Supporting information for

A *trans*-bidentate *bis*-pyridinyl ligand with a transition metal hinge

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General Methods

THF, Et_2O, and CH_2Cl_2 were dried and degassed using an Innovative Technology Inc. solvent purification system before use. All other materials were reagent grade and used as received. Reactions were performed under a dry Ar atmosphere implementing standard Schlenk procedures unless otherwise noted. UV-Visible absorption spectra were recorded using a Cary-50 spectrophotometer. NMR spectra were obtained using a Varian 400-MR or an INOVA 500 spectrometer. Infrared spectra were measured on solid samples using a Perkin-Elmer Spectrum 100 series FT-IR spectrometer equipped with an ATR accessory. Cyclic voltammograms were recorded using a BASi Epsilon electrochemical workstation and a BASi cell stand. Elemental analyses were performed by Midwest Microlabs in Indianapolis, IN.

Experimental Procedures

$Cp^*_2Ti(C_2$2-py)$_2$. (**1**) To an oven-dried 100 mL two-neck round-bottom flask under a positive pressure of argon was added Et_2O (40 mL) and 2-ethynylpyridine (0.49 mL, 4.85 mmol). After the pale-yellow solution was cooled in a dry ice/acetone bath for 10 min, n-butyllithium (2.5 M, 1.94 mL, 4.85 mmol) was added. The solution was stirred in the bath for 10 min and then was removed for 10 min. $Cp^*_2TiCl_2$ (924 mg, 2.37 mmol) was added and the mixture was allowed to stir at room temperature in the absence of light for 4 h. The following workup was performed without the need of an inert atmosphere and with minimal light exposure to avoid degradation of **1**. The reaction mixture was concentrated and loaded onto a triethylamine treated silica gel column (2.5 x 12 cm) and eluted using a 5% solution of triethylamine in CH_2Cl_2. A dark-red band was collected and the solvent was then removed using rotary evaporation. The resulting solid was dissolved in minimal THF (approximately 5 mL), precipitated with hexanes (approximately 50 mL), collected using vacuum filtration, and dried under vacuum, yielding 812 mg (65.5%) of a purple powder. UV/Vis (THF), λ/nm (ϵ/dm^3 mol^{-1} cm^{-1}): 475 (2505), 363 (sh, 13,238). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.52 (ddd, *J* = 4.9, 1.8, 0.9, 2H), 7.51 (td, *J* = 7.7, 1.9 Hz, 2H), 7.25 (dt, *J* = 7.9, 1.1, 2H), 7.01 (ddd, *J* = 7.5, 4.9, 1.2, 2H), 2.09 (s, 30H); ^{13}C {^{1}H} NMR (400 MHz, $CDCl_3$) δ 161.4, 149.8, 146.2, 135.6, 126.1, 124.2, 122.3, 120.4, 13.3. Anal. Calcd (found) for $C_{34}H_{38}N_2Ti$: C, 77.89 (78.15); H, 7.15 (7.33); N, 5.27 (5.36). IR (neat) $\nu_{C\equiv C}$ = 2077 cm^{-1}.

$Cp^*_2Ti(C_2$2-py)$_2CuOH_2PF_6$. (**2**) To an oven-dried two-neck round-bottom flask under a positive pressure of argon was added CH_2Cl_2 (60 mL) and $Cp^*_2Ti(C_2$2-py)$_2$ (150 mg, 0.29 mmol). After the dark-red solution was stirred at room temperature for 5 min, $Cu(CH_3CN)_4PF_6$ (107 mg, 0.29 mmol) was added and the mixture was allowed to stir at room temperature in the absence of light for 1 h. After Cu(I) insertion, the following workup was performed under ambient lighting without the need of an inert atmosphere. The solvent was removed and the resulting solid was dried under vacuum

for 1 h. The product was dissolved in minimal CH_2Cl_2 (approximately 15 mL), precipitated with hexanes (approximately 70 mL), collected using vacuum filtration, and dried under vacuum, yielding 120 mg (57.8%) of an orange powder. UV/Vis (THF), λ/nm (ϵ/dm^3 mol^{-1} cm^{-1}): 465 (sh, 755), 335 (sh, 14,494). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 (d, *J* = 4.0 Hz, 2H), 7.85 (t, *J* = 7.6 Hz, 2H), 7.61 (d, *J* = 7.9 Hz, 2H), 7.35 (t, *J* = 6.1, 2H), 6.48 (bs, 2H), 1.97 (s, 30H); ^{13}C {^{1}H} NMR (400 MHz, $CDCl_3$) δ 151.7, 148.9, 143.8, 138.4, 128.1, 126.0, 123.7, 123.5, 13.0. Anal. Calcd (found) for $C_{34}H_{40}N_2OCuTiPF_6 \bullet H_2O$: C, 53.24 (53.40); H, 5.52 (5.30); N, 3.65 (3.64). IR (neat) $\nu_{C\equiv C}$ = 1958 cm^{-1}.

