Supporting information for

(η^3-Allyl)Ni(II), Pd(II), and Pt(II) Complexes Bearing a Bidentate Titanium(IV) Phosphinoamide Ligand: a Ti ← M Dative Bond Enhances the Electrophilicity of the π-Allyl Moiety

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Contents

Experimental Procedure

General. Manipulation of air and moisture sensitive organometallic compounds was carried out under a dry argon atmosphere using standard Schlenk tube techniques associated with a high-vacuum line. All solvents were distilled over appropriate drying reagents prior to use (THF, hexane; Ph_2CO/Na, CH_2Cl_2; CaH_2, acetone; MS 4A). ^1H, ^{13}C, ^{19}F, ^{31}P NMR spectra was recorded on a JEOL Lambda 600 or a Lambda 400 spectrometer at ambient temperature unless otherwise noted. ^1H, ^{13}C, and ^{31}P NMR chemical shifts (δ values) were given in ppm relative to the solvent signal (^1H, ^{13}C) or standard resonances (^{19}F; external CF_3COOH, ^{31}P; external 85% H_3PO_4). ESI mass spectra were recorded on a JEOL JMS-T100CS apparatus. Melting points were measured on a Yanaco SMP3 micro melting point apparatus. Elemental analyses were performed by a Perkin Elmer 2400II/CHN analyzer. Starting materials, titanium phosphinoamide [1], $[(\eta^3\text{-methallyl})NiCl]_2$ [2], $[(\eta^3\text{-methallyl})PdCl]_2$ [3], $[(\eta^3\text{-methallyl})PtCl]_2$ [4] were synthesized by the method reported in the literature.

Preparation of $[(\eta^3\text{-methallyl})Ni(Ph_2PN^tBu)_2TiCl_2](OTf)$ (2a). In a glove box, $[(\eta^3\text{-methallyl})NiCl]_2$ (70.3 mg, 0.24 mmol) and acetone (350 μL, 4.8 mmol) was mixed in CH_2Cl_2 (5 mL), and AgOTf (122 mg, 0.48 mmol) was added to this solution. The mixture was stirred at room temperature for 10 min, then CH_2Cl_2 solution (5 mL) of titanium phosphinoamide $(Ph_2PN^tBu)_2TiCl_2$ (**1**) (300 mg, 0.48 mmol) was added dropwise to this solution. The resulting mixture was stirred at room temperature for 30 min during which time the color of the solution changed from orange to dark red. The solvent was evaporated and the residue extracted with CH_2Cl_2. The insoluble materials were filtered off through a pad of Celite, and the resulting filtrate was collected. Removal of volatiles followed by washing with hexane gave desired heterobimetallic complex (**2a**) as a red powder (242 mg, 57 %). Single crystals of **2a** were grown from CH_2Cl_2/pentane. M.p.: 112 °C. ^1H NMR (CD_2Cl_2, r.t.) δ 1.41 (s, 3H, $(CH_2)_2C(CH_3)$), 1.45 (s, 18H, ^{t}Bu), 3.66 (br s, 4H, $(CH_2)_2C(CH_3)$), 7.23 – 7.25 (m, 4H, Ph), 7.26 – 7.30 (m, 4H, Ph), 7.47 – 7.49 (m, 2H, Ph), 7.53 – 7.57 (m, 4H, Ph), 7.60 – 7.62 (m, 2H, Ph), 7.92 - 7.94 (m, 4H, Ph). ^1H NMR (CD_2Cl_2, -90 °C) δ 1.25 (s, 3H, $(CH_2)_2C(CH_3)$), 1.31 (s, 18H, ^{t}Bu), 3.74 (br s, 2H, $(CH_2)_2C(CH_3)$), 3.86 (br s, 2H, $(CH_2)_2C(CH_3)$), 7.12 – 7.14 (m, 4H, Ph), 7.19 – 7.23 (m, 4H, Ph), 7.38 –

7.41 (m, 2H, Ph), 7.55 – 7.59 (m, 4H, Ph), 7.60 – 7.62 (m, 2H, Ph), 8.31 – 8.37 (m, 4H, Ph). ^{13}C NMR (CD_2Cl_2) δ 27.9 (*C*H_3-methallyl), 32.3 (s, C*Me*$_3$), 71.5 (br s, *C*Me$_3$), 81.60 (br s, *C*H_2=C(Me)), 128.7, 129.9, 130.0, 132.4, 132.9, 133.0, 133.9, 134.5 (Ph), 139.2 (br s, *C*H_2=C(Me)). ^{19}F {^{1}H} NMR (CD_2Cl_2, r.t.) δ -82.0 (s). ^{31}P {^{1}H} NMR (CD_2Cl_2, r.t.) δ 14.1 (br s). ^{31}P {^{1}H} NMR (CD_2Cl_2, -90 ^{o}C) δ 13.2 (br s). Anal. Calcd. for $C_{37}H_{45}Cl_2N_2P_2O_3F_3STiNi$: C, 49.70; H, 5.07; N, 3.13. Found: C, 49.52; H, 4.87; N, 2.98 %. Exact mass (ESI-TOF): Calcd. for $^{12}C_{36}{}^1H_{45}{}^{14}N_2{}^{31}P_2{}^{35}Cl_2{}^{48}Ti_1{}^{58}Ni_1$: 743.12680. Found: 743.12751.

Preparation of [(η^3-methallyl)Pd(Ph$_2$PN^{t}Bu)$_2$TiCl$_2$](OTf) (2b). In a glove box, [(η^3-methallyl)PdCl]$_2$ (40.3 mg, 0.1 mmol) and acetone (151 μL, 2.0 mmol) was mixed in CH_2Cl_2 (5 mL), and AgOTf (52.7 mg, 0.2 mmol) was added to this solution. The mixture was stirred at room temperature for 10 min, then CH_2Cl_2 solution (5 mL) of titanium phosphinoamide ($Ph_2PN^tBu)_2TiCl_2$ (**1**) (130 mg, 0.2 mmol) was added dropwise to this solution. The resulting mixture was stirred at room temperature for 30 min during which time the color of the solution changed from orange to red. The solvent was evaporated and the residue extracted with CH_2Cl_2. The insoluble materials were filtered off through a pad of Celite, and the resulting filtrate was collected. Removal of volatiles followed by washing with hexane gave desired heterobimetallic complex (**2b**) as a red powder (140 mg, 73 %). Single crystals of **2b** were grown from CH_2Cl_2/pentane. M.p.: 131 ^{o}C. ^{1}H NMR (CD_2Cl_2, r.t.) δ 1.50 (s, 18H, ^{t}Bu), 1.52 (s, 3H, $(CH_2)_2C(CH_3)$), 3.76 (br s, 4H, $(CH_2)_2C(CH_3)$), 7.13 – 7.16 (m, 4H, Ph), 7.21 – 7.24 (m, 4H, Ph), 7.38 – 7.41 (m, 2H, Ph), 7.55 – 7.59 (m, 4H, Ph), 7.58 – 7.62 (m, 2H, Ph), 7.89 – 7.93 (m, 4H, Ph). ^{1}H NMR (CD_2Cl_2, -90 ^{o}C) δ 1.40 (s, 18H, ^{t}Bu), 1.42 (s, 3H, $(CH_2)_2C(CH_3)$), 3.70 (br s, 4H, $(CH_2)_2C(CH_3)$), 7.03 – 7.06 (m, 4H, Ph), 7.13 – 7.17 (m, 4H, Ph), 7.32 – 7.34 (m, 2H, Ph), 7.45 – 7.50 (m, 4H, Ph), 7.53 – 7.56 (m, 2H, Ph), 8.27 – 8.31 (m, 4H, Ph). ^{13}C NMR (CD_2Cl_2) δ 27.5 (*C*H_3-methallyl), 33.8 (s, C*Me*$_3$), 72.1 (t, *C*Me$_3$, $J_{C\text{-}P}$ = 5.8 Hz), 83.0 (t, *C*H_2=C(Me), $J_{C\text{-}P}$ = 11.6 Hz), 128.5, 129.3, 129.6, 129.7, 131.4, 132.0, 132.3, 132.8 (Ph), 141.1 (t, *C*H_2=C(Me), $J_{C\text{-}P}$ = 4.3 Hz). ^{19}F {^{1}H} NMR (CD_2Cl_2, r.t.) δ -82.1 (s). ^{31}P {^{1}H} NMR (CD_2Cl_2, r.t.) δ 9.75 (s). ^{31}P {^{1}H} NMR (CD_2Cl_2, -90 ^{o}C) δ 8.56 (s). Anal. Calcd. for

$C_{37}H_{45}Cl_2N_2P_2O_3F_3STiPd$: C, 47.18; H, 4.82; N, 2.97. Found: C, 46.82; H, 4.54; N, 2.68 %. Exact mass (ESI-TOF): Calcd. for $^{12}C_{36}{}^{1}H_{45}{}^{14}N_2{}^{31}P_2{}^{35}Cl_2{}^{48}Ti_1{}^{106}Pd_1$: 791.09493. Found: 791.09391.

Preparation of [(η^3-methallyl)Pt($Ph_2PN^tBu)_2TiCl_2$](OTf) (2c). In a glove box, [(η^3-methallyl)PtCl]$_2$ (45 mg, 0.08 mmol) and acetone (116 μL, 1.6 mmol) was mixed in CH_2Cl_2 (5 mL), and AgOTf (40.7 mg, 0.16 mmol) was added to this solution. The mixture was stirred at room temperature for 10 min, then CH_2Cl_2 solution (5 mL) of titanium phosphinoamide ($Ph_2PN^tBu)_2TiCl_2$ (**1**) (100 mg, 0.16 mmol) was added dropwise to this solution. The resulting mixture was stirred at room temperature for 30 min during which time the color of the solution changed from orange to dark red. The solvent was evaporated and the residue extracted with CH_2Cl_2. The insoluble materials were filtered off through a pad of Celite, and the resulting filtrate was collected. Removal of volatiles followed by washing with hexane gave desired heterobimetallic complex (**2c**) as a orange powder (128 mg, 81 %). Single crystals of **2c** were obtained by cooling the saturated toluene solution at - 35 ^oC. M.p.: 138 ^oC. ^1H NMR (CD_2Cl_2, r.t.) δ 1.51 (s, 18H, ^tBu), 1.76 (s, 3H, $(CH_2)_2C(CH_3)$), 3.46 (br s, 2H, $(CH_2)_2C(CH_3)$), 3.55 (br s, 2H, $(CH_2)_2C(CH_3)$), 7.12 – 7.15 (m, 4H, Ph), 7.18 – 7.22 (m, 4H, Ph), 7.34 – 7.37 (m, 2H, Ph), 7.44 – 7.46 (m, 4H, Ph), 7.53 – 7.57 (m, 2H, Ph), 7.80 – 7.84 (m, 4H, Ph). ^1H NMR (CD_2Cl_2, -90 ^oC) δ 1.40 (s, 18H, ^tBu), 1.68 (s, 3H, $(CH_2)_2C(CH_3)$), 3.70 (br s, 4H, $(CH_2)_2C(CH_3)$), 7.15 – 7.19 (m, 4H, Ph), 7.26 – 7.30 (m, 4H, Ph), 7.33 – 7.38 (m, 2H, Ph), 7.49 – 7.54 (m, 4H, Ph), 7.60 – 7.62 (m, 2H, Ph), 8.16 – 8.20 (m, 4H, Ph). The measurement of satisfactory ^{13}C NMR spectrum was unsuccessful due to its poor solubility. ^{31}P $\{^1H\}$ NMR (CD_2Cl_2, r.t.) δ 0.60 (s with a satellite signal due to the coupling with ^{195}Pt, $J_{Pt\text{-}P}$ = 3262 Hz). ^{31}P $\{^1H\}$ NMR (CD_2Cl_2, -90 ^oC) δ -0.16 (s with a satellite signal due to the coupling with ^{195}Pt, $J_{Pt\text{-}P}$ = 3216 Hz). Anal. Calcd. for $C_{37}H_{45}Cl_2N_2P_2O_3F_3STiPt$: C, 43.12; H, 4.40; N, 2.72. Found: C, 43.48; H, 4.68; N, 3.01 %. Exact mass (ESI-TOF): Calcd. for $^{12}C_{36}{}^{1}H_{45}{}^{14}N_2{}^{31}P_2{}^{35}Cl_2{}^{48}Ti_1{}^{195}Pt_1$: 880.15622. Found: 880.15738.

