Rhodium and Palladium Complexes of a Pyridyl-centred Polyphenylene Derivative

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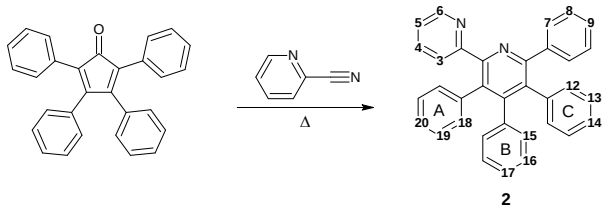
2-(2' pyridyl)-3,4,5,6-tetraphenylpyridine **2** (HL), a ligand with both N,N-bidentate and N,N,C-terdentate coordination potential, was prepared in excellent yield by the Diels-Alder [2+4] cycloaddition of 2-cyanopyridine and tetraphenylcyclopentadien-1-one. Monometallic Pd(II) and Rh(III) complexes were formed which exhibit both types of ligand coordination (*trans*-$[RhCl_2(L)(NCMe)]$ **3**, *cis*-$[RhCl(L)(NCMe)_2]PF_6$ **4**, *cis*-$[RhCl_2(HL)_2]PF_6$ **6**, $[RhCl(L)(HL)]PF_6$ **7**, $[Rh(L)_2]PF_6$ **8**, $[Pd(OAc)(L)]$ **9** and $[Pd(\eta^3\text{-methallyl})(HL)]PF_6$ **10**). The molecular structures of the ligand and six complexes, including the chloro-bridged dimer $[RhCl(L)(\mu\text{-}Cl)]_2$ **5**, were obtained by single crystal X-ray diffraction.

Introduction

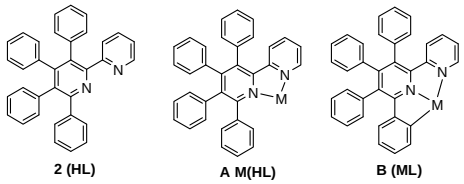
In a recent report we demonstrated the versatility of the Diels Alder [4+2]cycloaddition of a tetraarylcyclopenta-2,4-dien-1-one and an appropriately substituted acetylene in the generation of heteroatom oligo-polyphenylenes [1]. The result was a new set of propellor-like hexaarylsubstituted benzenes for structural analysis and as precursors to heteroatom graphenes [2,3]. One unexplored variation in the synthetic procedure was to replace the acetylene with an arylcyanide to generate not superbenzenes but superpyridines. In the search for such polyaromatics 2-(2' pyridyl)-3,4,5,6-tetraphenylpyridine **2** (HL) is a necessary first step.



Scheme 1 Synthesis of **2** and the atom labelling used for the assignment of NMR data.

2 is an interesting polyaromatic compound. It can be considered either as a substituted pyridine (2-(2'-pyridyl)-3,4,5,6-tetraphenylpyridine) or as an asymmetrically substituted bulky bipyridine (3,4,5,6-tetraphenyl-2,2'-bipyridine). In either case the presence of two pyridyl nitrogen atoms confers ligand potential to the molecule and two possible coordination modes emerge: (i) bidentate N,N-coordination and (ii) anionic N,N,C-terdentate coordination via orthometallation (**A** and **B** in Scheme 2).

To explore these two facets of the ligand chemistry of **2**, metal centres were chosen with rich coordination and orthometallation chemistry, Rh(III) and Pd(II). The coordination of bulky asymmetric ligands to such catalytic metals has relevance to investigations into bond formation processes. In addition transition metal complexes of derivatives of 6-phenyl-2,2'-bipyridine have shown interesting photo-physical properties [4] and the coordination chemistry of (N-N)-donor ligands such as 2,2'-bipyridine and related ligands are well reviewed [5].



Scheme 2 Coordination modes of **2** to a metal centre M

Results and Discussion

Synthesis of the ligand

Polyaromatic **2** (HL) has been synthesised previously [6] by a similar method [6a], and by reacting 2-cyanopyridine with two equivalents of diphenyl acetylene in a trimerisation process [6b] but no complexes were prepared. Here we report its full characterization. Data (IR, ^{1}H-NMR, ^{13}C-NMR, mass spectometric, and micro-analytical) for **2** and other compounds are given in the Experimental section; some selected proton NMR data are given in Table 1. The synthetic procedure adopted in this work, the Diels Alder [4+2] cycloaddition of a tetraphenylcyclopenta-2,4-dien-1-one and 2-cyanopyridine (scheme 1) resulted in a 95% yield of **2**.

The Rhodium complexes

Treatment of **2** on reflux, with one equivalent of $RhCl_3.xH_2O$ in aqueous acetonitrile results in the formation of the *trans*-dichloro cyclometallated product $[RhCl_2(L)(NCMe)]$ **3** which was obtained by filtration. The monochloro *cis*-$[RhCl(L)(NCMe)_2]PF_6$ **4** in which one of the chloride ligands

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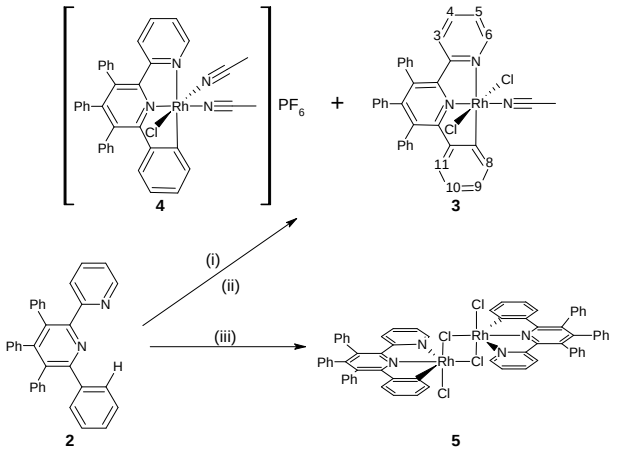
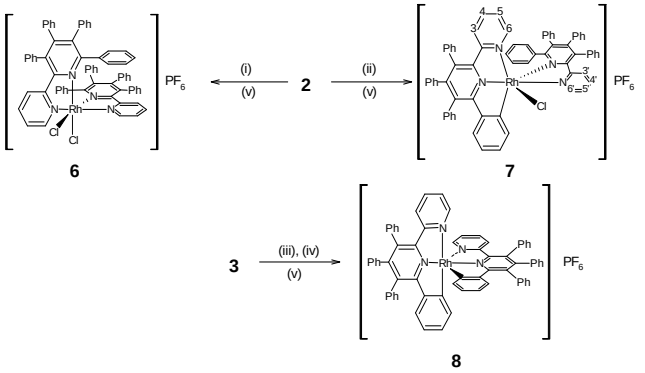
is replaced by MeCN could also be obtained from this reaction by treatment of the mother liquor with aqueous KPF_6 (scheme 3). In both cases only the *mer*-isomers are produced allowing



Scheme 3 (i) $RhCl_3.xH_2O$, aq. acetonitrile, reflux, 16 h, (ii) aq. KPF_6, (iii) $RhCl_3.xH_2O$, ethanol, reflux, 16 h and the atom labelling of cyclometallated complexes for the assignment of NMR data.

the cyclometallated ligand to be planar.