$Cp^*_2Ti(C_2$2-py)$_2PdCl_2$. (**3**) To an oven-dried two-neck round-bottom flask under a positive pressure of argon was added CH_2Cl_2 (3 mL) and $Cp^*_2Ti(C_2$2-py)$_2$ (143 mg, 0.27 mmol). After the dark-red solution was stirred at room temperature for 5 min, $Pd(CH_3CN)_2Cl_2$ (88 mg, 0.34 mmol) in CH_3CN (12 mL) was transferred by cannula and the mixture was allowed to stir at room temperature in the absence of light for 18 h. After Pd(II) insertion, the following workup was performed under ambient lighting without the need of an inert atmosphere. The solvent was removed by rotary evaporation. The resulting solid was sonicated in CH_3CN (5mL) and filtered using vacuum filtration. The solid was collected and loaded onto a triethylamine treated silica gel column (1 x 20 cm) and eluted using a 5% solution of triethylamine in CH_2Cl_2. The solvent was then removed using rotary evaporation. A light red band was collected and the solvent was removed using rotary evaporation. The resulting solid was dissolved in minimal THF (approximately 2 mL), precipitated with hexanes (approximately 50 mL), collected using vacuum filtration, and dried under vacuum, yielding 55.1 mg (28.8%) of a pink powder. UV/Vis (THF), λ/nm (ϵ/dm^3 mol^{-1} cm^{-1}): 475 (sh, 1948), 350 (sh, 16,765). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.64 (ddd, *J* = 5.8, 1.6, 0.7, 2H), 7.48 (td, *J* = 7.7, 1.6 Hz, 2H), 7.11 (ddd, *J* = 8.0, 1.5, 0.7, 2H), 7.00 (ddd, *J* = 7.4, 5.8, 1.5, 2H), 2.12 (s, 30H); ^{13}C {^{1}H} NMR (400 MHz, $CDCl_3$) δ 173.3, 152.2, 147.1, 137.1, 126.0, 124.9, 121.1, 116.8, 13.2. Anal. Calcd (found) for $C_{34}H_{38}N_2TiPdCl_2 \bullet H_2O$: C, 57.13 (56.89); H, 5.53 (5.62); N, 3.93 (3.90). IR (neat) $\nu_{C\equiv C}$ = 2079 cm^{-1}.

X-ray Crystallography. For **1** and **3**, crystals suitable for diffraction were grown from THF by slow evaporation. Crystals of **2** were grown by layering hexanes onto a solution of **2** in CH_2Cl_2. The crystal structures were determined by single crystal X-ray diffraction measured using a Bruker D8 Venture diffractometer. Crystals were mounted on a low-scatter loop using paratone, and immediately cooled to 100 ± 2 K in a cold nitrogen gas stream. Data were collected by phi and omega scans using Mo Kα (λ = 0.71073 Å) radiation from an Incoatec microfocus source, and a Photon 100 detector. Data were processed and scaled (multi-scan absorption correction) using the SAINT and SADABS routines in the Apex3 software suite.[1] The space groups were determined based on the systematic absences, and the structures were solved by intrinsic phasing (SHELXT) and subsequently refined by Fourier difference techniques using full-matrix-least-squares on F^2 (SHELXL) using the SHELXTL package.[2] All non-hydrogen atoms were refined anisortropically. Hydrogen atoms attached to carbon atoms were placed in

geometrically idealized positions and refined using appropriate riding models. In the case of the coordinated H_2O molecule in **2**, the hydrogen atoms were identified from the difference electron density map, and their positions freely refined using appropriate distance fixing restraints. Here, the hydrogen atoms of the water molecule and the nitrogen atoms of the pyradinyl groups were oriented in favorable positions for intramolecular hydrogen bonding, with D-H---A distances of 2.689(11)-2.790(2) Å.

Several instances of disorder were included in the models of **1**-**3**. In **1**, one of the Cp* groups attached to the Ti center was found to exhibit a rotational disorder. The two components were distinguished from the difference electron density map and their occupancies freely refined in approximately 62:38 ratio. The majority ratio was selected for the graphical renderings in the manuscript and SI. The fluorine atoms of the $[PF_6]^-$ counterion of **2** were also found to be disordered, and their occupancies freely refined. In the case of **3**, a disordered acetonitrile solvent molecule was found to cocrystallize with the target complex, and two partially-occupied arrangements were modeled in disorder about an inversion center. Details of the data collection and refinements are summarized in Table S1. In addition to the thermal ellipsoid plots in the manuscript, a comparison of the molecular geometries, as well as additional packing diagrams are included as Figures S1-S4 here in the Supporting Information.

Table S1: Crystallographic data for complexes **1**-**3**.