Preparation of [(dppp)M_2(η^3-methallyl)](OTf) (M = Ni (3a), Pd (3b), Pt (3c)).

The complexes **3a** – **3c** were prepared according to the method reported in the literature [5] with slight modification. In a typical example, $[(\eta^3\text{-methallyl})NiCl]_2$ (29 mg, 0.10 mmol) and acetone (140 μL, 2.0 mmol) was mixed in CH_2Cl_2 (5 mL), and AgOTf (50 mg, 0.20 mmol) was added to this solution. The mixture was stirred at room temperature for 10 min, and then dppp (80 mg, 0.20 mmol) was added to this solution. The resulting mixture was stirred at room temperature for 30 min, then the solvent was evaporated, and the residue extracted with CH_2Cl_2. The insoluble materials were filtered off through a pad of Celite, and the resulting filtrate was collected. Removal of volatiles followed by washing with hexane gave desired complex (**3a**) as white powder (102 mg, 74 %). ^{1}H NMR (CD_2Cl_2, r.t.) δ 1.89 (s, 3H, CH_3), 2.50 – 2.91 (m, 6H, CH_2), 2.72 (br s, 2H, C*H*$_2$=C(CH_3)), 3.43 (br s, 2H, C*H*$_2$=C(CH_3)) 7.17 – 7.69 (m, 20H, Ph). ^{31}P {^{1}H} NMR (CD_2Cl_2, r.t.) δ -6.1 (s).

Using similar procedures, **3b** and **3c** were synthesized. **3b:** ^{1}H NMR (CD_2Cl_2, r.t.) δ 1.88 (s, 3H, CH_3), 1.91 – 2.18 (m, 2H, CH_2), 2.62 – 2.81 (m, 4H, CH_2), 3.12 (t, $J_{P\text{-}H}$ = 6.9 Hz, 2H, C*H*$_2$=C(CH_3)), 3.82 (br s, 2H, C*H*$_2$=C(CH_3)) 7.26 – 7.55 (m, 20H, Ph). ^{13}C NMR (CD_2Cl_2, r.t.) δ 19.2 (s, CH_3), 24.1 (s, -CH_2-), 24.3 (t, $J_{P\text{-}C}$ = 15.9 Hz, P-CH_2), 73.4 (t, $J_{P\text{-}C}$ = 15.9 Hz, *C*H$_2$=C(CH_3)), 129.5 (t, $J_{P\text{-}C}$ = 5.8 Hz, *meta*-Ph), 131.6 (d, $J_{P\text{-}C}$ = 24.5 Hz, *para*-Ph), 132.0 (t, $J_{P\text{-}C}$ = 21.7 Hz, *ipso*-Ph), 132.7 (dt, $J_{P\text{-}C}$ = 5.8, 44.8 Hz, *ortho*-Ph), 138.2 (t, $J_{P\text{-}C}$ = 5.8 Hz, CH_2=*C*(CH_3)). ^{31}P {^{1}H} NMR (CD_2Cl_2, r.t.) δ 8.70 (s). **3c:** ^{1}H NMR (CD_2Cl_2, r.t.) δ 1.92 (s with a satellite signal due to the coupling with ^{195}Pt, $J_{Pt\text{-}H}$ = 59.8 Hz, 3H, CH_3), 1.98 – 2.27 (m, 2H, CH_2), 2.58 – 2.95 (m, 4H, CH_2, and 2H, C*H*$_2$=C(CH_3)), 3.55 (br s, 2H, C*H*$_2$=C(CH_3)) 7.24 – 7.58 (m, 20H, Ph). ^{31}P {^{1}H} NMR (CD_2Cl_2, r.t.) δ 0.25 (s with a satellite signal due to the coupling with ^{195}Pt, $J_{Pt\text{-}P}$ = 3512 Hz).

Reaction of Ti-M_2 dinuclear complexes with amines. A mixture of the Ti-M_2 dinuclear complex [for **2a** (9 mg, 0.01 mmol), for **2b** (9 mg, 0.01 mmol), for **2c** (10 mg, 0.01 mmol)] and CD_2Cl_2 (0.3 mL) was transferred into a flame dried NMR tube in a glove box. A solution of amine [for $HNEt_2$ (10 μl, 0.1 mmol), for aniline (9.2 μl, 0.1 mmol)] in CD_2Cl_2 (0.2 mL) was added to this solution, and the solution

was quickly frozen, and connected to a vacuum line. The tube was evacuated at -78 ^{o}C, sealed by flame, quickly warmed, and shaken several times. The NMR measurement was carried out periodically at 25 ^{o}C in CD_2Cl_2.

The reaction of dppp complexes (**3a**, **3b**, **3c**) with $HNEt_2$ or aniline were performed using similar method.

Catalytic allylation of diethylamine catalyzed by 2b. Methallyl chloride (9.4 μl, 0.1 mmol) and diethylamine (20 μl, 0.2 mmol) was dissolved in CD_2Cl_2, and 10 mol % of **2b** (9 mg, 0.01 mmol) was added to this solution. This reaction mixture was quickly transferred into a flame dried NMR tube in a glove box, and the mixture was quickly frozen. The tube was evacuated at lower temperature, sealed by flame, quickly warmed, and shaken for 5 min. Complete conversion of methallyl chloride was confirmed by the NMR measurement at 25 ^{o}C.

The reaction of dppp complexes (**3a**, **3b**, **3c**) with $HNEt_2$ or aniline were performed using similar method.

X-ray data collection and reduction. X-ray crystallography was performed on a Rigaku Saturn CCD area detector with graphite monochromated Mo-Kα radiation (λ = 0.71070A). The data were collected at 123(2) K using ω scan in the θ range of $3.0 \leq \theta \leq 27.5$ deg (**2a**), $3.1 \leq \theta \leq 27.5$ deg (**2b**), $3.0 \leq \theta \leq 27.5$ deg (**2c**). The data obtained were processed using Crystal-Clear (Rigaku) on a Pentium computer, and were corrected for Lorentz and polarization effects. The structure was solved by direct methods[6] for **2a**, **2b**, and **2c**, and expanded using Fourier techniques.[7] The non-hydrogen atoms were refined anisotropically except for the solvent atoms (toluene for **2a** and **2c**, and CH_2Cl_2 for **2b**). Hydrogen atoms were refined using the riding model. In complex **2c**, there is a large void in the unit cell, however, it was difficult to find the solvated molecule inside the void due to the low quality of the crystal. The final cycle of full-matrix least-squares refinement on F^2 was based on 8,528 observed reflections and 601 variable parameters for **2a**, 9,835 observed reflections and 530 variable parameters for **2b**, 10,987

observed reflections and 521 variable parameters for **2c**. Neutral atom scattering factors were taken from Cromer and Waber.[8] All calculations were performed using the CrystalStructure[9,10] crystallographic software package. Details of final refinement as well as the bond distances and angles are summarized in the supporting information, and the numbering scheme employed is also shown in the supporting information, which were drawn with ORTEP at 50% probability ellipsoid.

