Supporting Materials for

Activation of C-H Bonds of Arenes: Selectivity and Reactivity in Bis(pyridyl) Platinum(II) Complexes

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General methods

All reactions were carried under an N_2 atmosphere using standard Schlenk techniques or using a drybox. NMR spectra were recorded by using a Varian Mercury 400 or 600 MHz spectrometer. ^{1}H and ^{19}F NMR chemical shifts are reported relative to TMS and $CFCl_3$ respectively.

Preparation of the complexes.

[$PtMe_2$(DPM)], 1c. To a solution of [$Pt_2Me_4(\mu$-$SMe_2)_2$] (0.385 g, 0.670 mmol) in ether (15 mL) was added a solution containing DPM (0.228 g, 1.34 mmol) in ether (10mL). The solution immediately turned pale orange, and the product precipitated as pale orange solid over 30 min. The product was collected by filtration, washed with ether/pentane and dried under vacuum. Yield: 89%. NMR in $CDCl_3$: $\delta(^{1}H)$ = 0.90 [s, 6H, ^{2}J(PtH) = 83 Hz, 2PtMe]; 4.00 [br, 1H, CH_2]; 4.74 [br, 1H, CH_2]; 7.19 [m, 2H, Py H^5]; 7.37 [d, 2H, Py H^3]; 7.77 [td, 2H, Py H^4]; 8.87 [m, 2H, ^{3}J(PtH) = 22 Hz, Py H^6]; ^{13}C NMR($CDCl_3$): -18.3 [s, ^{1}J(PtC) = 813 Hz, 2PtMe]; 47.5 [s, ^{3}J(PtC) = 52 Hz, CH_2]; 124.3 [s, ^{2}J(PtC) = 22 Hz, Py C^2]; 124.7 [s, Py C^3]; 136.9 [s, Py C^4]; 150.5 [s, ^{2}J(PtC) = 25 Hz, Py C^6]; 155.1 [s, Py C^5]. ESI-MS (m/z): 417 [$PtMe_2$(DPM)+Na]$^+$. NaI was used as the ionizing reagent. The dimethylplatinum(II) complexes **1a** and **1b** were prepared similarly.[1]

[PtMe{HOB(C_6F_5)$_3$}(DPK)], 2a. To a solution of [$PtMe_2$(DPK)], **1a**, (0.41 g, 1 mmol) in CF_3CH_2OH (30 mL) was added a solution of $B(C_6F_5)_3$ (0.54 g, 1mmol) in CF_3CH_2OH (10 mL). The color changed from purple to yellow orange. The mixture was stirred for 6h, and the yellow precipitate of the product was separated by filtration and washed with ether (3×2 mL) and pentane (3×10 mL), and dried under vacuum. Yield: 86%. Anal. Calcd for $C_{30}H_{12}BF_{15}N_2O_2Pt$: C, 39.03; H, 1.31; N, 3.03. Found: C, 39.54; H, 1.34; N, 3.27%. NMR in CD_2Cl_2: $\delta(^{1}H)$ = 0.96 [s, 3H, ^{2}J(PtH) = 73 Hz, Pt-Me]; 3.30 [m, 1H, OH]; 7.50 – 8.80 [8H, py]. $\delta(^{19}F)$ = -134.3 [br m, 6F, *o*-F]; -160.2 [t, 3F, *p*-F]; -165.4 [dt, 6F, *m*-F]. $\delta(^{13}C)$ = -13.9 [PtMe]; 125.4, 127.4, 129.1, 129.2, 137.8, 139.1, 149.5, 149.9, 153.5, 153.9 [py]; 135.6; 138.2; 146.5; 148.8 [C_6F_5]; 185.9 [CO].

[PtMe{HOB(C_6F_5)$_3$}(DPA)], 2b. This was prepared in a similar way from [$PtMe_2$(DPA)], and isolated as a pale brown solid. Yield 84%. Anal. Calcd for $C_{29}H_{13}BF_{15}N_3OPt$: C, 38.26; H, 1.44; N, 4.62. Found: C, 38.59; H, 1.33; N, 4.47%. NMR in CD_2Cl_2: δ(^{1}H) = 0.86 [s, 3H, ^{2}J(PtH) = 72 Hz, Pt-Me]; 3.70 [m, 1H, OH]; 5.70 [1H, NH]; 6.38 – 8.51 [8H, py]. δ(^{19}F) = -134.1 [br m, 6F, *o*-F]; -160.1 [t, 3F, *p*-F]; -165.2 [dt, 6F, *m*-F].

[PtMe{O(H)B(C_6F_5)$_3$}(DPM)], 2c. This was prepared in a similar way from [$PtMe_2$(DPM)], and isolated as a pale brown solid. Yield: 91 %. ^{1}H NMR (acetone-d_6): 0.86 [s, 3H, ^{2}J(PtH) = 74 Hz, PtMe]; 3.64 [sept., 1H, OH]; 4.10 [d, 1H, ^{2}J(HH) = 14 Hz, CH_2]; 4.48 [d, 1H, ^{2}J(HH) = 14 Hz, CH_2]; 7.33 [t, 1H, Py H$^{5'}$]; 7.44 [t, 1H, Py H^5]; 7.67 [d, 1H, PyH$^{3'}$]; 7.70 [d, 1H, PyH^3]; 7.96 [t, 1H, Py H$^{4'}$]; 8.01 [t, 1H, Py H^4]; 8.64 [d, 1H, ^{3}J(PtH) = 68 Hz , PyH$^{6'}$]; 8.76 [d, 1H, Py H^6]. ^{19}F NMR (acetone-d_6): -134.1 [br, 6F, *o*-F]; -162.0 [t, 3F, *p*-F]; -166.9 [t, 6F, *m*-F]. ESI-MS (m/z): 922 [$PtMe_2$(DPM){O(H)B(C_6F_5)$_3$}+Na]$^+$. NaI was used as the ionizing reagent.

[PtMe(DPK)(CO)]$^+$[O(H)B(C_6F_5)$_3$]$^-$, 3a. Yield: 88 %. NMR in CD_2Cl_2: δ(^{1}H) = 1.09 [s, 3H, ^{2}J(PtH) = 70 Hz, PtMe]; 4.17 [m, 1H, O(H)B]; 7.42 [t, br, 2H, Py H^5 & H$^{5'}$]; 7.92 [d, 2H, ^{3}J((HH) = 8 Hz, Py H^3, H$^{3'}$]; 8.03 [t, 2H, ^{3}J(HH) = 7 Hz, Py H^4, H$^{4'}$]; 8.60 [d, br, 2H, Py H^6, H$^{6'}$]. δ(^{19}F) = -136.3 [d, 6F, *o*-F]; -162.1 [t, br, 3F, *p*-F]; -166.6 [t, 6F, *m*-F]. IR: 2073 cm^{-1} (CO). ESI-MS (m/z): 422 (M$^+$).