The ^{1}H NMR resonances of **3** are fully assigned (Figure 1) and evidence for the cyclometallation appears in the ^{13}C NMR spectrum with the ^{1}J(RhC) coupling for the orthometallated carbon atom occuring in the expected range [7] (δ 165.0 ppm, ^{1}J(RhC) = 23.2 Hz). In the absence of a coordinating solvent such as acetonitrile i.e. when **2** is treated with $RhCl_3.xH_2O$ in aqueous ethanol, the cyclometallated chloride-bridged dimer



Scheme 4 (i) $RhCl_3.xH_2O$, aq. acetonitrile, reflux, 16 h, (ii) $RhCl_3.xH_2O$, N-ethylmorpholine, ethanol, reflux, 3 h, (iii) $AgNO_3$, acetone/ethanol, reflux, 3 h, (iv) (**2**), reflux, 16 h, (v) aq. KPF_6.

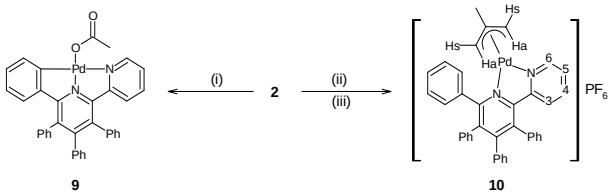
$[RhCl(L)(\mu\text{-}Cl)]_2$ **5** (Scheme 3) is produced.

On changing the stoichiometry of the reaction bis-chelate complexes of rhodium (Scheme 4) can be formed. Reaction of **2** with 0.33 equivalents of $RhCl_3.xH_2O$ in aqueous acetonitrile and the subsequent addition of saturated KPF_6(aq) gives a mixture of products as shown by ^{1}H-NMR spectroscopy. These on isolation proved to be the dichloro bis-chelate *cis*-$[RhCl_2(HL)_2]PF_6$ **6** (43%), **3** (14%), **4** (9%), and an unidentified product (33%).

Reaction of **2** with 0.5 equivalents of $RhCl_3.xH_2O$ in the presence of a non-coordinating base, N-ethylmorpholine, results in the mono-cyclometallated bis-chelate complex $[RhCl(L)(HL)]PF_6$ **7** (67%). There was no evidence of the di-cyclometallated product even on heating and in order to generate the elusive $[Rh(L)_2]PF_6$ **8** the *trans* dichloro ligands of **3** were first removed with silver nitrate before bringing to reflux in the presence of one equivalent of **2**.

The Palladium Complexes

In order to investigate the ease of formation of Pd(II) cyclometallated and N-donor complexes, $[Pd(OAc)_2]$ and $[(\eta^3\text{-methallyl})Pd(\mu\text{-}Cl)]_2$ were reacted with **2** in



Scheme 5 (i) $[Pd(OAc)_2]$, dichloromethane, reflux, 3 h, (ii) $[(\eta^3\text{-methallyl})Pd(\mu\text{-}Cl)]_2$ dichloromethane (iii) NH_4PF_6/Methanol.

dichloromethane in Pd:**2** ratios of 1:1. The result was mono-orthometallated [Pd(OAc)(L)] **9**, produced in 94% yield on reflux and the N,N-chelate complex $[(\eta^3\text{-methallyl})Pd(HL)]PF_6$ **10**, produced in over 90% yield.

Spectroscopic characterisation

The complexes were fully characterised using NMR spectroscopy, mass spectrometry and elemental analysis. For the cationic complexes **4**, **6**, **7**, **8** and **10**, the ESI-MS gave signals in agreement with the theoretically expected masses and isotopic distributions of $[M\text{-}PF_6]^+$ or $[M\text{-}OAc]^+$. The neutral complexes **3** and **5** did not yield ESI-MS spectra.

The ^{1}H and ^{13}C NMR chemical shifts were assigned by performing H-H and C-H COSY and NOE experiments. The asymmetric character of bulky **2** resulted in complex NMR spectra and the proton chemical shifts of the mono substituted 2-pyridyl group of **2** (H3, H4, H5, H6, see Scheme 1) are given in Table 1 for comparison with those in the complexes.

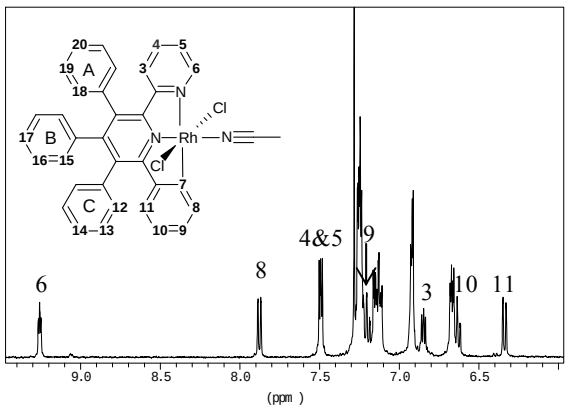


Fig. 1 The aromatic region of the ^{1}H NMR spectrum of **3** in $CDCl_3$ at 20 °C. Only the assignments made to the protons in metal coordinated aromatic rings are presented.

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In the ^{1}H NMR spectrum of [Rh(L)Cl$_2$(CH$_3$CN)] **3** (Figure 1) the phenyl rings *meta* (A and C) and *para* (B) to the central pyridine nitrogen give rise to four sets of overlapping multiplets. The two most upfield sets of these signals include a multiplet integrating for two protons for the *ortho* protons of ring B (H15 at δ 6.66 ppm) and a multiplet integrating for three protons for the *meta* and *para* protons of ring B (H16, H17 at δ 6.92 ppm). The chemical shifts of these signals are very similar to those obtained for the protons of ring B in the ligand prior to coordination. The two more downfield groups of signals include a multiplet integrating for four protons at δ 7.10-7.16 ppm (assigned to H18 and H12, the *ortho* protons of rings A and C) and a multiplet integrating for six protons at δ 7.22-7.27 ppm (assigned to H13, H14, H19 and H20, the *meta* and *para* protons of rings A and C). Again the chemical shifts of these signals compare well to those of the protons of rings A and C in the ligand prior to coordination (slight downfield shift of about δ 0.2 ppm). The proton resonances for H6 and H8 of **3** (and also for **4** and **5**) are deshielded whereas those of H3 are shielded.

for H3 in complexes **4**, **5**, **9** and **10** compared to the same protons in **2**. This can be explained by the locked conformation of H3 on complexation which causes it to be shielded by the adjacent phenyl ring. The shifts for orthometallated phenyl ring protons (H8, H9, H10, H11) are very similar in all three rhodium complexes. The signals for the palladium complex **9** appear more upfield than that of the rhodium complexes. In the proton NMR of **10** the four non-equivalent proton resonances of the allyl group appeared as broad peaks at δ 3.91, 3.28, 2.51 and 1.78 ppm and are similar to other allyl compounds reported [8].

