*H*-Pd
5a-H	8.32 (d, 4.0 Hz)	7.20 (d, 7.0 Hz, 2H), 7.16 (app t, 7.7 Hz, 2H), 6.93 (d, 7.5 Hz, 2H)	4.12 (br)	2.32 (m)	1.33 (dd, 7.5, 2.0), 1.30 (m)	-	-9.19 (t, 13.5 Hz)
5b-H	8.34 (d, 4.0 Hz)	7.20 (d, 5.5 Hz, 2H), 7.17 (dd, 7.0, 5.5 Hz, 2H), 6.95 (d, 7.0 Hz, 2H),	4.40, 3.62, 2.50-2.43 (m – overlapped with *i*Pr C*H*Me), 1.90	2.50-2.43 (m – overlapped with CH_2), 2.32 (h, 7.5 Hz)	1.37 (dd, 15.0, 7.0 Hz), 1.34-1.30 (m), 1.23 (dd, 17.2, 6.7 Hz)	-	-8.42 (t, 13.5 Hz)
6a-H	7.70 (d, 12.5 Hz)	7.31 (dd, 9.0, 3.5 Hz, 2H), 7.12 (d, 3.5 Hz, 2H), 7.10 (2H), 7.07 (d, 2.5 Hz, 2H), 7.04 (2H), 7.02 (dd, 9.0, 2.5 Hz, 2H)	4.73 (d, 11.5 Hz), 4.34 (d, 13.0 Hz)	2.48 (h, 6.5 Hz), 2.22 (m)	1.36 (dd, 17.5, 6.5 Hz), 1.08 (dd, 19.0, 6.5 Hz)	2.31, 2.25	-20.08 (t, 15.2 Hz)

Table SI-4. Selected ^{13}C{^{1}H}, ^{31}P{^{1}H} and ^{19}F NMR data for bridging hydrides **5-H** and **6a-H** (CD_2Cl_2).

	H*C*=N	Ar *C*	CH_2	*i*Pr *C*HMe	CH*Me*	Ar *Me*	^{31}P{^{1}H}	^{19}F
5a-H	178.3 (d, 3.3 Hz)	162.9 (d, 6.2 Hz), 158.2, 146.5, 128.4, 123.2, 115.1 (d, 15.3 Hz)	64.6	30.6 (d, 26.9 Hz)	18.7 (d, 4.9)	-	207.1	-79.8
5b-H	178.7 (d, 3.3 Hz)	162.6 (d, 5.5 Hz), 157.9, 146.5, 128.5, 122.9, 115.0 (d, 15.7 Hz)	62.3, 27.1	30.7 (d, 26.7 Hz), 30.3 (d, 27.1 Hz)	18.7 (d, 7.3 Hz), 18.6 (d, 2.8 Hz), 16.1 (d, 4.1 Hz)	-	207.5	-79.7
6a-H	161.7	160.7 (d, 18.7 Hz), 148.7, 135.3, 134.4 (d, 1.4 Hz), 133.4, 131.9, 130.4 (7.5 Hz), 127.7, 127.0, 119.6 (d, 13.6 Hz), 118.2, 117.7 (d, 47 Hz)	68.5	27.9 (d, 24.8 Hz), 22.4 (31.7 Hz)	18.9, 18.7, 18.4, 16.4	20.5, 20.3	83.4	-80.2