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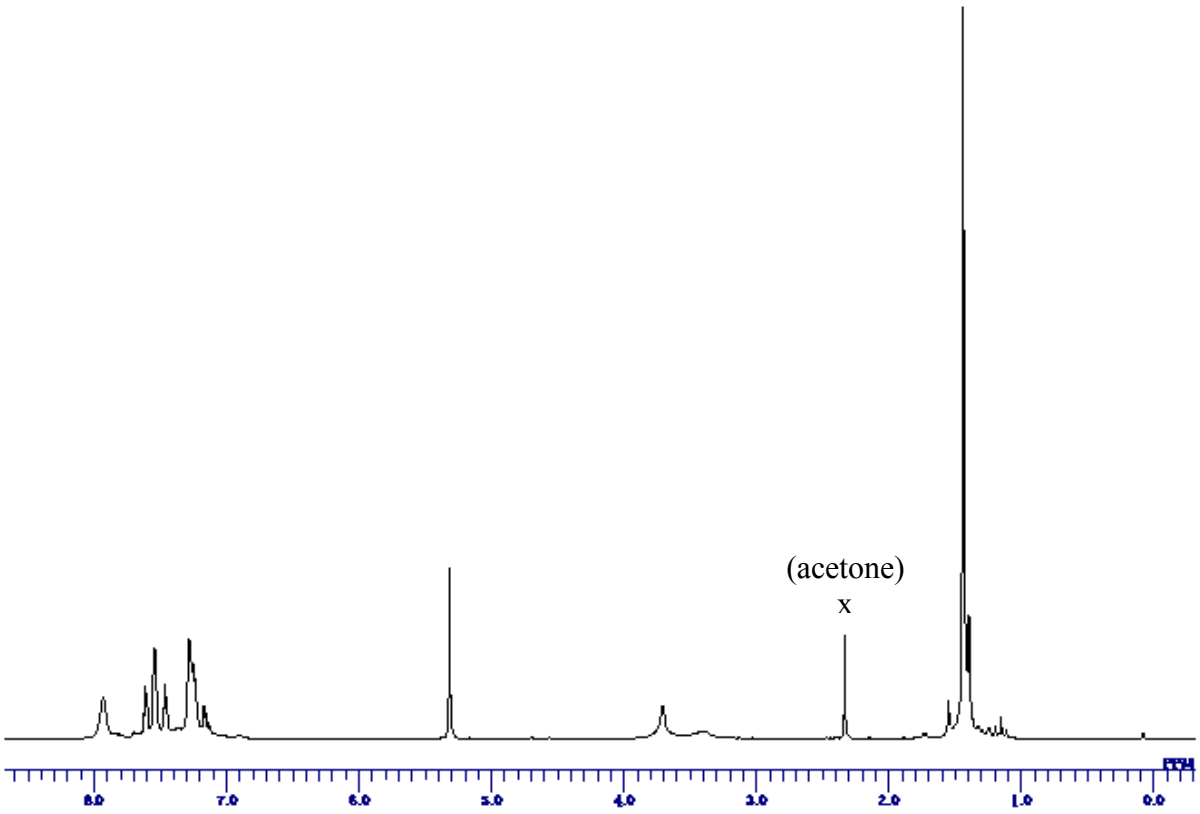
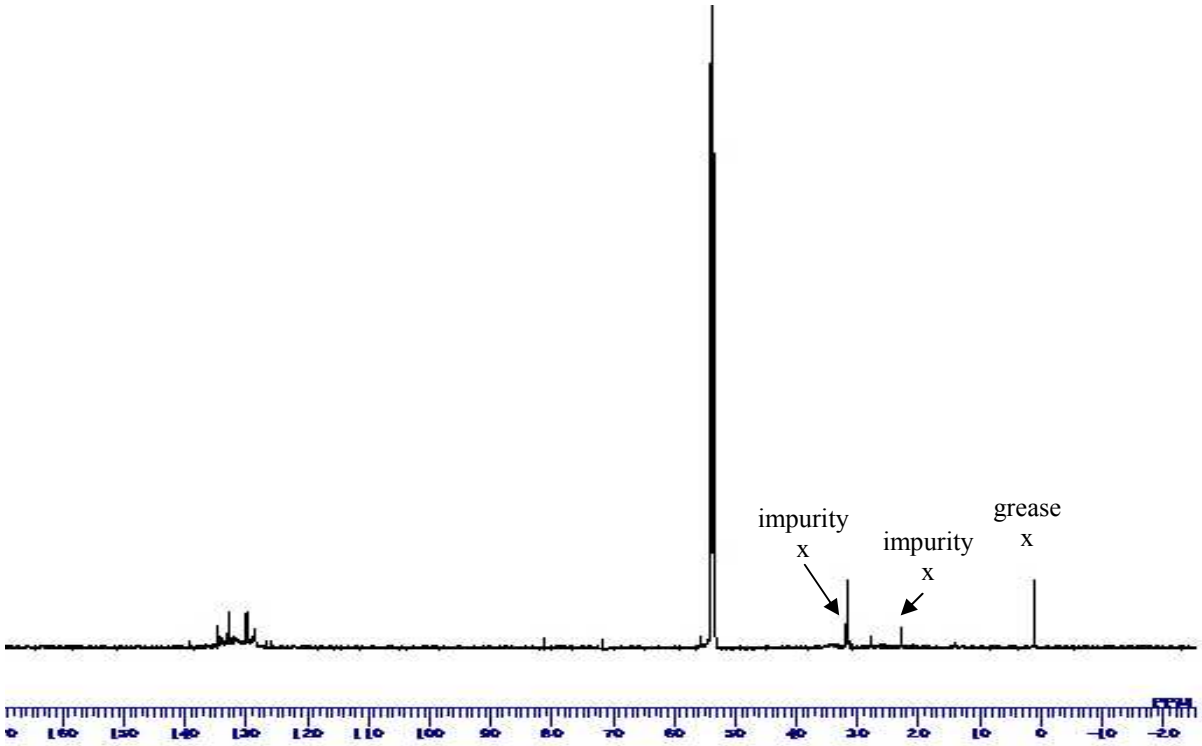
Figure S1. ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR spectra of [(η^3-methallyl)Ni($Ph_2PN^tBu)_2TiCl_2$](OTf) (**2a**)

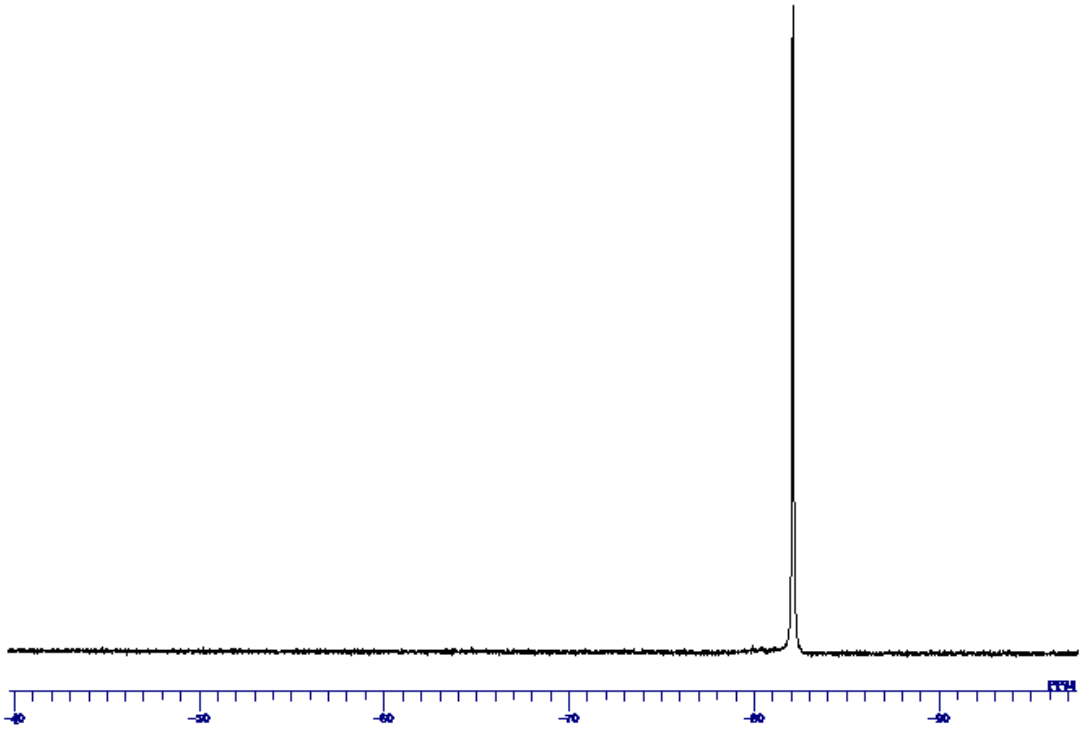


^{1}H NMR (600 MHz, in CD_2Cl_2)

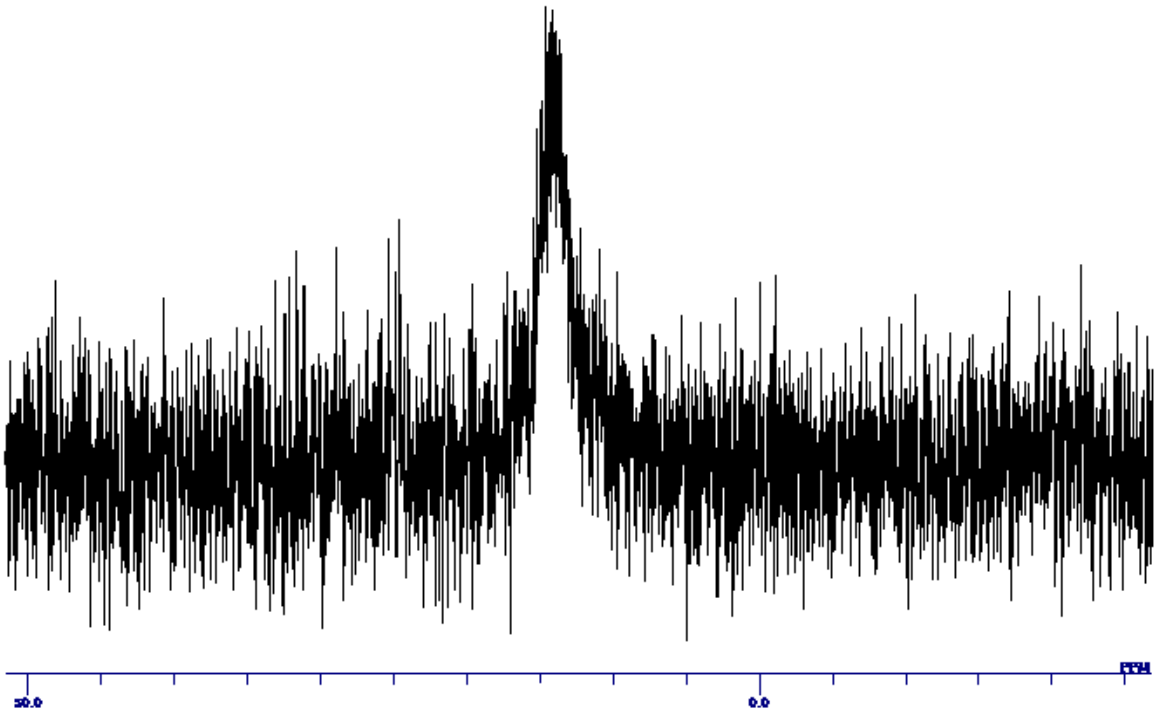


^{13}C NMR (150 MHz, in CD_2Cl_2)

Figure S1. ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR spectra of [(η^3-methallyl)Ni($Ph_2PN^tBu)_2TiCl_2$](OTf) (**2a**) (continued)