[PtMe(DPA)(CO)]$^+$[O(H)B(C_6F_5)$_3$]$^-$ 3b. Yield: 91 %. NMR in CD_2Cl_2: δ(^{1}H) = 1.00 [s, 3H, ^{2}J(PtH) = 68 Hz, PtMe]; 7.10 [t, 1H, Py H^5]; 7.12 [t, 1H, Py H$^{5'}$]; 7.46 [d, 1H, Py H^4]; 7.52 [d, 1H, Py H$^{4'}$]; 7.82 [t, br, 2H, Py H^3, H$^{3'}$]; 8.17 [d, 1H, ^{3}J(PtH) = 34 Hz, Py H^6]; 8.28 [d, 1H, Py H$^{6'}$]; 12.08 [s, 1H, NH]. NMR(CD_2Cl_2): δ(^{13}C) = -13.9 [s, ^{1}J(PtC) = 520 Hz, PtMe]; 163.2 [s, ^{1}J(PtC) = 1821 Hz, PtCO]. δ(^{19}F) = -136.3 [d, 6F, *o*-F]; -161.8 [t, 3F, *p*-F]; -166.3 [t, 6F, *m*-F]. IR: 2105 cm^{-1} (CO). ESI-MS (m/z): 409 (M$^+$).

[PtMe(DPM)(CO)]$^+$[O(H)B(C_6F_5)$_3$]$^-$, 3c. Yield: 91 %. NMR in CD_2Cl_2: δ(^{1}H) = 1.26 [s, 3H, ^{2}J(PtH) = 70 Hz, PtMe]; 4.42 [br, 1H, CH_2]; 4.64 [br, 1H, CH_2]; 7.52 [t, 1H, Py H^5]; 7.61 [t, 1H, Py H$^{5'}$]; 7.76 [d, 1H, Py H^4]; 7.8 [d, 1H, Py H$^{4'}$]; 8.03 [t, 1H, Py H^3]; 8.09 [t, 1H, Py H$^{3'}$]; 8.52 [d, 1H, ^{3}J(PtH) = 44 Hz, Py H^6]; 8.72 [d, 1H, Py H$^{6'}$]. δ(^{13}C) = -14.2 [PtMe]; 45.7 [CH_2]. δ(^{19}F) = -136.4 [d, 6F, ^{3}J(FF) = 23 Hz, *o*-F]; -163.8 [t, 3F, ^{3}J(FF) = 20 Hz, *p*-F]; -167.3 [t, 6F, ^{3}J(FF) = 19 Hz, *m*-F]. IR: 2109 cm^{-1} (CO). ESI-MS (m/z): 408 (M$^+$).

[PtPh{HOB(C_6F_5)$_3$}(DPK)], 4a. To a solution of complex **1a** (0.41 g, 1 mmol) in CF_3CH_2OH (30 mL) was added a solution of B(C_6F_5)$_3$ (0.54 g, 1 mmol) in CF_3CH_2OH (10 mL), followed by addition of C_6H_6 (30 mmol), to give a yellow-orange solution. After 4 days, the yellow precipitate of the product was separated by filtration, washed with ether (3×2 mL) and pentane (3×10 mL), and dried under vacuum. Yield: 88%. Anal. Calcd for $C_{35}H_{14}BF_{15}N_2O_2Pt$: C, 42.66; H, 1.43; N, 2.84. Found: C, 42.31; H, 1.41; N, 2.77%. NMR in C_6D_6: δ(^{1}H) = 3.93 [br, 1H, PtOH]; 5.58 – 8.68 [8H, py]; 7.05 [t, 1H, ^{5}J(PtH) = 31 Hz, Ph, *p*-H]; 7.08 [t, 2H, ^{4}J(PtH) = 47 Hz, Ph, *m*-H]; 7.16 [br, m, 2H, Ph, *o*-H]. δ(^{19}F) = -132.6 [br m, 6F, *o*-F]; -158.9 [t, 3F, *p*-F]; -164.4 [dt, 6F, *m*-F].

[PtPh{O(H)B(C_6F_5)$_3$}(DPA)], 4b. This was prepared similarly but using [$PtMe_2$(DPA)] (0.40 g, 1 mmol). Yield: 78%. Anal. Calcd for $C_{34}H_{15}BF_{15}N_3O_2Pt$: C, 41.32; H, 1.53; N, 4.25. Found: C, 41.68; H, 1.49; N, 4.64. NMR in C_6D_6: δ(^{1}H) = 3.91 [br, 1H, PtOH]; 5.62 [td, 1H]; 6.42 [td, 1H]; 6.63 [td, 1H]; 6.92 [td, 1H]; 6.96 [dd, 1H]; 7.13 [t, br, 1H, Ph, *p*-H]; 7.17 [t, br, 2H, Ph, *m*-H]; 7.22 [br, 2H, Ph, *o*-H]; 7.31 [d, 2H]; 7.82 [dd, 1H, ^{3}J(PtH) = 74 Hz, PtNCH *trans* to O]; 8.75 [dd, 1H, NCH *trans* to Ph]. δ(^{19}F) = -132.6 [b, 6F, *o*-F]; -158.9 [t, 3F, *p*-F]; -164.4 [td, 6F, *m*-F].

[PtPh{O(H)B(C_6F_5)$_3$}(DPM)], 4c. This was prepared similarly but using [$PtMe_2$(DPM)] (0.40 g, 1 mmol). Yield: 78%. NMR in CD_2Cl_2: δ(^{1}H) = 3.51 [septet, 1H, O(H)B(C_6F_5)$_3$]; 4.10 [d, 1H, ^{2}J(HH) = 14 Hz, CH_2]; 4.42 [d, 1H, ^{2}J(HH) = 14 Hz, CH_2]; 6.88 [t, br, 2H, Ph, *m*-H]; 6.90 [t, br, 1H, Ph, *p*-H]; 6.93 [t, 1H, Py H^5]; 7.04 [d, br, 2H, Ph, o-H]; 7.33 [t, Py H$^{5'}$]; 7.40 [d, 1H, Py H^3]; 7.42 [d, 1H, Py H$^{3'}$]; 7.77 [td, 1H, Py H^4]; 7.81 [td, 1H, Py H$^{4'}$]; 8.34 [d, 1H, Py H^6]; 8.71 [d, 1H, Py H$^{6'}$]. δ(^{13}C) = 46.2 [CH_2]; 123.9, 124.2, 124.3, 124.6; 125.5, 127.0, 135.1, 135.8, 138.9, 139.3, 150.4, 152.9, 154.8, 156.1; 136.0, 137.5, 138.3, 140.0, 146.9, 148.5. δ(^{19}F) = -133.5 [br, 6F, *o*-F]; -161.1 [t, 3F, *p*-F]; -165.9 [t, 6F, *m*-F]. ESI-MS (m/z): 994 [PtPhX(DPM)+Na]$^+$. NaI was used as the ionizing reagent.