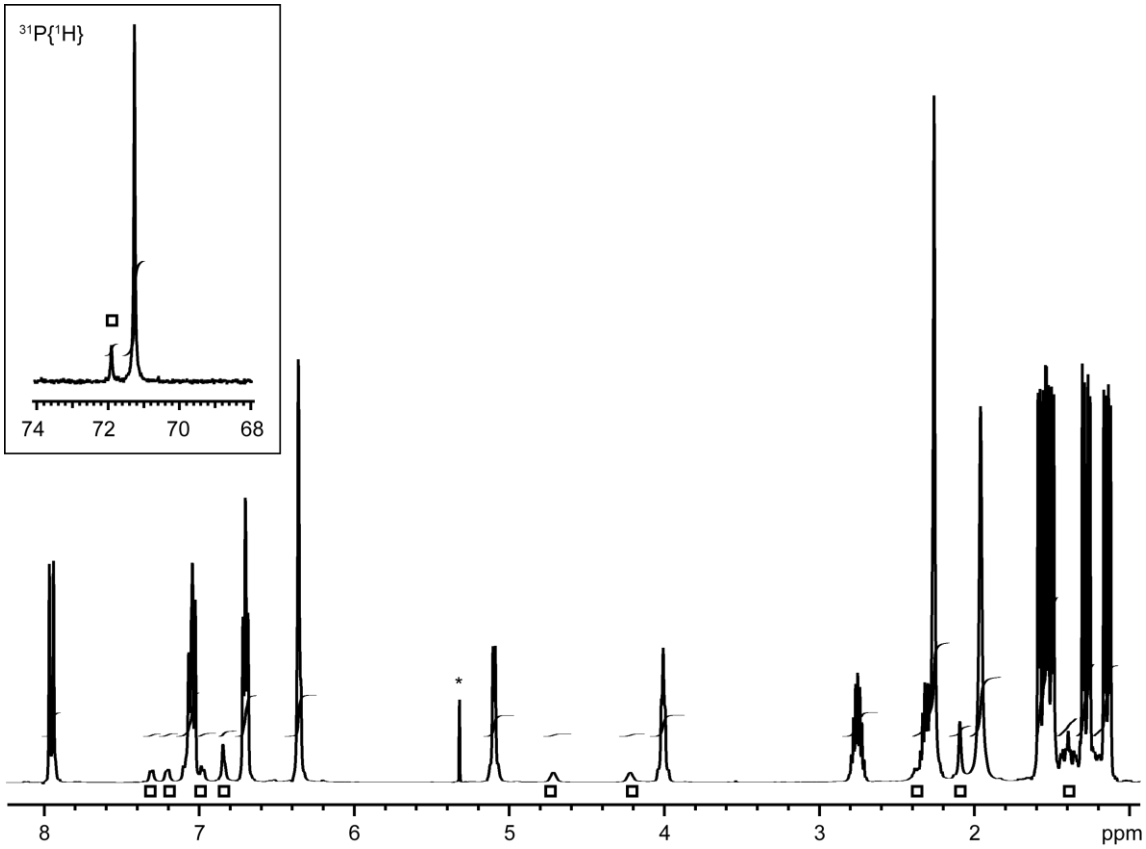

Figure SI-1. ^{1}H NMR spectrum (inset: $^{31}P\{^{1}H\}$ NMR spectrum) of $(PNN\text{-}C_2)Pd_2Cl_2$ **6a-Cl** in CD_2Cl_2 (solvent peak marked by *). Peaks from minor isomer marked by □.

