Electronic Supplementary Information for Dalton Transactions

Supporting Information Pertaining to:

“Click” 1,2,3-triazoles as tunable ligands for late transition metal complexes

Bart M. J. M. Suijkerbuijk,[a] Bas N. H. Aerts,[a] Harm P. Dijkstra,[a] Martin Lutz,[b] Anthony L. Spek,[b] Gerard van Koten,[a] Robertus J. M. Klein Gebbink[a]

[a]*Organic Chemistry and Catalysis, Faculty of Science, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands*
[b]*Crystal and Structural Chemistry, Faculty of Science, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands*

Experimental Section

General. All air-sensitive reactions were performed under a nitrogen atmosphere using standard Schlenck techniques. CH_2Cl_2 was distilled from CaH_2, Et_2O from sodium/benzophenone, and MeOH from $Mg(OEt)_2$ prior to use. Other solvents and all standard reagents were purchased and used as received. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded at 300 MHz and 75 MHz, respectively, on a Varian 300 spectrometer operating at 298 K. If the signals were detected, they are denoted by (b). UV/Vis spectra were recorded on a Cary 50 scan UV-visible spectrophotometer and solid state UV/Vis spectra were recorded on a Varian Cary 5 UV-Vis-NIR spectrophotometer. Elemental microanalyses were performed by Dornis und Kolbe, Mikroanalytisches Laboratorium, Müllheim a/d Ruhr, Germany.

1-benzyl-4-phenyl-1,2,3-triazole (L1)[1]

^1H NMR (acetone-d_6, 298 K): $\delta = 8.37$ (s, 1H, triazole-H), 7.90 (ps d, 2H, 4-phenyl-H_{ortho}), 7.45-7.26 (m, 8H, ArH), 5.68 (s, 2H, CH_2) ppm; ^{13}C NMR (acetone-d_6, 298 K): δ = 148.2, 137.0, 132.2, 129.7, 129.6, 129.1, 128.8, 128.6, 126.2, 121.5, 54.3 ppm.

1,4-dibenzyl-1,2,3-triazole (L2)

Benzylazide (2.0 g, 15 mmol) was dissolved in acetonitrile. Next, 2,6-lutidine (1.2 mL, 10 mmol) was added, followed by 3-phenyl-propyne (1.25 mL, 10 mmol). Finally, $Cu(CH_3CN)_4PF_6$ (48 mg, 0.013 mmol) was added. After stirring for 24 hours at room temperature, the mixture was concentrated in vacuo and washed with Et_2O to yield a slightly pink solid. The solid was taken up in CH_2Cl_2 (20 mL) and washed with ammonia solution (2 × 20 mL) to remove Cu^{2+} salts. The organic layer was dried ($MgSO_4$), filtered and concentrated to dryness to afford **L2** as a white solid (1.73 g, 65%). ^1H NMR (acetone-d_6, 298 K): δ 7.69 (s, 1H, H_{triazole}), 7.33 (m, 5H, ArH) 7.16 (m, 5H, ArH), 5.57 (s, 2H, NCH_2), 4.01 (s, 2H, ArCH_2) ppm; Anal. calcd. for $C_{16}H_{15}N_3$: C 77.08, H 6.06, N 16.85%; found: C 76.92, H 6.15, N 16.75%.

1,4-dihexyl-1,2,3-triazole (L3)

This reaction was carried out under a N_2 atmosphere. Hexylazide (2.0 g, 23 mmol) was dissolved in 25 mL of acetonitrile. Next, 2,6-lutidine (1.86 mL, 16 mmol) was added, followed by 1-octyne (2.33 mL, 16 mmol). Finally, $Cu(CH_3CN)_4PF_6$ (77 mg, 0.021 mmol) was added. After stirring for 24 hours at room temperature, the mixture was concentrated in vacuo, yielding a white solid. The product was purified by column chromatography. Remains of 2,6-lutidine were removed by washing with hexane (30 mL) whereas 1,4-dihexyl-1,2,3-triazole was eluted with CH_2Cl_2. All the fractions containing the product were combined and concentrated in vacuo. The product was obtained as a blue oily substance, which was taken up in CH_2Cl_2 (20 mL) and washed with ammonia solution (2 × 20 mL) to remove Cu^{2+} salts. The organic layer was dried ($MgSO_4$), filtered and concentrated to dryness to afford **L3** as a white solid (1.19 g, 31%).

