Supplementary Information: J. S. Hart, G. S. Nichol, J. B. Love, "Directed secondary interactions in metal complexes of tripodal imine and amide ligands."

Experimental procedures

The synthesis of $[Ti(O^iPr)_2(HL^2)]$ (R' = Me, Cy) were carried out using standard Schlenk procedures or dry box techniques under an atmosphere of dry dinitrogen and using solvents dried by a Vacuum Atmospheres solvent purification assembly. Deuterated C_6D_6 was dried over potassium, trap-to-trap vacuum distilled, and freeze-pump-thaw degassed three times prior to use. All other synthetic procedures were carried out using commercial-grade solvent in air. Pyrrole was distilled under reduced pressure prior to use. The syntheses of 2,2',2''-tripyrrylethane and *tris*(5,5',5''-formyl-2,2',2''-pyrryl)ethane were carried out as described in the literature.(REF) All other chemicals were used as purchased.

^{1}H NMR spectra were recorded at 298 K, unless otherwise stated on Bruker DPX250, DPX360, AVA400, and AVA500 spectrometers at operating frequencies of 250.13, 360.13, 399.90, and 500.13 MHz, respectively. $^{13}C\{^1H\}$ spectra were recorded on the DPX360 and AVA500 spectrometers at operating frequencies of 90.55 and 125.76 MHz, respectively. ^{1}H and $^{13}C\{^1H\}$ spectra were referenced internally to residual protio solvent (^{1}H) or solvent (^{13}C) resonances and are reported relative to tetramethylsilane (δ = 0 ppm). Mass spectra were recorded by Mr Alan Taylor of the mass spectrometry service of the University of Edinburgh's School of Chemistry using a Thermo LCQ instrument. IR spectra were recorded on a Perkin Elmer Spectrum 65 FTIR or a JASCO FT/IR-410 spectrometer as solids or KBr disks. UV-Vis spectra were recorded on a Varian Cary 50 scan UV-Visible spectrophotometer. Elemental analyses were carried out by Mr Stephen Boyer at London Metropolitan University.

Crystallography

Data for $[CuCl(H_2L^1)]$ were collected at 150(2) K using an Oxford Cryosystems low temperature device attached to an Oxford diffraction SuperNova dual wavelength diffractometer equipped with an Atlas CCD detector and using mirror monochromated Cu*K*a radiation (λ = 1.54180 Å).

Data for $[Pd(HL^1)]$ and $[Pd(ClH_2L^1)]$ were collected at 150(2) K using and Oxford Cryosystems low temperature device attached to an Oxford diffraction Eos diffractometer equipped with an Eos detector and using graphite monochromated Mo*K*a radiation (λ = 0.71073 Å).

Data for $[Ti(O^iPr)_2(H_3L^{2b})]$ were collected at 160(2) K using a Rigaku Mercury375R/M CCD (XtaLABmini) diffractometer using graphite monochromated Mo*K*a radiation (λ = 0.71075 Å).

The structures were solved by direct methods using the WinGX suite of programs[1] and refined using full-matrix least square refinements on $|F^2|$ using SHELXTL-97.[2] Unless otherwise stated, all non hydrogen atoms were refined with anisotropic displacement parameters and all hydrogen atoms were placed at calculated positions and refined as part of a riding model. For $[CuCl(H_2L^1)]$, the acetonitrile molecule has a partial occupancy of 60% and was refined as such. The ether molecule of crystallisation was handled using an isotropic whole molecule disorder model with a refined occupancy ratio of 0.670(5):0.330(5). The Flack (1983) parameter is refined based on 7243 Friedel pairs. Despite the value of 0.488(14), the structure shows no missed inversion symmetry and is refined as an inversion twin. The data for $[Pd(ClH_2L^1)]$ was complete up to 0.95 Å and was cut at this distance, giving rise to an A-alert in the Check CIF.

