## Supporting Information

for

# Reactivity studies of pincer bis-protic $\mathbf{N}$-heterocyclic carbene complexes of platinum and palladium under basic conditions 

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Figure S1: NMR data for 6-Pt in $\mathrm{CD}_{2} \mathrm{Cl}_{2}$.

| $\mathrm{H}-{ }^{15} \mathrm{~N} \mathbf{g H M B C A D}$ |  |  |
| :---: | :---: | :---: |
| H | bonds | N |
| 8.01 | 3 | -215.3 |
| 8.01 | 2 | -197.8 |
| 7.72 | 3 | -197.8 |
| 7.53 | 3 | -197.0 |
| 7.41 | 3 | -209.9 |
| 7.41 | 2 | -197.0 |
| ${ }^{\mathrm{a}} \mathrm{J}_{\mathrm{nxh}}=5 \mathrm{~Hz}$ |  |  |
| $\mathbf{J}_{1 \times \mathrm{ln}}=90 \mathrm{~Hz}$ |  |  |


| ${ }^{1} \mathrm{H}-{ }^{13} \mathrm{C}$ |  |
| :---: | :---: |
| HSQCAD |  |
| H | C |
| 8.15 | 115.3 |
| 8.08 | 113.7 |
| 8.01 | 111.9 |
| 7.72 | 109.8 |
| 7.53 | 110.8 |
| 7.41 | 109.3 |
| 1.58 | 32.6 |
| 1.52 | 32.6 |
| 1.33 | 31.7 |
| 1.09 | 29.9 |


| $\mathbf{g C O S Y}$ |
| :---: |
| $8.19 \leftrightarrow 7.41$ |
| $8.15 \leftrightarrow 7.53$ |
| $8.08 \leftrightarrow 7.72$ |

Red $=$ Proton, Black $=$ carbon, Blue $=$ Nitrogen

| ${ }^{\mathbf{1}} \mathbf{H}{ }^{\mathbf{1 3}} \mathbf{C} \mathbf{~ g H M B C}$ |  |  |
| :---: | :---: | :---: |
| b |  |  |
| H | bonds | C |
| 8.19 | 2 | 166.4 |
| 8.19 | 2 | 142.2 |
| 8.19 | 3 | 109.3 |
| 8.15 | 3 | 133.1 |
| 8.15 | 2 | $126.9(\mathrm{w})$ |
| 8.15 | 3 | 125.9 |
| 8.15 | 4 | $124.5(\mathrm{w})$ |
| 8.15 | 3 | 110.8 |
| 8.15 | 3 | 35.4 |
| 8.08 | 3 | 133.6 |
| 8.08 | 3 | 126.9 |
| 8.08 | 2 | $125.9(\mathrm{w})$ |
| 8.08 | 3 | 109.8 |
| 8.08 | 3 | 35.5 |
| 8.01 | 3 | 170.5 |
| 8.01 | 2 | 153.1 |
| 8.01 | 3 | $125.8(\mathrm{w})$ |
| 7.72 | 2 | $140.5(\mathrm{w})$ |
| 7.72 | 3 | 133.6 |
| 7.72 | 4 | 125.9 |
| 7.72 | 3 | 113.7 |
| 7.72 | 3 | 35.5 |


| $\mathbf{H}^{\mathbf{1}}$$\mathbf{1 3} \mathbf{C ~ g H M B C A D}$ <br> Continued |  |  |
| :---: | :---: | :---: |
| H | bonds | C |
| 7.53 | 2 | $139.8(\mathrm{w})$ |
| 7.53 | 3 | 133.0 |
| 7.53 | 4 | $126.9(\mathrm{w})$ |
| 7.53 | 2 | 124.5 |
| 7.53 | 3 | 115.3 |
| 7.53 | 3 | 35.4 |
| 7.41 | 3 | 166.4 |
| 7.41 | 2 | 142.2 |
| 7.41 | 3 | $124.5(\mathrm{w})$ |
| 1.58 | 3 | 140.5 |
| 1.58 | 2 | 35.5 |
| 1.58 | 1,3 | 32.6 |
| 1.52 | 3 | 139.8 |
| 1.52 | 2 | 35.4 |
| 1.52 | 1,3 | 32.6 |
| 1.33 | 3 | 153.1 |
| 1.33 | 2 | 33.5 |
| 1.33 | 1,3 | 31.7 |
| 1.09 | 3 | 142.2 |
| 1.09 | 2 | 30.6 |
| 1.09 | 1,3 |  |
| $J_{\text {nxh }}=8.0$ |  |  |
|  | $J_{1 \times h}=140.0$ |  |