[Pt(C_6H_4Me){HOB(C_6F_5)$_3$}(DPK)], 5a. This was prepared in a similar way to **4a** but using toluene (30 mmol). Yield: 86%. Anal. Calcd for $C_{36}H_{16}BF_{15}N_2O_2Pt$: C, 43.27; H, 1.61; N, 2.80. Found: C, 42.83; H, 1.31; N, 3.27%. NMR in CD_2Cl_2: *meta*-**8**: δ(^{1}H) = 2.15 [s, 3H, Me]; 3.53 [1H, OH]; 6.73 [d, 1H, tolyl H^4]; 6.77 [t, 1H, tolyl H^5]; 6.78 [s, 1H, tolyl H^2]; 6.84 [d, 1H, tolyl H^6]; 7.21 – 8.89 [8H, py]; δ(^{19}F) = -133.2 [br m, 6F, *o*-F]; -160.5 [t, 3F, *p*-F]; -165.7 [m, 6F, *m*-F]. *para*-**8**: δ(^{1}H) = 2.24 [s, 3H, Me]; 3.48 [1H, OH]; 6.68, 6.70 [m, 4H, tolyl]; 7.21 – 8.89 [8H, py]; δ(^{19}F) = -133.0 [br m, 6F, *o*-F]; -160.7 [t, 3F, *p*-F]; -165.6 [m, 6F, *m*-F]. *ortho*-**8**: 2.34 [3H, Me]; 3.32 [1H, OH]; 7.14, 6.96 [m, tolyl]; other tolyl protons obscured. Isomer ratio obtained by integration of methyl resonances of the *o*-, *m*-, and *p*-tolyl groups.

[Pt(C_6H_4Me){HOB(C_6F_5)$_3$}(DPA)], 5b. This was prepared in a similar way using [$PtMe_2$(DPA)] and toluene. The product formed as an off-white precipitate. Yield: 84%. Anal. Calcd for $C_{35}H_{17}BF_{15}N_3OPt$: C, 43.22; H, 1.91; N, 4.28. Found: C, 42.93; H, 1.99; N, 4.37%. NMR in CD_2Cl_2: *meta*-**9**: δ(^{1}H) = 2.15 [s, 3H, Me]; 3.53 [1H, OH]; 6.74 [d, 1H, tolyl H^4]; 6.86 [d, 1H, tolyl H^6]; 7.03 [t, 1H, tolyl H^5]; 7.13 [s, 1H, tolyl H^2]; 6.60 – 8.52 [8H, py]; δ(^{19}F) = -133.2 [br m, 6F, *o*-F]; -160.5 [t, 3F, *p*-F]; -165.7 [m, 6F, *m*-F]. *para*-**9**: δ(^{1}H) = 2.24 [s, 3H, Me]; 3.40 [1H, OH]; 6.62, 6.68 [m, 4H, tolyl]; 6.77 – 8.52 [8H, py]; *ortho*-**8**: Tol-Me: 2.34 [3H, Me]; 3.32 [1H, OH]; 6.96, 7.14, [m, tolyl]; other tolyl protons obscured. Isomer ratio obtained by integration of methyl resonances of the *o*-, *m*-, and *p*-tolyl groups.

[Pt(3,4-$C_6H_3Me_2$){HOB(C_6F_5)$_3$(DPK)], 6a. This was prepared in the same way as complex **4a**, but using *o*-xylene (30 mmol). Reaction was complete in 4 h. Yield: 87%. Anal. Calcd for $C_{37}H_{18}BF_{15}N_2O_2Pt$: C, 43.85; H, 1.79; N, 2.76. Found: C, 43.66; H, 1.98; N, 2.51%. NMR in CD_2Cl_2: δ(^{1}H) = 2.06 [s, 3H, Me]; 2.17 [s, 3H, Me]; 3.49 [m, 1H, OH]; 6.63 [d, 1H, Xy H^6]; 6.67 [d, 1H, Xy H^5]; 6.74 [s, 1H, Xy H^2]; 7.22-8.90 [8H, py]. δ(^{19}F) = -133.1 [br m, 6F, *o*-F]; -160.7 [t, 3F, *p*-F]; -165.8 [m, 6F, *m*-F]. δ(^{13}C) = 18.7,

19.2; 125.3, 127.6, 128.4, 128.8, 128.8, 132.8, 132.9, 135.1, 136.3, 139.6, 139.7, 150.0, 150.1, 154.9; 186.0.

[Pt(3,4-$C_6H_3Me_2$){O(H)B(C_6F_5)$_3$}(DPM)], 6c. This was prepared similarly but using [$PtMe_2$(DPM)] (0.40 g, 1 mmol). Yield: 78%. NMR in CD_2Cl_2: δ(^{1}H) = 2.06 [s, 3H, *o*-xylene Me]; 2.18 [s, 3H, *o*-xylene Me]; 3.48 [sept., 1H, O(H)B(C_6F_5)$_3$]; 4.08 [d, 1H, ^{2}J(HH) = 14 Hz, CH_2]; 4.42 [d, 1H, ^{2}J(HH) = 14 Hz, CH_2]; 6.69 [d, 1H, ^{3}J(HH) = 7 Hz, *o*-xylene H^6]; 6.76 [d, 1H, ^{3}J(HH) = 7 Hz, *o*-xylene H^5]; 6.79 [s, ^{3}J(PtH) = 37 Hz, *o*-xylene H^2]; 6.94 [t, 1H, Py H^5]; 7.32 [t, 1H, Py $H^{5'}$]; 7.40 [d, 2H, Py H^3 & $H^{3'}$]; 7.70 [td, 1H, Py H^4]; 7.80 [td, 1H, ^{4}J(HH) = 1 Hz, Py $H^{4'}$]; 8.45 [d, 1H, ^{3}J(PtH) =72 Hz, Py H^6]; 8.69 [d, 1H, Py $H^{6'}$]. δ(^{13}C) = 17.5, 20.0 [Me]; 47.0 [CH_2]. δ(^{19}F) = -132.6 [br, 6F, *o*-F]; -160.6 [t, 3F, *p*-F]; -165.4 [t, 6F, *m*-F]. EI-MS (m/z): 999 [M].