Synthesis of [CuCl(H_2L^1)]

To a mixture of H_3L^1 (0.48 g, 0.87 mmol) in MeOH (50 mL) and NEt_3 (0.48 g, 4.8 mmol), was added a solution of $CuCl_2$ (0.11 g, 0.82 mmol) in MeOH (20 mL). The resulting solution was stirred for 8 h at room temperature after which it was filtered and solvents were evaporated under reduced pressure to afford 0.37 g, 65 % of [CuCl(H_2L^1)] as a green powder. Single crystals were grown by slow diffusion of Et_2O into a saturated CH_3Cl solution.

Analysis Found: C, 64.69, H, 7.32, N, 12.84 % $C_{35}H_{47}CuClN_6$ requires C, 64.59, H, 7.28, N, 12.91 %; ESMS (+ve ion): *m/z* 438.34 ($[CuL]^+$ loss of protonated arm, 46 %), 614.17 ($[Cu\text{-}H_2L]^+$, 100 %), 650.05 ($[M+H^+]$, 12 %); IR (KBr): υ 3417 (NH), 1660 (C=N), 1581 (C=C) cm^{-1}; UV-vis ($CHCl_3$, 25 °C): 314 nm (ε = 28478 $dm^3mol^{-1}cm^{-1}$), 370 nm (ε = 19739 $dm^3mol^{-1}cm^{-1}$). μ_{eff} (Evans' method) = 1.94 BM.

Synthesis of [Cu(HL^1)]

To a suspension of H_3L (1.1 g, 1.9 mmol) in MeCN (50 mL), was added a solution of $Cu(OAc)_2$ (0.38 g, 1.9 mmol) in MeCN (200 mL). The reaction was stirred at room temperature 2 h after which the solvents were evaporated under reduced pressure. The residual solids were dissolved in THF (10 mL) and precipitated by the addition of hexane (50 mL). The liquors were decanted and the precipitate was washed with hexane (3 × 10 mL) and dried under reduced pressure affording 0.71 g, 60 % of [Cu(HL^1)] as green solids.

Analysis Found: C, 68.43, H, 7.55, N, 13.68 % $C_{35}H_{46}N_6Cu$ requires C, 68.37, H, 7.46, N, 13.59 %; ESMS (+ve ion): *m/z* 438.29 ($[CuL]^+$ loss of protonated arm, 37 %), 614.26 (M^+, 100 %); IR (KBr): υ 3446 (NH), 1653 (C=N), 1576 (C=C) cm^{-1}; UV-vis ($CHCl_3$, 25 °C): 280 nm (ε = 64693 $dm^3mol^{-1}cm^{-1}$), 290 nm (ε = 32237 $dm^3mol^{-1}cm^{-1}$), 320 nm (ε = 40570.2 $dm^3mol^{-1}cm^{-1}$); μ_{eff} (Evans' method) = 2.23 BM

Synthesis of [Pd(H_2L^1)][Cl]

To a mixture of H_3L (0.099, 0.18 mmol) in CH_2Cl_2 (10 mL) and NEt_3 (0.70 mL), was added a solution of $PdCl_2(MeCN)_2$ (0.052 g, 0.20 mmol) in CH_2Cl_2 (15 mL). The resulting mixture was stirred at room temperature for 3 h after which the addition of hexane (20 mL) ensured the precipitation of the product which was filtered, washed with hexane (2 × 10 mL) and dried under reduced pressure affording 0.075 g, 60 % of [Pd(H_2L^1)][Cl] product as a yellow powder. Single crystals were grown by slow diffusion of hexane into a saturated CH_2Cl_2 solution.