Figure S2: NMR data for 6-Pd in $\mathrm{CD}_{2} \mathrm{Cl}_{2}$.

| ${ }^{1} \mathrm{H}-{ }^{15} \mathrm{~N} \mathbf{g H M B C A D}{ }^{\text {a }}$ |  |  |
| :---: | :---: | :---: |
| H | bonds | N |
| 8.06 | 2 | -195.8 |
| 8.06 | 3 | -193.5 |
| 7.73 | 4 | -284.0 |
| 7.73 | 3 | -195.8 |
| 7.50 | 4 | -284.0 |
| 7.50 | 3 | -192.6 |
| 7.35 | 3 | -208.3 |
| 7.35 | 2 | -192.6 |
| $\begin{aligned} & { }^{\mathrm{a}} \mathrm{~J}_{\mathrm{nxh}}=5 \mathrm{~Hz} \\ & \mathrm{~J}_{\mathrm{lxh}}=90 \mathrm{~Hz} \end{aligned}$ |  |  |


| ${ }^{1} \mathrm{H}-{ }^{13} \mathrm{C}$ HSQCAD |  |
| :---: | :---: |
| H | C |
| 8.13 | 115.3 |
| 8.07 | 113.6 |
| 8.06 | 112.1 |
| 7.73 | 109.6 |
| 7.50 | 110.7 |
| 7.35 | 110.2 |
| 1.58 | 32.6 |
| 1.51 | 32.6 |
| 1.36 | 31.8 |
| 1.01 | 29.7 |


| gCOSY |
| :---: |
| $8.13 \leftrightarrow 7.50$ |
| $8.07 \leftrightarrow 7.73$ |
| $8.02 \leftrightarrow 7.35$ |


| ${ }^{\mathbf{1}} \mathbf{H}{ }^{\mathbf{1 3}} \mathbf{C} \mathbf{~ g H M B C}$ |  |  |
| :---: | :---: | :---: |
|  |  |  |
| H | bonds | C |
| 8.13 | 3 | 134.8 |
| 8.13 | 3 | 126.0 |
| 8.13 | 3 | 110.7 |
| 8.13 | 3 | 35.4 |
| 8.07 | 3 | 134.9 |
| 8.07 | 3 | 127.1 |
| 8.07 | 2 | $126.0(\mathrm{w})$ |
| 8.07 | 3 | 109.6 |
| 8.07 | 3 | 35.5 |
| 8.06 | 3 | 169.9 |
| 8.06 | 2 | 155.1 |
| 8.02 | 2 | $170.9(\mathrm{w})$ |
| 8.02 | 2 | $142.5(\mathrm{w})$ |
| 8.02 | 3 | $110.2(\mathrm{w})$ |
| 7.73 | 3 | 134.9 |
| 7.73 | 2 | $125.9(\mathrm{w})$ |
| 7.73 | 3 | 113.6 |
| 7.73 | 3 | 35.5 |
| 7.50 | 3 | 134.8 |
| 7.50 | 2 | $124.5(\mathrm{w})$ |
| 7.50 | 3 | 115.3 |
| 7.50 | 3 | 35.4 |