^{1}H NMR (acetone-d_6, 298 K): δ = 7.72 (s, 1H, triazole-*H*), 4.35 (t, 2H, $^3J_{HH}$ = 7.2 Hz, NCH_2), 2.66 (t, 2H, $^3J_{HH}$ = 7.5 Hz, ArCH_2), 1.87 (qui, 2H, $^3J_{HH}$ = 7.2 Hz, NCH_2CH_2), 1.64 (qui, 2H, $^3J_{HH}$ = 7.5 Hz, $ArCH_2CH_2$), 1.31 (m, 12H, CH_2), 0.87 (m, 6H, CH_3) ppm; ^{13}C NMR (acetone-d_6, 298 K): δ = 148.4, 121.9, 50.4, 32.3, 31.9, 31.0, 30.3, 29.6, 26.8, 26.3, 23.2, 23.1, 14.3, 14.2 ppm; Anal. calcd. for $C_{14}H_{27}N_3$: C 70.83, H 11.46, N 17.70%; found: C 70.80, H 11.41, N 17.68%.

1-benzyl-4-phenyl-1*H*-1,2,3-triazole, 2,6-bis[(dimethylamino)methyl]-1-palladio(II)-benzene complex (1L1)

$AgBF_4$ (74 mg, 380 μmol) was suspended in dry CH_2Cl_2 (15 mL) and after 5 min of stirring **1** (140 mg, 371 μmol) was added at once. Almost immediately an off-white precipitate started to form (AgBr) and stirring was continued for 15 min. 1-Benzyl-4-phenyl-1,2,3-triazole (**L1**, 90.2 mg, 383 μmol) was then added and the suspension was shielded from ambient light with Al foil and stirred for an additional 4 h. The mixture was subsequently filtered over a pad of Celite® and the residue was washed twice with 10 mL of CH_2Cl_2. The filtrate was concentrated to 10 mL and Et_2O (80 mL) was quickly added to give a cream-colored solid, which was isolated by means of centrifugation and dried *in vacuo*. Yield: 220 mg (96%).

^{1}H NMR (acetone-d_6, 298 K): δ = 8.84 (br, 1H, triazole-*H*), 8.49 (d, 2H, Ar*H*), 7.70-7.35 (m, 8H, Ar*H*), 7.07 (dd, 1H, Ar*H*), 6.90 (d, 2H, Ar*H*), 5.90 (s, 2H, ArCH_2NNN), 4.18 (s, 4H, Ar$CH_2$$NMe_2$), 2.63 (s, 12H, $N(CH_3)_2$) ppm; ^{13}C NMR (acetone-d_6, 298 K): δ = 149.0, 146.7, 144.1, 130.3, 129.9, 129.6, 129.2, 127.5, 126.4, 121.1, 74.9, 55.7, 52.8 ppm; all other signals were not resolved due to extreme line-broadening;

Anal. calcd. for $C_{27}H_{32}BF_4N_5Pd$: C 52.32, H 5.20, N 11.30%; found: C 52.19, H 5.28, N 11.23%; Light yellow crystals suitable for X-ray crystal structure determination were obtained by slow evaporation of a CH_2Cl_2/hexanes solution of the product.

Synthesis of NCN-pincer Pt complexes **2L1**, **2L2**, and **2L3**:

General procedure: $AgBF_4$ (1.05 eq) was suspended in dry CH_2Cl_2 (30 mM) and after 5 min of stirring **2** (1 eq) was added at once. Almost immediately an off-white precipitate started to form (AgBr) and stirring was continued for 15 min. The respective **Ln** was then added and the suspension was shielded from ambient light with Al foil and stirred for an additional 5 h. The mixture was subsequently filtered over a pad of Celite® and the residue was washed twice with 10 mL of CH_2Cl_2. The filtrate was concentrated to 10 mL and Et_2O (80 mL) was quickly added to give **2Ln**, which was isolated by centrifugation and dried *in vacuo*.

1-benzyl-4-phenyl-1,2,3-triazole, 2,6-bis[(dimethylamino)methyl]-1-platino(II)-benzene complex (2L1)

White powder. Yield: 630 mg (96%).