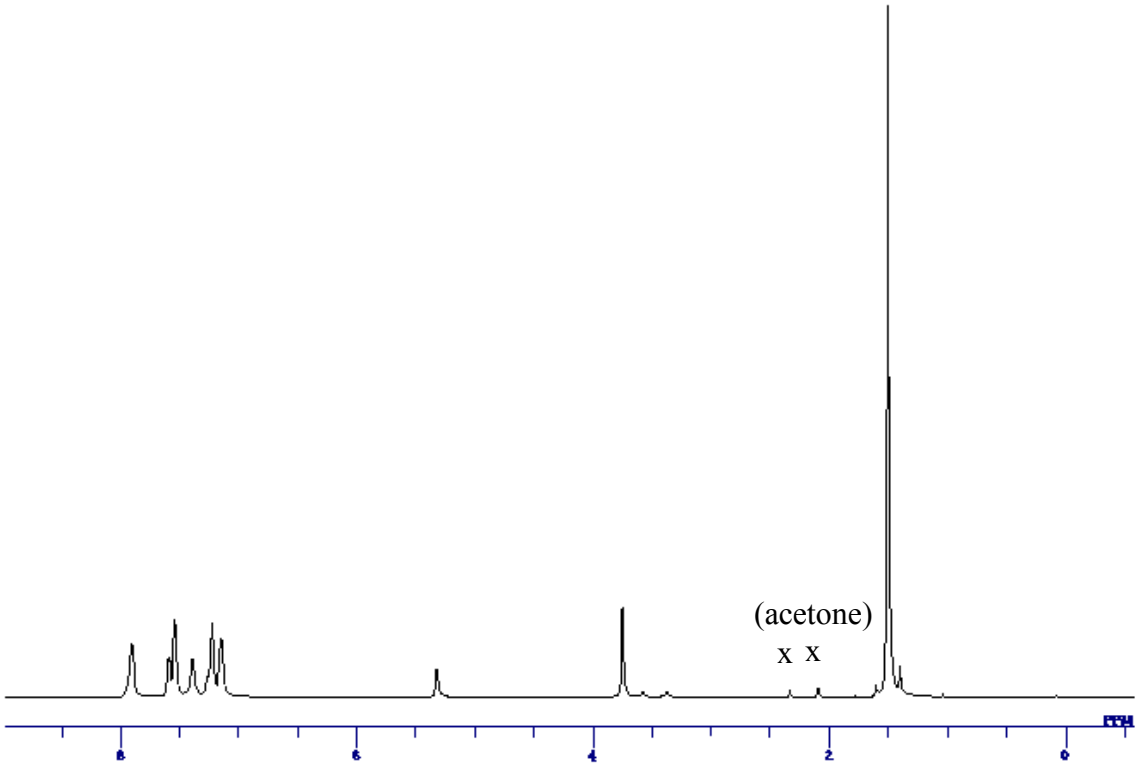


^{19}F NMR (565 MHz, in CD_2Cl_2)

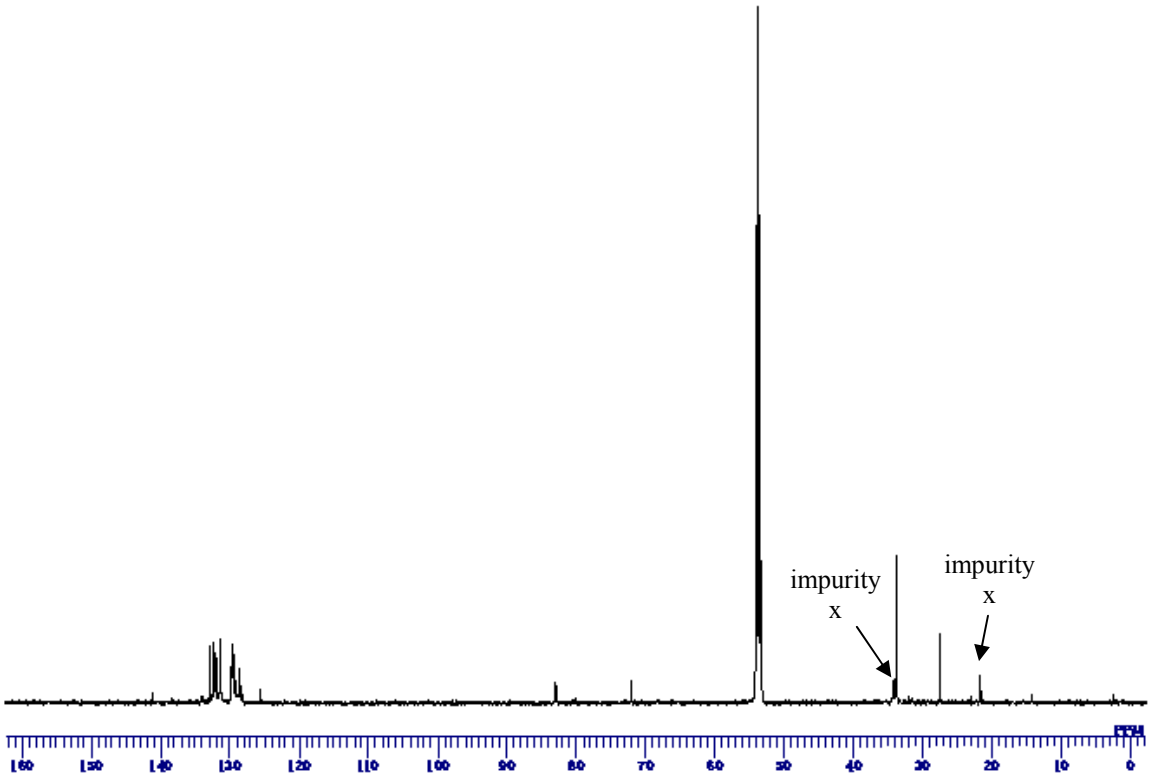


^{31}P NMR (243 MHz, in CD_2Cl_2)

Figure S2. ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR spectra of [(η^3-methallyl)Pd($Ph_2PN^tBu)_2TiCl_2$](OTf) (**2b**)

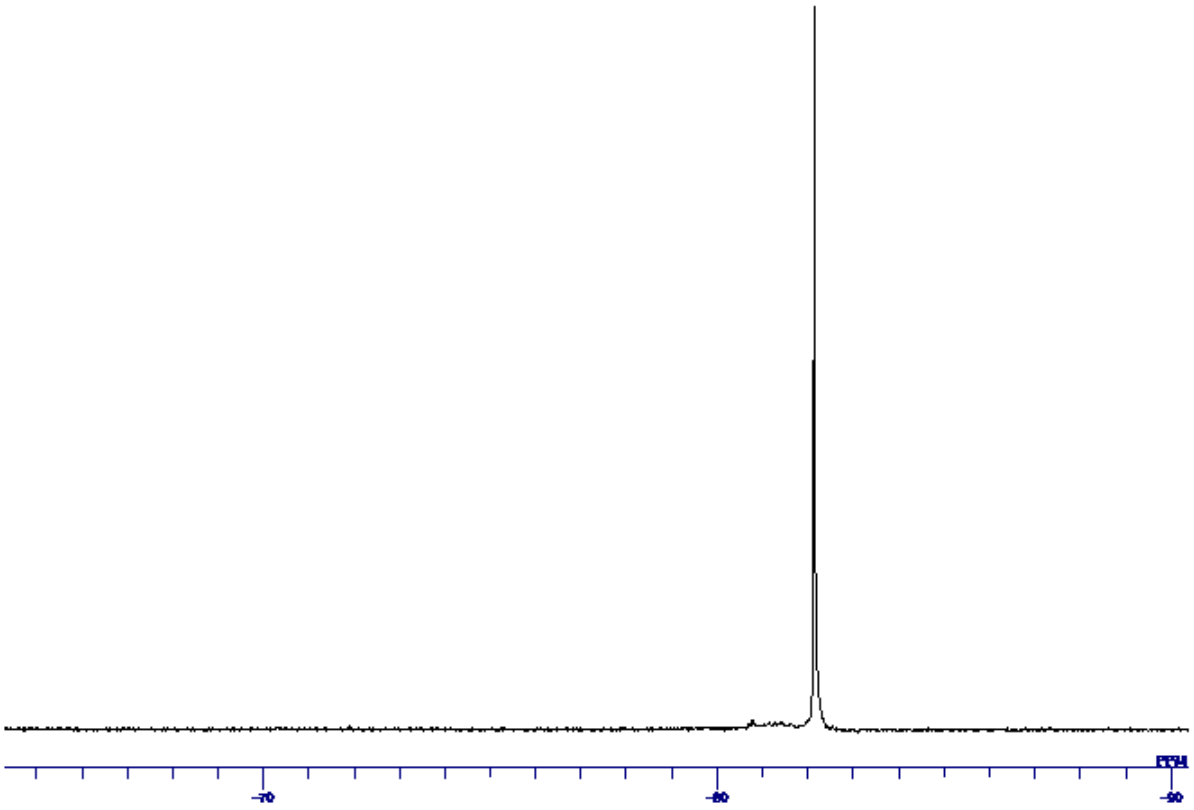


^{1}H NMR (600 MHz, in CD_2Cl_2)

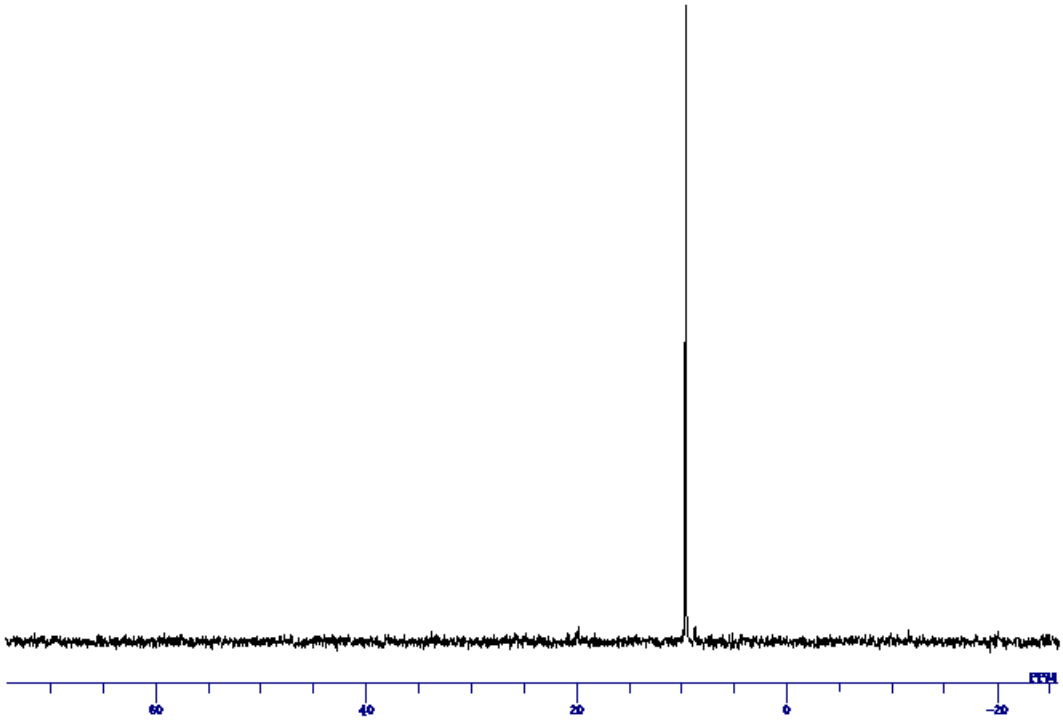


^{13}C NMR (150 MHz, in CD_2Cl_2)

Figure S2. ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR spectra of [(η^3-methallyl)Pd($Ph_2PN^tBu)_2TiCl_2$](OTf) (**2b**) (continued)