The ^{1}H NMR spectra of complexes **6**, **7** and **8** were too complex for full assignment. However one signal is distinctive; a multiplet integrating for one proton at δ 9.58 ppm in **6** and δ 8.14 ppm in **8** which is due to the H6 proton. In both spectra the remaining twenty-three protons give rise to a number of doublets and multiplets between δ 6.37 and 7.50 ppm.

The detailed analysis of the NMR spectra allowed us to determine which of the two possible conformations of **7** was

Table 1 ^{1}H NMR data and assignments for the pyridyl ring and the orthometallated phenyl ring protons in ligand **2** and complexes **3**, **4**, **5**, **9** and **10**. Chemical shifts (δ) are in ppm. Coupling constants, in Hz, are in brackets (when available).

	H3	H4	H5	H6	H7	H8	H9	H10	H11
2	7.46 (7.5)	7.55 (7.5, 1.5)	7.09 (7.5, 5.0, 1.5)	8.48 (5.0)	7.18	7.41	7.18	_	_
3 (Rh)	6.84	7.49	7.49	9.25	_	7.87 (7.7, 1.5)	7.19	6.62	6.33 (8.4, 1.5)
4 (Rh)	6.85 (8.3)	7.56 (8.3, 2.0)	7.66	9.36 (5.5, 2.0)	_	7.81 (8.2, 1.5)	~ 7.3	6.75	6.33 (8.2, 1.4)
5 (Rh)	6.87	7.48 (7.7, 1.9)	~7.3	9.06 (5.5, 1.9, 0.7)	_	7.89 (7.7, 1.5)	6.87	6.69 (8.0, 1.5)	6.39 (8.0, 1.5)
9 (Pd)	6.61 (8.0)	7.44 (8.0, 2.0)	7.35 (7.5, 5.0, 1.0)	8.61 (5.0)	_	7.30 (7.5, 1.5)	7.01 (7.5, 1.5)	6.60	5.95 (8.0, 1.0)
10 (Pd)	6.91 (8.0)	7.54 (8.0, 1.5)	7.46 (7.5, 5.0, 1.5)	8.81 (5.0)	6.84-7.32				

The ^{13}C NMR spectrum of **3** is very complex but shows the expected number of signals for the quaternary (eleven, δ 165.0-135.3 ppm) and aromatic **C**H carbon atoms (eleven small signals accounting for one carbon each and six larger signals accounting for two, δ 149.7-122.7 ppm) as well as a resonance for the coordinated acetonitrile molecule at δ 4.51 ppm. The orthometallated carbon (C7) at δ 165.0 ppm is the most downfield signal.

Whereas **3** has a plane of symmetry in the plane of the tridentate ligand due to the *trans* arrangement of the chloride ligands, **4** and **5** do not, increasing the number and complexity of the signals in their ^{1}H NMR spectra. For instance, the uncoordinated phenyl rings no longer give rise to two simple sets of spin systems. Fortunately however, the 2-pyridyl ring and the orthometallated phenyl ring still give rise to two distinct sets of four resonances that could be assigned using TOCSY experiments. Table 1 summarises this data for complexes **3**, **4**, **5** and **9** and **10** for comparison to the free ligand **2**.

A general downfield shift is noticeable for the 2-pyridyl signals of H6 and H5, and an upfield shift of about δ 0.6 ppm

formed (**a** or **b** in Figure 2). For steric reasons, conformation **b** is favoured and this is supported from the ^{1}H NMR data which shows that the most downfield signal assigned to H6B, is a doublet at δ 9.94 ppm with a coupling constant J = 5.0 Hz. The deshielding of this proton is due to its proximity to the

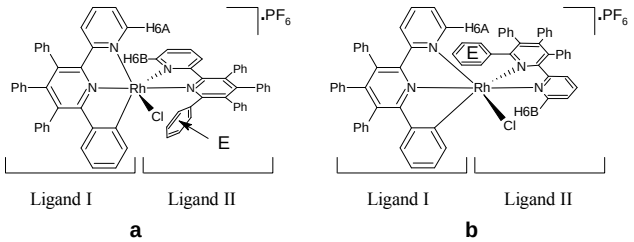


Fig. 2 Two possible orientations for the NN-coordinated ligand in complex **7**

chloride ligand. In conformation **a** both H6A and H6B lie above the plane of a pyridine ring which would be expected to shift their resonances upfield. The inability to convert **7** to **8** also fits with the former existing in the **b** conformation.

Molecular Structure Determination

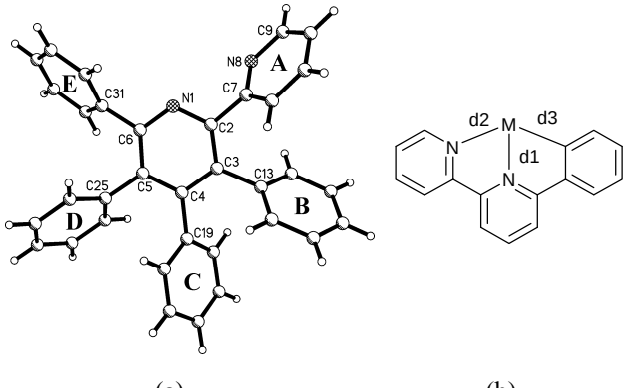
Ligand **2** and complexes **3**, **4**, **5**, **6**, **8** and **9** were structurally characterised by single crystal X-ray diffraction. The crystallographic data are summarised in Table 2. Apart from **9** which contains a methanol solvate per asymmetric unit, the other structures contain a significant quantity of chlorinated solvent: dichloromethane for **2**, **6** and **8** (one, one and three molecules per asymmetric unit respectively), and deuterated chloroform for **4**, **3** and **5** (2.5, four and three molecules per asymmetric unit respectively).

The geometry of the metal centres is as expected in all structures. The rhodium(III) complexes **3**, **4**, **5**, **6** and **8** are octahedral and the palladium(II) complex **9** is square planar. The octahedral and square planar geometries are distorted primarily due to the geometric constraints of the terdentate or bidentate ligand. The extent of distortion is similar in the six complexes, with the smallest angles at the metal centre ranging from 79.8(2)° in **3** to 80.1(2)° in **5** and the largest angles ranging from 99.93(2)° in **5** to 102.7(2)° in **6**.

Figure 3a gives a representation of ligand **2**, with the atom numbering and peripheral ring labelling (letters A to E) that will be used for consistent discussion of all the structures. Figure 3b shows the designated numbering of the metal to ligand distances.

Confirmation of the orthometallation in **3**, **4**, **5**, **9** and **8** is provided from the crystallographically determined molecular structures. These are presented in Figures 4, 5, and 6.

In the case of the chloro-bridged complex **5** (Figure 6), there is a centre of symmetry such that the asymmetric unit comprises only half of the dimer (as well as three molecules of chloroform). Despite being slightly longer than the Rh-$Cl_{terminal}$ bonds, the Rh-μCl bonds (2.387(2)Å and 2.377(2)Å) are between 0.15 Å and 0.18 Å shorter than Rh-μCl distances in the literature [9].