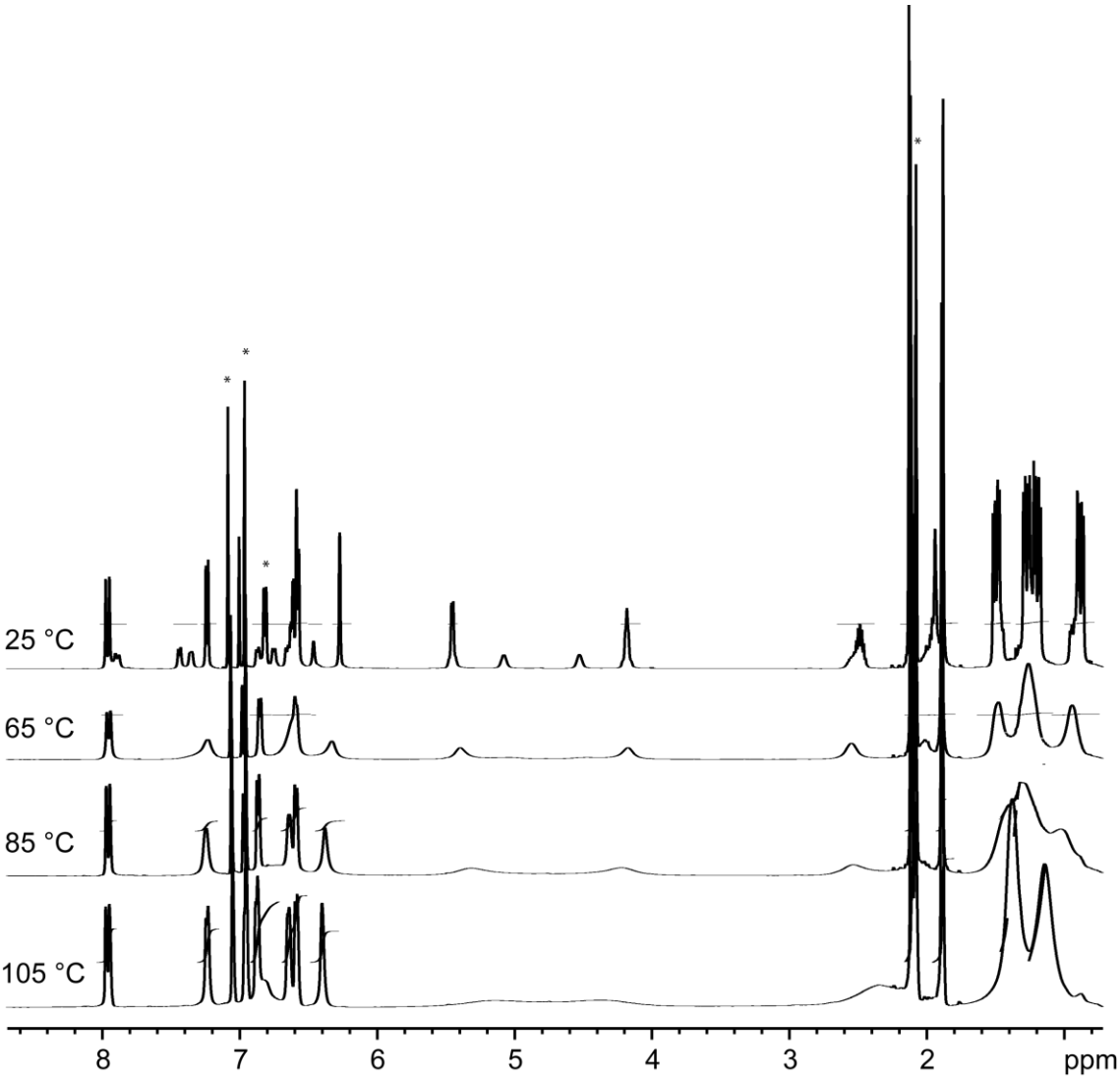

Figure SI-2. Variable temperature ^{1}H NMR spectrum of (PNN-C_2)Pd_2Cl_2 **6a-Cl** in $CD_3C_6D_6$ (solvent peak marked by *).

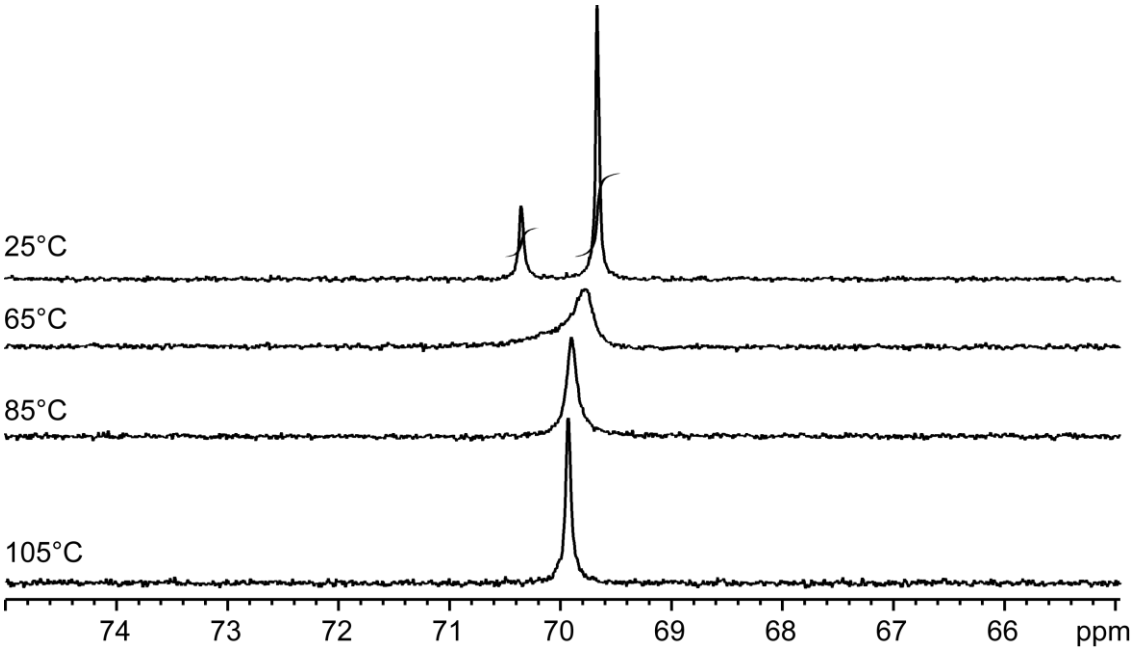

Figure SI-3. $^{31}P\{^{1}H\}$ NMR spectrum of (PNN-C_2)Pd_2Cl_2 **6a-Cl** in $CD_3C_6D_6$.