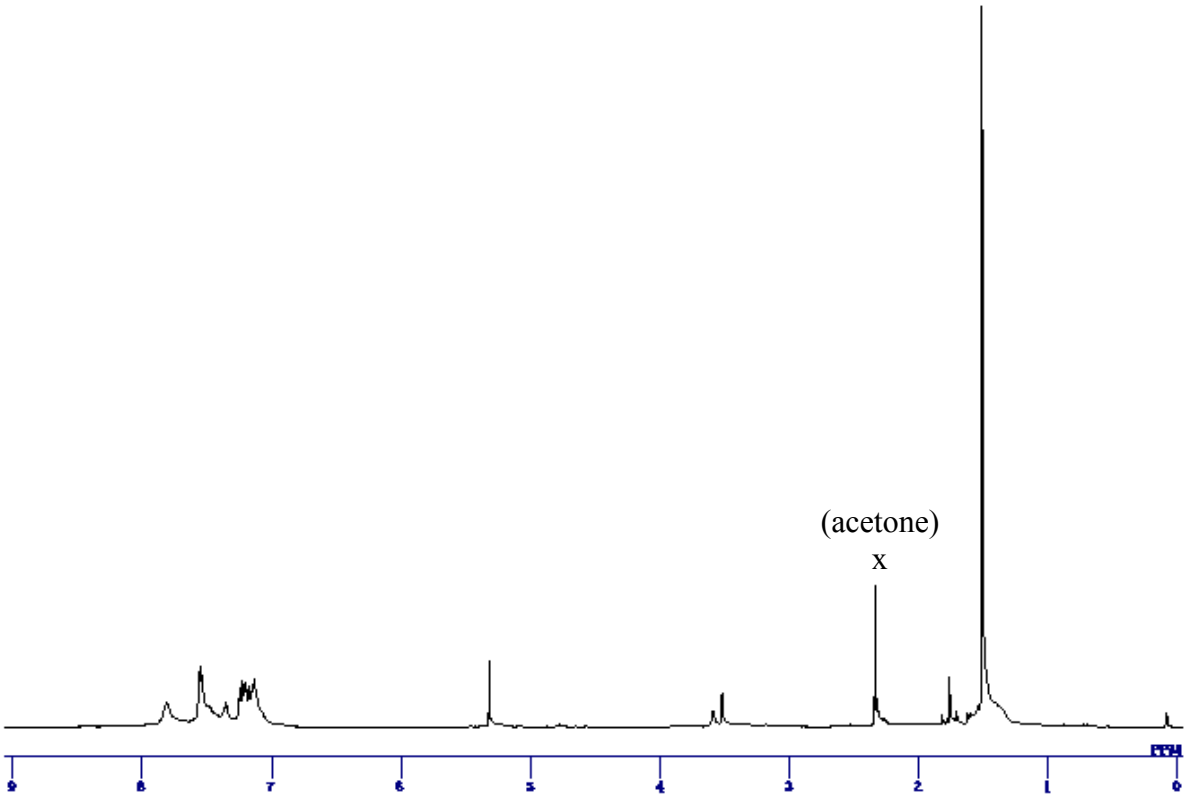


^{19}F NMR (565 MHz, in CD_2Cl_2)

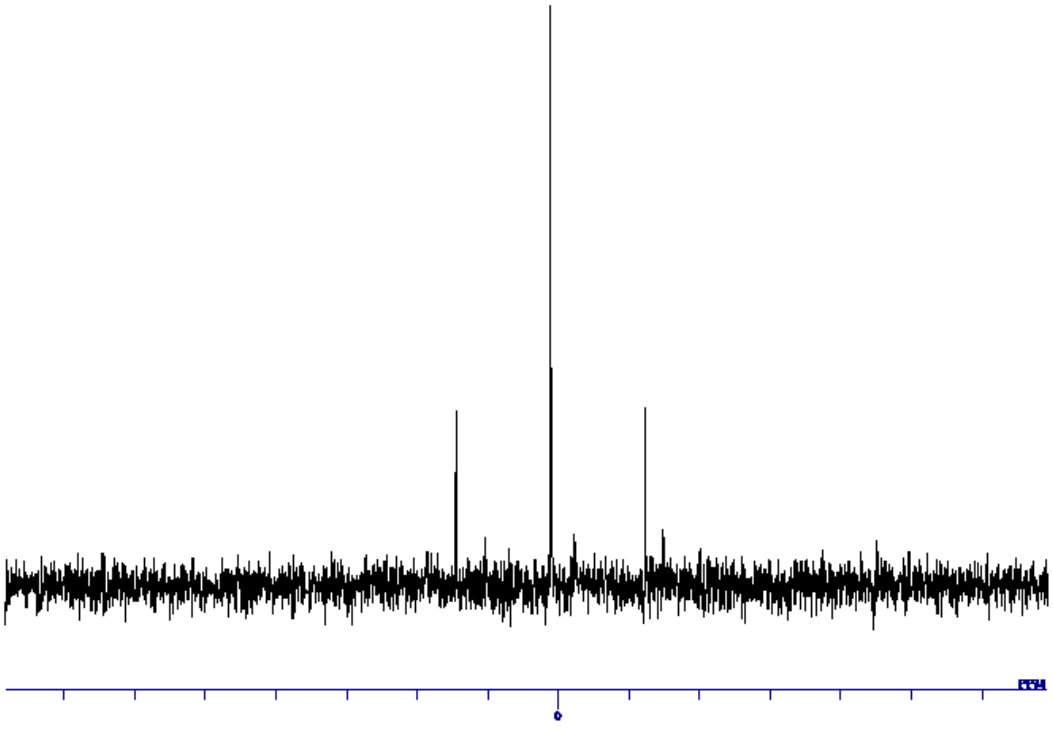


^{31}P NMR (243 MHz, in CD_2Cl_2)

Figure S3. ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR spectra of [(η^3-methallyl)Pt($Ph_2PN^tBu)_2TiCl_2$](OTf) (**2c**)

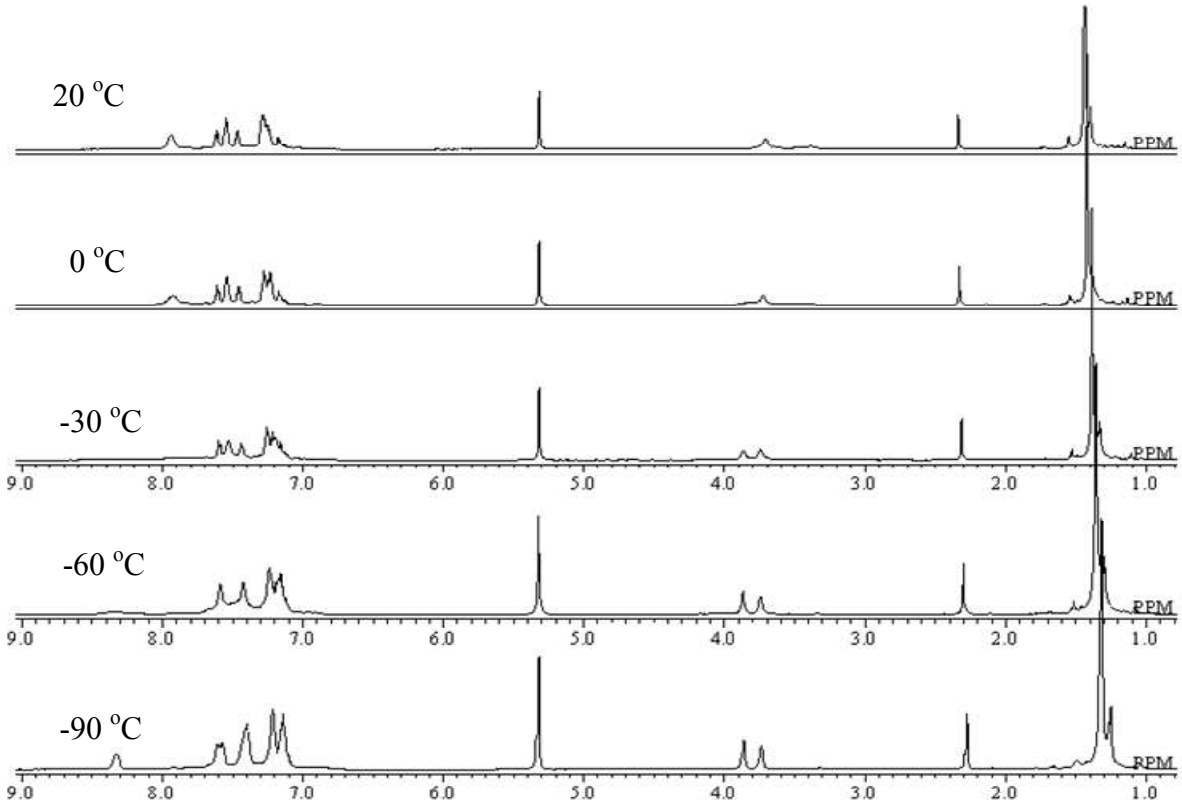


^{1}H NMR (600 MHz, in CD_2Cl_2)

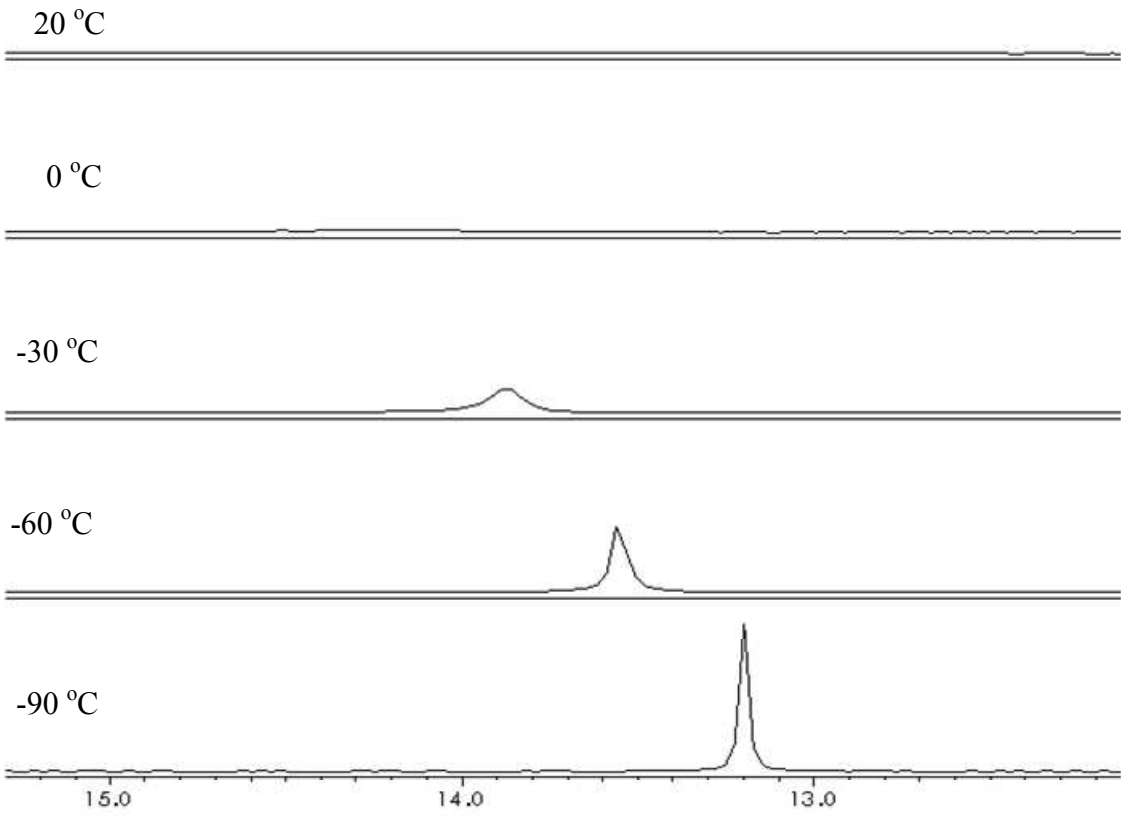


^{31}P NMR (243 MHz, in CD_2Cl_2)

