Supplementary Information

"Chlorometallate and palladium cluster complexes of wide-span diimine and diamine ligands"

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General experimental details

The synthesis of 1,4-dibromomethyl-2,3,5,6-tetramethylbenzene and 2,3,5,6-tetramethylterephthalaldehyde were carried out as described in the literature.[1, 2] All synthetic procedures were carried out using commercial-grade solvent in air and all chemicals were used as purchased. ^{1}H spectra were recorded at 298 K on a Bruker AVA400 at 399.90 MHz and ^{13}C{^{1}H} NMR spectra were recorded at 298 K on a Bruker AVA500 at 125.76. All ^{1}H NMR were referenced internally to residual protio-solvent resonances. Electrospray mass spectra were recorded using a Thermo Finnigan LCQ Classic ion trap mass spectrometer, IR spectra on a Perkin Elmer Spectrum 65 FTIR or a JASCO FT/IR-410 spectrometer as solids or KBr disks and UV-Vis spectra were recorded on a Varian Cary 50 scan UV-Visible spectrophotometer. Elemental analyses were carried out by Mr. Stephen Boyer at the London Metropolitan University.

Synthesis of L^{ImAr}

To solution of 2,3,5,6-tetramethylterephthalaldehyde (2.0 g, 11 mmol) in MeCN (50 mL), was added 2,6-di(isopropyl)aniline (3.72 g, 22 mmol). Trifluoroacetic acid (1 mL) was added to the solution dropwise. The mixture was stirred for 1 h at room temperature after which it was neutralised using KOH (aq). The yellow precipitate was filtered and washed with MeCN (3 x 10 mL) and dried under vacuum to afford 4.82 g, 86 % of L^{ImAr} as a colourless solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.67 (s, 2H, imine CH), 7.27–7.15 (m, 6H, aromatic), 3.18 (sep, $^{3}J_{HH}$ = 6.81 Hz, 4H, isopropyl CH), 2.55 (s, 12H, Me), 1.25 (d, $^{3}J_{HH}$ = 6.81 Hz, 24H, Me); ^{13}C{^{1}H} NMR (500 MHz, $CDCl_3$): δ_C 164.6, 149.6 (q), 137.9 (q), 135.8 (q), 134.6 (q), 124.4, 123.3, 28.0, 24.0, 16.8; Found: C, 84.76, H, 9.57, N, 5.47 % $C_{36}H_{48}N_2$ requires: C, 84.98, H, 9.51, N, 5.51 %; ESIMS (+ve ion): m/z 509.22 ($[M+H]^+$, 100 %); IR (ATR): υ 1630 (C=N), 1588 (C=C) cm^{-1}.

Synthesis of L^{ImR}

To a solution of 2,3,5,6-tetramethylterephthalaldehyde (4.29 g, 23 mmol) in MeCN (100 mL) was added tert-butylamine (4.12 g, 56 mmol). Trifluoroacetic acid (0.5 mL) was added dropwise and the mixture stirred for 1 h at room temperature. The resulting colourless precipitate was filtered, washed with MeCN (3 x 10 mL), and dried under vacuum to afford 4.9 g, 70 % of the L^{ImR}.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.55 (s, 2H, CH imine), 2.17 (s, 12H, Me), 1.38 (s, 18H, ^{t}Bu); ^{13}C{^{1}H} NMR (500 MHz, $CDCl_3$): δ_C 158.1, 136.8 (q), 131.7 (q), 58.2 (q), 29.7, 16.3; Found: C, 80.03, H, 10.57, N, 9.05 % $C_{20}H_{32}N_2$ requires: C, 79.94, H, 10.73, N, 9.32 %; ESIMS (+ve ion): m/z 301.09($[M]^+$, 100 %), 245.10 ($[M-^{t}Bu]^+$, 14.5 %); IR (ATR): υ 1651 (C=N) cm^{-1}

Synthesis of L^{AmAr}

Method 1: To a mixture of 1,4-dibromomethyl-2,3,5,6-tetramethylbenzene (5.6 g) in MeCN (150 mL), triethylamine (5 mL) was added, followed by 2,6-diisopropylaniline. The mixture was boiled for 8 h, after which the solvents were evaporated under reduced pressure. The residues were dissolved in water, extracted into CH_2Cl_2 (100 mL), and evaporated to dryness. The crude colourless solids were recrystallised from hot MeCN to afford 4.8 g, 53 % of L^{AmAr} as colourless microcrystals.