Attempted synthesis of [Pt(3,4-$C_6H_3Me_2$){O(H)B(C_6F_5)$_3$}(bu_2bpy)], 6d. The reaction of [$PtMe_2$(bu_2bpy)], **1d**, (0.40 g, 1 mmol) with *o*-xylene was carried out as above and monitored by ^{1}H NMR. After one day at room temperature, the known complex [PtMe{O(H)B(C_6F_5)$_3$}(bu_2bpy)] was still present. At 60°C, a complex reaction occurred and eventually led to formation of crystals of [Pt_2(μ-OH)$_2$(bu_2bpy)$_2$][B(OH)(C_6F_5)$_3$]$_2$, which was identified crystallographically. There was no evidence for formation of xylylplatinum complexes.

[Pt(3,5-$C_6H_3Me_2$){HOB(C_6F_5)$_3$}(DPK)], 7a. This was prepared similarly to **4a** but using *m*-xylene (30 mmol). Yield: 86%. Anal. Calcd for $C_{37}H_{18}BF_{15}N_2O_2Pt$: C, 43.85; H, 1.79; N, 2.76. Found: C, 43.51; H, 2.08; N, 2.59%. NMR in CD_2Cl_2: δ(^{1}H) = 2.08 [s, 6H, Me]; 3.49 [m, 1H, OH]; 6.51 [s, 2H, Xy H^2, H^6]; 6.48 [s, 1H, Xy H^4]; 7.20-8.89 [8H, py]. δ(^{19}F) = -133.2 [br, m, 6F, *o*-F]; -160.7 [t, 3F, *p*-F]; -165.8 [m, 6F, *m*-F]. δ(^{13}C) = 20.9; 125.3, 126.6, 127.5, 128.8, 128.8, 132.9, 134.4, 136.2, 139.6, 139.7, 150.1, 153.2, 155.0; 186.0.

[Pt(3,5-$C_6H_3Me_2$){O(H)B(C_6F_5)$_3$}(DPA)], 7b. This was prepared similarly using [$PtMe_2$(DPA)] (0.117 g, 0.3 mmol). Yield: 88%. Anal. Calcd for $C_{36}H_{19}BF_{15}N_3OPt$: C, 43.22; H, 1.91; N, 4.20. Found: C, 42.51; H, 2.06; N, 4.52. NMR in C_6D_6: δ(^{1}H) = 2.33 [s, 6H, 2Me of *m*-xy]; 3.83 [m, 1H, O(H)B(C_6F_5)$_3$]; 5.23 [d, 1H]; 5.42 [t, 1H]; 5.50 [s, NH]; 5.57 [d, 1H]; 6.34 [t, 1H]; 6.40 [t, 1H]; 6.73 [s, 1H, *m*-xy H^4]; 6.79 [t, 1H]; 7.05 [s, 2H, *m*-xy $H^{2,6}$]; 8.05 [d, 1H, ^{3}J(PtH) = 80Hz, PtNCH, *trans* to O]; 8.53 [d, 1H, PtNCH, trans to *m*-xy]. δ(^{19}F) = 132.7 [br, 6F, *o*-F]; -161.2 [t, 3F, *p*-F]; -165.8 [td, 6F, *m*- F].

[Pt(C_6H_4OMe){HOB(C_6F_5)$_3$}(DPK)], 8a. This was prepared similarly, but using anisole (30 mmol). Yield: 48%. Anal. Calcd for $C_{36}H_{16}BF_{15}N_2O_3Pt$: C, 42.58; H, 1.61; N, 2.80. Found: C, 42.64; H, 1.81; N, 2.72%. NMR in CD_2Cl_2: *ortho*-**12**: δ(^{1}H) = 4.01 [s, 3H, OMe]; 4.81 [m, br, 1H, OH]; 6.29 [d, 1H, An H^6]; 6.39 [t, 1H, An H^5]; 6.68 [d, 1H, An H^3]; 6.90 [dt, 1H, An H^4]; 7.21-9.01 [8H, py]. δ(^{19}F) = -134.5 [br m, 6F, *o*-F]; -161.7 [t, 3F, *p*-F]; -166.9 [m, 6F, *m*-F]. *meta*-**12**: δ(^{1}H) = 3.75 [s, 3H, OMe]; 3.70 [m, br, 1H, OH]; 6.51 [s, 1H, An H^2]; 6.56 [d, 1H, An H^6]; 6.83 [t, 1H, An H^5]; 6.90 [d, 1H, An H^4]; 7.25-8.97 [8H, py]. *para*-**12**: δ(^{1}H) = 3.72 [s, 3H, OMe]; 3.69 [m, br, 1H, OH]; 6.44 [d, 2H, An $H^{2,6}$]; 6.54 [d, 2H, An $H^{3,5}$]; 7.3-8.9 [8H, py].

[Pt{2,4-$C_6H_3(OMe)_2$}{$HOB(C_6F_5)_3$}(DPK)], 9a. This was prepared similarly, but using 1,3-dimethoxybenzene (30 mmol). Yield: 40%. Anal. Calcd for $C_{37}H_{18}BF_{15}N_2O_4Pt$: C, 42.51; H, 1.74; N, 2.68. Found: C, 42.67; H, 1.86; N, 2.59%. NMR in CD_2Cl_2: $\delta(^1H)$ = 3.71 [s, 3H, 4-OMe]; 3.90 [s, 3H, 2-OMe]; 4.71 [m, br, 1H, OH]; 6.02 [d, 1H, Ar H5]; 6.21 [d, 1H, Ar H6]; 6.33 [s, 1H, Ar H3]; 7.24 – 9.23 [8H, py]. $\delta(^{19}F)$ = -133.5 [br m, 6F, *o*-F]; -160.7 [t, 3F, *p*-F]; -165.9 [m, 6F, *m*-F].

[Pt(2-MeO-4-Me-C_6H_3){$HOB(C_6F_5)_3$}(DPK)], 10a. This was prepared similarly, but using 3-methylanisole (30 mmol). Yield: 49%. NMR in CD_2Cl_2: $\delta(^1H)$ = 2.28 [s, 3H, Me]; 3.99 [s, 3H, OMe]; 4.75 [m, br, 1H, OH]; 6.14 [d, 1H, Ar H^6]; 6.25 [d, 1H, Ar H^5]; 6.50 [s, 1H, Ar H^3]; 7.2 – 8.99 [8H, py]. $\delta(^{19}F)$ = -133.2 [br m, 6F, *o*-F]; -160.8 [t, 3F, *p*-F]; -165.8 [m, 6F, *m*-F]. ESI-MS in the presence of NaI to aid ionization: m/z = 1052 [**14**+Na]$^+$.