	1 $C_{34}H_{38}N_2Ti$	**2** $[C_{34}H_{40}CuN_2OTi][PF_6]$	**3** $C_{34}H_{38}Cl_2N_2PdTi \cdot 0.5(CH_3CN)$
CCDC reference no.	1571228	1571229	1571227
Formula weight (g/mol)	522.56	749.09	720.39
Temperature (K)	100(2) K	100(2)	100(2)
Wavelength (Å)	0.71073 Å	0.71073	0.71073
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/n$	Triclinic, P-1
a, Å	10.3807(12)	14.5015(7)	8.8432(3)
b, Å	16.385(2)	15.9769(8)	12.3352(5)
c, Å	16.9043(19)	15.0401(7)	16.4088(7)
α º	90	90	104.000(2)
β, º	101.544(4)	105.672(2)	93.8680(10)
γ, º	90	90	96.8550(10)
V, Å^3	2817.1(6)	3355.1(3)	1715.69(12)
Z, D_{cal} g/cm^3	4, 1.232	4, 1.483	2, 1.394
μ, mm^{-1}	0.329	0.983	0.939
F(000)	1112	1544	738
Crystal size, mm	0.191 × 0.204 × 0.208	0.131 × 0.142 × 0.541	0.031 × 0.031 × 0.322
Theta range for data collection	2.36 to 25.25	1.94 to 26.50°	2.33 to 26.07°
Index ranges	-12<=h<=12 -19<=k<=19 -20<=l<=20	-18<=h<=18 -20<=k<=20 -18<=l<=18	-10<=h<=10 -15<=k<=15 -20<=l<=20
Reflections collected	48697	102006	27680
Independent reflections	5104 [R(int) = 0.0750]	6942 [R(int) = 0.0421)	6778 [R(int) = 0.0441]
Max. and min. transmission	1.0000 and 0.9619	1.0000 and 0.8431	1.0000 and 0.9371
Data / restraints / parameters	5104 / 192 / 440	6942 / 95 / 495	6778 / 82 / 427
Goodness-of-fit on F^2	1.060	1.173	1.042
Final R indices [I>2 σ(I)]	R1 = 0.0684 wR2 = 0.1756	R1 = 0.0289 wR2 = 0.0802	R1 = 0.0376 wR2 = 0.1009
R indices (all data)	R1 = 0.0893 wR2 = 0.1922	R1 = 0.0353 wR2 = 0.0937	R1 = 0.0520 wR2 = 0.1100
Largest diff. peak and hole (e·Å^{-3})	1.050 and -0.394	0.657 and -0.846	0.993 and -0.881