^{1}H NMR (acetone-d_6, 298 K): δ = 9.01 (s, 1H, triazole-*H*), 8.69 (d, $^3J_{HH}$ = 6.9 Hz, 2H, 4-phenyl-H_{ortho}), 7.63-7.30 (m, 8H, Ar*H*), 7.06 (dd, 1H, Ar*H*), 6.93 (d, $^3J_{HH}$ = 7.5 Hz, 2H, Ar*H*), 5.93 (s, 2H, $ArCH_2NNN$), 4.24 (m, 4H, $ArCH_2NMe_2$), 2.85 (s, 6H, $^3J_{PtH}$ = 39.6 Hz, $N(CH_3)_2$), 2.62 (s, 6H, $^3J_{PtH}$ = 39.3 Hz, $N(CH_3)_2$) ppm; ^{13}C NMR (acetone-d_6, 298 K): δ = 149.3 (C_{ipso}), 145.6, 144.1, 135.7, 130.8, 130.2, 130.0, 129.7, 129.3, 129.0, 128.3, 126.3, 125.7, 120.3, 77.8, 56.1, 54.5, 54.0 ppm; Anal. calcd. for $C_{27}H_{32}BF_4N_5Pt$: C 45.77, H 4.55, N 9.89%; found: C 45.87, H 4.62, N 9.84%; White crystals suitable for X-ray crystal structure determination were obtained by shaking the amorphous solid with acetone.

1,4-dibenzyl-1,2,3-triazole, 2,6-bis[(dimethylamino)methyl]-1-platino(II)-benzene complex (2L2)

White powder. Yield: 90 mg (98%).

^{1}H NMR (acetone-d_6, 298 K): δ = 8.36 (s, 1H, triazole-*H*), 7.38 (m, 10H, benzyl-Ar*H*) 7.05 (dd, 1H, Ar*H*), 6.93 (d, $^3J_{HH}$ = 7.6 Hz, 2H, Ar*H*), 5.84 (s, 2H, triazole-NCH_2), 4.63 (s, 2H, triazole-CCH_2), 4.22 (m, 4H, $ArCH_2NMe_2$), 2.85 (s, 6H, $^3J_{PtH}$ = 39.6 Hz, N(C*H*$_3$)$_2$), 2.70 (s, 6H, $^3J_{\mathrm{PtH}}$ = 39.6 Hz, N(C*H*$_3$)$_2$), ppm; ^{13}C NMR (acetone-d_6, 298 K): δ = 149.2 (C_{ipso}), 145.7, 144.9, 138.3, 135.8, 129.8, 129.7 (2×), 129.6, 129.1, 128.0, 127.3, 125.7, 120.3, 77.7, 55.8, 54.3, 54.0, 32.6 ppm; Anal. calcd. for $C_{28}H_{34}BF_4N_5Pt$: C 46.55, H 4.74, N 9.69%; found: C 46.65, H 4.78, N 9.78%; White crystals suitable for X-ray crystal structure determination were obtained by slow diffusion of Et_2O into a concentrated solution of **2L2** in CH_2Cl_2.

1,4-dihexyl-1,2,3-triazole, 2,6-bis[(dimethylamino)methyl]-1-platino(II)-benzene complex (2L3)

Colorless oily substance. Yield: 90 mg (98%).

^{1}H NMR (acetone-d_6, 298 K): δ = 8.44 (s, 1H, triazole-*H*), 7.06 (dd, 1H, Ar*H*), 6.93 (d, $^3J_{\mathrm{HH}}$ = 7.5 Hz, 2H, Ar*H*), 4.61 (t, 2H, $^3J_{\mathrm{HH}}$ = 7.2 Hz, NC*H*$_2$), 4.28 (m, 4H, ArC*H*$_2$NMe$_2$), 3.27 (t, 2H, $^3J_{\mathrm{HH}}$ = 7.5 Hz, ArC*H*$_2$), 2.89 (s, 6H, $^3J_{\mathrm{PtH}}$ = 39.6 Hz, N(C*H*$_3$)$_2$), 2.87 (s, 6H, $^3J_{\mathrm{PtH}}$ = 39.6 Hz, N(C*H*$_3$)$_2$), 2.02 (qui, 2H, $^3J_{\mathrm{HH}}$ = 6.9 Hz, NCH$_2$C*H*$_2$), 1.87 (qui, 2H, $^3J_{\mathrm{HH}}$ = 7.5 Hz, ArCH$_2$C*H*$_2$), 1.50 (qui, 2H, $^3J_{\mathrm{HH}}$ = 7.5 Hz, ArCH$_2$CH$_2$C*H*$_2$), 1.33 (m, 10H, C*H*$_2$), 0.87 (m, 6H, C*H*$_3$) ppm; ^{13}C NMR (acetone-d_6, 298 K): δ = 149.8 (C_{ipso}), 145.7, 145.2, 125.9, 125.6, 120.1, 77.8, 54.5, 54.0, 52.2, 32.2, 31.7, 30.7, 30.4, 29.8, 29.3, 26.8, 26.6, 23.1, 23.0, 14.3, 14.2 ppm; This compound was obtained as a highly viscous oil. A satisfactory elemental analysis could not be obtained.