Figure S4. VT- ^{1}H and ^{31}P NMR spectra of [(η^3-methallyl)Ni($Ph_2PN^tBu)_2TiCl_2$](OTf) (**2a**)

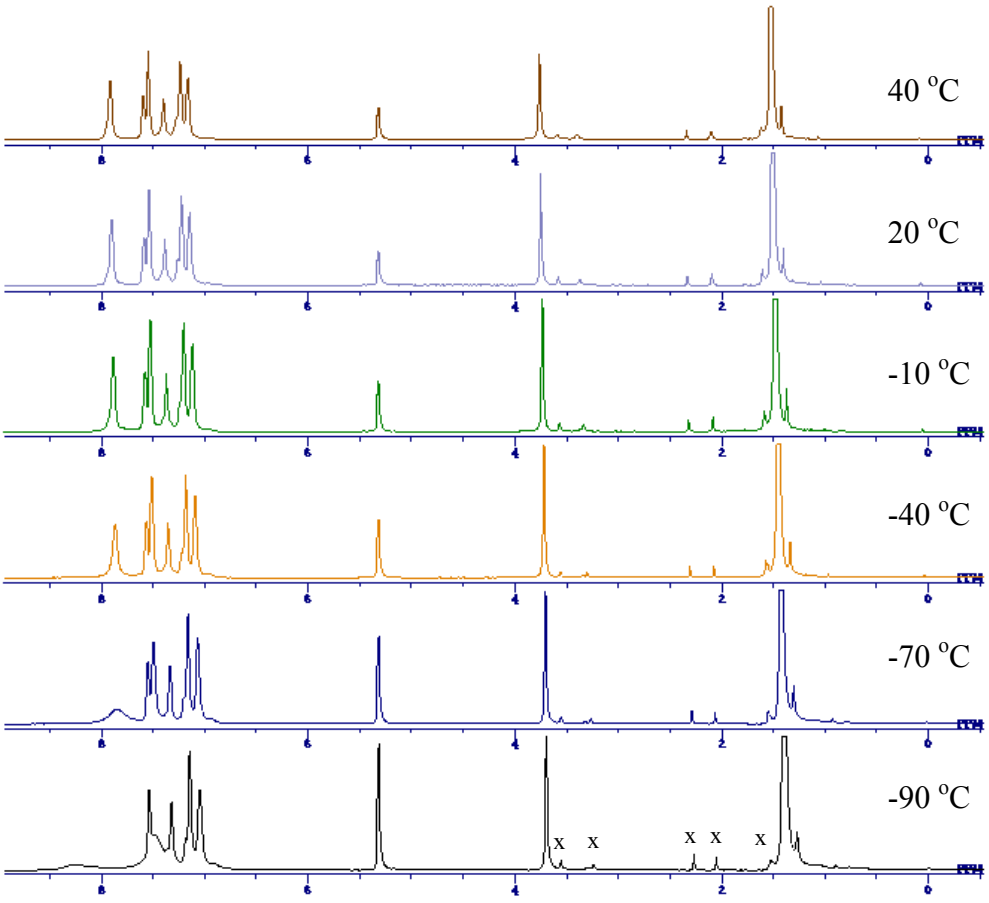


^{1}H NMR (600 MHz, in CD_2Cl_2)

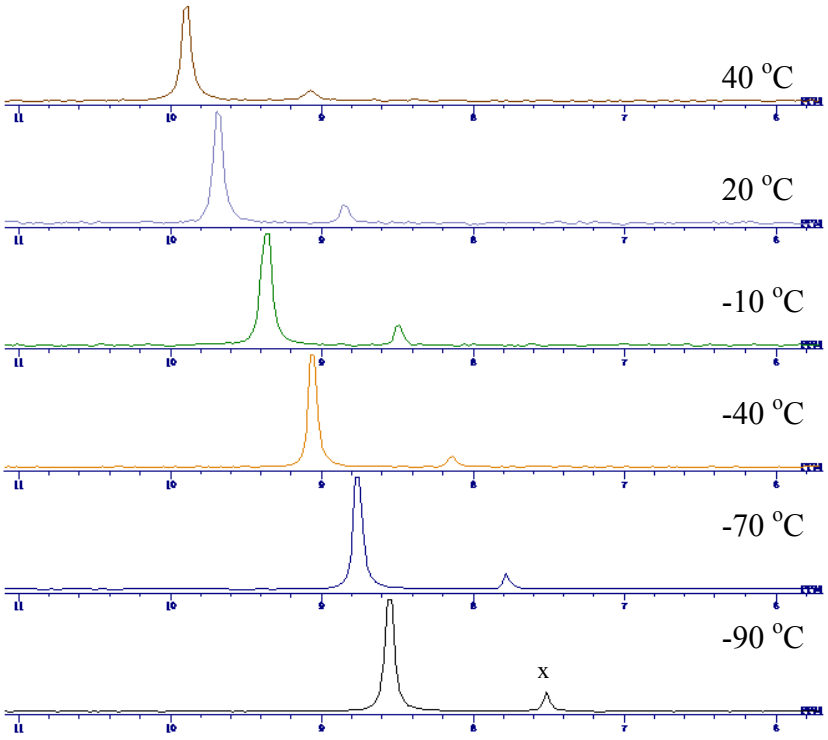


^{31}P NMR (243 MHz, in CD_2Cl_2)

Figure S5. VT- ^{1}H and ^{31}P NMR spectra of [(η^3-methallyl)Pd($Ph_2PN^tBu)_2TiCl_2$](OTf) (**2b**)



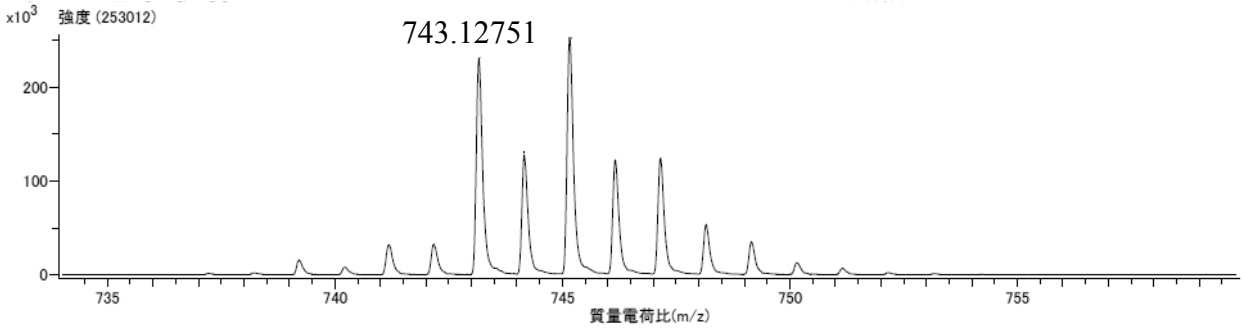
(x = impurity) ^{1}H NMR (600 MHz, in CD_2Cl_2)



(x = impurity) ^{31}P NMR (243 MHz, in CD_2Cl_2)

Figure S6. ESI-(tof)-MS spectrum of [(η^3-methallyl)Ni($Ph_2PN^tBu)_2TiCl_2$](OTf) (**2a**)

Actual spectrum



Simulated

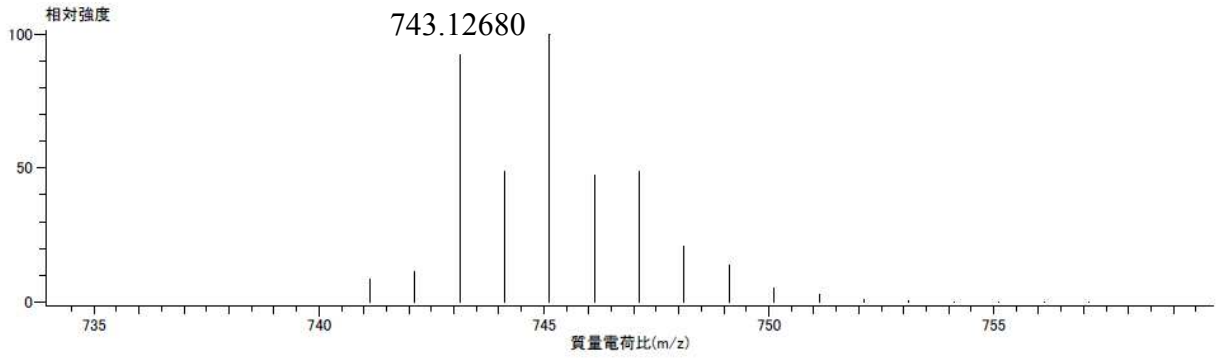
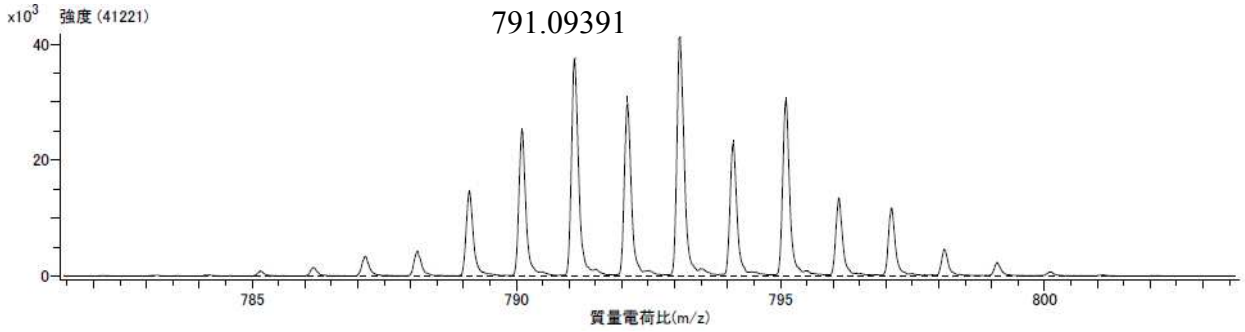