H/D Exchange Experiments.
The reaction of **1** with *o*-xylene-d_{10} or anisole-d_8 was carried out in a similar way to synthesis of complex **6a** and **8a**, but using the perdeuterated arene. The extent of H/D exchange at each position of the aryl group of the product complex was determined by integration of the corresponding resonance in the ^{1}H NMR spectrum, using an adjacent pyridyl resonance for calibration.
In a separate experiment, the complexes **6a** and **8a** were dissolved in deuterated alcohol in an NMR tube, but negligible H/D exchange was observed over several days at room temperature under these conditions.

Competition Reactions
The syntheses were carried out in a similar way as above, but using equimolar amounts of the two arenes. Thus, the relative reactivities of *m*-xylene and *m*-dimethoxybenzene, of *o*-xylene and *o*-xylene-d_{10}, and of anisole and anisole- d_8 were determined by isolation of the products followed by analysis by using ^{1}H NMR. Aliquots were taken during reaction, evaporated, and analysed as a cross-check.

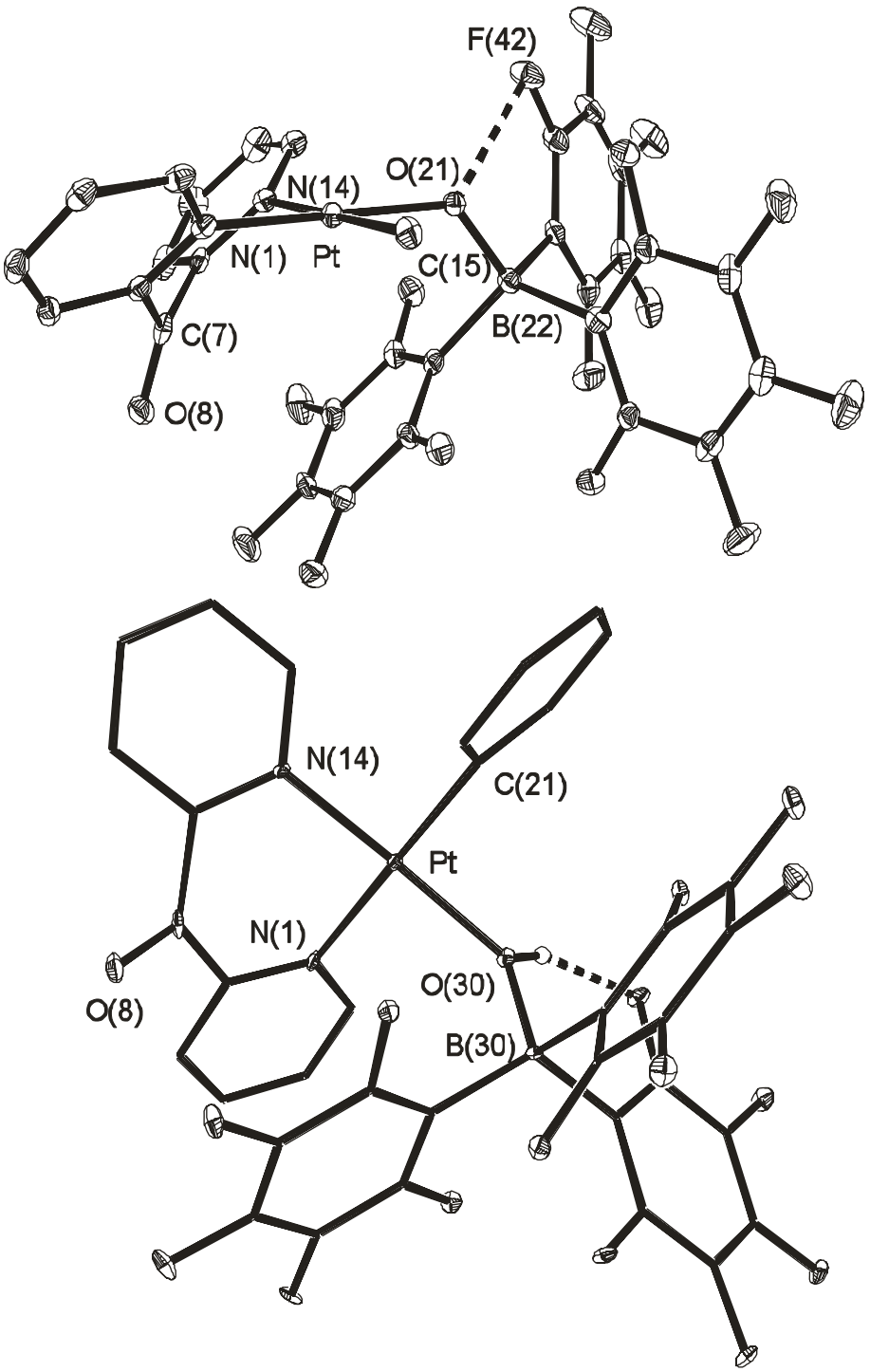
X-ray Structure Determinations. A suitable crystal was mounted on a glass fiber, and data were collected by using a Nonius Kappa-CCD diffractometer. Details of the data collections and structure refinements are given in the CIF files, and the individual structures are illustrated below.

Reference:
1. Zhang, F.; Jennings, M. C.; Puddephatt, R. J. *Organometallics*, **2004**, *23*, 1396. Scott, J.D.; Puddephatt, R.J. *Organometallics*, **1983**, *2*, 1643.