^{1}H NMR (399.90 MHz, $CDCl_3$): δ_H 13.34 (br. s, 1H, pyrrole NH), 12.86 (br. m, 1H, NH), 7.57 (s, 2H, imine), 7.38 (d, 1H, $^3J_{HH}$ = 15.5 Hz, protonated imine), 6.72 (dd, 1H, $^3J_{HH}$ = 4.1 Hz, $^4J_{HH}$ = 2.0 Hz, pyrrole), 6.65 (d, 2H, $^3J_{HH}$ = 3.91 Hz, pyrrole), 6.35 (d, 2H, $^3J_{HH}$ = 3.91 Hz, pyrrole), 5.71 (dd, 1H, $^3J_{HH}$ = 4.1 Hz, $^4J_{HH}$ = 2.0 Hz, pyrrole), 3.42 (m, 1H, CH Cy), 3.23 (m, 2H, CH Cy), 2.31 (s, 3H, CH_3), 2.24 - 1.13 (m, 30H, Cy) ppm; $^{13}C\{^1H\}$ NMR (125.76 MHz, $CDCl_3$): δ_C 158.3 (q), 156.5, 147.3, 145.5 (q), 137.1 (q), 129.8, 121.6 (q), 116.4, 113.1, 108.5, 63.2, 61.3, 47.2 (q), 34.1, 32.7, 27.3, 26.2, 26.1, 24.7 ppm; Analysis Found: C, 60.47, H, 6.68, N, 11.92 % $C_{35}H_{47}N_6PdCl$ requires C, 60.60, H, 6.83, N, 12.12 %; ESMS (+ve ion): *m/z* 481.29 [PdL^+ loss of protonated arm, 19.1 %], 657.27 [$Pd(H_2L)^+$, 100 %]; IR (KBr): υ 3417 (NH), 1658 (C=N), 1568 (C=C) cm^{-1}