Method 2: To a solution of 2,3,5,6-tetramethylterephthalaldehyde (0.1 g, 0.192 mmol) in THF (5 mL) was added a solution of $NaBH_4$ (0.08 g, 2.11 mmol) in MeOH (5 mL). The mixture was stirred vigorously for 2 h, after which the solvents were evaporated under reduced pressure. The residues were taken up in water (10 mL) and extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$, and the solvents evaporated under reduced pressure to yield a colourless crude solid that was recrystallised from MeCN to afford 0.02 g, 20 % of L^{AmAr} as a colourless solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.16 – 7.05 (m, 6H, aromatics), 4.22 (s, 4H, CH_2), 3.30 (sep, $^{3}J_{HH}$ = 6.63 Hz, 4H, CH), 3.07 (br. s, 2H, NH), 2.35 (s, 12H, CH_3), 1.25 (d, $^{3}J_{HH}$ = 6.63 Hz, 24H, CH_3); ^{13}C{^{1}H} NMR (500 MHz, $CDCl_3$): δ_C 144.2 (q), 141.7 (q), 136.2 (q), 133.5 (q), 123.8, 123.3, 50.8,

28.1, 24.4, 16.9. Found: C, 84.46, H, 10.13, N, 5.51 % $C_{36}H_{52}N_2$ requires: C, 84.32, H, 10.22, N, 5.46 %; ESIMS (+ve ion): m/z 1022.69 ([2M-3H$^+$], 71%), 513.18 ([M+H]$^+$, 69 %), 336.23 ([M-2,6-di(isopropyl)amine]$^+$, 100 %), IR (KBr): υ 3400 (NH), 1442 (C-N) cm^{-1}.

Synthesis of L^{AmR}

Method 1: To a solution of L^{ImR} (2.5 g, 8.2 mmol) in MeOH (40 mL) was added $NaBH_4$ (1.56 g, 41.1 mmol). The resulting solution was stirred for 2 h at room temperature after which the solvent was evaporated under reduced pressure. The residues were extracted into a mixture of CH_2Cl_2 (10 mL) and water (10 mL) and the organic phase dried over $MgSO_4$. The solvents were evaporated under reduced pressure to afford 2.3 g, 92 % of L^{AmR} as a colourless solid.

Method 2: A mixture of tert-butylamine (2 mL) and 1,4-dibromomethyl-2,3,5,6-tetramethylbenzene (0.1 g, 0.313 mmol) was heated to reflux for 8 h. The resulting precipitate was isolated by filtration under reduced pressure and dried under vacuum to afford 0.038 mg, 40 % L^{AmR} as a colourless solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 3.73 (s, 4H, CH_2), 2.31 (s, 12H, Me), 1.22 (s, 18H, ^{t}Bu); ^{13}C{^{1}H} NMR (500 MHz, $CDCl_3$): δ_C 135.8 (q), 133.2 (q), 50.5 (q), 41.6, 29.1, 15.1; Found: C, 78.91, H, 12.00, N, 9.24 % $C_{20}H_{36}N_2$ requires: C, 78.88, H, 11.92, N, 9.20 %; ESIMS (+ve ion): m/z 304.97 ([M]$^+$, 100%), 232.05 ([M-^{t}BuN]$^+$, 44.1 %), IR (KBr): υ 3334 (NH), 1473 (C-C), 1228 (CN) cm^{-1}

Synthesis of $[H_2L^{AmR}][CoCl_4]$

To a solution of L^{AmR} (0.1 g, 0.328 mmol) in Et_2O (10 mL) was added a solution HCl (0.024 g, 0.657 mmol) in Et_2O (2 mL). The resulting solution was stirred for 30 min after which a suspension of $CoCl_2$ (0.043 g, 0.33 mmol) in Et_2O (5 mL) was added. The resulting mixture was stirred at room temperature for 1 h after which the resulting precipitate was filtered under reduced pressure and washed with Et_2O (3 x 5mL) to afford 0.138 g, 63 % of $[H_2L^{AmR}][CoCl_4]$ as blue solids.