Determination of K_{ass}'.

2L1 and 1.1-1.3 eq. of **Lx** were weighed in an NMR tube and dissolved in 500 µL of boiling acetone-d_6. After equilibration of the mixture (as inferred from three identical, consecutive ^{1}H NMR spectra), the equilibrium concentrations of all compounds were determined by the average of two independent integrations of the appropriate signals. In all cases, at least one signal of each of the components of the equilibrium mixture was independent in the spectrum and could thus be reliably integrated. Figure S1 shows a representative example.

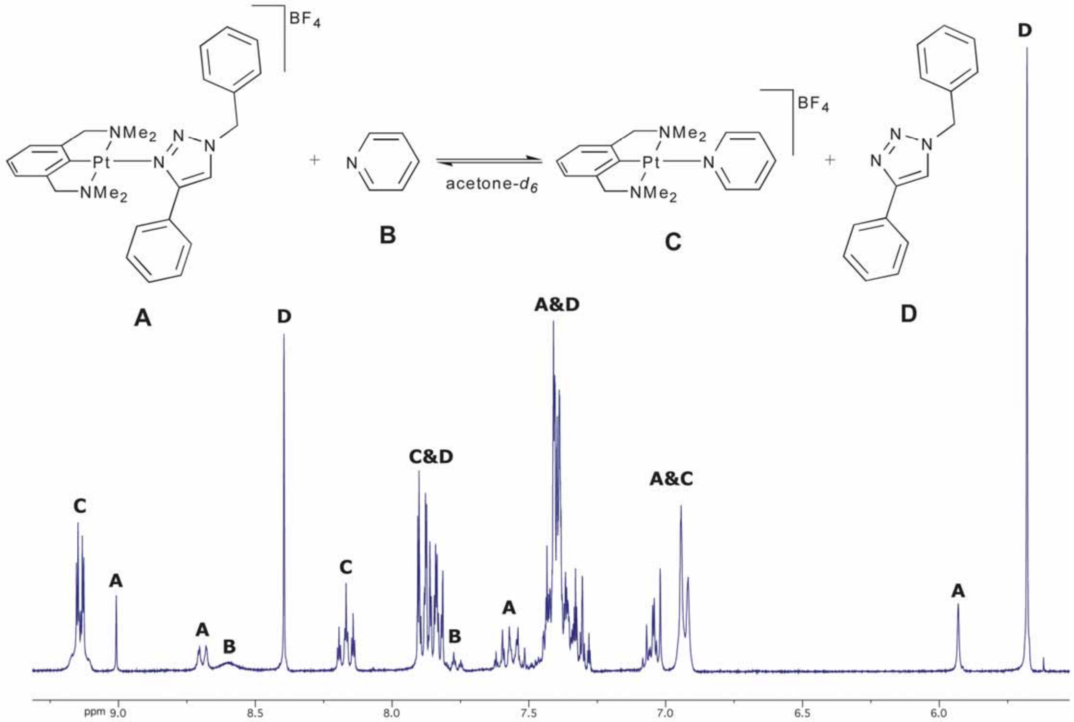

Figure S1. Low field region of the ^{1}H NMR spectrum of the equilibrium mixture of **1L1** (**A**) and pyridine (**B**) in acetone-d_6 at 298 K.