Figure S7. ESI-(tof)-MS spectrum of [(η^3-methallyl)Pd($Ph_2PN^tBu)_2TiCl_2$](OTf) (**2b**)

Actual spectrum



Simulated

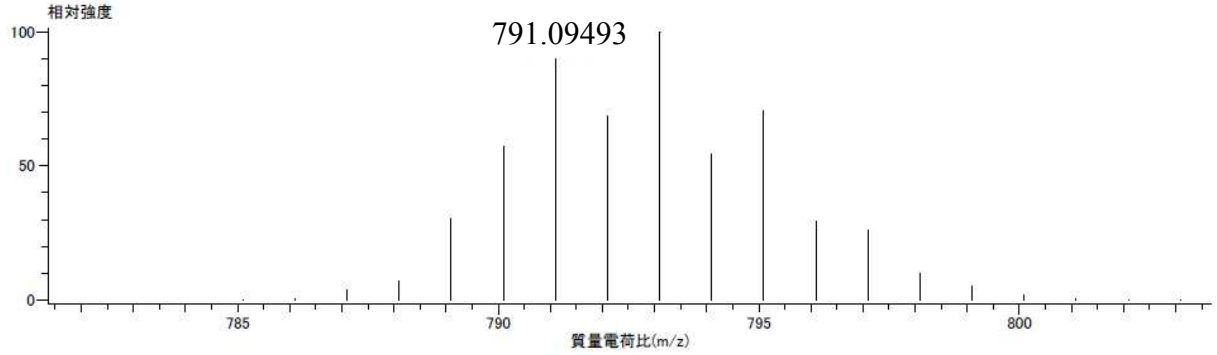
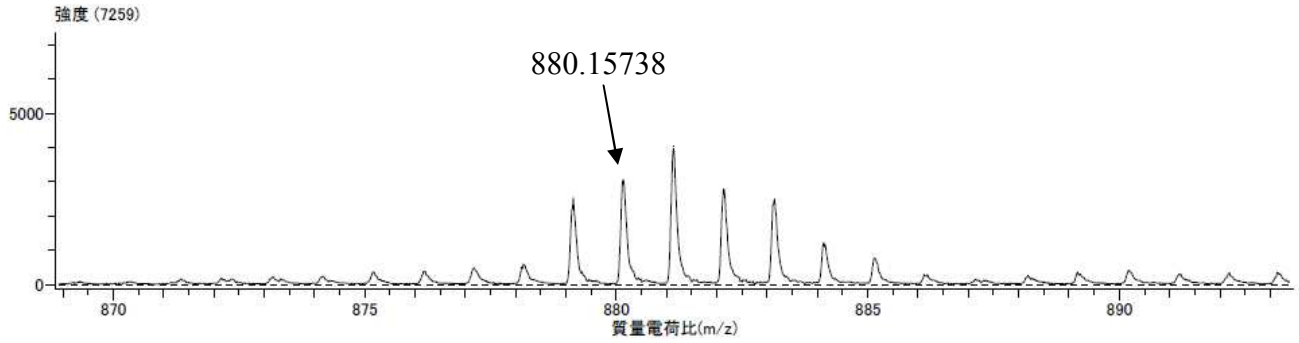


Figure S8. ESI-(tof)-MS spectrum of [(η^3-methallyl)Pt($Ph_2PN^tBu)_2TiCl_2$](OTf) (**2c**)

Actual spectrum



Simulated

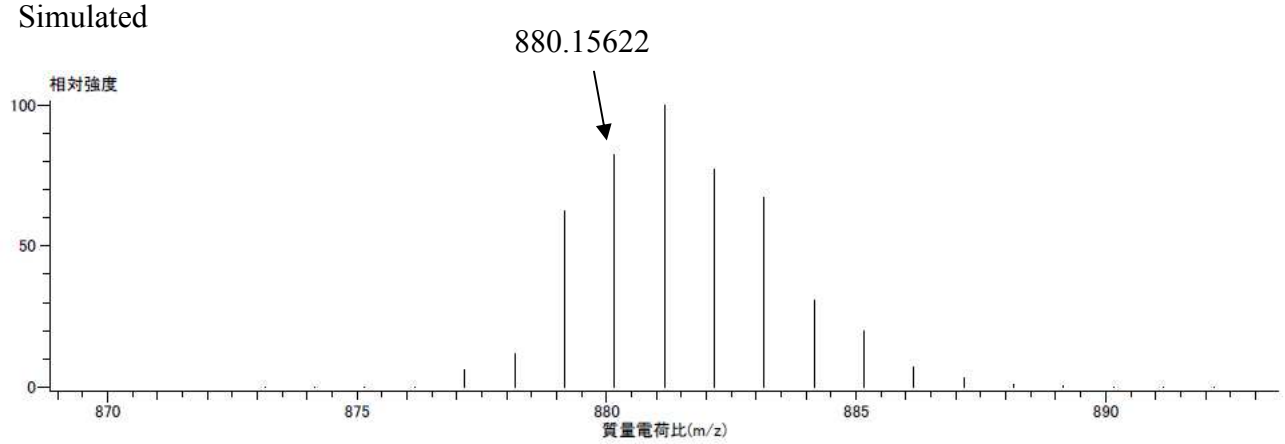


Table S1. Crystallographic data for **2a**, **2b**, and **2c**.

	2a	**2b**	**2c**
Empirical Formula	$C_{37}H_{45}Cl_2F_3N_2NiO_3P_2STi \cdot 1.5C_7H_8$	$C_{37}H_{45}Cl_2F_3N_2O_3P_2PdSTi \cdot 0.5\ CH_2Cl_2$	$C_{37}H_{45}Cl_2F_3N_2O_3P_2PtSTi \cdot 0.5\ C_7H_8$
Formula Weight	1010.47	992.65	1076.74
Crystal System	monoclinic	monoclinic	monoclinic
Lattice Type	Primitive	Primitive	Primitive
Space Group	$P2_1/c$ (#14)	$P2_1/n$ (#14)	$P2_1/c$ (#14)
a, Å	20.222(7)	11.1976(13)	19.813(3)
b, Å	15.556(5)	18.604(2)	15.645(2)
c, Å	15.826(5)	21.654(2)	15.723(2)
α, deg.	90	90	90
β, deg.	102.066(6)	101.6701(17)	99.555(2)
γ, deg.	90	90	90
Volume, $Å^3$	4869(3)	4417.6(8)	4806.2(12)
Z value	4	4	4
$D_{calc,}\ g/cm^3$	1.378	1.492	1.488
F(000)	2102.00	1952.00	2148.00
μ(MoKα), cm^{-1}	8.207	9.978	33.302
Crystal Color, Habit	Dark red, block	Red, block	red, platelet
Crystal Dimensions, mm	0.18 x 0.16 x 0.05	0.25 x 0.20 x 0.10	0.10 x 0.05 x 0.03
No. Observations (All reflections)	8528	9835	10987
No. Variables	601	530	521
Reflection/Parameter Ratio	14.19	18.56	21.09
R (All reflections)	0.1460	0.0617	0.0652
$R_1(I>2.00\sigma(I))$ [a]	0.0961	0.0552	0.0866
wR_2 (All reflections) [b]	0.2857	0.1946	0.2077
GOF	1.000	1.003	1.002
Max Shift/Error in Final Cycle	0.000	0.000	0.000
Maximum peak in Final Diff. Map, $e^-/Å^3$	3.46	4.37	5.92
Minimum peak in Final Diff. Map, $e^-/Å^3$	-0.95	-2.03	-3.11

[a] $R_1 = \Sigma||F_0| - |F_c||/\Sigma|F_0|$. [b] $wR_2 = [\Sigma(w(F_0^2 - F_c^2)^2)/\Sigma(w(F_0^2)^2)]^{1/2}$

Table S2. Representative bond lengths and angles for **2a**, **2b**, and **2c**.

	2a	**2b**	**2c**
bond length (Å)			
M-Ti	2.6036(18)	2.8155(5)	2.7653(15)
M-Cl(1)	2.692(2)	3.0291(9)	3.124(2)
M-C(1)	2.082(8)	2.222(3)	2.179(10)
M-C(2)	2.093(9)	2.245(3)	2.247(10)
M-C(3)	2.041(10)	2.171(3)	2.205(9)
M-P(1)	2.240(2)	2.3244(9)	2.2889(17)
M-P(2)	2.237(2)	2.3061(9)	2.2903(17)
Ti-Cl(1)	2.313(2)	2.2958(11)	2.286(2)
Ti-Cl(2)	2.246(2)	2.2337(9)	2.229(3)
Ti-N(1)	1.942(6)	1.939(3)	1.951(5)
Ti-N(2)	1.945(5)	1.946(2)	1.957(5)
Ti-P(1)	2.689(2)	2.7495(10)	2.780(2)
Ti-P(2)	2.699(2)	2.7534(10)	2.764(2)
N(1)-P(1)	1.656(7)	1.676(2)	1.658(6)
N(2)-P(2)	1.657(7)	1.664(2)	1.635(6)
bond angle (deg.)			
P(1)-M-P(2)	111.33(8)	107.37(3)	108.17(6)
C(1)-M-C(2)	39.4(3)	36.71(13)	36.1(4)
C(1)-M-C(3)	70.1(3)	66.00(13)	65.5(3)
C(2)-M-C(3)	40.0(3)	37.49(13)	36.9(3)
P(1)-M-C(1)	88.9(2)	93.44(9)	93.1(2)
P(1)-M-C(2)	111.6(2)	121.84(9)	121.8(2)
P(1)-M-C(3)	156.5(2)	158.78(9)	158.1(2)
P(2)-M-C(1)	156.1(2)	156.50(9)	156.5(2)
P(2)-M-C(2)	117.0(2)	119.99(9)	120.6(2)
P(2)-M-C(3)	87.3(2)	92.02(9)	92.3(2)
N(1)-Ti-N(2)	116.4(2)	116.38(12)	116.2(2)
N(1)-Ti-Cl(1)	117.35(19)	114.56(9)	117.99(19)
N(1)-Ti-Cl(2)	102.8(2)	102.71(8)	102.5(2)
N(2)-Ti-Cl(1)	117.5(2)	121.56(8)	119.29(19)
N(2)-Ti-Cl(2)	103.9(2)	100.78(8)	101.7(2)
Cl(1)-Ti-Cl(2)	93.05(9)	94.15(3)	91.53(11)

Figure S9. ORTEP representation of the molecular structure of [(η^3-methallyl)Ni($Ph_2PN^tBu)_2TiCl_2$](OTf) (**2a**) showing 50 % probability ellipsoids. Counter anion, solvent molecules (toluene), and hydrogen atoms were omitted for clarity.