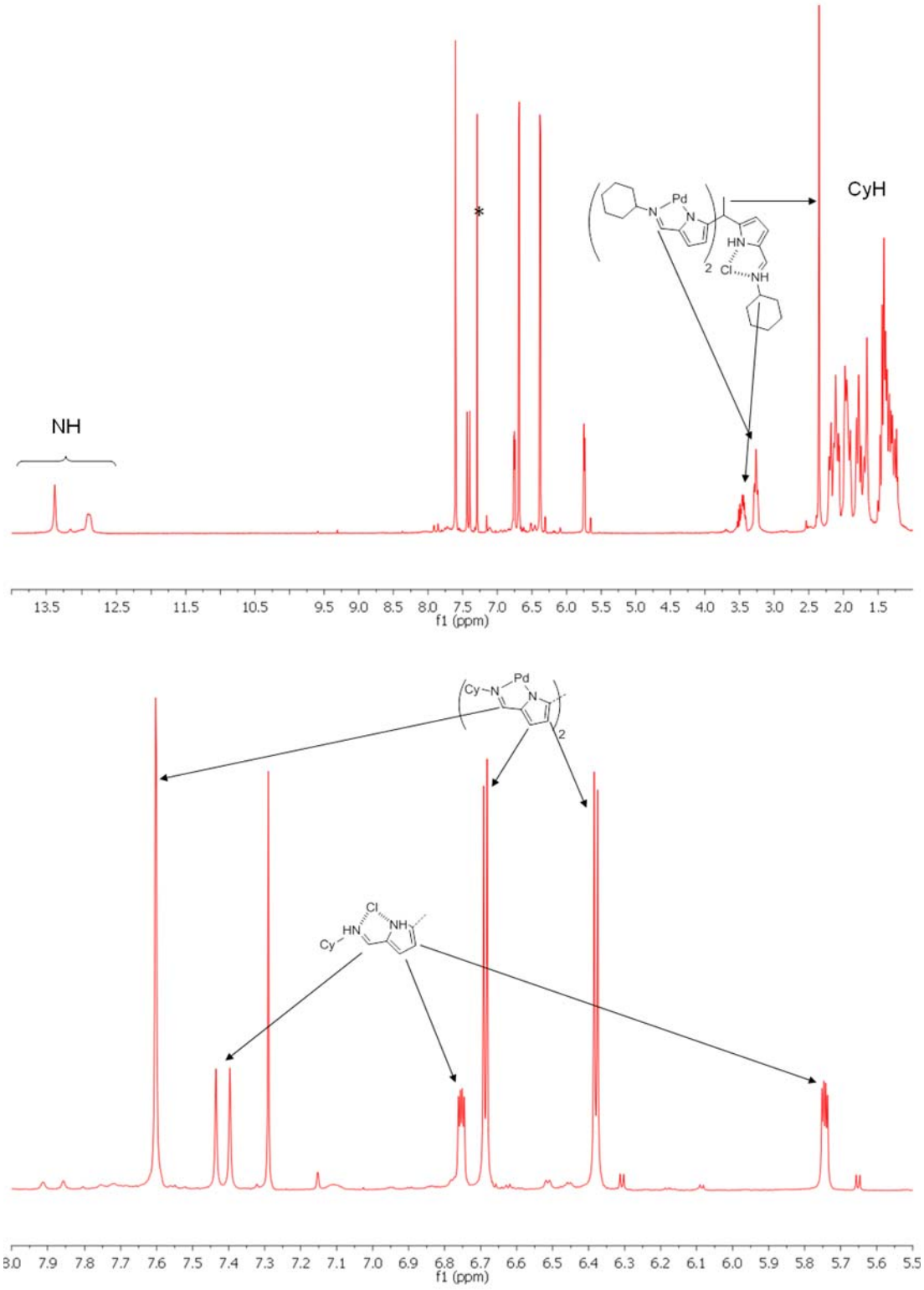

Figure S1: ^{1}H NMR spectrum of [Pd(H_2L^1)][Cl] in $CDCl_3$ (top) and the expansion of its aromatic region.

Synthesis of [Pd(HL^1)]

To a mixture of H_3L (0.50 g, 0.91 mmol) in MeCN (10 mL) and NEt_3 (2 mL), was added a solution of $Pd(OAc)_2$ (0.21 g, 0.94 mmol) in MeCN (50 mL). The reaction was stirred for 2 h at room temperature. The precipitate was filtered, washed with MeCN (2 × 10 mL) and dried overnight under

high vacuum affording 0.39 g, 62 % of [Pd(HL[1])] as a yellow solid. Single crystals were obtained by cooling of a saturated solution of MeCN.

^{1}H NMR (400MHz, $CDCl_3$): δ_H 7.59 (s, 1H, imine), 7.57 (s, 2H, imine), 6.65 (d, 2H, $^{3}J_{HH}$ = 3.4 Hz, pyrrole), 6.60 (d, 1H, $^{3}J_{HH}$ = 3.9 Hz, pyrrole), 6.16 (d, 2H, $^{3}J_{HH}$ = 3.4 Hz, pyrrole), 5.89 (d, 1H, $^{3}J_{HH}$ = 3.9 Hz, pyrrole), 3.24 (m, 2H, CH Cy), 3.23 (m, 1H, CH Cy), 2.06 (s, 3H, CH_3), 2.22 - 1.00 (m, 30H, Cy) ppm; ^{13}C{^{1}H} NMR (125.76 MHz, $CDCl_3$): δ_C 156.4 (q), 149.2, 147.5, 142.0 (q), 136.8 (q), 129.8, 116.1 (q), 114.3, 107.7, 106.5, 69.3, 63.2, 46.9 (q), 34.5, 34.1, 31.0, 26.2, 25.8, 25.0; Analysis. Found: C, 63.81, H, 6.93, 12.67 % $C_{35}H_{46}N_6Pd$ requires C, 63.96, H, 7.05, N, 12.79 % ; ESMS (+ve ion): *m/z* 481.29 [PdL^+ loss of free arm, 52 %], 657.36 [Pd(HL), 100 %]; IR (KBr): υ 3410 (NH), 1637 (C=N), 1569 (C=C); UV-vis ($CHCl_3$, 25 °C): 390 nm (ε =11851 $dm^3mol^{-1}cm^{-1}$), 295 nm (ε = 22734 $m^3mol^{-1}cm^{-1}$).