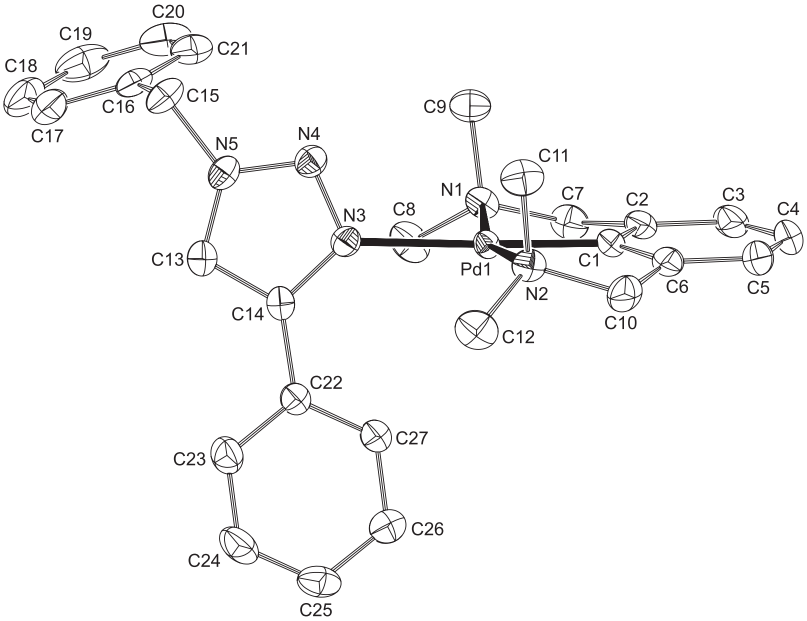

Figure S2. Displacement ellipsoid plot of **1L1**, drawn at the 50% probability level. Hydrogen atoms and BF_4 anion are omitted for clarity.

X-ray crystal structure determination of 1L1

$[C_{27}H_{32}N_5Pd](BF_4)$, Fw = 619.79, colourless block, 0.15 x 0.15 x 0.15 mm^3, orthorhombic, Pbca (no. 61), a = 18.7077(2), b = 13.95732(10), c = 20.6417(3) Å, V = 5389.74(10) $Å^3$, Z = 8, D_x = 1.528 g/cm^3, μ = 0.74 mm^{-1}. 102749 Reflections were measured on a Nonius Kappa CCD diffractometer with rotating anode (graphite monochromator, λ = 0.71073 Å) up to a resolution of $(\sin \theta/\lambda)_{max}$ = 0.65 $Å^{-1}$ at a temperature of 150 K. An absorption correction based on multiple measured reflections was applied (0.77-0.89 correction range). 6200 Reflections were unique (R_{int} = 0.0410). Initial coordinates were taken from the isostructural **2L1**. The structure was then refined with SHELXL-97[2] against F^2 of all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located in the difference Fourier map and refined with a riding model. 347 Parameters were refined with no restraints. R1/wR2 [$I > 2\sigma(I)$]: 0.0263/0.0531. R1/wR2 [all refl.]: 0.0436/0.0591. S = 1.035. Residual electron density between -0.35 and 0.47 e/$Å^3$. Geometry calculations and checking for higher symmetry was performed with the PLATON program.[3]

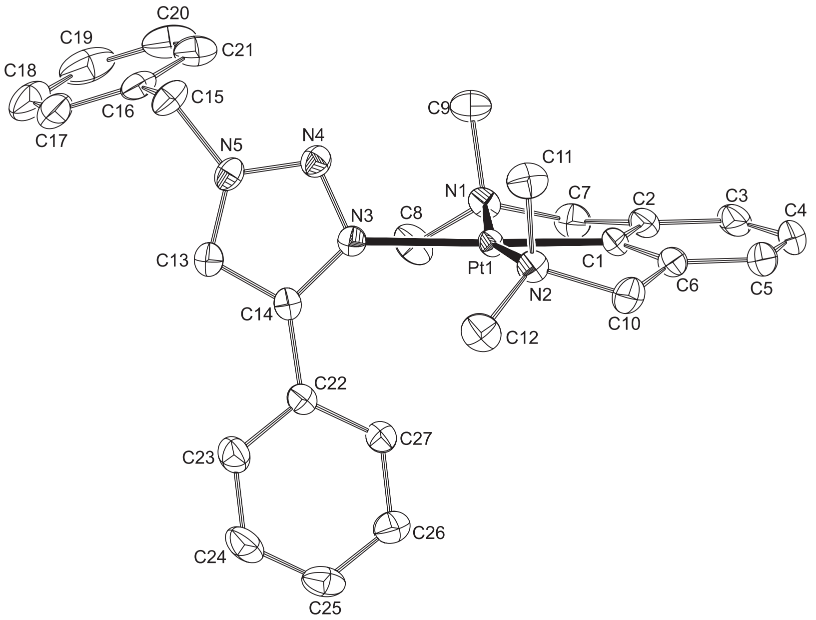

Figure S3. Displacement ellipsoid plot of **2L1**, drawn at the 50% probability level. Hydrogen atoms and BF_4 anion are omitted for clarity.