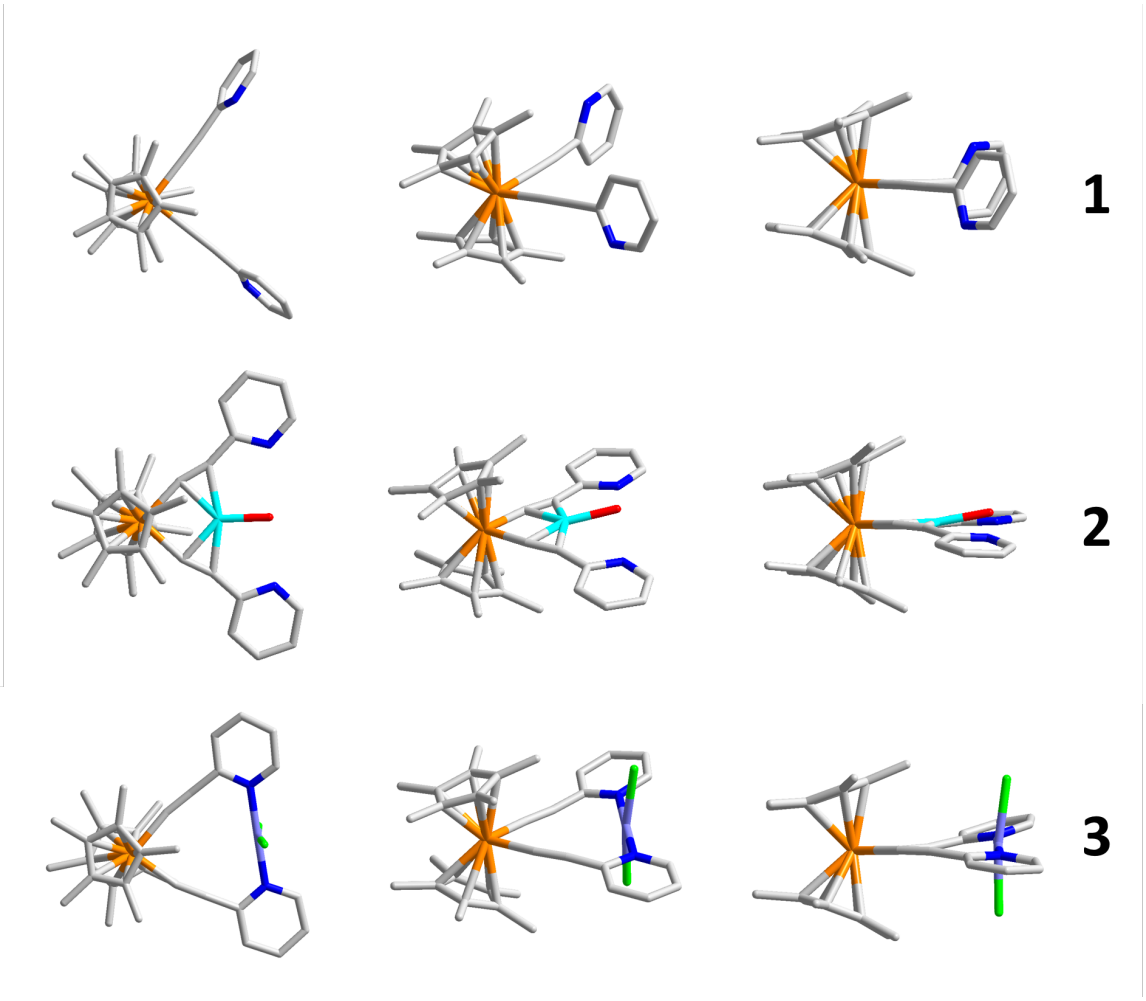

Figure S1: Comparison of three different orientations of the Ti-hinged *trans*-bidentate *bis*-pyridinyl ligand (**1**), the bimetallic Cu(I) complex (**2**), and the bimetallic Pd(II) complex (**3**) of the present study. Wireframe color scheme: Orange = Ti, cyan = Cu, purple = Pd, green = Cl, red = O, blue = N, silver = C; hydrogen atoms omitted for clarity.

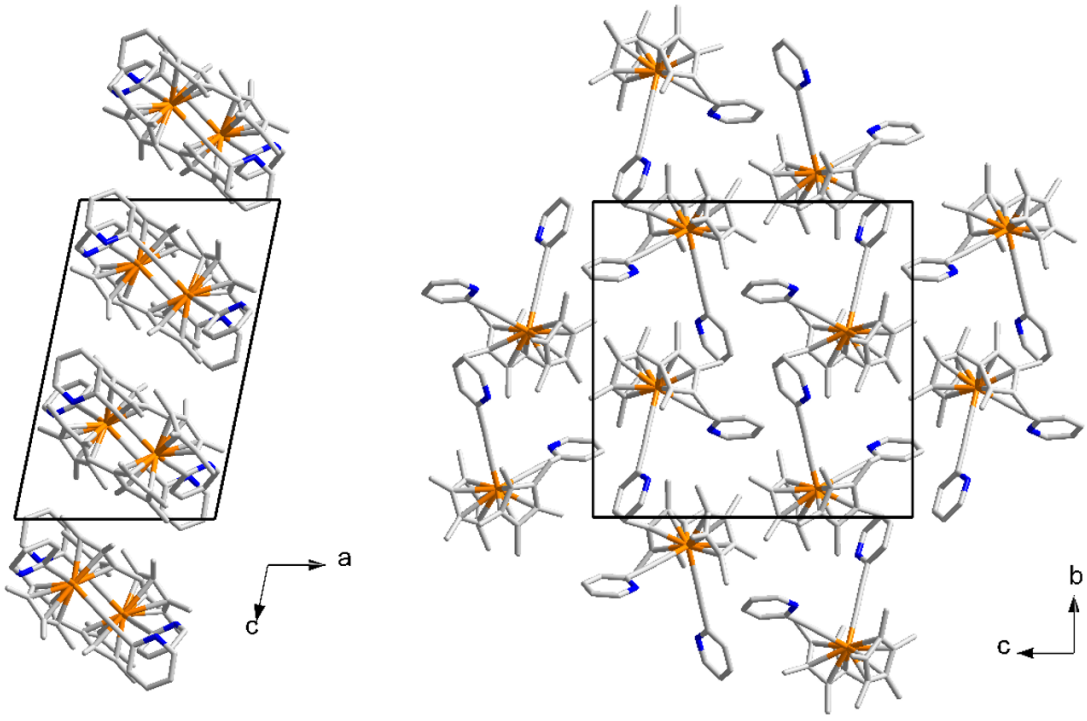

Figure S2: Packing arrangement in **1** along [010] (left) and [100] (right) projections. Wireframe color scheme: Orange = Ti, blue = N, silver = C; hydrogen atoms omitted for clarity.