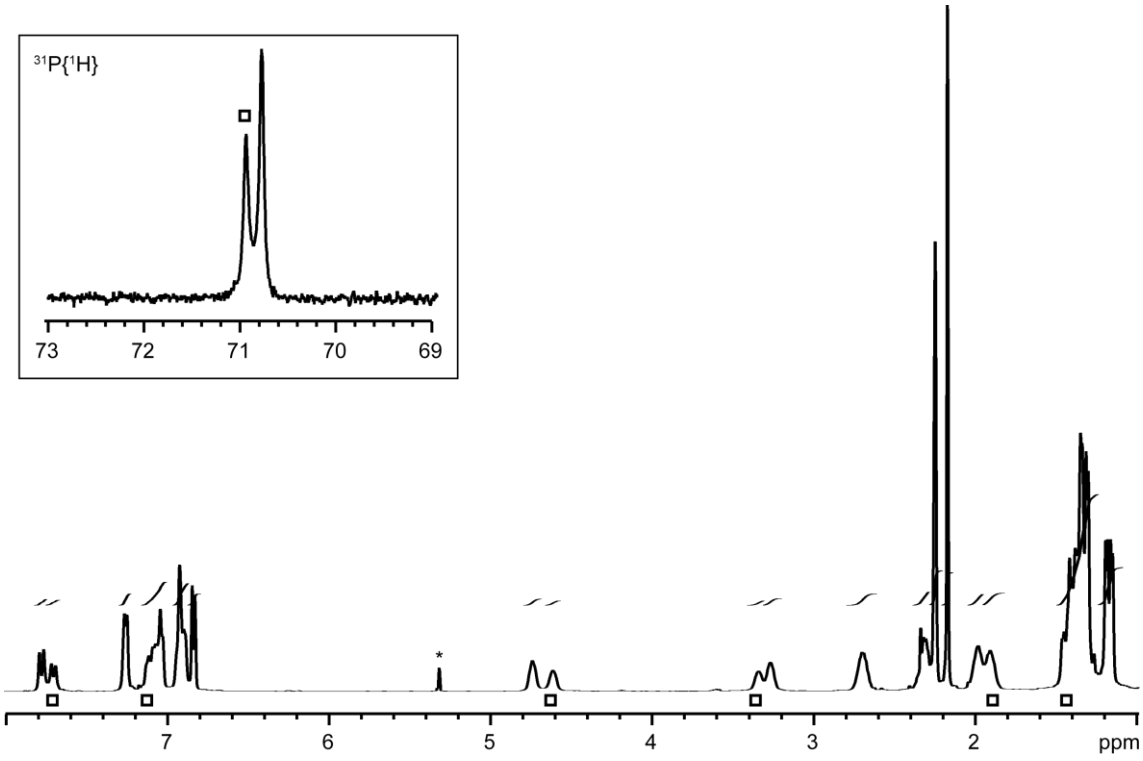

Figure SI-4. ^{1}H NMR spectrum (inset: $^{31}P\{^{1}H\}$ NMR spectrum) of (PNN-C_4)Pd_2Cl_2 **6b-Cl** in CD_2Cl_2 (solvent peak marked by *). Peaks from minor isomer marked by □.

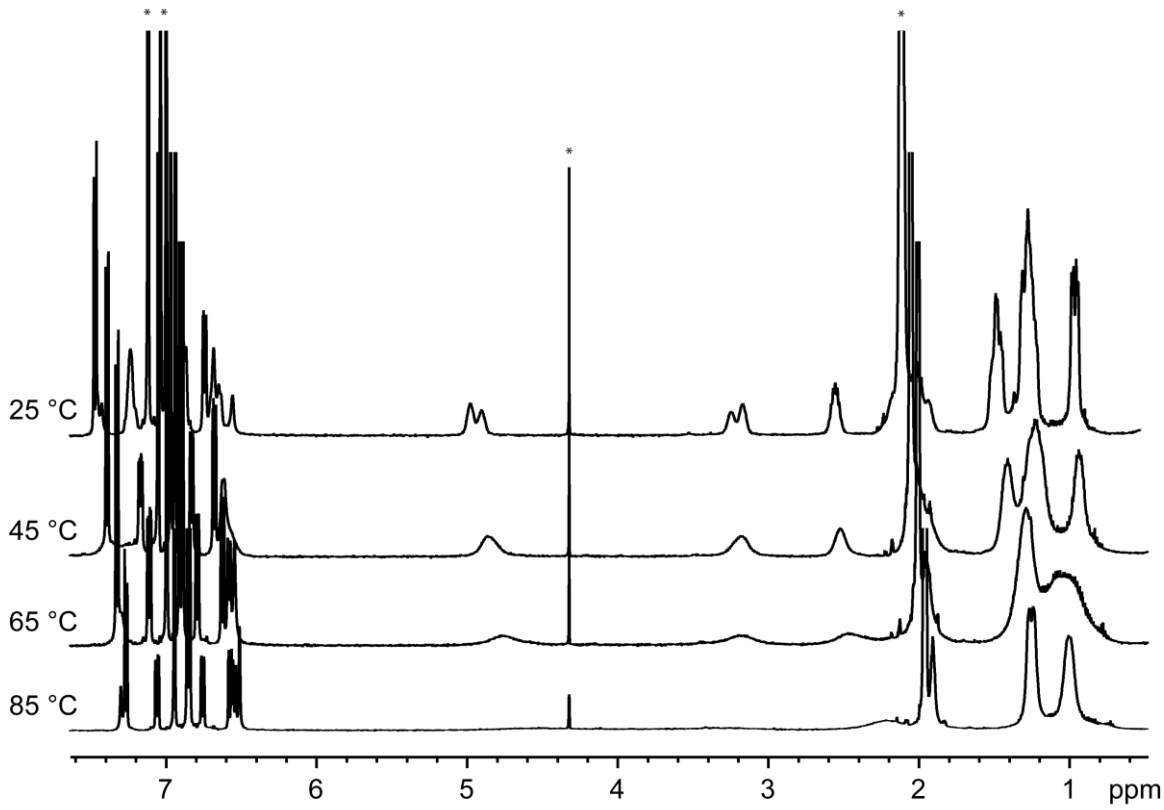

Figure SI-5. Variable temperature ^{1}H NMR spectrum of (PNN-C_4)Pd_2Cl_2 **6b-Cl** in $CD_3C_6D_6$ (solvent peak and residual CH_2Cl_2 marked by *).