Found: C, 47.45, H, 7.58, N, 5.37 % $C_{20}H_{36}Cl_4CoN_2$ requires: C, 47.54, H, 7.18, N, 5.54 %; IR (KBr): υ 3419 (NH), 1635 (C-C aromatic), 1593 (C=N) cm^{-1}

Synthesis of $[H_2L^{ImAr}][Zn_4Cl_{10}]$

To a solution of L^{ImAr} (0.1 g, 0.195 mmol) in Et_2O (10 mL), was added a solution HCl (0.0142 g, 0.4 mmol) in Et_2O (2 mL). The resulting solution was stirred for 30 minutes after which a solution of $ZnCl_2$ (0.106 g, 0.78 mmol) in Et_2O (5 mL) was added. The mixture was stirred at room temperature for 1 h and the resulting precipitate filtered under reduced pressure and washed with Et_2O (3 x 5mL) to afford 0.138 g, 63 % of $[H_2L^{ImAr}][Zn_4Cl_{10}]$ as a colourless solid.

Found: C, 38.46, H, 4.52, N, 2.31 % $C_{36}H_{50}Cl_{10}N_2Zn_4$ requires: C, 38.37, H, 4.47, N, 2.49 %; IR (KBr): υ 3587 (NH), 1653 (C=N), 1608 (C=C) cm^{-1}

Synthesis of $[Pd_3Cl_6(L^{ImAr})]$

A solution of $PdCl_2(MeCN)_2$ (0.15 g, 0.585 mmol) in CH_2Cl_2 (15 mL) was added slowly to a solution of L^{ImAr} (0.1 g, 0.192 mmol) in CH_2Cl_2 (5 mL). The mixture was stirred for 3 h at room temperature, after which the precipitate was filtered, washed with hexane (3 x 5 mL), and dried under vacuum to afford 0.140 g, 70 % of $[Pd_3Cl_6(L^{ImAr})]$ as a red solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ_H 8.38 (s, 2H, imine CH), 7.50–7.25 (m, 6H, aromatic), 3.75 (s, 6H, aryl CH_3), 3.56 (sep, $^3J_{HH}$ = 6.97 Hz, 2H, isopropyl CH), 3.49 (sep, $^3J_{HH}$ = 6.97 Hz, 2H, isopropyl CH), 2.09 (s, 6H, aryl CH_3), 1.85 (d, $^3J_{HH}$ = 6.97 Hz, 6H, Me), 1.48 (d, $^3J_{HH}$ = 6.97 Hz, 6H, Me), 1.25 (d, $^3J_{HH}$ = 6.97 Hz, 6H, Me), 1.23 (d, $^3J_{HH}$ = 6.97 Hz, 6H, Me); ^{13}C{^{1}H} NMR (500 MHz, $CDCl_3$): δ_C 180.5, 145.5 (q), 141.7 (q), 141.5 (q), 137.4 (q), 135.7 (q), 133.8 (q), 129.2, 125.3, 124.7, 29.1, 28.6, 26.1, 25.2, 24.4, 23.7, 20.9, 17.0; Found: C, 41.39, H, 4.58, N, 2.54 % $C_{36}H_{48}Cl_6N_2Pd_3$ requires: C, 41.55, H, 4.65, N, 2.69 %; ESIMS (+ve ion): m/z 507.49 ([L-H]$^+$, 92 %), 613.21 ([L + Pd]$^+$, 27 %) 717.17 ([L + 2Pd]$^+$, 82 %), 757.15 ([L + Pd_2Cl]$^+$, 80 %), 860.96 ([L + Pd_2Cl_4]$^+$, 100 %) ; IR (ATR): υ 1608 (C=N), 1590 (C=C) cm^{-1}; UV-vis ($CHCl_3$, 25 °C): λ_{max} 431 nm (ε = 2711.4 dm^{3}mol^{-1}cm^{-1}).