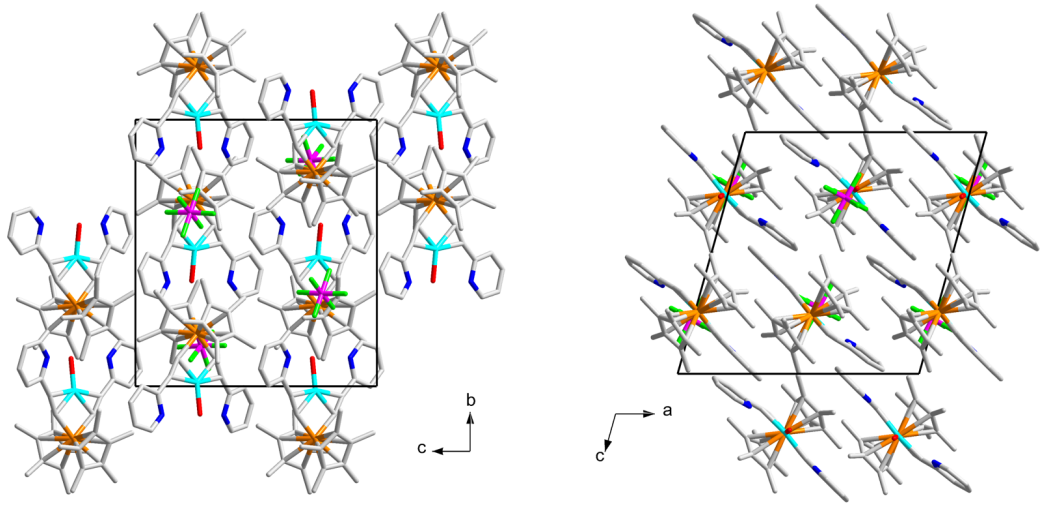

Figure S3: Packing arrangement in **2** along [100] (left) and [010] (right) projections. Wireframe color scheme: Orange = Ti, cyan = Cu, pink = P, green = F, red = O, blue = N, silver = C; hydrogen atoms omitted for clarity.

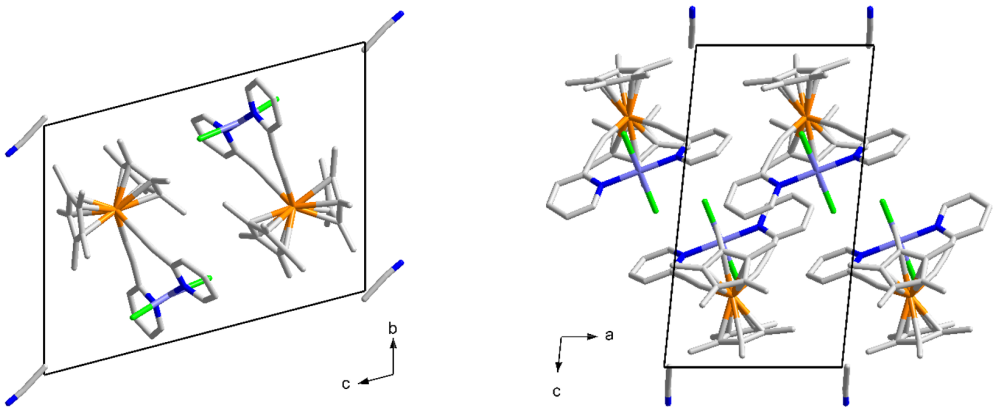

Figure S4: Packing arrangement in **3** along [100] (left) and [010] (right) projections. Wireframe color scheme: Orange = Ti, purple = Pd, green = Cl, blue = N, silver = C; hydrogen atoms omitted for clarity.

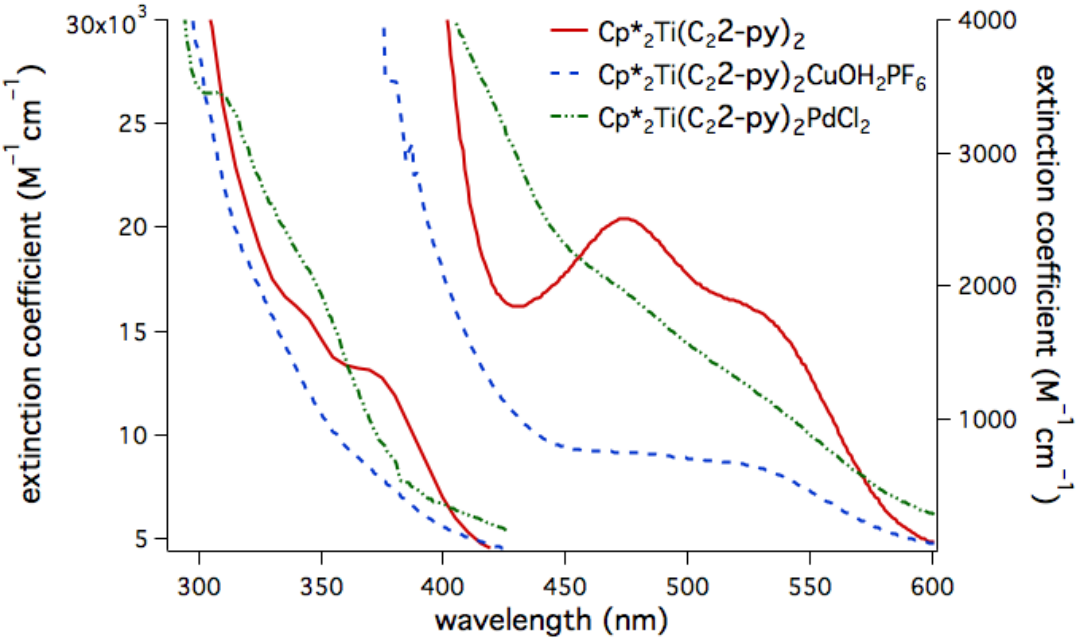

Figure S5: UV-Visible Spectra in CH_2Cl_2.