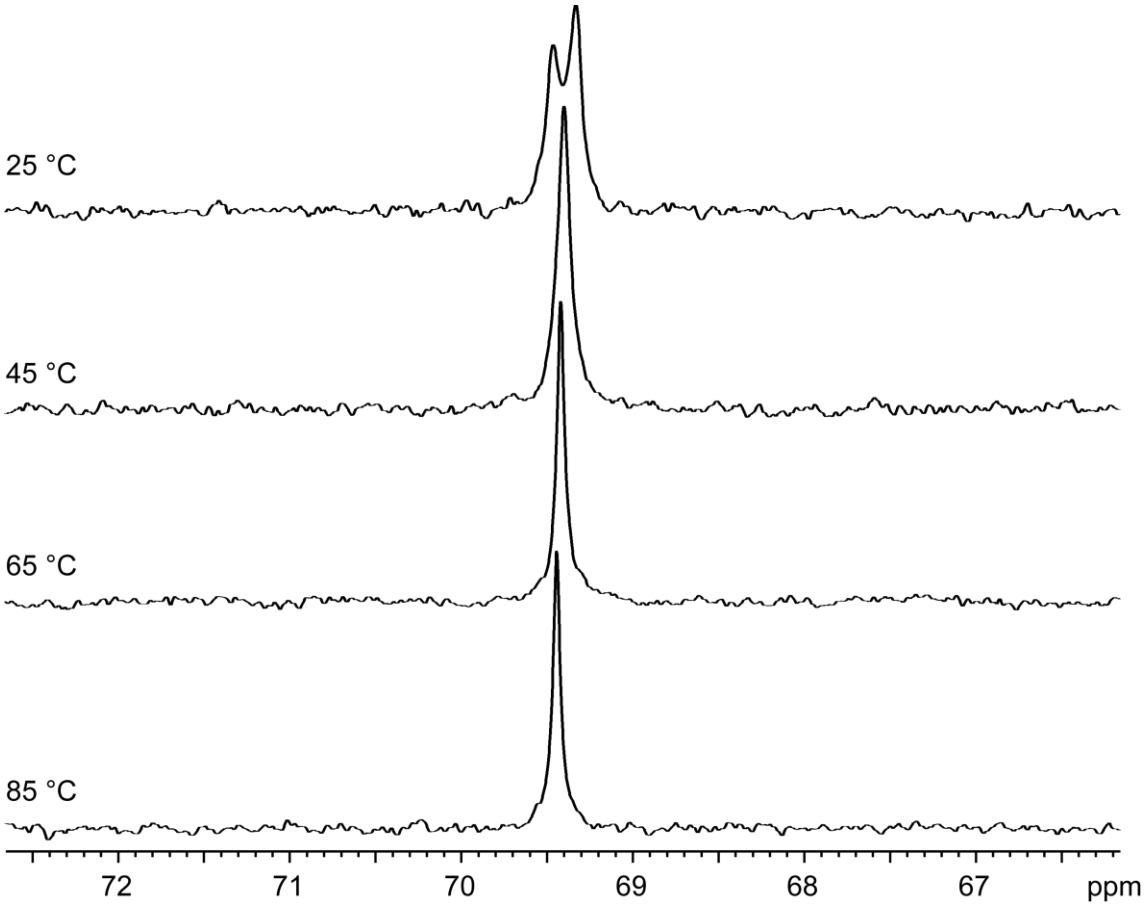

Figure SI-6. $^{31}P\{^{1}H\}$ NMR spectrum of (PNN-C_4)Pd_2Cl_2 **6b-Cl** in $CD_3C_6D_6$.