X-ray crystal structure determination of 2L1

$[C_{27}H_{32}N_5Pt](BF_4)$, Fw = 708.48, colourless plate, 0.24 x 0.15 x 0.06 mm^3, orthorhombic, Pbca (no. 61), a = 18.6226(4), b = 13.9422(7), c = 20.7557(6) Å, V = 5389.0(3) Å^3, Z = 8, D_x = 1.746 g/cm^3, μ = 5.26 mm^{-1}. 133892 Reflections were measured on a Nonius Kappa CCD diffractometer with rotating anode (graphite monochromator, λ = 0.71073 Å) up to a resolution of $(\sin \theta/\lambda)_{max}$ = 0.65 Å^{-1} at a temperature of 150 K. An analytical absorption correction was applied (0.32-0.70 correction range). 6195 Reflections were unique (R_{int} = 0.0507). The structure was solved with automated Patterson methods[4] and refined with SHELXL-97[2] against F^2 of all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located in the difference Fourier map and refined with a riding model. 347 Parameters were refined with no restraints. R1/wR2 [$I > 2\sigma(I)$]: 0.0162/0.0340. R1/wR2 [all refl.]: 0.0244/0.0371. S = 1.053. Residual electron density between -0.55 and 0.67 e/Å^3. Geometry calculations and checking for higher symmetry was performed with the PLATON program.[3]

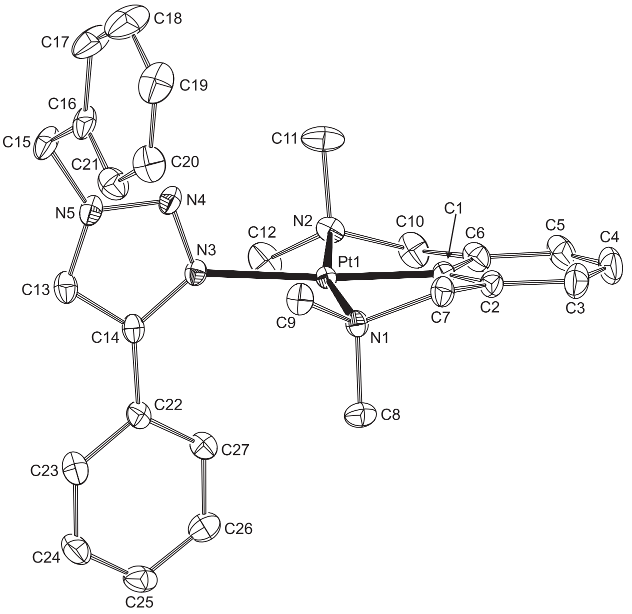

Figure S4. Displacement ellipsoid plot of **2L1 · 0.5CH$_2$Cl$_2$**, drawn at the 50% probability level. Hydrogen atoms, BF$_4$ anion, and CH$_2$Cl$_2$ solvent molecule are omitted for clarity.

X-ray crystal structure determination of 2L1 · 0.5CH$_2$Cl$_2$

[C$_{27}$H$_{32}$N$_5$Pt](BF$_4$) · 0.5CH$_2$Cl$_2$, Fw = 750.94, colourless block, 0.12 x 0.12 x 0.12 mm^3, triclinic, P $\overline{1}$ (no. 2), a = 11.1861(3), b = 12.05785(13), c = 12.9754(4) Å, α = 78.165(1), β = 68.692(1), γ = 63.542(1)°, V = 1457.75(6) Å^3, Z = 2, D$_x$ = 1.711 g/cm^3, μ = 4.96 mm^{-1}. 39400 Reflections were measured on a Nonius Kappa CCD diffractometer with rotating anode (graphite monochromator, λ = 0.71073 Å) up to a resolution of (sin $\theta/\lambda)_{max}$ = 0.65 Å^{-1} at a temperature of 110 K. An absorption correction based on multiple measured reflections was applied (0.42-0.55 correction range). 6685 Reflections were unique (R$_{int}$ = 0.0299). The structure was solved with automated Patterson methods[4] and refined with SHELXL-97[2] against F^2 of all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located in the difference Fourier map and refined with a riding model. Due to the proximity to a crystallographic inversion center the CH$_2$Cl$_2$ solvent molecule has only an occupancy of 0.5. 374 Parameters were refined with no restraints. R1/wR2 [I > 2σ(I)]: 0.0182/0.0366. R1/wR2 [all refl.]: 0.0227/0.0377. S = 1.049. Residual electron density between -0.96 and 1.21 e/Å^3. Geometry calculations and checking for higher symmetry was performed with the PLATON program.[3]