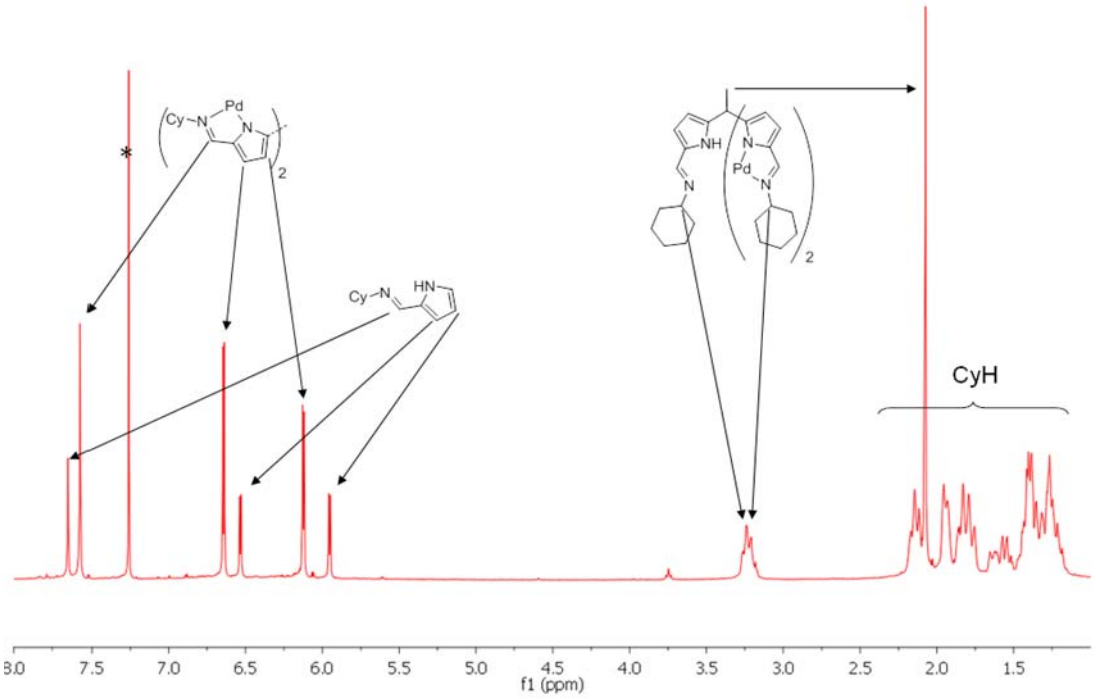

Figure S2: ^{1}H NMR spectrum of [Pd(HL[1])] in $CDCl_3$.

Synthesis of H_3L^{CCl3}

To a degassed solution of trichloroacetyl chloride (12 g, 67 mmol) in Et_2O (10 mL) at 0 °C under N_2, was slowly added a solution of 2,2',2''-tripyrrylethane (3.0 g, 13 mmol) in Et_2O (200 mL). The mixture was allowed to warm to room temperature and stirred for 2 h after which the precipitate was filtered, washed with Et_2O (3 × 25 mL) and dried in air to yield 5.6 g, 65 % of H_3L^{CCl3} as a dark pink solid.

^{1}H NMR (250.13 MHz, $CDCl_3$): δ_H 10.07 (br. s, 3H, NH), 7.37 (dd, 3H, $^{3}J_{HH}$ = 4.13 Hz, $^{4}J_{HH}$ = 2.31 Hz, pyrrole), 6.27 (dd, 3H, $^{3}J_{HH}$ = 4.13 Hz, $^{4}J_{HH}$ = 2.81 Hz, pyrrole), 2.23 (s, 3H, CH_3) ppm; ^{13}C{^{1}H} NMR (90.15 MHz, $CDCl_3$): δ_C 173.4 (q), 143.5 (q), 123.1, 122.6 (q), 110.8, 94.4 (q), 41.8 (q), 27.7 ppm; Analysis. Found: C, 36.76, H, 1.62, N, 6.26 % $C_{20}H_9Cl_9N_3O_3$ requires C, 36.49, H, 1.38, N, 6.38 %; ESMS (+ve ion): *m/z* 659.1 (M^+, 100 %); IR (KBr): υ 3331 (pyrrole NH), 1642 (C=O) cm^{-1}