Synthesis of $[Pd_3Cl_6(L^{ImR})]$

To a solution of $PdCl_2(MeCN)_2$ (0.26 g, 0.985 mmol) in CH_2Cl_2 (15 mL) was slowly added to a solution of L^{ImR} (0.1 g, 0.328 mmol) in CH_2Cl_2 (5 mL). The mixture was stirred for 3 h at room temperature, after which the resulting precipitate was filtered, washed with hexane (3 x 5 mL), and dried under vacuum to afford 0.21 g, 77 % of $[Pd_3Cl_6(L^{ImR})]$ as red solids.

^1H NMR (400MHz, $CDCl_3$): δ_H 8.45 (s, 2H, CH imine), 2.94 (s, 6H, CH_3), 1.90 (s, 6H, CH_3), 1.86 (s, 18H, ^{t}Bu); $^{13}C\{^1H\}$ NMR (500 MHz, $CDCl_3$): δ_C 176.8, 136.4 (q), 134.3 (q), 132.2 (q), 68.0 (q), 32.5, 20.5, 17.2; Found: C, 29.01, H, 3.71, N, 3.26 % $C_{20}H_{32}Cl_6N_2Pd_3$ requires: C, 28.86, H, 3.87, N, 3.37 %; ESIMS (+ve ion): m/z 299.28 ([L-2H$^+$], 100 %), 549.04 ([L+2Pd+Cl], 81 %), 682.01 ([L+Pd_3Cl_5], 73 %), IR (ATR): υ 1628 (C=N) cm^{-1}, UV-vis ($CHCl_3$, 25 °C): λ_{max} 310 nm (ε = 5421.8 $dm^3mol^{-1}cm^{-1}$).