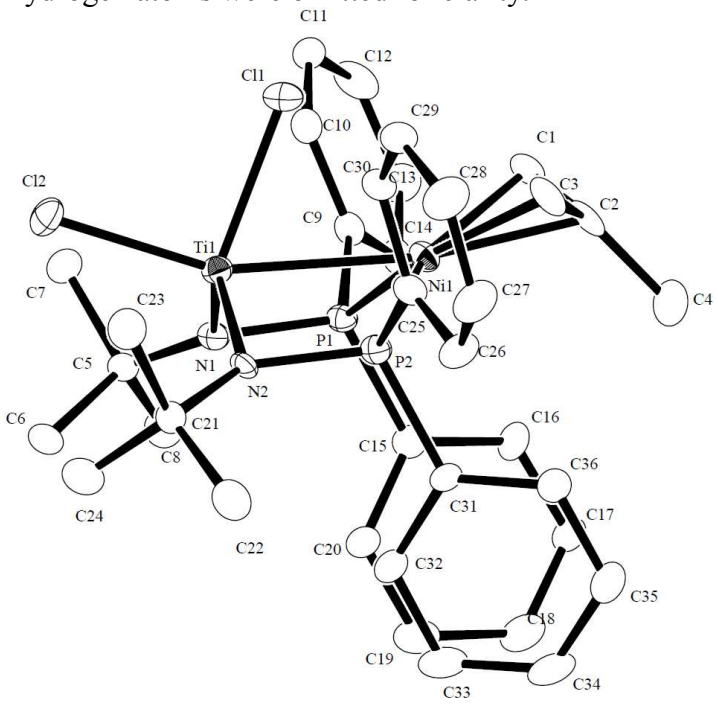


Figure S10. Gaussview depiction of HOMO for the calculated complex [(η^3-methallyl)Ni($Ph_2PN^tBu)_2TiCl_2$](OTf) (**2b**)

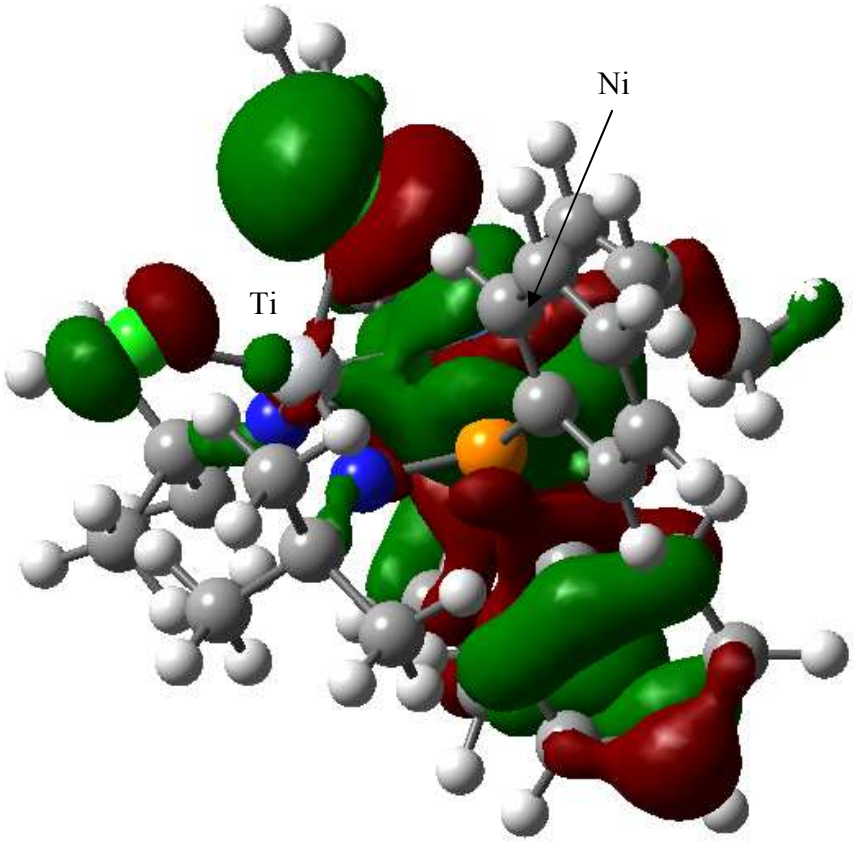


Figure S11. ORTEP representation of the molecular structure of [(η^3-methallyl)Pd($Ph_2PN^tBu)_2TiCl_2$](OTf) (**2b**) showing 50 % probability ellipsoids. Counter anion, solvent molecule (CH_2Cl_2), and hydrogen atoms were omitted for clarity.

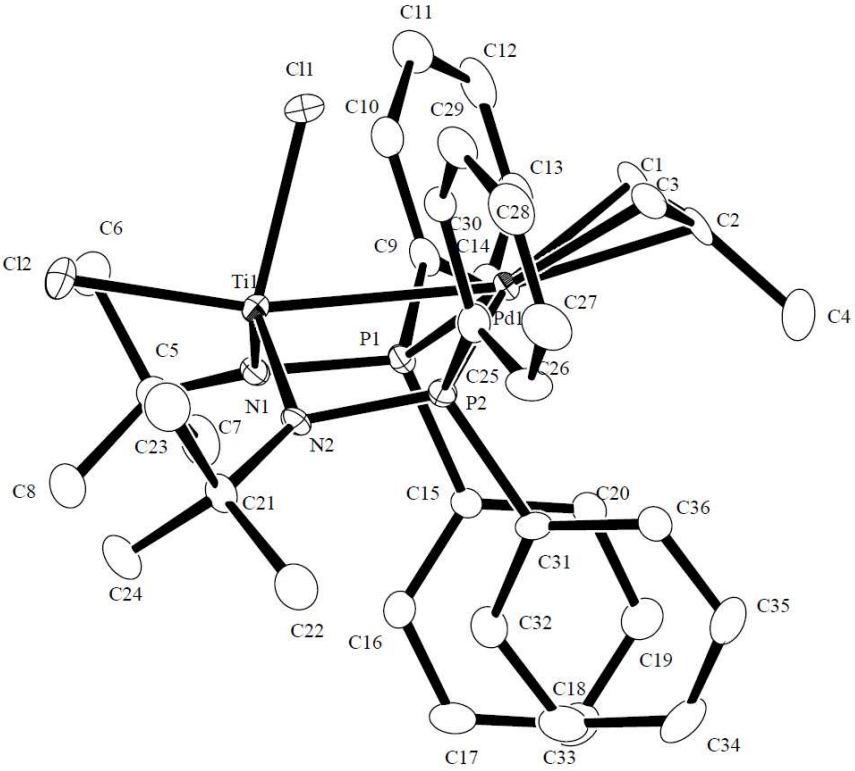


Figure S12. Gaussview depiction of HOMO-1 for the calculated complex [(η^3-methallyl)Pd($Ph_2PN^tBu)_2TiCl_2$](OTf) (**2b**)

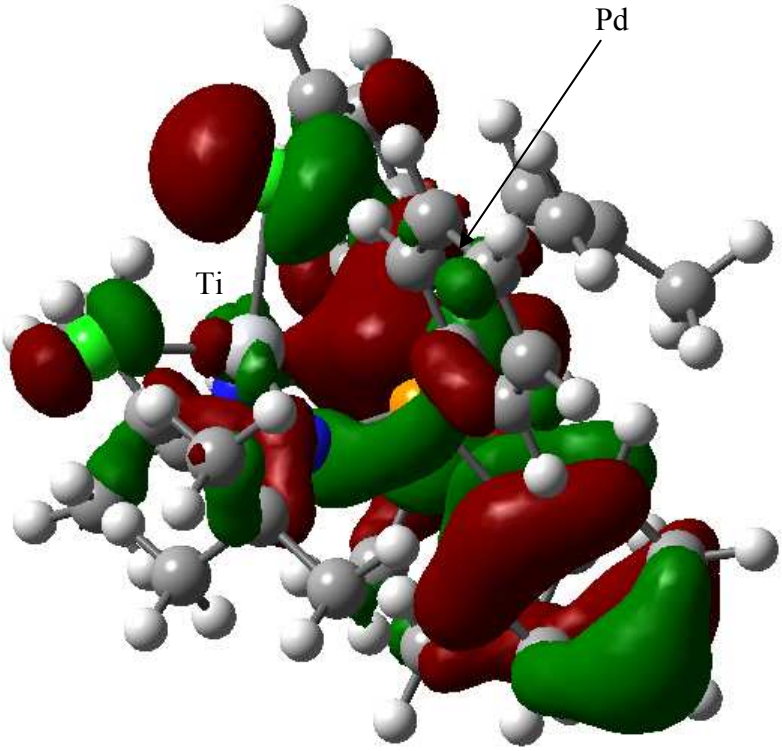


Figure S13. ORTEP representation of the molecular structure of [(η^3-methallyl)Pt($Ph_2PN^tBu)_2TiCl_2$](OTf) (**2c**) showing 50 % probability ellipsoids. Hydrogen atoms were omitted for clarity. Counter anion, solvent molecule (toluene), and hydrogen atoms were omitted for clarity.

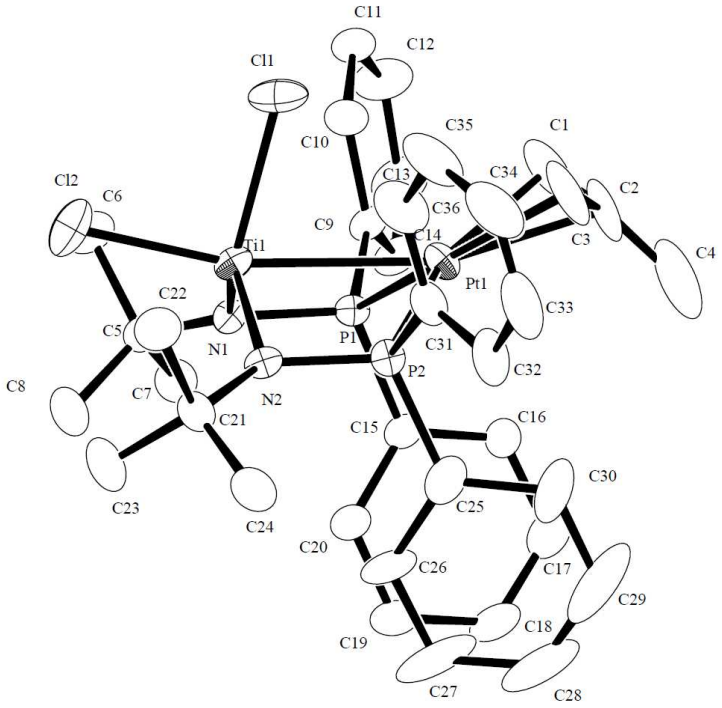


Figure S14. Gaussview depiction of HOMO for the calculated complex [(η^3-methallyl)Pt($Ph_2PN^tBu)_2TiCl_2$](OTf) (**2c**)