Synthesis of H_6L^{2a} (R' = Cy)

Neat cyclohexylamine (4.5 g, 45 mmol) was added to H_3L^{CCl3} (3.0 g, 4.5 mmol) and the resulting mixture stirred at room temperature for 16 h. The colourless precipitate was filtered and washed with Et_2O (3 × 10 mL) affording 2.6 g, 95 % of H_6L^{2a} as a colourless powder.

^{1}H NMR (360.13 MHz, DMSO): δ_H 10.9 (br. s, 3H, pyrrole NH), 7.78 (d, 3H, $^3J_{HH}$ = 7.30 Hz, amide NH), 6.71 (s, 3H, pyrrole), 5.77 (s, 3H, pyrrole), 3.78 (br. s, 3H, CH Cy), 1.84 (s, 3H, CH_3), 1.90 - 1.33 (m, 15H, Cy), 1.13 - 0.75 (m, 15H, Cy) ppm; $^{13}C\{^1H\}$ NMR (90.55 MHz, DMSO): δ_C 159.7 (q), 139.7 (q), 126.4 (q), 110.0, 106.9, 47.6, 32.9, 26.7, 25.4, 25.1 ppm; Analysis. Found: C, 69.97, H, 8.05, N, 13.99 % $C_{35}H_{48}N_6O_3$ requires C, 69.91, H, 7.93, N, 13.87 %; ESMS (+ve ion): *m/z* 644.8 ($[M+2Na]^+$, 100 %), 600.8 (M^+, 45 %); IR (KBr): υ 3436 (amide NH), 3288 (pyrrole NH), 1633 (amide C=O) cm^{-1}.

Synthesis of $[Ti(O^iPr)_2(H_4L^{2a})]$ (R' = Cy)

To solution of H_6L^{2a} (0.23 g, 0.38 mmol) in THF (15 mL), was added a solution of $Ti(O^iPr)_4$ (0.12 g, 0.42 mmol) in THF (5 mL) at -20 °C. The mixture was stirred for 2 h and allowed to warm to room temperature after which the solvent was evaporated under reduced pressure to afford 0.18 g, 62 % of $[Ti(O^iPr)_2(H_4L^{2a})]$ as a pale yellow powder.

^{1}H NMR (360.13 MHz, $CDCl_3$): δ_H 9.32 (br. s, 1H, NH), 6.65 (d, 2H, $^3J_{HH}$ = 3.67 Hz, pyrrole), 6.42 (d, 2H, $^3J_{HH}$ = 3.67 Hz, pyrrole), 6.36 (d, 1H, $^3J_{HH}$ = 18.1 Hz, amide NH), 5.90 (d, 2H, $^3J_{HH}$ = 7.34 Hz, pyrrole), 5.33 (d, 1H, $^3J_{HH}$ = 7.34 Hz, pyrrole), 5.08 (sep, 1H, $^3J_{HH}$ = 5.79 Hz, CH), 4.95 (sep, 1H, $^3J_{HH}$ = 5.36 Hz, CH), 4.08 (m, 2H, CH Cy), 4.01 (m, 1H, CH Cy), 2.31 (s, 3H, CH_3), 1.35 (d, 6H, $^3J_{HH}$ = 5.36 Hz, CH_3), 1.20 (d, 3H, $^3J_{HH}$ = 5.79 Hz, CH_3), 2.00 - 0.80 (m, 30H, Cy) ppm; $^{13}C\{^1H\}$ NMR (125.76 MHz, C_6D_6/THF): δ_C 164.8, 159.5 (q), 148.4, 143.0 (q), 134.4, 125.7 (q), 109.4 (q), 107.8, 105.4 (q), 105.0, 100.4 (q), 83.7, 71.3, 67.4, 62.6, 60.9, 58.9, 58.5, 56.8, 50.6, 49.2, 47.4, 42.5, 33.5, 29.5 (q), 13.0 ppm; Analysis. Found: C, 64.25, H, 8.02, N, 10.90 % $C_{41}H_{64}N_6O_5Ti$ requires C, 64.05, H, 8.39, N, 10.93 %; IR (KBr): υ 3290 (pyrrole NH), 1591 (C=O), 1540 (C=O free) cm^{-1}