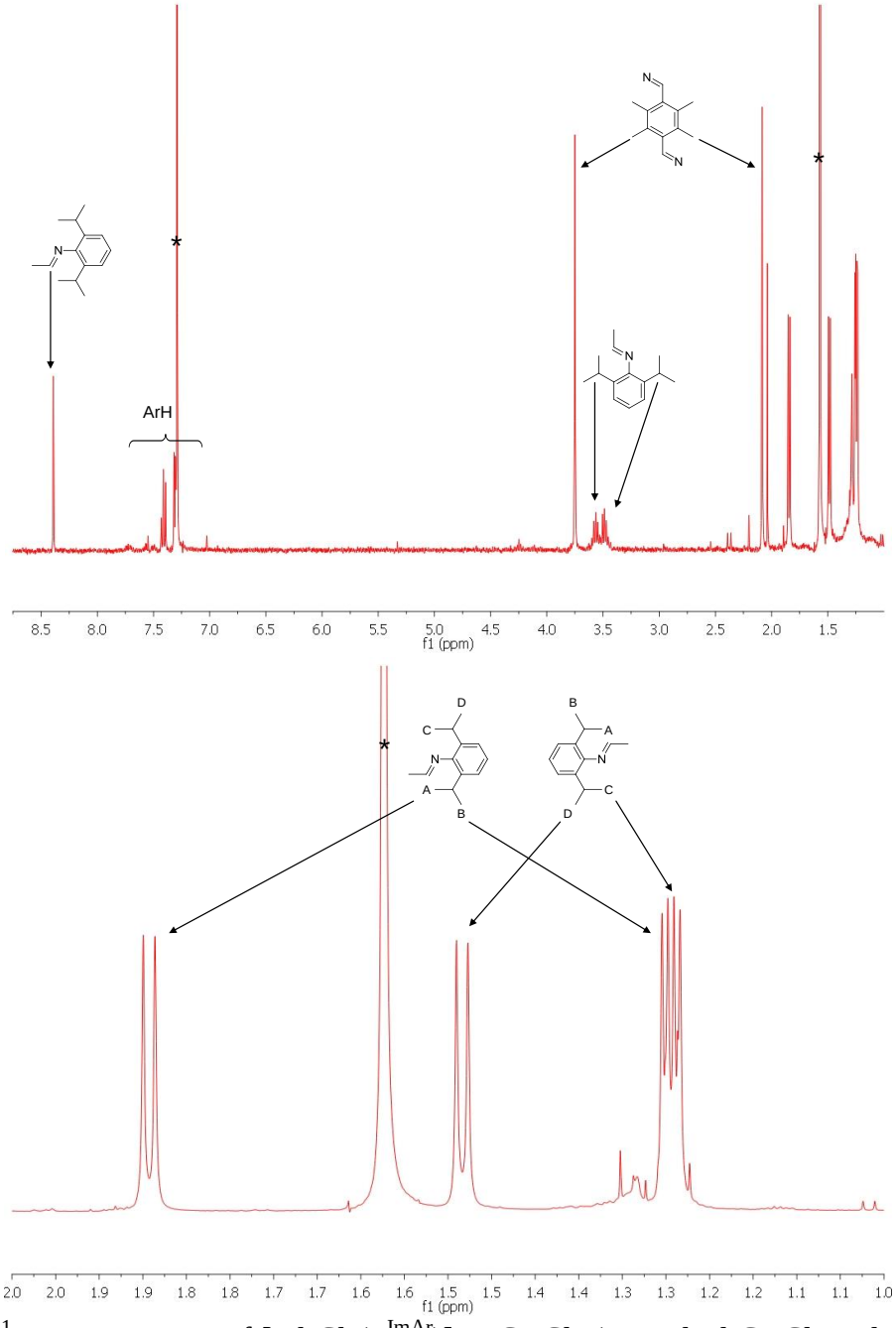

Figure S1 ^1H NMR spectra of $[Pd_3Cl_6(L^{ImAr})]$ in $CDCl_3$ (* residual $CHCl_3$ and H_2O). Top: full spectrum; Bottom: expansion of 2.0-1.0 ppm region.

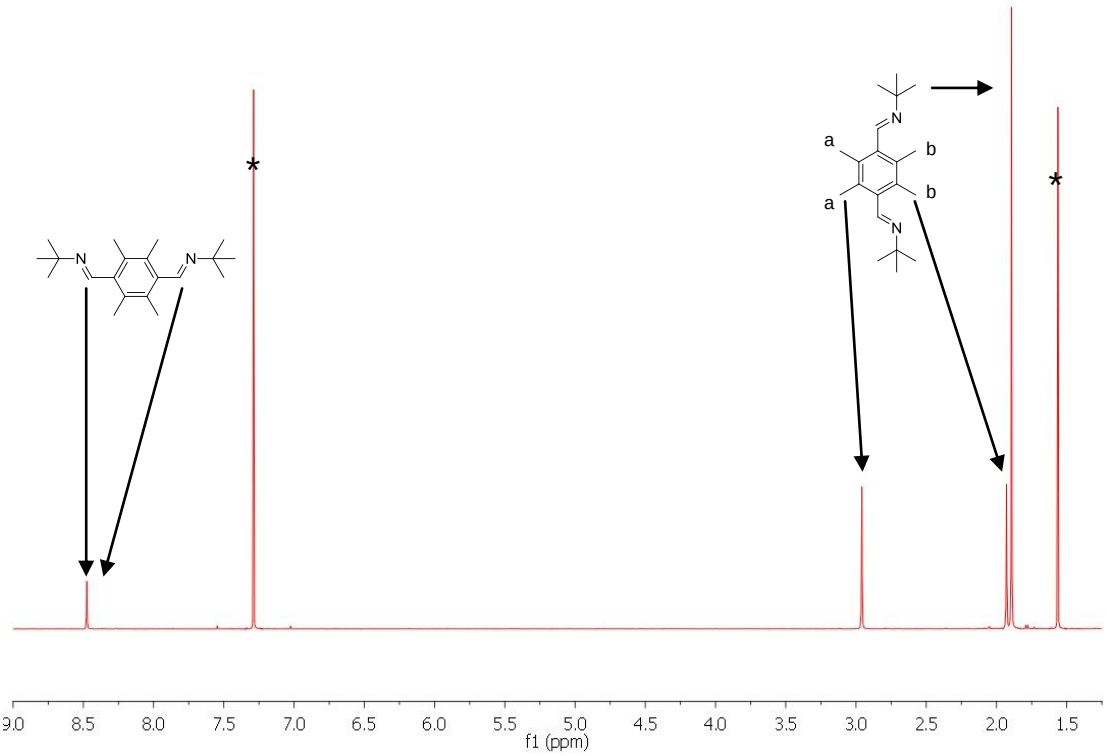

Figure S2 ^{1}H NMR spectrum of $[Pd_3Cl_6(L^{ImR})]$ in $CDCl_3$ (* residual $CHCl_3$ and H_2O)