| $\begin{gathered} { }^{1} \mathrm{H}-{ }^{{ }^{13} \mathrm{C} \text { gHMBCAD }} \\ \text { Continued }{ }^{\mathrm{b}} \end{gathered}$ |  |  |
| :---: | :---: | :---: |
| H | bonds | C |
| 7.35 | 3 | 170.9 |
| 7.35 | 2 | 142.5 |
| 1.58 | 3 | 140.3 |
| 1.58 | 2 | 35.5 |
| 1.58 | 1,3 | 326 |
| 1.51 | 3 | 139.6 |
| 1.51 | 2 | 35.4 |
| 1.51 | 1,3 | 32.6 |
| 1.36 | 3 | 155.1 |
| 1.36 | 2 | 33.0 |
| 1.36 | 1,3 | 31.8 |
| 1.01 | 3 | 142.5 |
| 1.01 | 2 | 30.7 |
| 1.01 | 1,3 | 29.7 |
| $\begin{gathered} J_{\mathrm{nxx}}=8.0 \mathrm{~Hz} \\ J_{1 \times \mathrm{h}}=146.0 \mathrm{~Hz} \end{gathered}$ |  |  |



Figure S3: NMR data for $\mathbf{4 - P t C I}$ in $\operatorname{THF}(0.6 \mathrm{~mL})$ and $d_{6}$-benzene $(0.1 \mathrm{~mL})$.

| $\mathbf{H} \mathbf{~}^{\mathbf{1 3}} \mathbf{C} \mathbf{~ g H M B C A D}$ |  |  |
| :---: | :---: | :---: |
|  |  |  |
| H | bonds | C |
| 8.11 | 3 | 35.5 |
| 8.11 | 3 | 111.3 |
| 8.11 | 2 | $127.0(\mathrm{w})$ |
| 8.11 | 3 | 131.8 |
| 7.91 | 2 | 142.5 |
| 7.91 | 3 | $160.6(\mathrm{w})$ |
| 7.74 | 3 | 35.5 |
| 7.74 | 3 | 115.2 |
| 7.74 | 2 | $124.5(\mathrm{w})$ |
| 7.74 | 3 | 131.8 |
| 1.43 | 1,3 | 32.5 |
| 1.43 | 2 | 35.5 |
| 1.43 | 3 | 140.2 |
| 1.28 | 1,3 | 29.8 |
| 1.28 | 2 | 31.2 |
| 1.28 | 3 | 142.5 |
| ${ }^{\mathrm{b}} J_{\mathrm{nxh}}=8.0 \mathrm{~Hz}$ |  |  |
| $J_{1 \times \mathrm{h}}=146.0 \mathrm{~Hz}$ |  |  |


| ${ }^{1} \mathrm{H}-{ }^{15} \mathrm{~N} \mathbf{~ g H M B C A D}$ |  |  |
| :---: | :---: | :---: |
| H | bonds | N |
| 7.91 | 2 | -197.9 |
| 7.91 | 3 | -211.0 |
| 7.74 | 3 | -197.9 |
| 7.74 | 4 | -299.5 |
| ${ }^{\mathrm{a}} \mathrm{J}_{\mathrm{nxh}}=5 \mathrm{~Hz}$ |  |  |
| $\mathrm{~J}_{1 \times \mathrm{hh}}=90 \mathrm{~Hz}$ |  |  |
|  |  |  |


| $\mathbf{g C O S Y}$ |
| :---: |
| $10.92 \leftrightarrow 7.92$ |
| $8.11 \leftrightarrow 7.74$ |



Figure S4: NMR data for $\mathbf{7 - P t}$ in $\operatorname{THF}(0.6 \mathrm{~mL})$ and $d_{6}$-benzene $(0.1 \mathrm{~mL})$.

| $\mathrm{H}-{ }^{15} \mathrm{~N}$ gHMBCAD ${ }^{\mathrm{a}}$ |  |  |
| :---: | :---: | :---: |
| H | bonds | N |
| 7.77 | 3 | -212.7 |
| 7.77 | 2 | -198.4 |
| 7.57 | 4 | -304.9 |
| 7.57 | 3 | -198.4 |
| 7.55 | 2 | -197.3 |
| 7.55 | 3 | -129.9 |
| 7.54 | 4 | -304.9 |
| 7.54 | 3 | -197.3 |
| ${ }^{\mathrm{a}} \mathrm{J}_{\mathrm{nxh}}=5 \mathrm{~Hz}$ |  |  |
| $\mathrm{~J}_{1 \times \mathrm{h}}=90 \mathrm{~Hz}$ |  |  |