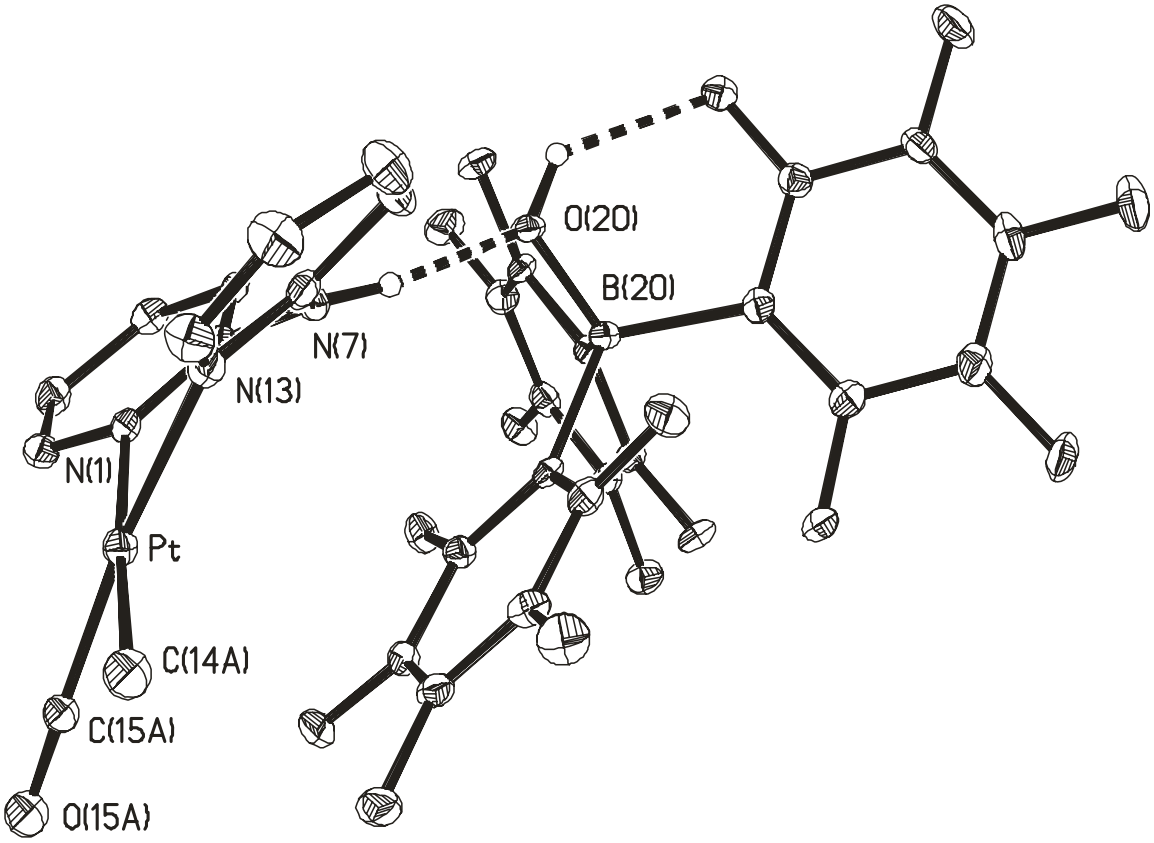
Table S1. Crystal Data and Structure Refinement for the Complexes

	2a $0.4CH_2Cl_2$. $0.6C_6H_{14}$	**4a**	**6a** $1.5CH_2Cl_2$	**6c**	**7a**	**8a** $0.5CH_2Cl_2$
formula	$C_{34}H_{21.2}BCl_{0.8}F_{15}N_2O_2Pt$	$C_{35}H_{14}BF_{15}N_2O_2Pt$	$C_{38.5}H_{21}BF_{15}N_2O_2Pt$	$C_{37}H_{20}BF_{15}N_2OPt$	$C_{37}H_{18}BF_{15}N_2O_2Pt$	$C_{36.5}H_{17}BF_{15}N_2O_3Pt$
fw	1008.99	985.38	1140.82	999.45	1013.43	1057.87
temp/K	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
λ (Mo Kα)/Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
cryst syst	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
space group	*P*2(1)/n	P2(1)/c	P2(1)/c	P2(1)/c	P2(1)/c	P2(1)/c
cell dimens *a*/Å	7.7332(2)	11.3484(4)	14.6798(5)	8.5660(2)	8.58600(10)	10.4214(3)
b/Å	19.3491(5)	20.7294(6)	20.7799(6)	17.8544(4)	17.7719(4)	15.1698(4)
c/Å	23.5497(6)	27.3470(9)	25.5737(8)	22.6002(6)	22.8225(6)	22.6241(4)
α/deg	90	90	90	90	90	90
β/deg	93.034(2)	95.8700	91.802(2)	90.040(2)	91.9220(10)	96.695(2)
γ/deg	90	90	90	90	90	90
volume/$Å^3$	3518.81(16)	6399.5(4)	7797.3(4)	3456.49(14)	3480.52(13)	3552.27(15)
Z	4	8	8	4	4	4
d(calc)/Mg m^{-3}	1.905	2.045	1.944	1.921	1.934	1.978
abs coeff/ mm^{-1}	4.164	4.512	3.917	4.176	4.151	4.147
F(000)	1947	3776	4408	1928	1952	2036
no. of reflns/ind reflns	45149/7197	55253/17650	58886/17756	38148/6096	35132/7972	39646/6279
abs corr	Integration	Integration	Integration	Integration	Integration	Integration
no. of data/restr/params	7197/11/460	17650/18/894	17756/8/1043	6096/1/469	7972/0/532	6279/0/515
R1, wR2 [$I > 2\sigma(I)$]	0.0457, 0.1175	0.0599, 0.1309	0.0605, 0.1380	0.0356, 0.0813	0.0354, 0.0780	0.0353, 0.0845