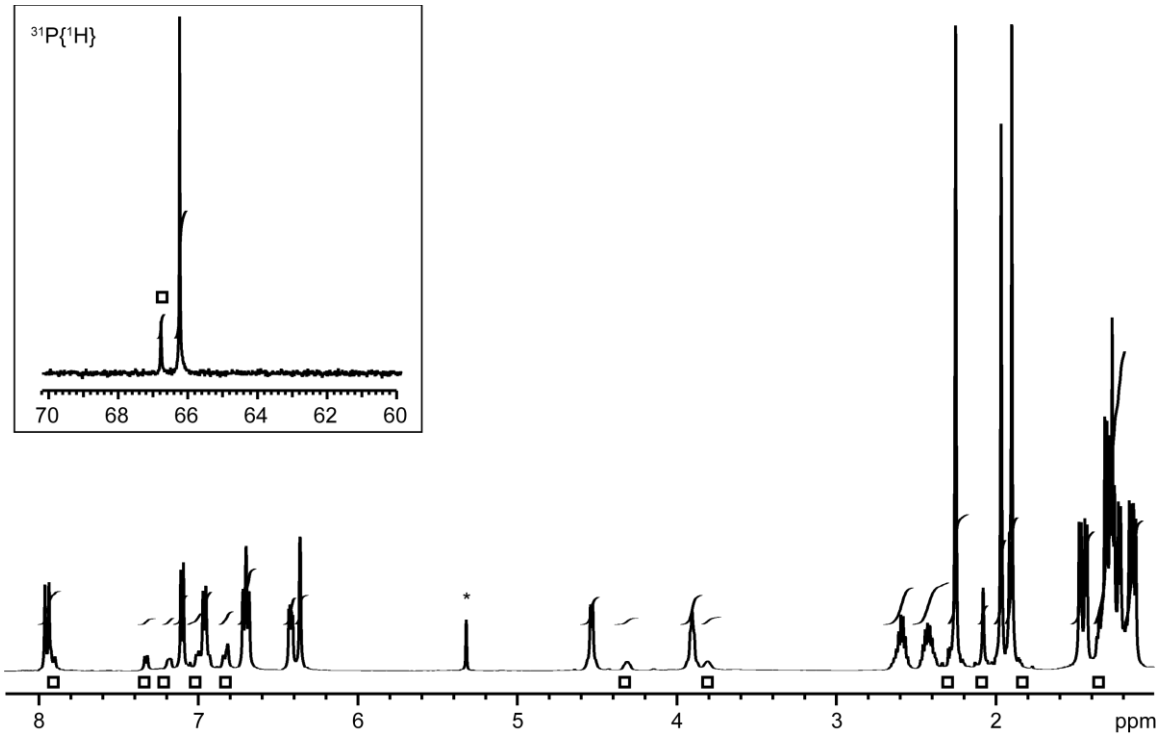

Figure SI-7. ^{1}H NMR spectrum (inset: $^{31}P\{^{1}H\}$ NMR spectrum) of (PNN-C_2)Pd_2OAc_2 **6a-OAc** in CD_2Cl_2 (solvent peak marked by *). Peaks from minor isomer marked by □.

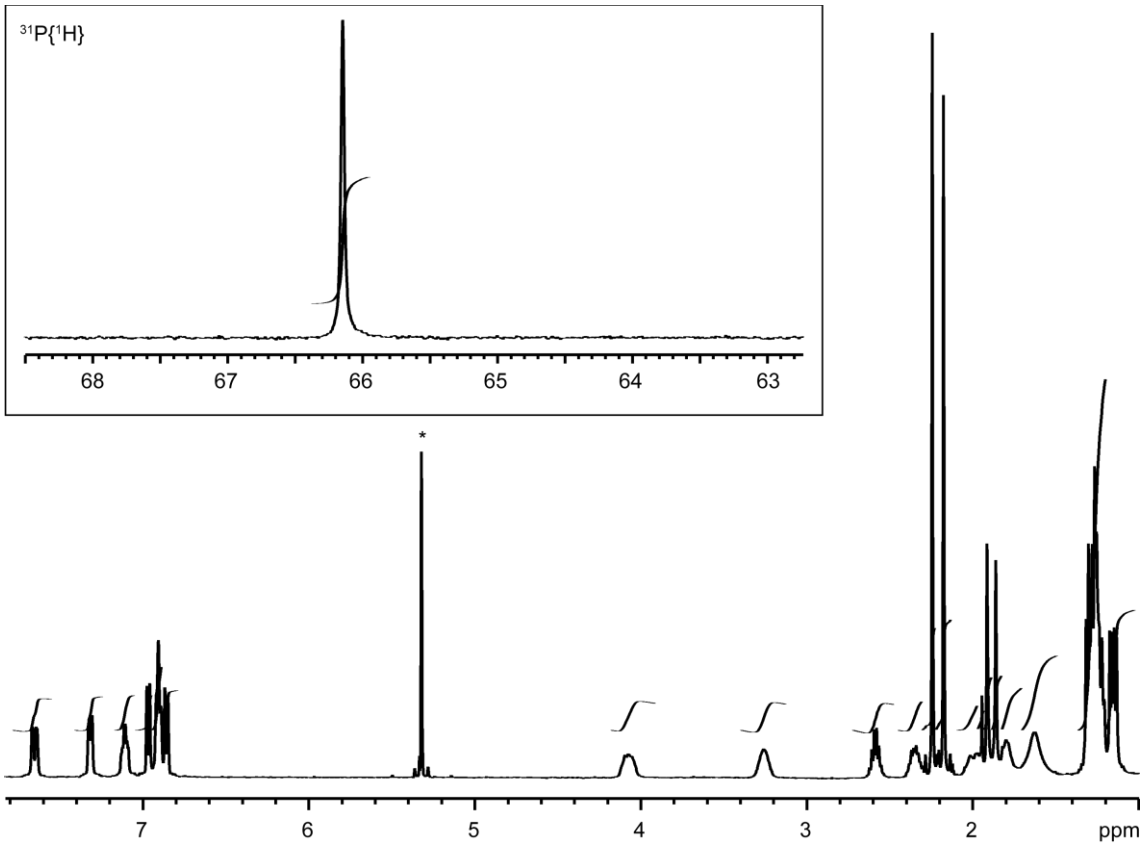

Figure SI-8. ^{1}H NMR spectrum (inset: $^{31}P\{^{1}H\}$ NMR spectrum) of (PNN-C_4)Pd_2OAc_2 **6b-OAc** in CD_2Cl_2 (solvent peak marked by *).