| ${ }^{1} \mathrm{H}-^{13} \mathrm{C}$ HSQCAD |  |
| :---: | :---: |
| H | C |
| 8.00 | 114.6 |
| 7.85 | 111.9 |
| 7.77 | 109.2 |
| 7.57 | 110.0 |
| 7.55 | 107.5 |
| 7.54 | 110.2 |
| 1.41 | 32.6 |
| 1.40 | 32.7 |
| 1.28 | 30.9 |
| 1.26 | 29.8 |


| ${ }^{1} \mathrm{H} \cdot{ }^{15} \mathrm{~N}$ gHSQC |  |
| :---: | :---: |
| H | N |
| 10.90 | -212.7 |

Red $=$ Proton, Black $=$ carbon, Blue $=$ Nitrogen

| ${ }^{\mathbf{H}} \mathbf{H}^{\mathbf{1 3}} \mathbf{C}$ gHMBCAD |  |  |
| :---: | :---: | :---: |
| H | bonds | $\mathbf{C}$ |
| 8.00 | 3 | 110.0 |
| 8.00 | 4 | $124.3(\mathrm{w})$ |
| 8.00 | 3 | 125.8 |
| 8.00 | 2 | $127.5(\mathrm{w})$ |
| 8.00 | 3 | 132.0 |
| 8.00 | 3 | 35.4 |
| 7.85 | 3 | 110.2 |
| 7.85 | 2 | $125.8(\mathrm{w})$ |
| 7.85 | 3 | 127.5 |
| 7.85 | 3 | 132.0 |
| 7.85 | 3 | 35.4 |
| 7.77 | 2 | 141.6 |
| 7.77 | 3 | 163.9 |
| 7.57 | 3 | 114.6 |
| 7.57 | 2 | $124.3(\mathrm{w})$ |
| 7.57 | 4 | $127.5(\mathrm{w})$ |
| 7.57 | 3 | 132.0 |
| 7.57 | 2 | $138.8(\mathrm{w})$ |
| 7.57 | 3 | 35.4 |
| 7.55 | 2 | 152.1 |
| 7.55 | 3 | 162.8 |


| $\begin{gathered} { }^{1} \mathrm{H}-{ }_{-13}{ }^{13} \text { Continued }{ }^{\mathrm{b}} \end{gathered}$ |  |  |
| :---: | :---: | :---: |
| H | bonds | C |
| 7.54 | 3 | 111.9 |
| 7.54 | 4 | 125.8(w) |
| 7.54 | 2 | 127.0 |
| 7.54 | 3 | 132.0 |
| 7.54 | 2 | 139.6(w) |
| 7.54 | 3 | 35.4 |
| 1.41 | 1,3 | 32.6 |
| 1.41 | 2 | 35.4 |
| 1.41 | 3 | 138.8 |
| 1.40 | 1,3 | 32.7 |
| 1.40 | 2 | 35.4 |
| 1.40 | 3 | 139.6 |
| 1.28 | 1,3 | 30.9 |
| 1.28 | 2 | 32.2 |
| 1.28 | 3 | 152.1 |
| 1.26 | 1,3 | 29.8 |
| 1.26 | 2 | 31.0 |
| 1.26 | 3 | 141.6 |
| $\begin{gathered} J_{\text {bxh }}=8.0 \mathrm{~Hz} \\ J_{1 \times \mathrm{hh}}=146.0 \mathrm{~Hz} \end{gathered}$ |  |  |



Figure S5: NMR data for 8-Pt in THF ( 0.6 mL ) and $d_{6}$-benzene $(0.1 \mathrm{~mL})$.