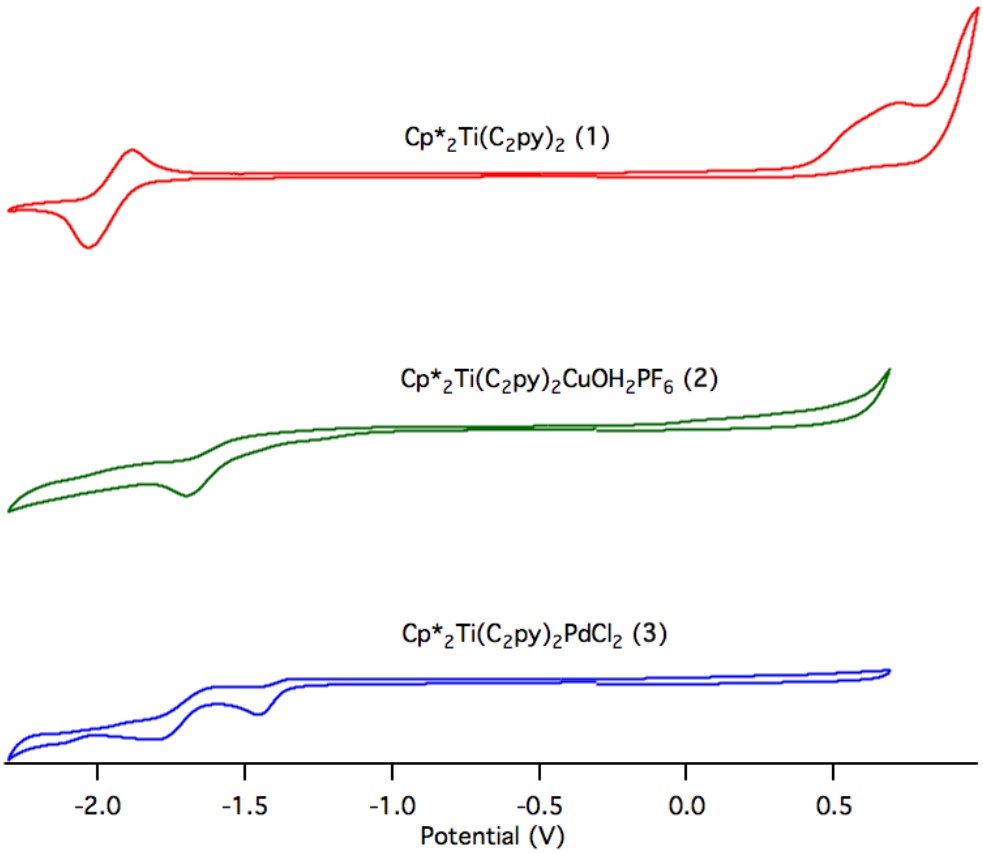

Figure S6: Cyclic voltammagram in CH_2Cl_2. Conditions: [Ti] ~1mM in CH_2Cl_2 (0.1 M TBAP), Pt working electrode, Ag/Ag^+ reference electrode. The x-axis reports voltages vs. $FcH^{+/0}$ as determined by running a voltammogram of FcH before and after data collection.