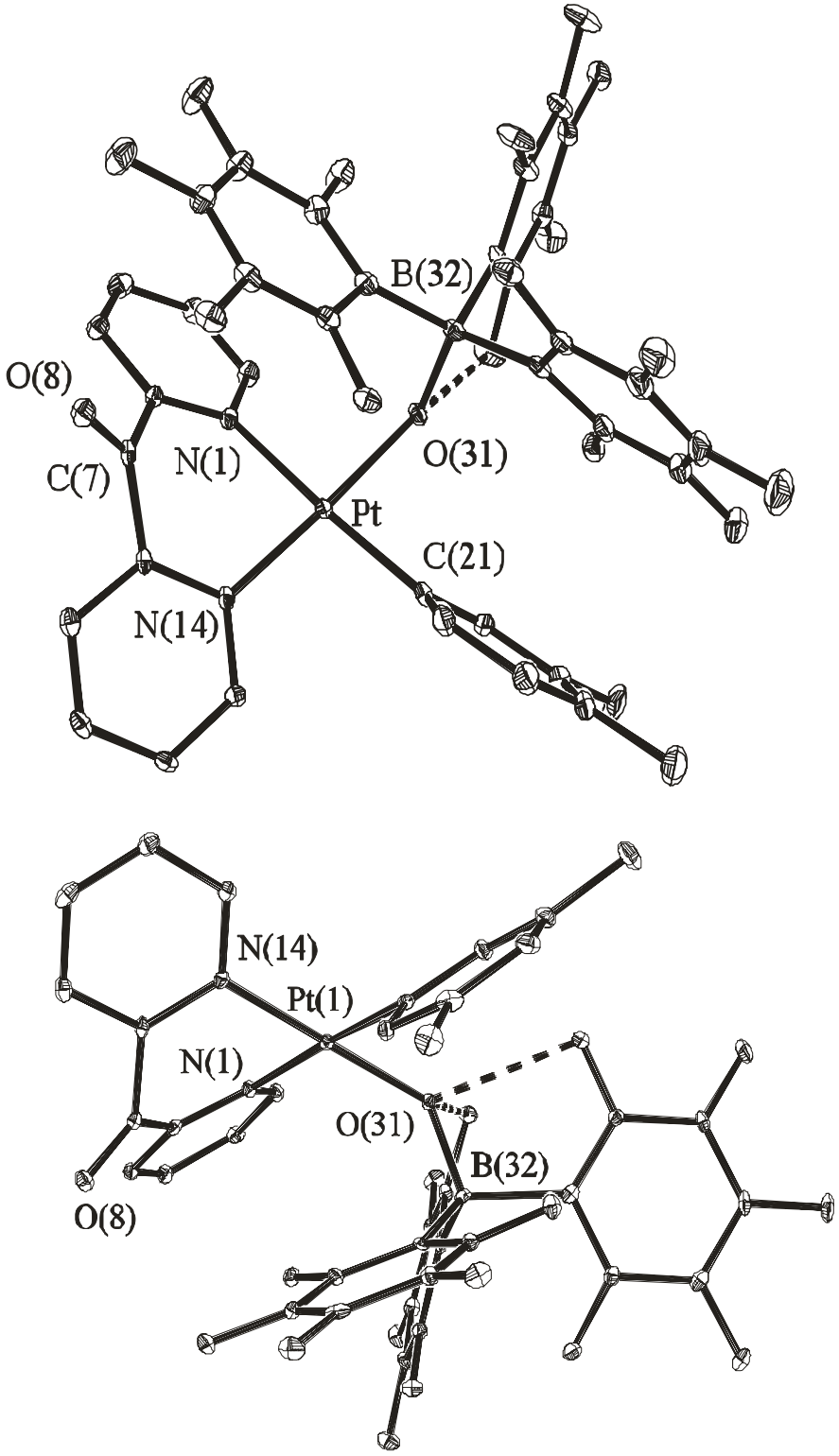
	9a $0.5CH_2Cl_2$	**10a** $0.5CH_2Cl_2$	**3b**
formula	$C_{37.5}H_{19}BClF_{15}N_2O_4Pt$	$C_{37.5}H_{19}BClF_{15}N_2O_3Pt$	$C_{30}H_{13}BF_{15}N_3O_2Pt$
fw	1087.90	1071.90	938.33
temp/K	150(2)	150(2)	150(2)
λ (Mo Kα)/Å	0.71073	0.71073	0.71073
cryst syst	Triclinic	Monoclinic	Monoclinic
space group	P2(1)/c	P2(1)/c	C2/c
cell dimens *a*/Å	10.6163(4)	10.4892(3)	37.1201(15)
b/Å	15.4527(6)	15.4986(5)	7.3349(3)
c/Å	22.3982(2)	22.3102(6)	23.0216(9)
α/deg	90	90	90
β/deg	92.257(2)	95.735(2)	106.850 (2)
γ/deg	90	90	90
volume/$Å^3$	3671.6(3)	3608.77(18)	5999.0(4)
Z	4	4	8
d(calc)/Mg m^{-3}	1.968	1.973	2.078
abs coeff/mm^{-1}	4.017	4.083	4.808
F(000)	2100	2068	3584
no. of reflns/ind reflns	31649/6386	34948/6347	26807/5275
abs corr	Integration	Integration	Integration
no. of data/restr/params	6386/0/532	6347/2/523	5275/0/431
R1, wR2 [$I > 2\sigma(I)$]	0.0416, 0.0844	0.0680, 0.1690	0.0402, 0.0943



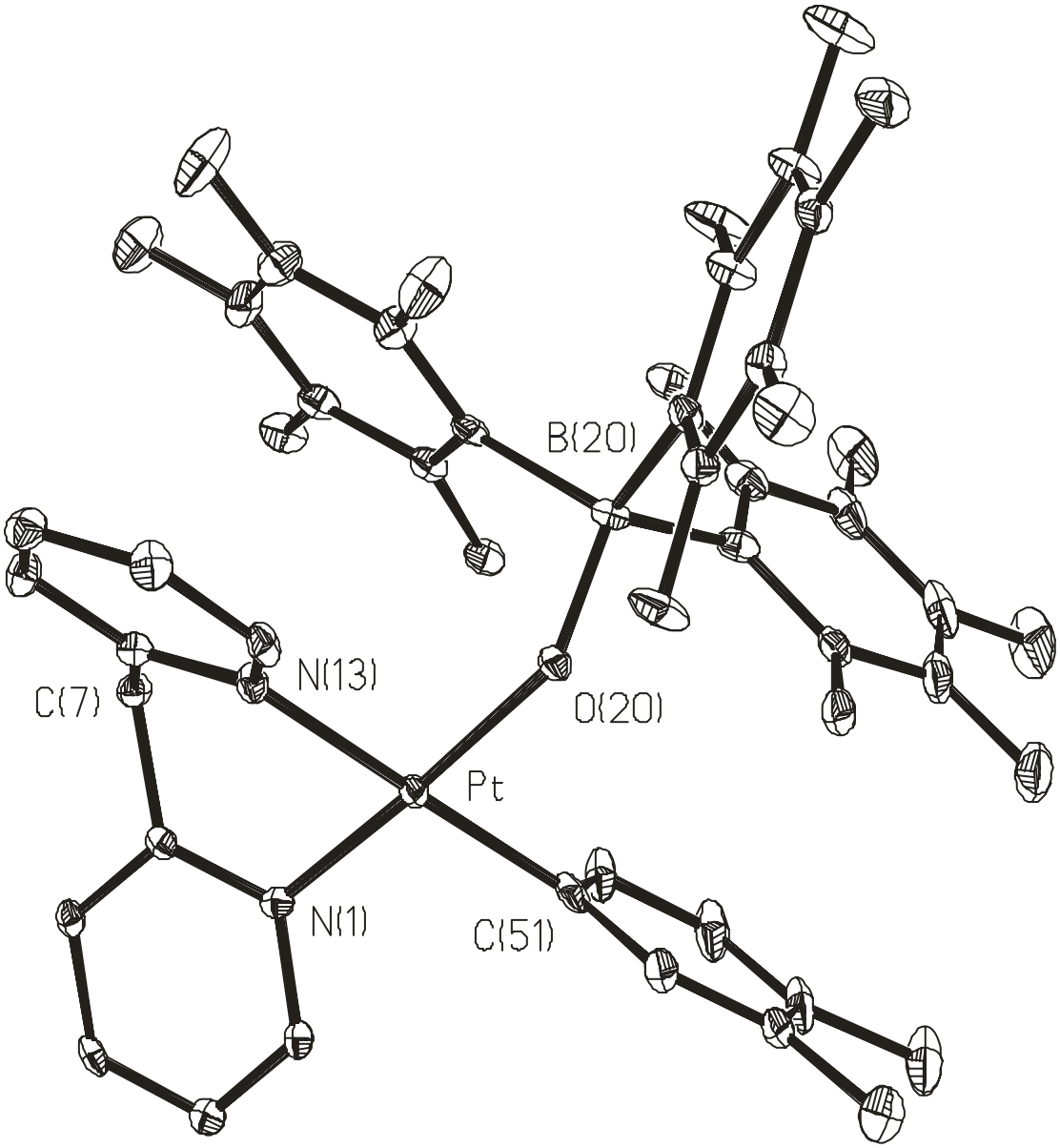
Structures of complexes **2a** and **4a**