Crystallographic details

Single-crystal X-ray diffraction data were collected at 150 K using either a Bruker Apex II CCD diffractometer or an Oxford Diffraction Xcalibur Eos diffractometer equipped with an Eos detector, with graphite monochromated Mo*K*α radiation (λ = 0.71073Å) or using an Oxford Diffraction SuperNova Dual Atlas diffractometer with graphite-monochromated Cu*K*α radiation (λ = 1.54180 Å) (see Table S1 for details). The structures were solved by direct methods using the WinGX suite of programs[3] and refined using full-matrix least square refinement on $|F^2|$ using SHELXTL-97.[4] Unless otherwise stated, all non-hydrogen atoms were refined with anisotropic displacement parameters while hydrogen atoms were placed at calculated position and included as part of a riding model. The amine hydrogens in L^{AmAr}, ammonium hydrogens in $[H_2L^{AmR}][CoCl_4]$ and iminium hydrogens in $[H_2L^{ImAr}][Zn_4Cl_{10}]$ were located from the difference Fourier map and refined with riding thermal parameters and bond distance restraints. In $[Pd_3Cl_6(L^{ImR})]$, one tertiary butyl group had 3-fold rotational disorder and was modelled over two sites with 0.66:0.34 occupancy and anisotropic atomic displacement parameters. In $[Pd_3Cl_6(L^{ImAr})]$, the structure suffers from whole molecule disorder, with an occupancy ratio of 0.8878(18):0.1122. Within the minor component the Pd atoms were refined freely and isotropically; the Cl positional parameters were refined, but a common isotropic displacement parameter was refined. The ligand atoms were treated as an overall rigid group with an isotropic displacement parameter fixed at 0.06 Å^2. Both molecules were restrained to be geometrically similar. Within the major component, only the Pd and Cl atoms were refined isotropically. Allowing the light atoms to refine with adps reduced R1 only modestly, but led to a number of atoms adopting physically unreasonable adps. This is probably a consequence of the whole-molecule disorder.

1. A. W. Van der Made and R. H. Van der Made, *J. Org. Chem.*, 1993, **58**, 1262-1263.
2. Y.-T. Chan, X. Li, M. Soler, J.-L. Wang, C. Wesdemiotis and G. R. Newkome, *J. Am. Chem. Soc.*, 2009, **131**, 16395-16397.
3. L. J. Farrugia, *J. Appl. Cryst.*, 1999, **32**, 837-838.
4. G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112-122.

Table S1 Crystal data for L^{ImAr}, L^{AmAr}, $[H_2L^{AmR}][CoCl_4]$

	L^{ImAr}	L^{AmAr}	$[H_2L^{AmR}][CoCl_4]$
Chemical formula	$C_{36}H_{48}N_2$	$C_{36}H_{52}N_2$	$C_{20}H_{38}N_2{\cdot}Cl_4Co{\cdot}CHCl_3{\cdot}H_2O$
M_r	508.76	512.80	644.64
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $C2/c$	Monoclinic, $P2_1/c$
Temperature (K)	150	171	150
a, b, c (Å)	8.4355 (9), 23.1135 (12), 9.0064 (9)	23.679 (3), 10.692 (1), 26.106 (4)	14.0602 (13), 12.1270 (9), 18.9923 (17)
α, β, γ (°)	90, 117.123 (13), 90	109.228 (14)	90, 107.588 (9), 90
V (Å^3)	1562.9 (2)	6240.7 (12)	3087.0 (5)
Z	2	8	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.06	0.06	1.18
Crystal size (mm)	0.25 × 0.10 × 0.02	0.22 × 0.09 × 0.02	0.03 × 0.02 × 0.01
Diffractometer	Xcalibur, Eos diffractometer	Xcalibur, Eos diffractometer	Xcalibur, Eos diffractometer
Absorption correction	Multi-scan CrysAlisPro, Agilent Technologies,	Multi-scan CrysAlisPro, Agilent Technologies,	Multi-scan CrysAlisPro, Oxford Diffraction Ltd.
T_{min}, T_{max}	0.897, 1.000	0.335, 1.000	0.814, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	11022, 3937, 2837	40816, 8429, 5606	23685, 6533, 4804
R_{int}	0.031	0.053	0.040
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.065, 0.176, 1.02	0.064, 0.171, 1.01	0.050, 0.117, 1.02
No. of reflections	3937	8429	6533
No. of parameters	178	363	317
No. of restraints	0	0	0
H-atom treatment	H-atom parameters constrained	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	0.41, -0.28	0.31, -0.24	1.29, -0.72