| $\mathrm{H} \cdot{ }^{\mathbf{1} 5} \mathrm{~N}$ gHMBCAD ${ }^{\mathrm{a}}$ |  |  |
| :---: | :---: | :---: |
| H | bonds | N |
| 7.74 | 4 | -189.2 |
| 7.44 | 2 | -192.0 |
| 7.44 | 3 | -127.4 |
| 7.38 | 3 | -192.0 |
| ${ }^{\mathbf{a}} \mathbf{J}_{\text {nxh }}=5 \mathrm{~Hz}$ |  |  |
| $\mathbf{J}_{1 \times \mathrm{h}}=90 \mathrm{~Hz}$ |  |  |


| ${ }^{1} \mathrm{H}-{ }^{13} \mathrm{C}$ |  |
| :---: | :---: |
| HSQCAD |  |
| H | C |
| 7.74 | 111.4 |
| 7.44 | 107.1 |
| 7.38 | 109.1 |
| 1.39 | 32.8 |
| 1.26 | 30.9 |


| gCOSY |
| :---: |
| $7.74 \leftrightarrow 7.38$ |

Red $=$ Proton, Black $=$ carbon, Blue $=$ Nitrogen

| ${ }^{\mathbf{1}} \mathbf{H}{ }^{\mathbf{1 3}} \mathbf{C} \mathbf{~} \mathbf{~ H M B C A D}$ |  |  |
| :---: | :---: | :---: |
|  |  |  |
| H | bonds | C |
| 7.74 | 3 | 109.1 |
| 7.74 | 2 | 126.2 |
| 7.74 | 4 | $127.2(\mathrm{w})$ |
| 7.74 | 3 | 132.5 |
| 7.44 | 2 | 151.6 |
| 7.44 | 3 | 166.7 |
| 7.38 | 3 | 111.4 |
| 7.38 | 2 | 127.2 |
| 7.38 | 3 | 132.5 |
| 1.39 | 1,3 | 32.8 |
| 1.39 | 2 | 35.2 |
| 1.39 | 3 | 138.3 |
| 1.26 | 1,3 | 30.9 |
| 1.26 | 2 | 32.2 |
| 1.26 | 3 | 151.6 |
| $J_{\text {nxh }}=8.0 \mathrm{~Hz}$ |  |  |
| $J_{\text {lxh }}=146.0 \mathrm{~Hz}$ |  |  |



Figure S6: ROESY 1D spectrum of $\mathbf{6 - P t}$, irradiating peak at $8.01, \mathrm{C} 4$ on MNHC imidazole and seeing the correlating peaks at 7.72 ppm from the carbazole, and 8.19 ppm from the NH on the PNHC.


Figure S7: ${ }^{1} \mathrm{H}$ NMR spectra of 4-PtCl (red, 1), 7-Pt (green, 2), 19 h after bubbling $\mathrm{H}_{2}$ in solution (blue, 3 ) mostly still 7-Pt with some 4-PtCl, NMR after addition of $\operatorname{AgOTf}$ ( 1.25 equiv) (purple, 4), formation of dimer 6-Pt.


Figure S8: ${ }^{1} \mathrm{H}$ NMR spectra of 4-PtCl (red) in THF ( 0.6 mL ) and $d_{6}$-benzene $(0.1 \mathrm{~mL}),{ }^{1} \mathrm{H}$ NMR of 7-Pt (green), formed from 4-PtCl and $n-\mathrm{BuLi}$ ( $2.5 \mathrm{M}, 1$ equiv), ${ }^{1} \mathrm{H}$ NMR after bubbling ethylene gas through solution for 4 minutes (blue), showing mostly $\mathbf{4}-\mathbf{P t C l}$.


Figure S9: ${ }^{1} \mathrm{H}$ NMR spectra of $\mathbf{8 - P t}($ red, 1$)$ in THF $(0.6 \mathrm{~mL})$ and $d_{6}$-benzene $(0.1 \mathrm{~mL})$, after addition of 1-heptene (20 equiv) (green, 2 ), after heating for 4 h at $70^{\circ} \mathrm{C}$ (purple, 3 ).