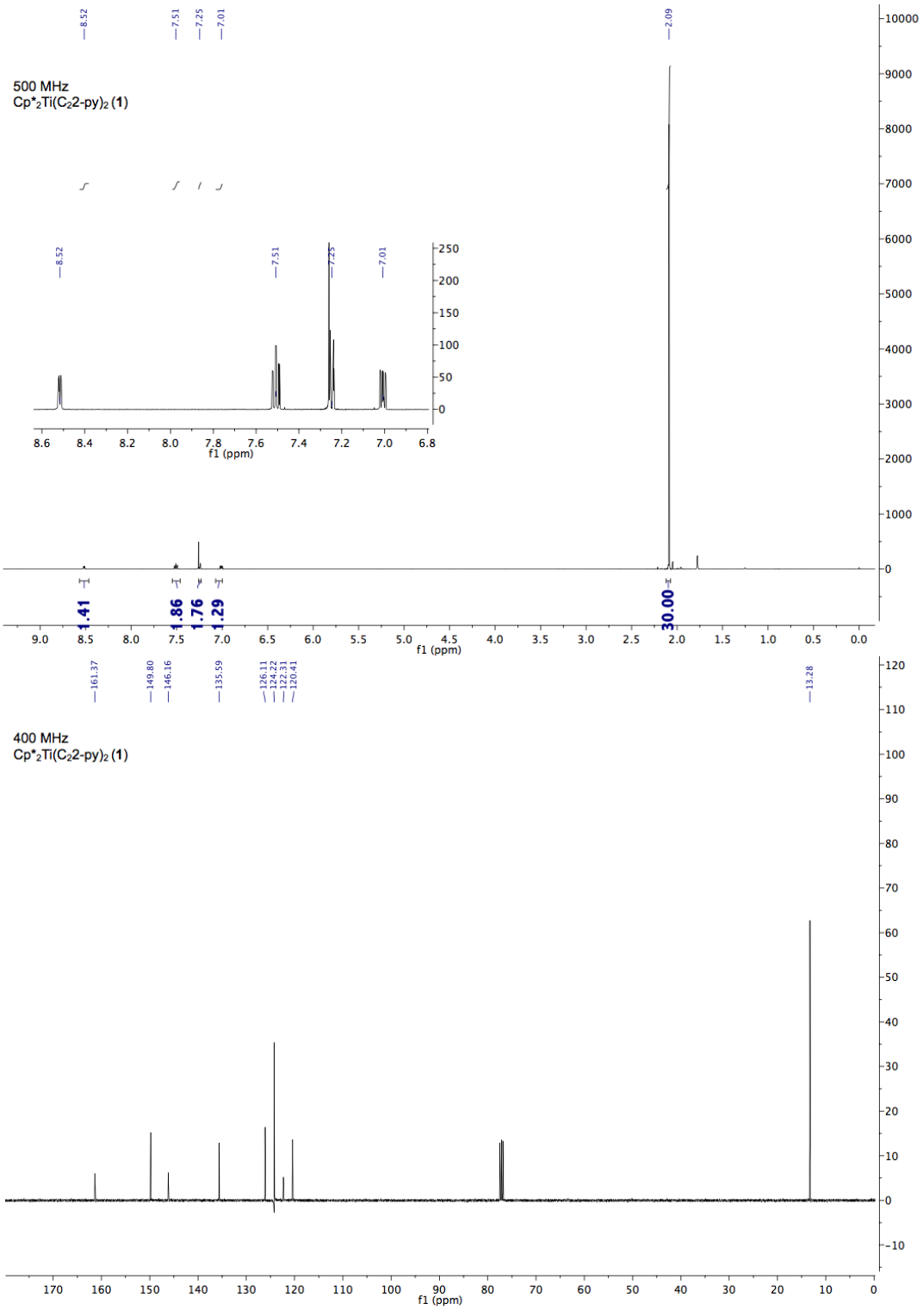

Figure S7: ^{1}H-NMR (500 MHz, top) and ^{13}C-NMR (400 MHz, bottom) of $Cp^*_2Ti(C_22\text{-}py)_2$ (**1**).