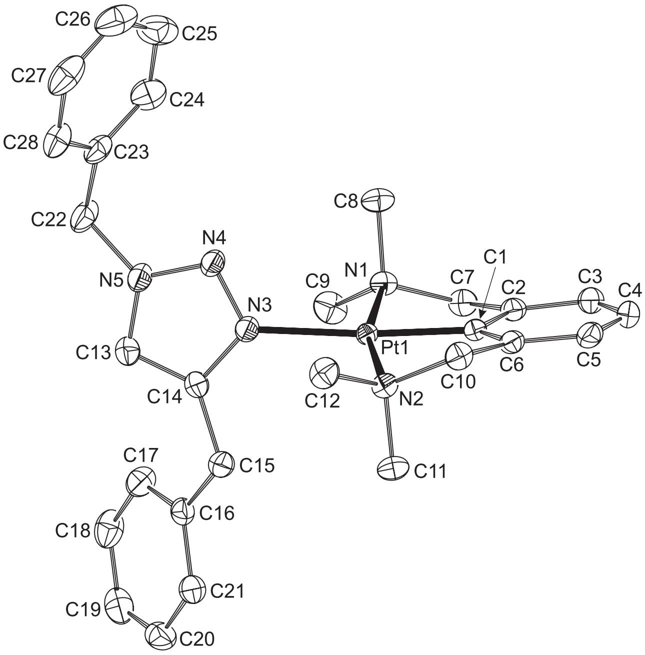

Figure S5. Displacement ellipsoid plot of **2L2**, drawn at the 50% probability level. Hydrogen atoms and disordered BF_4 anion are omitted for clarity.

X-ray crystal structure determination of 2L2

$[C_{28}H_{34}N_5Pt](BF_4)$, Fw = 722.50, colourless block, 0.30 x 0.21 x 0.18 mm^3, triclinic, $P\overline{1}$ (no. 2), a = 10.5401(5), b = 10.8373(5), c = 13.5859(5) Å, α = 90.459(2), β = 112.708(2), γ = 99.581(2)°, V = 1407.14(11) Å^3, Z = 2, D_x = 1.705 g/cm^3, μ = 5.04 mm^{-1}. 49444 Reflections were measured on a Nonius Kappa CCD diffractometer with rotating anode (graphite monochromator, λ = 0.71073 Å) up to a resolution of $(\sin \theta/\lambda)_{max}$ = 0.65 Å^{-1} at a temperature of 150 K. An absorption correction based on multiple measured reflections was applied (0.27-0.40 correction range). 6453 Reflections were unique (R_{int} = 0.0203). The structure was solved with automated Patterson methods[4] and refined with SHELXL-97[2] against F^2 of all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters. The BF_4 anion was refined with a disorder model. All hydrogen atoms were located in the difference Fourier map and refined with a riding model. 393 Parameters were refined with 142 restraints (restraints for BF_4 anion). R1/wR2 [$I > 2\sigma(I)$]: 0.0117/0.0272. R1/wR2 [all refl.]: 0.0132/0.0276. S = 1.074. Residual electron density between -0.47

and 0.35 e/Å^3. Geometry calculations and checking for higher symmetry was performed with the PLATON program.[3]

References

1. T. R. Chan, R. Hilgraf, K. B. Sharpless and V. V. Fokin, *Org. Lett.*, 2004, **6**, 2853.
2. G. M. Sheldrick, *SHELXL-97*, (1997) University of Göttingen, Germany.
3. A. L. Spek, *J. Appl. Cryst.*, 2003, **36**, 7.
4. P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, S. Garcia-Granda, R. O. Gould, J. M. M. Smits and C. Smykalla, *DIRDIF99*, (1999) University of Nijmegen, The Netherlands.