Synthesis of H_6L^{2b} (R' = Me)

A 40 % solution of methylamine in water (3.5 g, 45 mmol) was added to H_3L^{CCl3} (3.0 g, 4.5 mmol). The resulting mixture was stirred at room temperature for 2 h after which the precipitate was filtered and washed with Et_2O (3 × 10 mL) affording 1.6 g, 89 % of H_6L^{2b} as colourless solids.

^{1}H NMR (360.13 MHz, MeOD): δ_H 6.44 (d, 3H, $^3J_{HH}$ = 3.42 Hz, pyrrole), 5.77 (br. s, 3H, pyrrole), 2.69 (s, 9H, branch CH_3), 1.96 (s, 3H, CH_3) ppm; $^{13}C\{^1H\}$ NMR (90.55 MHz, MeOD): δ_C 162.3 (q), 139.9 (q), 124.9 (q), 109.7, 106.2, 40.2 (q), 25.8, 24.4 ppm; Analysis. Found: C, 60.46, H, 5.98, N, 21.07 % $C_{20}H_{24}N_6O_3$ requires C, 60.59, H, 6.10, N, 21.20 %; ESMS (+ve ion): *m/z* 418.92 ($[M+Na]^+$, 46.62 %), 814.46 ($2[M+Na]^+$, 100 %); IR (KBr): υ 3306 (NH), 1612(C=O), 1538 (C=C) cm^{-1}

Synthesis of $[Ti(O^iPr)_2(H_4L^{2b})]$ (R' = Me)

To solution of $Ti(O^iPr)_4$ (0.099 g, 0.35 mmol) in MeCN (5 mL), was added a solution of H_6L^{2b} (0.14 g, 0.35 mmol) in THF (15 mL). The reaction mixture was stirred for 2 h at -20 °C upon which a precipitate formed. The solvents were decanted and the crystalline precipitate was washed with hexane (2 × 5 mL) to afford 0.13 g, 66 % of $[Ti(O^iPr)_2(H_4L^{2b})]$. Single crystals were obtained by slow cooling a saturated MeCN solution.