(a) (b)

Fig. 3 Perspective view of the molecular structure of (a) **2** and (b) metal-ligand distances

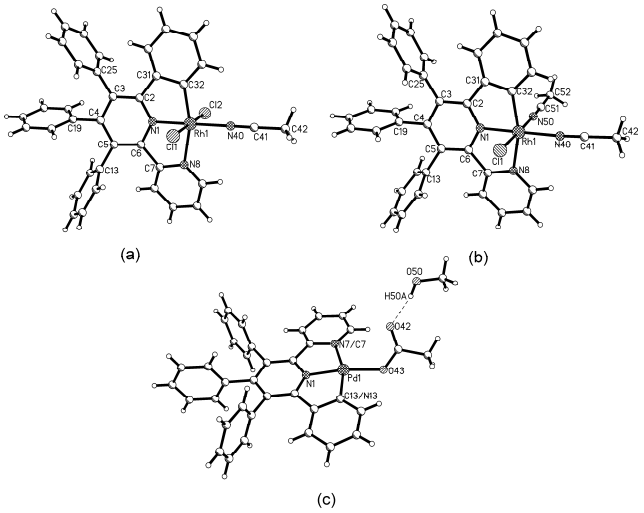


Fig. 4 Perspective view of the molecular structure of (a) **3**, (b) the cation in **4**, and (c) **9**.

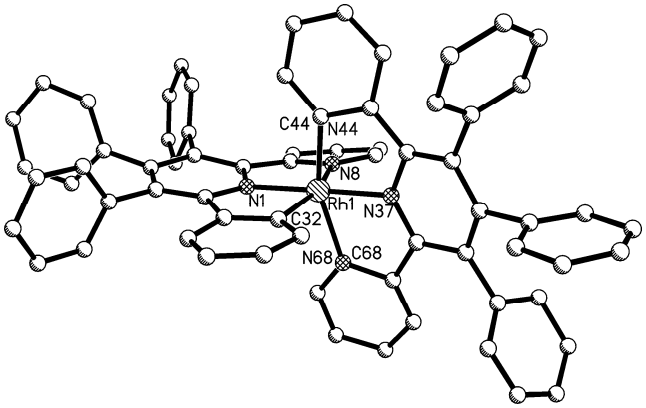


Fig. 5 Perspective view of the molecular structure of the cation in **8** with selected atomic labelling shown.

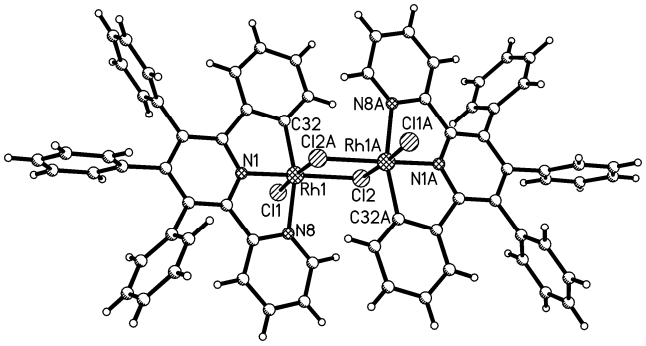


Fig. 6 Perspective view of the molecular structure of the cation in **5**.

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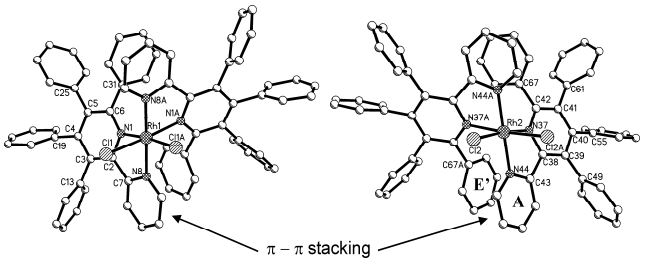
Table 2 Crystal data and X-ray experimental details for **2**, **3**, **4**, **5**, **6, 8** and **9**.

Compound	**2**	**3**	**4**	**5**	**6**	**8**	**9**
Empirical formula	$C_{35}H_{26}Cl_2N_2$	$C_{40}H_{30}Cl_{14}N_3Rh$	$C_{81}H_{63}Cl_{17}F_{12}N_8P_2Rh_2$	$C_{74}H_{52}Cl_{22}N_4Rh_2$	$C_{69}H_{50}Cl_4F_6N_4PRh$	$C_{71}H_{49}Cl_9F_6N_4OPRh$	$C_{37}H_{30}N_2O_3Pd$
Formula weight	545.48	1151.88	2246.80	1982.92	1324.81	1541.07	657.03
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	Fdd2	$P2_1/n$	$P2_1/c$	C2/c	C2/c	$P2_1/c$	P-1
Unit cell dimensions: a (Å)	25.057(3)	11.8530(9)	12.6221(8)	20.2841(12)	24.1740(12)	24.611(8)	10.2973(6)
b (Å)	43.374(4)	26.863(2)	34.842(2)	20.2395(13)	16.0642(8)	13.238(4)	12.3281(7)
c (Å)	10.3758(10)	15.1269(11)	11.6836(7)	21.0781(13)	31.4753(16)	21.081(7)	12.8367(8)
α (°)	90	90	90	90	90	90	94.3690(10)
β (°)	90	101.269(2)	110.2170(10)	112.6660(10)	104.9429(11)	91.501(7)	103.5000(10)
γ (°)	90	90	90	90	90	90	109.5570(10)
Volume($Å^3$)	11276.7(19)	4723.7(6)	4821.7(5)	7985.1(9)	11809.6(10)	6866(4)	1471.80(15)
Z	16	4	2	4	8	4	2
Density (calculated) (Mg/m^3)	1.285	1.620	1.548	1.649	1.490	1.491	1.483
Absorption coefficient (mm^{-1})	0.257	1.187	0.916	1.195	0.564	0.686	0.671
F(000)	4544	2296	2244	3952	5392	3112	672
Crystal size (mm)	0.40x0.30x0.30	0.12x0.08x0.02	0.15x0.14x0.12	0.24x0.22x0.02	0.20x0.16x0.12	0.21x0.15x0.03	0.51x0.41x0.34
Theta range for data collection (°)	1.88 to 25.00	1.57 to 25.02	1.72 to 26.00	1.48 to 26.00	1.54 to 26.00	0.83 to 25.00	1.66 to 27.50
Reflections collected	22078	36953	41199	33833	50481	35046	13720
Independent reflections [R(int)]	4968 [0.1035]	8307 [0.0766]	9479 [0.0340]	7853 [0.0654]	11586 [0.0454]	12083 [0.2245]	6708 [0.0217]
Data / restraints / parameters	4968 / 1 / 352	8307/0/524	9479/6/607	7853/0/460	11586/30/767	12083/1164/839	6708/0/391
Goodness-of-fit on F^2	0.998	1.038	1.145	1.134	1.018	1.311	1.069
R_1 [I>2sigma(I)]	0.0602	0.0570	0.0663	0.0640	0.0537	0.1414	0.0349
wR_2 (all data)	0.1423	0.1455	0.1763	0.1343	0.1545	0.3471	0.0951



(a) (b)

Fig. 7: Perspective views of (a) the Δ and (b) the Λ enantiomers of the cation in **6**, The solvate molecules, counter ions and the hydrogen atoms have been removed for clarity.