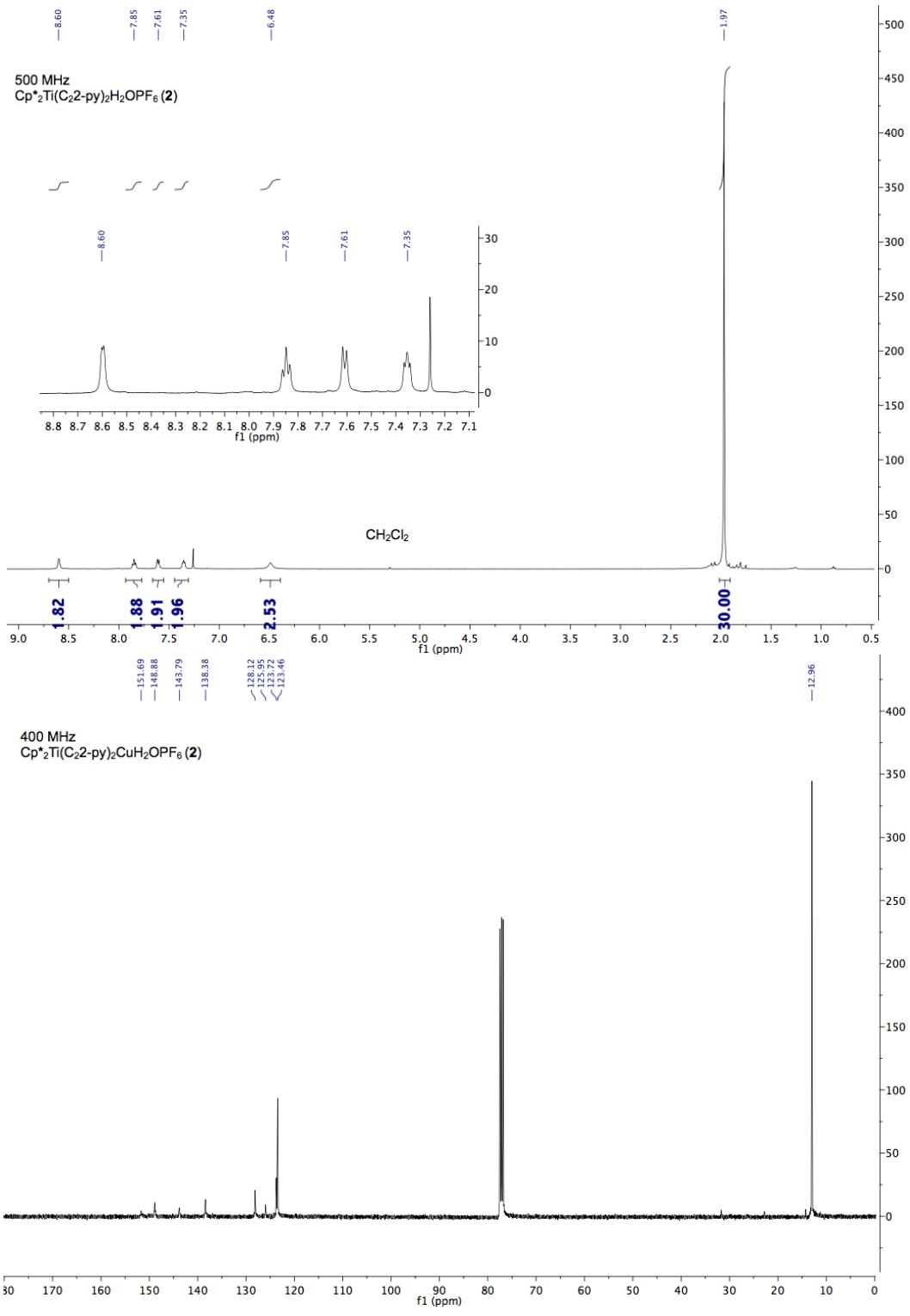

Figure S8: ^{1}H-NMR (500 MHz, top) and ^{13}C-NMR (400 MHz, bottom) of $Cp^*_2Ti(C_22\text{-}py)_2OH_2PF_6$ (**2**).

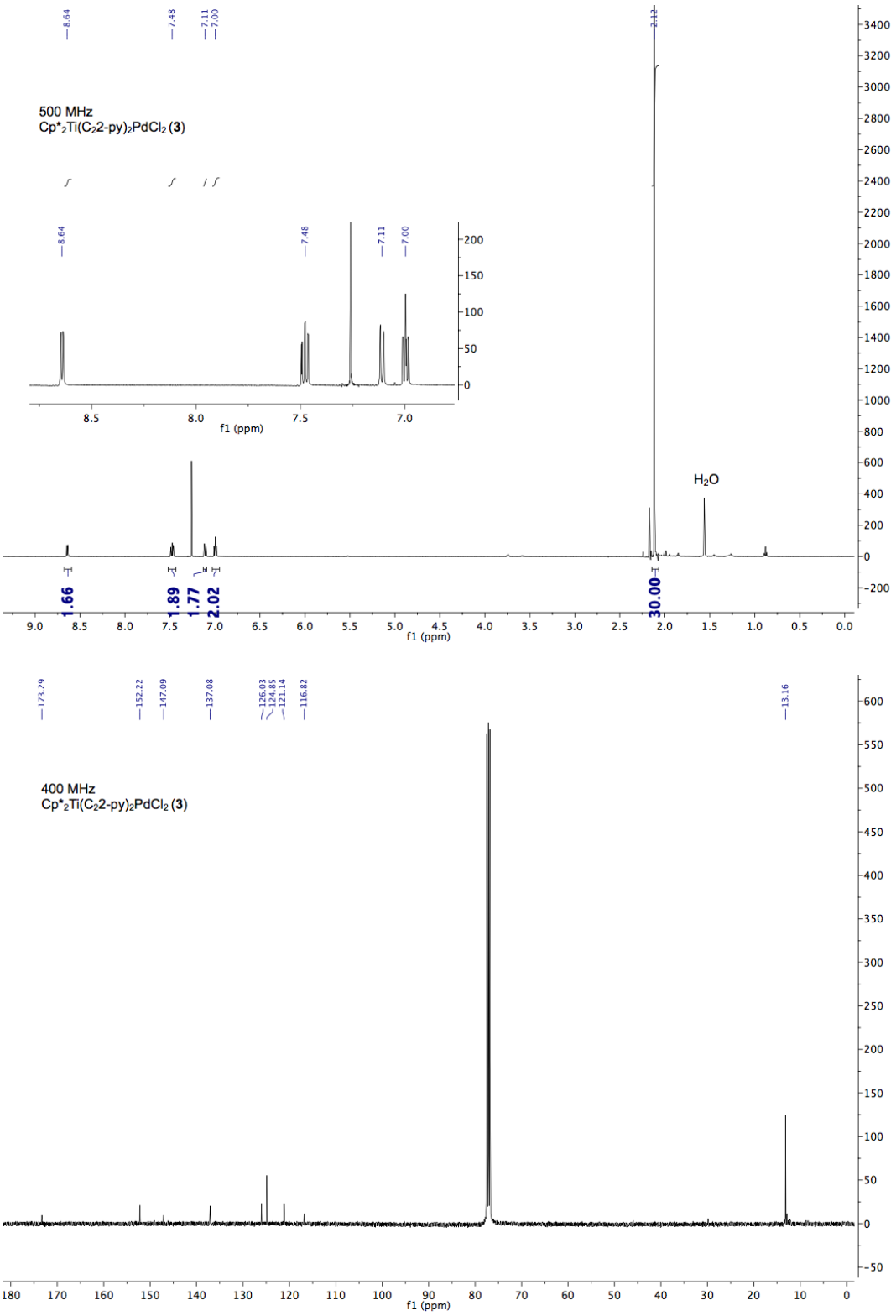

Figure S9: ^{1}H-NMR (500 MHz, top) and ^{13}C-NMR (400 MHz, bottom) of $Cp^*_2Ti(C_22\text{-}py)_2PdCl_2$ (**3**).

References:

1. Apex 3, **2015**, Bruker AXS, Inc.: Madison, WI.
2. G. Sheldrick, *Acta Crystallogr.,* 2008, **A64**, 112-122.