Figure S10: ${ }^{1} \mathrm{H}$ NMR spectra of 4-PtOTf (red, 1) in THF $(0.6 \mathrm{~mL})$ and $d_{6}$-benzene $(0.1 \mathrm{~mL})$, after addition of $\operatorname{LiN}(\mathrm{iPr})_{2}(1$ equiv) (green, 2 ), after sitting at room temperature for 27 h (blue, 3), 6-Pt (purple, 4) from Figure S7.


Figure S11: ${ }^{1} \mathrm{H}$ NMR spectra of $\mathbf{4}-\mathrm{PtOTf}(r e d, 1)$ in THF $(0.6 \mathrm{~mL}) d_{6}$-benzene ( 0.1 mL ); $\left[\mathbf{4 - P t}\left(\mathbf{C H}_{3} \mathbf{C N}\right)\right]^{+}$OTf (green, 2), after addition of $\mathrm{CH}_{3} \mathrm{CN}$ (10 equiv); 5 minutes after addition of $\operatorname{LiN}(\mathrm{iPr})_{2}$ ( 1 equiv) (blue, 3 ); 24 hours after addition of $\mathrm{LiN}(\mathrm{iPr})_{2}$ ( 1 equiv) (purple, 4).


Figure S12: Starting 4-PdCI complex in THF ( 0.6 mL ) and $d_{6}$-benzene $(0.1 \mathrm{~mL})($ red, 1$)$; after addition of $\operatorname{LiN}(\mathrm{iPr})_{2}(\sim 1$ equiv), giving a mixture of 7-Pd and $\mathbf{8 - P d}$ (light green, 2); after addition of 1 -heptene and heating at $70^{\circ} \mathrm{C}$ for 16 h (green, 3) giving the same mixture of 7-Pd and $\mathbf{8 - P d}$; after addition of more $\operatorname{LiN}\left(\mathrm{iPr}_{2}\right.$ ( 1 equiv), giving $\mathbf{8}$-Pd with impurities; after addition of $\operatorname{AgOTf}$ ( 1.5 equiv), giving what appears to be deprotonated dimer 6-Pd.

## General experimental

Manipulations were carried out in a nitrogen-filled glovebox or using Schlenk techniques unless otherwise specified. THF and diethyl ether were distilled from sodium and benzophenone, whereas dichloromethane and hexane were distilled from calcium hydride under nitrogen. $d_{6}$-benzene and $\mathrm{CDCl}_{3}$ were purchased from Cambridge Isotope Labs, dried over calcium hydride, and vacuum transferred prior to use. $d_{6}$-acetone and $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ were purchased from Cambridge Isotope Labs, was further deoxygenated by bubbling nitrogen gas through the liquid and transferred to a glovebox. ${ }^{1} \mathrm{H}$ NMR spectra were obtained on Varian spectrometers, $600 \mathrm{MHz} .{ }^{13} \mathrm{C}$ NMR and 2D NMR spectra were obtained on the same instrument. Both ${ }^{1} \mathrm{H}$ NMR and ${ }^{13} \mathrm{C}$ NMR chemical shifts were reported in parts per million downfield from tetramethylsilane and referenced to the solvent resonances ( ${ }^{1} \mathrm{H}$ NMR: 7.16 ppm for $\mathrm{C}_{6} \mathrm{HD}_{5} 7.27 \mathrm{ppm}$ for $\mathrm{CHCl}_{3}, 5.32 \mathrm{ppm}$ for $\mathrm{CHDCl}_{2}$ and 2.05 ppm for $d_{5}$-acetone . ${ }^{13} \mathrm{C}$ NMR: 128.39 ppm for $C_{6} \mathrm{D}_{6}, 77.23$ ppm for $\mathrm{CDCl}_{3}, 54.00 \mathrm{ppm}$ for $\mathrm{CD}_{2} \mathrm{Cl}_{2}$, and 29.92 ppm for $d_{6}$-acetone), where ${ }^{1} \mathrm{H}$ NMR chemical shifts are followed by multiplicity, coupling constants $J$ in hertz, and integration in parentheses.
${ }^{15} \mathrm{~N}$ chemical shifts on unlabeled materials were determined from gradient HSQC or HMBC experiments run on a Varian INOVA 600 MHz spectrometer. Sweep widths and the number of increments in the ${ }^{15} \mathrm{~N}$ dimension were chosen so as to give digital resolutions in the ${ }^{15} \mathrm{~N}$ dimension of less than 1.5 ppm . The ${ }^{15} \mathrm{~N}$ chemical shift of a standard reference sample of formamide solution in $d_{6}$-dimethylsulfoxide ( $90 \%$ ) was determined and set to be -267.8 ppm . Then, using the same sweep width and offsets, samples of nitromethane ( 1.0 M in $\mathrm{CDCl}_{3}$ ) and quinine ( 0.5 M in $\mathrm{CDCl}_{3}$ ) gave ${ }^{15} \mathrm{~N}$ chemical shifts of -4.2 for $\mathrm{CH}_{3} \mathrm{NO}_{2}$ and -72.4 and -349.2 ppm for the $\mathrm{sp}^{2}$ and $\mathrm{sp}^{3}$ hybridized nitrogens of quinine, respectively.