Table 3 Distances (Å) from the metal atom.

	d1	d2	d3	M-X	M-Cl
4	1.964(4)	2.119(4)	2.020(4)	2.019(4)[a] 2.013(4)[a]	2.314(2)
3	1.962(4)	2.158(5)	1.994(5)	2.027(4)[a]	2.345(2) 2.337(2)
5	1.953(4)	2.130(4)	2.005(5)	—	2.323(2)[d] 2.387(2)[e] 2.375(2)[f]
6	2.086(3) 2.079(3)	2.019(3) 2.018(3)	—	—	2.329(2) 2.344(2)
8	1.98(2) 2.011(2)	2.132(2)[c] 2.035(2)[c]	1.99(2)[c] 2.090(2)[c]	—	—
9	1.964(2)	2.024(2)	2.070(2)	2.047(2)[b]	—

[a]X = **N**CMe, [b]X = **O**Ac, [c] distances effected by disorder, [d] terminal Cl, [e] bridging Cl, [f] symmetry generated Cl (-x+1,-y,-z).

For the *cis* dichloro N,N-bidentate complex **6** (Figures 7) there are two independent cations, each with diad symmetry and both are subject to space group operations which invert configuration. The complexes containing Rh1 (Figure 7a) and Rh2 (Figure 7b) are the Δ and the Λ isomers respectively. In both the free phenyl ring E' of one ligand stacks with the 2-pyridyl ring A of the second ligand. Measuring from the centroid of ring E' to the mean-plane of ring A gives stacking distances of 3.16(1)Å and 3.19(1)Å (Figures 7a and 7b respectively). The two rings in each case are almost parallel (8.0º, 7.9(1)º) and the centre of one ring (E') is over the midpoint of a C-C bond in the other (A).

All the structures were examined for occupational CH or N disorder. When refined as mixed occupancy (C/N), the associated free variable was >0.9 (or <0.1) in all cases except **8** and **9**. In the former there was some evidence of twinning and the occupational disorder on the atoms linked to the metal is reflected in the labelling of N68 and C44 (Figure 5). Orthometallated complex **9** (Figure 4c) experienced the same type of disorder (occupancy of position 8 53% C and 47% N, occupancy of position 32 53% N and 47% C). Complex **9** is the only complex in which the solvate molecule hydrogen-bonds to the complex: the free oxygen of the coordinated acetate is hydrogen-bonded to the hydroxy group of the methanol solvate, with O50···O42 = 2.696(3)Å and O50–H50A···O42 = 164(1)°.

Table 4: The tilt angles made between the central 'NC5' ring and the peripheral aromatic rings in degrees. The rings are identified by a letter according to Figure 3 (a).

	A	B	C	D	E
H-**2**	53.1	62.2	61.4	61.9	51.4
3	16.6	65.8	75.8	81.8	10.5
4	12.2	69.9	83.5	89.6	8.3
5	11.1	71.4	80.2	74.8	6.3
6	15.7 / 15.6	74.3 /.73.0	73.6 / 66.4	71.4 / 72.0	67.8 / 70.5
8	17.3 / 18.3	81.7 / 68.5	80.3 / 88.3	89.7 / 87.2	8.4 / 14.6
9	7.6	89.4	88.9	86.4	10.4

Table 3 gives all the metal-atom bond distances and these are consistent with those found in the literature [9,10]. The

longest bonds are the metal-chlorine bonds (2.314(2)Å to 2.387(2)Å). In the orthometallated complexes **3**, **4** and **5**, the metal-C and metal-N bonds show the same d1 < d3 < d2 trend as the majority of the structures known of 6-phenyl-2,2'-bipyridine and its analogues [11], and reflect the trans influence of the sigma-C bonds. In complex **6**, the ligand is bidentate, free from the constraints imposed by a third ligand- and the distances are more similar and d1 > d2.

In the crystal structure of ligand **2**, the peripheral rings are tilted with respect to the central ring, with tilt angles ranging from 51.3° to 62.2°. Table 4 shows how the tilt angles are affected by coordination. The rings bound to the metal (A, and E' in the orthometallated complexes) see their tilt angles decreased almost to co-planarity (angles < 20°) to accommodate the geometric constraints of the metal. This induces an increase in the tilt angles of all the other rings. For the non-disordered orthometallated complexes **3**, **4** and **5**, the tilt angles for the orthometallated ring E' are smaller than those for the 2-pyridyl ring A.

Conclusion

2-cyanopyridine has been shown to be an effective dienophile in a [2+4] Diels-Alder cycloaddition reaction with tetraphenylcyclopenta-2,4-dien-1-one. The resulting formation of 2-(2'-pyridyl)-3,4,5,6-tetraphenylpyridine in excellent yield allows for the formation of metal complexes with potential catalystic use. For the two types of metal centre used (Rh(III), Pd(II)) the ligand has been shown to exhibit both N,N-bidentate and N,N,C- orthometallated binding modes. The type of coordination can be controlled by varying the reaction conditions. The introduction of a base results in the preferential formation of a mono cyclometallated bis chelate complex. Varying the ligand : $RhCl_3.xH_2O$ reaction stoichometry allows for the preparation of a range of mono orthometallated products. Subsequent substitution of the coordinated chloro or acetonitrile ligands in these complexes generates both monometallic and dimetallic bis-orthometallated complexes. The molecular structures of the Rh(III) complexes show the generation of the mer isomers exclusively with similar degrees of ring twisting

Experimental

General procedures and materials

IR spectra were recorded from KBr disks on a Perkin-Elmer Paragon 1000 Fourier transform spectrophotometer. NMR spectra were recorded on a DPX 400 spectrometer operating at 400.13 MHz for ^{1}H, and 100.62 MHz for ^{13}C, and were standardized with respect to TMS. Electrospray ionization mass spectra were recorded on a micromass LCT electrospray mass spectrometer. Tetraphenylcyclopentadienone, 2-cyanopyridine, $RhCl_3.xH_2O$ and $[Pd(OAc)_2]$ were purchased from Aldrich. $[(\eta^3\text{-metallyl})Pd(\mu\text{-Cl})]_2$ was prepared according to a literature procedure [12].