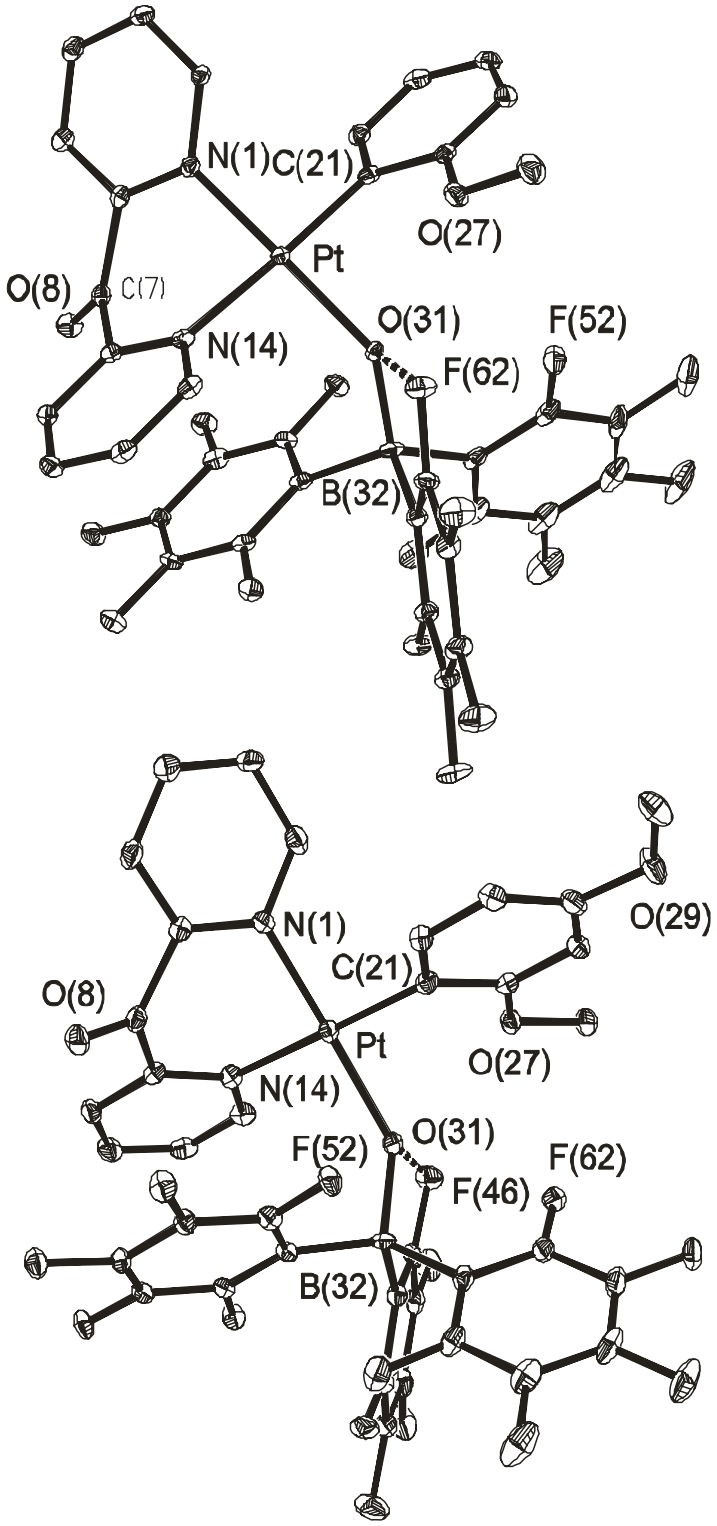
Structure of complex **3b**



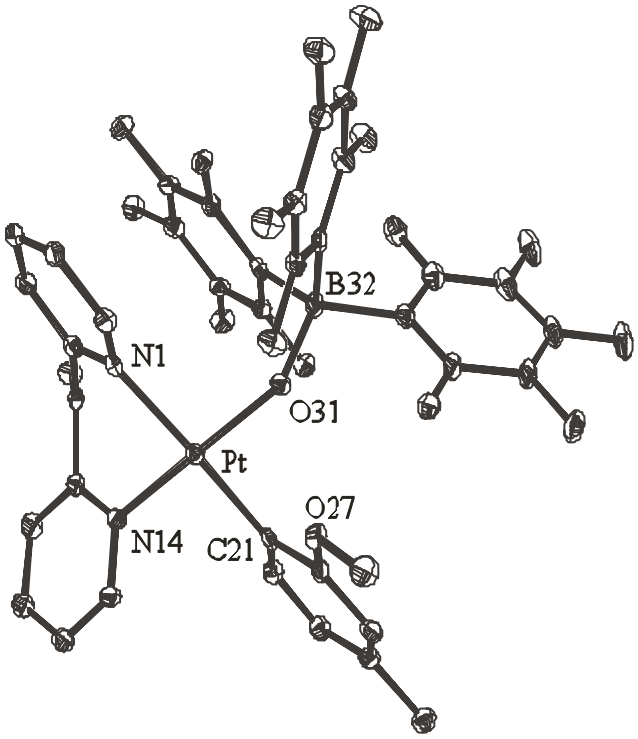
Structures of complexes **6a** and **7a**



Structure of complex **6c**



Stuctures of complexes **8a** and **9a**



Structure of complex **10a**