## Synthesis of 6-Pd

To a J. Young NMR tube in a glovebox was added $\mathbf{4 - P d C l}(40.1 \mathrm{mg}, 0.060 \mathrm{mmol})$, sodium tert-butoxide ( $7.0 \mathrm{mg}, 0.072 \mathrm{mmol}$ ), and $\mathrm{C}_{6} \mathrm{D}_{6}(2.0 \mathrm{~mL})$. After 45 minutes the reaction was transferred to a vial in the glovebox and solvent was reduced to approximately 0.75 mL . $\mathrm{Et}_{2} \mathrm{O}$ was then allowed to mix by vapor diffusion in a freezer. The yellow crystals were filtered through a pipet loaded with cotton and washed with pentanes ( $3 \times 0.25 \mathrm{~mL}$ ), then dissolved in $\mathrm{Et}_{2} \mathrm{O}$ and transferred to a vial and dried under oil pump vacuum with $\mathrm{P}_{2} \mathrm{O}_{5}$ yielding 6-Pd ( $19.3 \mathrm{mg}, 0.015 \mathrm{mmol}, 50 \%$ yield). Anal. calcd. for $\mathrm{C}_{68} \mathrm{H}_{86} \mathrm{~N}_{10} \mathrm{Pd}_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)$ (mol. wt. 1274.36): C, 64.09; H, 6.96; N, 10.99. Found C, 63.95; H, 6.91; N, 10.93.

Synthesis of 6-Pt

To a J. Young NMR tube in a glove box was added $4-\mathbf{P t C l}(50.0 \mathrm{mg}, 0.066 \mathrm{mmol})$, sodium tert-butoxide $(6.7 \mathrm{mg}, 0.070 \mathrm{mmol})$, and $\mathrm{C}_{6} \mathrm{D}_{6}(2.5 \mathrm{~mL})$. The solution was heated in a $70^{\circ} \mathrm{C}$ oil bath for 25 minutes,
which was then transferred into a vial in the glovebox and solvent was reduced to approximately 0.75 mL . $\mathrm{Et}_{2} \mathrm{O}$ was allowed to mix by vapor diffusion in a freezer where crystals formed. The yellow crystals were filtered through a pipet loaded with cotton and washed with pentanes ( $3 \times 0.1 \mathrm{~mL}$ ), then transferred to a vial by dissolving in $\mathrm{Et}_{2} \mathrm{O}$ and dried under oil pump vacuum with $\mathrm{P}_{2} \mathrm{O}_{5}$ yielding 6-Pt ( $27.4 \mathrm{mg}, 0.019$ $\mathrm{mmol}, 56 \%$ yield). Anal. calcd. for $\mathrm{C}_{68} \mathrm{H}_{86} \mathrm{~N}_{10} \mathrm{Pt}_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}$ (mol. wt. 1469.70): C, $55.57 ; \mathrm{H}, 6.17 ; \mathrm{N}, 9.53$. Found C, 55.43; H, 6.03; N, 9.60.