Crystallography

Single-crystal analyses of ligand **2** and complexes **3**, **4**, **5**, **6**, **8** and **9** were made using a Bruker SMART APEX CCD area detector using graphite monochromatised MoKα (λ□= 0.71073 Å) radiation at 153(2)K. The experimental and crystallographic data are summarized in Table 2. The data reductions were performed using SAINT [13]. Intensities were corrected for Lorentz and polarisation effects and for absorption in the case of the complexes using multi-scan techniques. Space groups were determined from systematic absences and checked for higher symmetry. A full sphere of data was obtained for each using the omega scan method. The structures were solved by direct methods using SHELXS [14,15], and refined on F^2 using all data by full-matrix least-squares procedures with SHELXL-97 [16]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in calculated positions with isotropic displacement parameters 1.2 times the isotropic equivalent of their carrier carbons. Final Fourier syntheses showed no significant residual electron density except in the case of **8**. Crystals of **8** were twinned; the poor nature of the data being manifest in the refinement and thermal parameters. The resulting structure is included for comparison only and without detailed analysis.

Suitable crystals of **2** and **6** were obtained by vapour diffusion of hexane into a dichloromethane solution of the respective compound. Crystals of **4** and **8** were grown by layering hexane onto a solution of the respective complex in $CDCl_3$ and dichloromethane respectively. Crystals of **3** and **5** were obtained in an NMR tube by slow evaporation of a $CDCl_3$ solution. Crystals of **9** were grown from dichoromethane/methanol.

Synthesis of [2-(2-pyridyl)-3,4,5,6-tetraphenyl]pyridine (2) Tetraphenylcyclopentadienone (1.00 g, 2.60 mmol) and 2-cyanopyridine (1.1 mL, 11.6 mmol) were combined and heated to reflux (external temperature 280° C) under nitrogen for 48 h. The resulting brown solution was allowed to cool to give a brown solid, which was crystallised from dichloromethane/acetone to give **2** as white crystals. Yield (1.13 g, 95%). **IR** (KBr): ν 3056, 3025, 1586, 1535, 1396, 761, 698 cm^{-1}. **^{1}H NMR** ($CDCl_3$): δ 8.48 (dm, 1H, *J* = 5.0 Hz, H6), 7.55 (ddd, app. td, 1H, *J* = 1.5, 7.5 and 7.5 Hz, H4) 7.46 (dm, 1H, *J* = 7.5 Hz, H3), 7.41 (m, 2H, H7), 7.18 (m, 3H, H8 and H9), 7.09 (ddd, 1H, *J* = 1.5, 5.0 and 7.5 Hz, H5), 6.92-7.03 (m, 13H), 6.81 (m, 2H, H15) ppm. **^{13}C NMR**: δ 158.5 (C_{quat}, C2), 156.3 (C_{quat}), 155.3 (C_{quat}), 149.9 (C_{quat}), 148.3 (**C**H, C6), 140.2 (C_{quat}), 137.8 (C_{quat}), 137.5 (C_{quat}), 137.4 (C_{quat}), 135.1 (**C**H, C4), 134.4 (C_{quat}), 133.9 (C_{quat}), 130.8 (2C, **C**H), 130.6 (2C, **C**H), 129.9 (2C, **C**H, C15), 129.8 (2C, **C**H, C7), 127.0 (2C, **C**H, C8), 126.9 (2C, **C**H), 126.8 (**C**H, C9), 126.7 (2C, **C**H), 126.5 (2C, **C**H), 125.8 (**C**H), 125.8 (**C**H), 125.6 (**C**H) (C14, C17 and C20), 124.4 (**C**H, C3), 121.5 (**C**H, C5) ppm. **MS** *m/z*: 461.1992 ($[M+H]^+$) (calcd. 461.2018). **m.p.** 216 °C (lit 217-219 °C [6a]).

Synthesis of $[Rh(L)Cl_2(CH_3CN)]$ (3) and $[Rh(L)Cl(CH_3CN)_2](PF_6)$ (4) $RhCl_3.xH_2O$ (39.5 mg, 0.19 mmol) in water (1.5 mL) was added to **2** (69.1 mg,

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0.15 mmol) in acetonitrile (1.5 mL) and the mixture was heated to reflux for 16h, after which a yellow precipitate had formed. The reaction mixture was cooled down on ice. The yellow precipitate was then filtered and washed with water and diethyl ether to yield complex **3** (61.6 mg, 0.091 mmol, 61%). The filtrate was evaporated, the resulting solid was dissolved in the minimum amount of acetonitrile and a solution of saturated aqueous KPF_6 was added to form a yellow precipitate. This was filtered and washed with water and diethyl ether to yield complex **4** (18.5 mg, 15%).

Complex 3: ^{1}H NMR ($CDCl_3$): δ 9.25 (m, 1H, H6), 7.87 (dd, 1H, *J* = 1.5 and 7.7 Hz, H8), 7.49 (m, 2H, H4 and H5), 7.22-7.27 (m, 6H, H13, H14, H19 and H20), 7.19 (m, 1H, H9), 7.10-7.16 (m, 4H, H12 and H18), 6.92 (m, 3H, H16 and H17), 6.84 (m, 1H, H3), 6.66 (m, 2H, H15), 6.62 (m, 1H, H10), 6.33 (dd, 1H, *J* = 1.5 Hz and 8.4 Hz, H11), 2.66 (s, 3H, C**H**$_3$CN) ppm. **^{13}C NMR**: δ 165.0 (d, J_{RhC} = 23.2 Hz, C7), 162.5 (C_{quat}), 156.4 (C_{quat}), 153.3 (C_{quat}), 151.7 (C_{quat}), 149.7 (**C**H, C6), 146.9 (C_{quat}), 137.2 (**C**H, C4), 136.4 (C_{quat}), 136.3 (C_{quat}), 136.0 (C_{quat}), 135.6 (C_{quat}), 135.3 (C_{quat}), 134.6 (**C**H, C8), 130.7 (**C**H, C9), 130.1 (2C, **C**H), 130.0 (2C, **C**H), 129.8(2C, **C**H), 129.8 (**C**H, C11), 129.0 (2C, **C**H), 128.5 (2C, **C**H), 128.2 (**C**H), 127.8 (**C**H), 127.4 (**C**H, C5), 127.0 (2C, **C**H), 126.6 (**C**H), 125.8 (**C**H, C3), 122.7 (**C**H, C10), 4.51 (**C**H$_3$CN) ppm. Anal. Calcd for $C_{36}H_{26}Cl_2N_3Rh.1.25CDCl_3$: C, 54.24; H, 3.18; N, 5.09. Found: C, 54.37; H, 2.85; N, 4.76.

Complex 4: ^{1}H NMR ($CDCl_3$): δ 9.36 (dd, 1H, *J* = 2.0 and 5.5 Hz, H6), 7.81 (dd, 1H, *J* = 1.4 and 8.2 Hz, H8), 7.66 (m, 1H, H5), 7.56 (ddd, app. td, 1H, *J* = 2.0 and 8.3 Hz, H4), 7.51 (m, 1H, H_{phenyl}), 7.24-7.31 (m, 6H and $CHCl_3$, H_{phenyl} and H9), 7.10-7.17 (m, 4H, H_{phenyl}), 6.94 (m, 3H, H_{phenyl}), 6.85 (d, 1H, *J* = 8.3 Hz, H3), 6.81 (m, 1H, H_{phenyl}), 6.75 (m, 1H, H10), 6.65 (m, 1H, H_{phenyl}), 6.33 (dd, 1H, *J* = 1.4 and 8.2 Hz, H11), 2.75 (s, 3H, C**H**$_3$CN), 2.19 (s, 3H, C**H**$_3$CN) ppm. **MS** *m/z*: 679.1164 $[M\text{-}PF_6]^+$, (calcd. 679.1136). Anal. Calcd for $C_{38}H_{29}ClF_6N_4PRh.CDCl_3$: C, 49.55; H, 3.09; N, 5.93. Found: C, 50.30; H, 2.32; N, 5.10.