^{1}H NMR (250.13 MHz, CD_3CN): δ_H 8.57 (br. s, 1H, NH), 7.07 (br. s, 2H, NH), 6.57 (d, 2H, $^{3}J_{HH}$ = 3.79 Hz, pyrrole), 6.29 (br. s, 1H, pyrrole NH), 6.25 (dd, 1H, $^{3}J_{HH}$ = 2.65 Hz, $^{4}J_{HH}$ = 1.08 Hz, pendant pyrrole), 6.02 (d, 2H, $^{3}J_{HH}$ = 3.79 Hz, pyrrole), 5.82 (dd, 1H, $^{3}J_{HH}$ = 2.65 Hz, $^{4}J_{HH}$ = 1.08 Hz, pendant pyrrole), 4.65 (sep, 1H, $^{3}J_{HH}$ = 5.91 Hz, CH), 4.53 (sep, 1H, $^{3}J_{HH}$ = 5.91 Hz, CH), 2.94 (d, 6H, $^{3}J_{HH}$ = 4.61 Hz, CH_3), 2.61 (d, 3H, $^{3}J_{HH}$ = 4.86 Hz, CH_3), 1.97 (s, 3H, CH_3), 1.16 (d, 6H, $^{3}J_{HH}$ = 5.91 Hz, CH_3), 1.00 (d, 3H, $^{3}J_{HH}$ = 5.91 Hz, CH_3), 0.87 (d, 3H, $^{3}J_{HH}$ = 5.91 Hz, CH_3) ppm; $^{13}C\{^{1}H\}$ NMR (125.76 MHz, C_6D_6/MeCN): δ_C 166.0, 161.3 (q), 147.8, 144.4 (q), 134.4, 125.0 (q), 116.6 (q), 110.2, 108.5 (q), 105.9, 104.3 (q), 77.1, 75.9, 67.4, 63.3, 41.8, 40.8 (q), 29.7, 26.0, 25.2 ppm; Analysis. Found: C, 56.01, H, 6.37, N, 15.18 % $C_{26}H_{36}N_6O_5Ti$ requires C, 55.72, H, 6.47, N, 14.99 %; IR (KBr): υ 3291 (pyrrole NH), 1600 (C=O), 1558 (C=O) cm^{-1}.

Table 1. Crystallographic details

	[Pd(HL^1)]	[Pd(ClH$_2$L^1)]	[CuCl(H$_2$L^1)]	[Ti(O^{i}Pr)$_2$(H$_4$L^{2b})]
Chemical formula	$C_{35}H_{46}N_6Pd$	$C_{36}H_{48}Cl_4N_6Pd$	$C_{75.20}H_{105.80}Cl_2Cu_2N_{12.60}O$	$C_{32}H_{45}N_9O_5Ti$
M_r	657.18	813.00	1399.45	683.67
Crystal system, space group	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/c$	Orthorhombic, $Pna2_1$	Monoclinic, $P2_1/c$
Temperature (K)	150	150	150	160
a, b, c (Å)	11.6995 (6), 13.0619 (7), 13.1928 (7)	17.130 (2), 11.0690 (14), 20.818 (3)	16.9395 (3), 16.1910 (3), 26.7675 (5)	11.704 (10), 35.30 (3), 9.483 (12)
α, β, γ (°)	115.965 (5), 113.289 (5), 94.036 (4)	90, 108.888 (14), 90	90, 90, 90	90, 112.407 (12), 90
V (Å^3)	1590.89 (15)	3734.7 (8)	7341.5 (2)	3622 (7)
Z	2	4	4	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Cu $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.62	0.82	1.78	0.29
Crystal size (mm)	0.92 × 0.14 × 0.08	0.24 × 0.12 × 0.11	0.30 × 0.10 × 0.06	0.20 × 0.20 × 0.20
Diffractometer	Agilent Technologies Xcalibur	Agilent Technologies Xcalibur	Agilent Technologies SuperNova	Rigaku Mercury375R
Absorption correction	Multi-scan	Analytical	Analytical	Multi-scan
T_{min}, T_{max}	0.818, 1.000	0.977, 0.986	0.6130, 0.8949	0.945, 0.945
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	35168, 7757, 6644	16832, 4554, 3473	57040, 14997, 14290	19852, 6022, 4080
R_{int}	0.047	0.057	0.041	0.124
θ_{max} (°)	29.2	22.0	75.9	25.0
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.032, 0.066, 1.02	0.042, 0.091, 1.04	0.046, 0.1250, 1.068	0.087, 0.209, 1.12
No. of reflections	7757	4554	14997	6022
No. of parameters	379	425	838	435
No. of restraints	0	0	8	0
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained	Riding
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	0.38, -0.64	0.64, -0.55	0.56, -0.35	0.32, -0.39
Absolute structure	–	–	Flack H D (1983), Acta Cryst. A39, 876-881	–
Flack parameter	–	–	0.488(15)	–