Table S1: Crystal data and structure refinement for 6-Pd.

| Identification code | 6-Pd |
| :---: | :---: |
| Empirical formula | C46.50 H56 Cl N5 Pd |
| Formula weight | 826.81 |
| Temperature | 100(2) K |
| Wavelength | 1.54178 £ |
| Crystal system | Monoclinic |
| Space group | C2/c |
| Unit cell dimensions | $a=28.1402(8) \AA$ A $\quad \alpha=90^{\circ}$. |
|  | $\mathrm{b}=15.7664(5) \AA \quad \beta=94.048(2)^{\circ}$. |
|  | $\mathrm{c}=19.0083(6) \AA \quad \gamma=90^{\circ}$. |
| Volume | 8412.4(4) $\AA^{3}$ |
| Z | 8 |
| Density (calculated) | $1.306 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $4.424 \mathrm{~mm}^{-1}$ |
| F(000) | 3464 |
| Crystal size | $0.15 \times 0.11 \times 0.08 \mathrm{~mm}^{3}$ |
| Theta range for data collection | 3.15 to $64.88^{\circ}$. |
| Index ranges | $-28<=\mathrm{h}<=32,-18<=\mathrm{k}<=18,-21<=1<=22$ |
| Reflections collected | 25380 |
| Independent reflections | $6990[\mathrm{R}(\mathrm{int})=0.0355]$ |
| Completeness to theta $=64.88^{\circ}$ | 97.9 \% |
| Absorption correction | Multi-scan |
| Max. and min. transmission | 0.7185 and 0.5566 |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Data / restraints / parameters | 6990 / 37 / 502 |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 1.052 |
| Final R indices [ $\mathrm{I}>2 \operatorname{sigma}(\mathrm{I})$ ] | $\mathrm{R} 1=0.0473, \mathrm{wR} 2=0.1300$ |
| R indices (all data) | $\mathrm{R} 1=0.0576, \mathrm{wR} 2=0.1394$ |
| Largest diff. peak and hole | 1.071 and -1.478 e. $\AA^{-3}$ |

Table S2: Crystal data and structure refinement for 6-Pt.

Identification code
Empirical formula
Formula weight
Temperature
Wavelength
Crystal system
Space group
Unit cell dimensions

Volume
Z
Density (calculated)
Absorption coefficient
F(000)
Crystal size
Crystal color, habit
Theta range for data collection
Index ranges
Reflections collected
Independent reflections
Completeness to theta $=25.00^{\circ}$
Absorption correction
Max. and min. transmission
Refinement method
Data / restraints / parameters
Goodness-of-fit on $\mathrm{F}^{2}$
Final R indices $[\mathrm{I}>2 \operatorname{sigma}(\mathrm{I})]$
R indices (all data)
Largest diff. peak and hole

## 6-Pt

C43 H56 N5 Pt
838.02

100(2) K
$0.71073 \AA$
Monoclinic
C2/c
$\mathrm{a}=28.6827(19) \AA \quad \alpha=90^{\circ}$.
$\mathrm{b}=15.2306(10) \AA \quad \beta=93.9130(10)^{\circ}$.
$\mathrm{c}=19.5645(13) \AA \quad \gamma=90^{\circ}$.
$8526.9(10) \AA^{3}$
8
$1.306 \mathrm{Mg} / \mathrm{m}^{3}$
$3.324 \mathrm{~mm}^{-1}$
3416
$0.34 \times 0.13 \times 0.11 \mathrm{~mm}^{3}$
Orange Block
1.87 to $27.49^{\circ}$.
$-37<=\mathrm{h}<=36,-19<=\mathrm{k}<=19,-19<=1<=25$
48497
$9509[\mathrm{R}(\mathrm{int})=0.0411]$
99.6 \%

Multi-scan
0.7113 and 0.3978

Full-matrix least-squares on $\mathrm{F}^{2}$
9509 / 0 / 526
1.048
$\mathrm{R} 1=0.0283, \mathrm{wR} 2=0.0675$
$R 1=0.0403, w R 2=0.0752$
1.246 and -0.696 e.$\AA^{-3}$