Synthesis of $[Rh(L)Cl(\mu\text{-}Cl)]_2$ (5)

2 (23.0 mg, 0.050 mmol) and $RhCl_3.xH_2O$ (13.2 mg, 0.063 mmol) were heated to reflux in ethanol (4 mL) for 16h. The solvent was removed in vacuo. Recrystallisation of the solid obtained from dichloromethane /hexane yielded complex **5** as a yellow powder (12.1 mg, 0.0095 mmol, 34%). **^{1}H NMR** ($CDCl_3$): δ 9.06 (ddd, 1H, *J* = 0.7, 1.9 and 5.1 Hz, H6), 7.89 (dd, 1H, *J* = 1.5 and 7.7 Hz, H8), 7.48 (ddd, app. td, 1H, *J* = 1.9 and 7.7 Hz, H4), 7.24-7.39 (m, 8H and $CHCl_3$, H_{phenyl} and H5), 7.17-7.22 (m, 2H, H_{phenyl}), 7.08 (d, 1H, *J* = 7.3 Hz, H_{phenyl}), 6.90-7.00 (m, 3H, H_{phenyl}), 6.87 (m, 2H, H3 and H9), 6.80 (d, 1H, *J* = 7.3 Hz, H_{phenyl}), 6.69 (dt, 1H, *J* = 1.5 and 8.0 Hz, H10), 6.63 (m, 1H, H_{phenyl}), 6.39 (dd, 1H, *J* = 1.5 and 8.0 Hz, 1H, H11) ppm.

Synthesis of $[Rh(HL)_2Cl_2](PF_6)$ (6)

$RhCl_3.xH_2O$ (10.5 mg, 0.05 mmol) in water (1.0 mL) was added to **2** (69.1 mg, 0.15 mmol) in acetonitrile (1.5 mL) and the mixture was heated to reflux for 16 h. After cooling down, a solution of saturated aqueous KPF_6 was added to the solution. A yellow precipitate formed, which was filtered and washed with water and diethyl ether. The ^{1}H NMR spectrum of this precipitate (28.5 mg) in the H6 proton region shows a mixture of four complexes: **6** (δ H6 9.59 ppm, 43%), **4** (δ H6 9.38 ppm, 9%), **3** (δ H6 9.25 ppm, 15%), and another unidentified compound (δ H6 8.84 ppm, 33%). Yellow crystals of complex **6**, suitable for single crystal X-Ray analysis, grew in the NMR tube by slow evaporation of the $CDCl_3$ solution. These crystals were then collected by filtration. Yield 6.3 mg (0.0052 mmol, 10%).

^{1}H NMR (CD_3CN): δ 9.58 (m, 1H, H6), 7.34-7.40 (m, 4H), 7.32 (m, 1H), 7.21 (m, 2H), 7.08 (d, 1H, *J* = 8.0 Hz), 6.95-7.04 (m, 4H), 6.92 (d, 1H, *J* = 7.0 Hz), 6.88 (m, 3H), 6.79-6.85 (m, 4H), 6.73 (d, 1H, *J* = 8.0 Hz), 6.44 (m, 2H). **MS** *m/z*: 1093.2275 $[M\text{-}PF_6]^+$, (calcd. 1093.2311).

Synthesis of $[Rh(HL)(L)Cl](PF_6)$ (7)

2 (69.0 mg, 0.15 mmol) and $RhCl_3.xH_2O$ (17.3 mg, 0.084 mmol) were combined and dissolved in ethanol (12 mL) containing N-ethylmorpholine (3 drops), and the mixture was heated to reflux for 3 h. The product was precipitated by adding a solution of saturated aqueous KPF_6. The solid was isolated *via* filtration, then washed with water and diethyl ether to yield **7** as a yellow powder (67 mg, 0.056 mmol, 67%). **^{1}H NMR** ($CDCl_3$): δ 9.94 (d, 1H, *J* = 5.0 Hz, H6'), 8.25 (m, 1H), 7.76 (m, 1H), 7.50-7.57 (m, 3H), 7.21-7.41 (m, probably 11H, contains $CHCl_3$), 7.15 (m, 2H), 7.06 (m, 4H), 6.78-6.94 (m, 11H), 6.67-6.76 (m, 4H), 6.55-6.62 (m, 3H), 6.47 (d, 1H), 6.47 (d, 1H, *J* = 7.5 Hz), 6.42 (d, 1H, *J* = 7.5 Hz), 6.32-6.38 (m, 3H), 6.22 (d, 1H, *J* = 7.5 Hz) ppm. **MS** *m/z*: 1057.2549 $[M\text{-}PF_6]^+$,(calcd. 1057.2544) Anal. Calcd for $C_{68}H_{47}ClF_6N_4PRh.CH_2Cl_2$: C, 64.32; H, 3.83; N, 4.35. Found: C, 64.89; H, 3.49; N, 4.30.

Synthesis of $[Rh(L)_2]PF_6$ (8)

Complex **3** (42.2 mg, 0.068 mmol) and silver nitrate (25.5 mg, 0.15 mmol) were heated to reflux in acetone / ethanol (6:1, 7 mL) under argon for 3 h. The solution was then filtered through celite to remove the silver chloride precipitate formed and evaporated to dryness. The yellow oil obtained was dissolved in butanol (8 mL) and **2** (31.3 mg, 0.068 mmol) was added. The mixture was heated to reflux under argon for 16 h to give a yellow solution. The solution was stirred with a saturated aqueous solution of KPF_6, and a yellow precipitate formed. This was isolated *via* filtration, washed with water and diethyl ether to yield **8** (22.3 mg, 0.019 mmol, 28%).