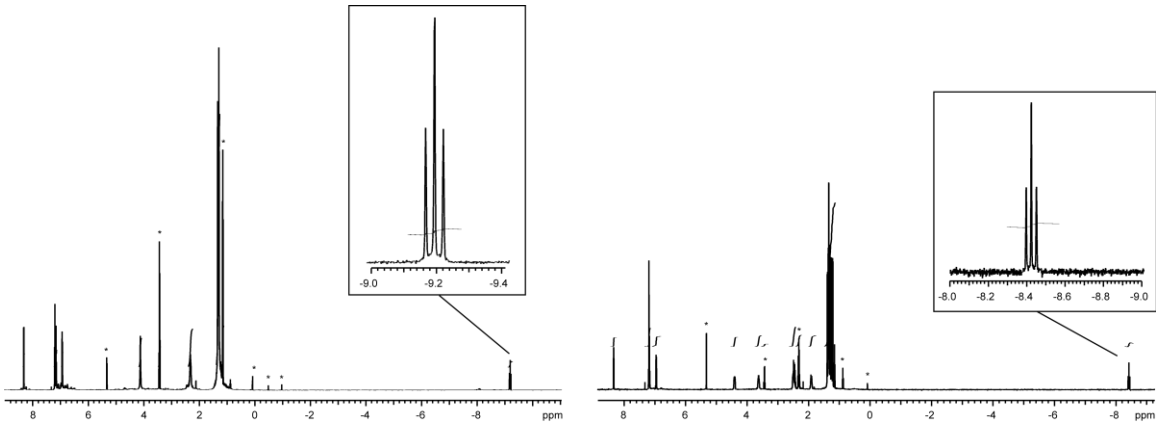

Figure SI-9. ^{1}H NMR spectra of bridging hydride, monocations **6a-H** (left) and **6b-H** (right) in CD_2Cl_2 (solvent peak, residual solvent and grease impurities marked by *).

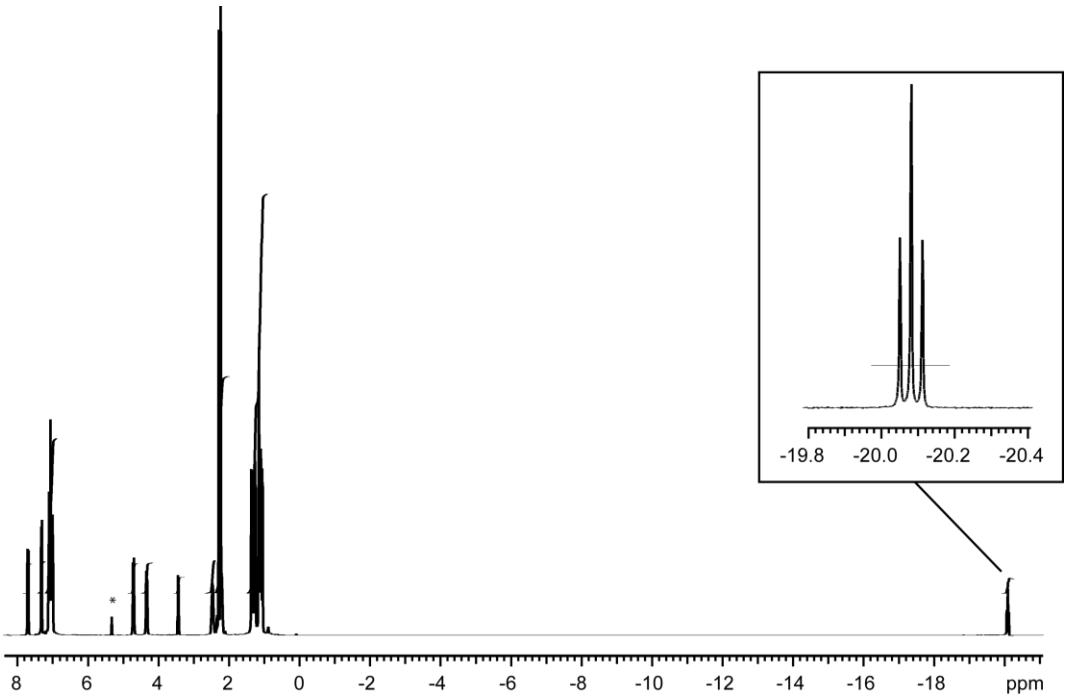

Figure SI-10. ^{1}H NMR spectrum of bridging hydride, monocation **6a-H** in CD_2Cl_2 (solvent peak marked by *).