Table S2 $[H_2L^{ImAr}][Zn_4Cl_{10}]$, $[Pd_3Cl_6(L^{ImAr})]$, $[Pd_3Cl_6(L^{ImR})]$

	$[H_2L^{ImAr}][Zn_4Cl_{10}]$	$[Pd_3Cl_6(L^{ImAr})]$	$[Pd_3Cl_6(L^{ImR})]$
Chemical formula	$C_{36}H_{50}N_2 \cdot Cl_{10}Zn_4$	$C_{36}H_{50}Cl_6N_2Pd_3$	$C_{20}H_{32}Cl_6N_2Pd_3 \cdot 2(CHCl_3)$
M_r	1126.76	1042.68	1071.11
Crystal system, space group	Triclinic, $P\bar{1}$	Monoclinic, *Cc*	Monoclinic, $P2_1/n$
Temperature (K)	150	150	150
a, *b*, *c* (Å)	9.5094 (8), 10.1009 (8), 13.8791 (10)	15.708 (3), 18.709 (3), 14.422 (2)	14.0862 (4), 12.8822 (3), 20.1228 (4)
α, β, γ (°)	88.205 (6), 85.706 (6), 61.321 (8)	90, 101.312 (18), 90	90, 96.349 (2), 90
V (Å^3)	1166.29 (16)	4155.9 (12)	3629.11 (15)
Z	1	4	4
Radiation type	Mo *K*α	Mo *K*α	Cu *K*α
μ (mm^{-1})	2.63	1.70	20.15
Crystal size (mm)	0.05 × 0.02 × 0.01	0.19 × 0.04 × 0.03	0.02 × 0.01 × 0.01
Diffractometer	Xcalibur, Eos diffractometer	Xcalibur, Eos diffractometer	SuperNova, Dual, Cu at zero, Atlas diffractometer
Absorption correction	Multi-scan CrysAlisPro, Oxford Diffraction Ltd.,	Multi-scan CrysAlisPro, Oxford Diffraction Ltd.,	Multi-scan CrysAlisPro, Agilent Technologies,
T_{min}, T_{max}	0.807, 1.000	0.956, 1.000	0.478, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	12460, 4663, 3703	14947, 7313, 5844	33867, 6914, 5952
R_{int}	0.028	0.057	0.065
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.031, 0.075, 1.01	0.064, 0.160, 1.06	0.043, 0.120, 1.05
No. of reflections	4663	7313	6914
No. of parameters	244	287	387
No. of restraints	0	143	0
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	Riding	H-atom parameters constrained
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	0.56, -0.31	1.79, -0.80	1.70, -1.37
Absolute structure	N/A	Flack H D (1983), Acta Cryst. A39, 876-881	N/A
Flack parameter	N/A	0.58 (7)	N/A

CrysAlisPro, Oxford Diffraction Ltd., Version 1.171.33.55 (release 05-01-2010 CrysAlis171 .NET) (compiled Jan 5 2010,16:28:46) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. Computer programs: *SMART* (Siemens, 1993), CrysAlisPro, Oxford Diffraction Ltd., Version 1.171.33.55 (release 05-01-2010 CrysAlis171 .NET) (compiled Jan 5 2010,16:28:46), *SAINT* (Siemens ,1995), *SHELXS97* (Sheldrick, 1990), *SHELXS97* (Sheldrick, 2008), *SHELXL97* (Sheldrick, 1997), *SHELXL97* (Sheldrick, 2008), *ORTEP* (Farrugia, 1997), *enCIFer* (Allen *et al.*, 2004).