^{1}H NMR ($CDCl_3$): δ 8.14 (d, 1H, *J* = 5.0 Hz, H6), 7.49 (d, 1H, *J* = 6.8 Hz), 7.44 (d, 1H, *J* = 7.5 Hz), 7.31-7.36 (m, 3H), 7.22-7.29 (m, probably 5H, contains $CHCl_3$), 7.21 (d, 1H, *J* = 5.4 Hz), 7.12 (m, 2H), 7.07 (m, 1H), 6.97 (m, 2H), 6.90 (d, 1H, *J* = 8.2), 6.84 (m, 1H), 6.80 (m, 1H), 6.44-6.51 (m, 2H), 6.37 (d, 1H, *J* = 8.2 Hz) ppm. **^{13}C NMR**: δ 167.4 (d, J_{RhC} = 32.8 Hz, RhC), 159.9 (C_{quat}), 155.2 (C_{quat}), 152.8 (C_{quat}), 149.9 (C_{quat}), 149.0 (**C**H, C6), 145.6 (C_{quat}), 137.1 (**C**H), 136.2 (C_{quat}), 136.1 (C_{quat}), 135.8 (C_{quat}), 135.7 (C_{quat}, 2 × C), 130.6 (**C**H), 130.4 (**C**H), 130.2 (**C**H), 130.0 (**C**H), 129.3(**C**H), 129.2 (**C**H), 129.2 (**C**H, 2 × C), 129.1 (**C**H), 129.0 (**C**H), 128.9 (**C**H), 128.5 (**C**H), 128.4 (**C**H), 128.2 (**C**H), 128.0 (**C**H), 127.5 (**C**H), 127.4 (**C**H), 126.9 (**C**H), 126.3 (**C**H), 126.2 (**C**H), 121.9 (**C**H) ppm. **MS** *m/z*:

1021.2798 $[M\text{-}PF_6]^+$, (calcd. 1021.2778). Anal. Calcd for $C_{68}H_{46}F_6N_4PRh.2.5CH_2Cl_2$: C, 61.39; H, 3.73; N, 4.06. Found: C, 61.00; H, 3.25; N 3.96.

Synthesis of [Pd(L)(OAc)] (9)

A solution containing **2** (60 mg, 0.130 mmol) and $[Pd(OAc)_2]$ (30 mg, 0.133 mmol) in dichloromethane (5 mL) was refluxed for 3 h. The solution was concentrated to a small volume (*ca.* 1 mL) then methanol (2 mL) was added to give the cyclometallated Pd(II) complex **9** as yellow crystals (76 mg, 94%). **^{1}H NMR** ($CDCl_3$): δ 8.61 (dm, 1H, *J* = 5.0 Hz, H6), 7.44 (td, 1H, *J* = 2.0 and 8.0 Hz, H4), 7.35 (ddd, 1H, *J* = 1.0, 5.0 and 7.5 Hz, H5), 7.30 (dd, 1H, *J* = 1.5 and 7.5 Hz, H8), 7.22-7.27 (m, 6H, H_{phenyl}), 7.04-7.07 (m, 4H, H_{phenyl}), 7.01 (td, 1H, *J* = 1.5 and 7.5 Hz, H9), 6.92 (m, 3H, H_{phenyl}), 6.68 (m, 2H, H_{phenyl}), 6.61 (dm, 1H, *J* = 8.0 Hz, H3), 6.60 (m, 1H, H10), 5.95 (dd, 1H, *J* = 1.0 and 8.0 Hz, H11), 3.50 (s, 3H, C**H$_3$**OH from crystallisation), 2.30 (s, 3H, OAc), 1.20 (br. S, 1H, CH_3**O**H from crystallisation) ppm. **^{13}C NMR**: δ 177.5 (C_{quat}, **C**=O), 161.9 (C_{quat}), 155.8 (C_{quat}), 155.6 (C_{quat}), 153.6 (C_{quat}), 150.7 (C_{quat}), 149.7 (**C**H, C6), 147.8 (C_{quat}), 137.6 (**C**H, C4), 135.6 (C_{quat}), 135.5 (C_{quat}), 135.3 (C_{quat}), 135.2 (C_{quat}), 134.2 (C_{quat}), 132.8 (**C**H, C8), 129.4 (2C, **C**H), 129.2 (2C, **C**H), 129.2 (**C**H), 129.1 (2C, **C**H), 128.7 (2C, **C**H), 128.2 (2C, **C**H), 128.0 (**C**H), 127.9 (**C**H), 127.6 (**C**H), 126.7 (2C, **C**H), 126.3 (**C**H), 125.8 (**C**H, C3), 125.3 (**C**H, C5), 123.8 (**C**H, C10), 50.4 (**C**H_3OH from crystallisation), 23.8 (**C**H_3) ppm. **IR** (Neat) 1615.7, 1592.9, 1574.8, 1369.4 and 1321.4. Anal. Calcd for $C_{36}H_{26}N_2O_2Pd.2MeOH$, C, 66.24; H, 4.69; N, 4.06. Found: C, 66.86; H, 4.48; N, 4.01. **MS** *m/z*: 565.0905 $[M\text{-}OAc]^+$, (calcd. 565.0896).

Synthesis of [(η^3-methallyl)Pd(HL)]PF_6 (10)

2 (20 mg, 0.0434 mmol) and $[(\eta^3\text{-metallyl})Pd(\mu\text{-}Cl)]_2$ (8.5 mg, 0.0217 mmol) were dissolved in dichloromethane (1 mL). After 15 min, a solution of NH_4PF_6 (20 mg, 0.122 mmol) in methanol (1 mL) was added to give a colourless solution. The solution was concentrated and the residue was triturated with methanol to yield **10** as an off-white solid (30 mg, 91%). **^{1}H NMR** ($CDCl_3$): δ 8.81 (dm, 1H, *J* = 5.0 Hz, H6), 7.54 (ddd, app. td, 1H, *J* = 1.5 and 8.0 Hz, H4), 7.46 (ddd, 1H, *J* = 1.5, 5.0 and 7.5 Hz, H5), 7.32-7.36 (m, 3H), 7.19-7.28 (m, probably 3H, contains $CHCl_3$), 7.06 (m, 1H), 6.95-7.03 (m, 8H), 6.91 (dm, 1H, *J* = 8.0 Hz, H3), 6.73-6.84 (m, 5H), 3.91 (s, 1H, Hs), 3.28 (s, 1H, H*a*), 2.51 (s, 1H, Hs), 1.98 (1H, 3H, C*H*$_3$), 1.78 (s, 1H, H*a*) ppm. **^{13}C NMR**: δ 160.3 (C_{quat}), 156.2 (C_{quat}), 154.2 (C_{quat}), 153.2 (**C**H, C6), 151.7 (C_{quat}), 142.7 (C_{quat}), 138.2 (C_{quat}), 137.9 (**C**H, C4), 137.0 (C_{quat}), 136.0 (C_{quat}), 135.9 (C_{quat}), 135.5 (C_{quat}), 133.9 (C_{quat}), 130.4 (**C**H), 130.3 (**C**H), 130.3 (**C**H), 130.2 (**C**H), 130.1 (**C**H), 130.1 (**C**H), 129.4 (**C**H), 129.3 (**C**H), 128.7 (**C**H), 128.6 (**C**H, 2 × C), 128.1 (**C**H), 127.9 (**C**H), 127.6 (**C**H, 2 × C), 127.1 (**C**H, 2 × C), 127.0 (**C**H, 2 × C), 126.7 (**C**H), 126.6 (**C**H), 125.9 (**C**H), 62.8 (allyl **C**H_2), 61.5 (allyl **C**H_2), 22.2 (**C**H_3) ppm. **MS** *m/z*: 621.1541 $[M\text{-}PF_6]^+$, (calcd. 621.1522).

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Table XX Caption

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[a] Footnote text.