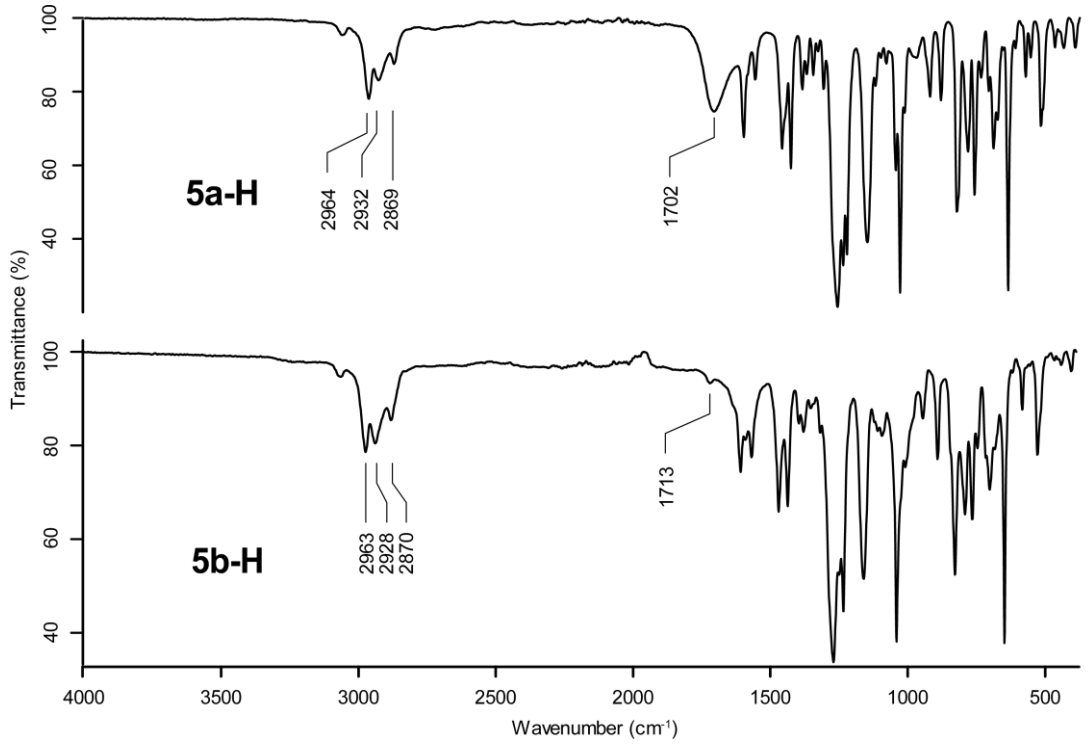

Figure SI-11. ATR FT-IR spectra of **5-H**.

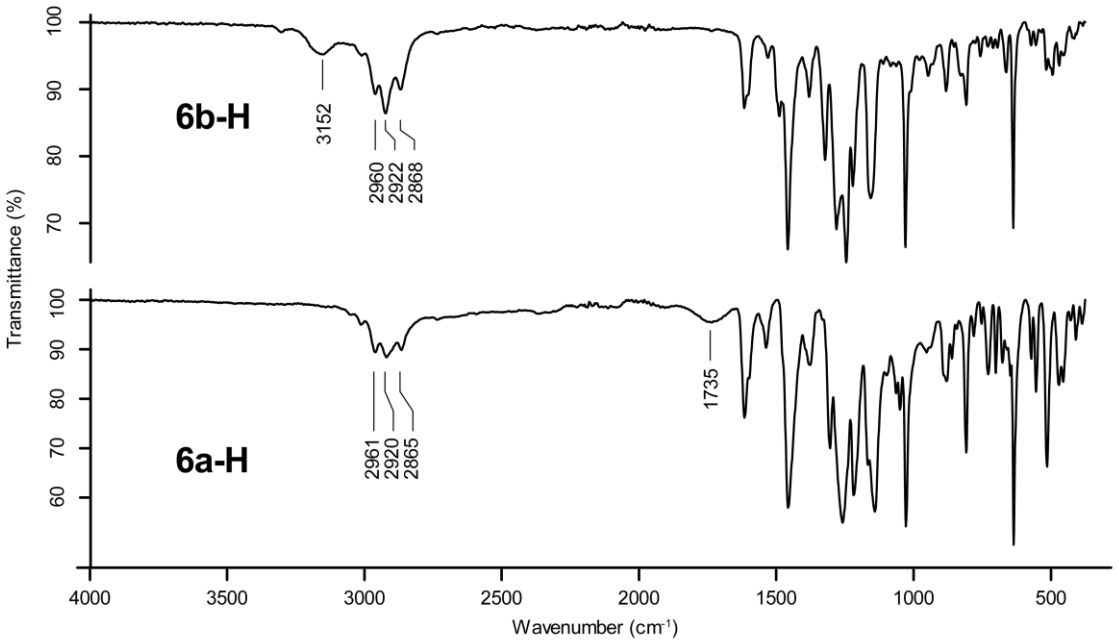

Figure SI-12. ATR FT-IR of **6-H** illustrating appearance of N-H stretch at 3150 cm^{-1}.