Rhodium and iridium complexes containing diphenyl-2-(3-methyl)indolylphosphine: synthesis, structure and application in the catalytic transfer hydrogenation of ketones†

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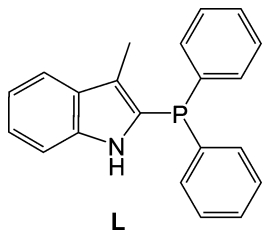
The synthesis and characterisation of a number of group nine complexes containing the recently reported ligand, diphenyl-2-(3-methyl)indolylphosphine, is presented herein. The complexes [RhCl(COD){$PPh_2(C_9H_8N)$}] (**1**), [IrCl(COD){$PPh_2(C_9H_8N)$}] (**2**), [RhCl(NBD){$PPh_2(C_9H_8N)$}] (**3**) and [Rh(COD)(MeCN){$PPh_2(C_9H_8N)$}]BF_4 (**4**) (where COD = 1,5-cyclooctadiene, NBD = 2,5-norbornadiene) have been structurally characterised by X-ray crystallography. The complex $[Rh_2(COD)_2\{N(Me)=C(H)Ph)\}\{PPh_2(C_9H_8N)\}][BF_4]_2$ (**8**) was also isolated and structurally characterised. Complex **8** contains a '[Rh(COD)]' fragment coordinated to the aromatic ring of the indolyl group, providing the first example of a η^6 coordination mode for this ligand. The synthesised complexes were investigated for their activity in the catalytic transfer hydrogenation of ketones and found to be moderately active catalysts.

Introduction

There has been great interest in the development of new complexes containing mixed phosphorus and nitrogen based ligands for the catalytic hydrogenation of unsaturated compounds following the report of the metal–ligand bifunctional catalysts by Noyori *et al*.[1] Since then, a broad range of such complexes have been developed[2–4] some of which have been shown to hydrogenate ketones with outstanding catalytic activities.[5] We became interested in this reaction as a means of exploring a potential cooperation effect from the close proximity of certain functional groups to the metal centre.[6] In the Noyori systems, the coordination of an NH functional group at the metal centre is key in determining the enhanced activities.[7] We were interested to explore whether any cooperation effect would result from the presence of an NH functional group in close proximity to the metal centre. In principle, the NH group would stabilize resulting hydride species, perhaps *via* hydrogen bonding interactions[8] or provide a means of directing substrates towards the metal centre.[6] We therefore set out to prepare some group nine complexes containing the relatively unexplored ligand, diphenyl-2-(3-methyl)indolylphosphine (**L**) (Fig. 1).[9,10,11]

Browning and coworkers reported the synthesis of diphenyl-2-indolylphosphine in 2004 together with some of its palladium complexes.[9,11] In these complexes the ligand coordinates to the metal centre *via* the phosphorus atom and the NH group was found to provide strong hydrogen bonding interactions with the coordinated halides.[10] A further report provided an unusual bridging coordination mode for the ligand (μ^3, η^2).[9]



L

Fig. 1 Diphenyl-2-(3-methyl)indolylphosphine, **L**.

More recently, derivatives of this ligand have been utilized in the Suzuki-Miyaura coupling of aryl chlorides.[12] Several monodentate and bidentate derivative ligands[13–16] have been reported and some of the latter examples have successfully been applied to asymmetric hydrogenation,[14,15] hydroformylation[15] and allylic alkylation reactions.[16] Most recently, Pérez-Prieto has published a new C3-symmetric tripodal ligand based on diphenyl-2-(3-methyl)indolylphosphine.[17] The coordination chemistry of this ligand however remains limited and we therefore wish to report the synthesis of a range of group nine transition metal complexes containing this ligand along with their catalytic performance in the transfer hydrogenation of ketones.

Results and discussion

Synthesis of complexes

The complexes [RhCl(COD)**L**] (**1**) and [IrCl(COD)**L**] (**2**) were prepared by the addition of two equivalents of diphenyl-2-(3-methyl)indolylphosphine[11] to dichloromethane solutions of $[RhCl(COD)]_2$ and $[IrCl(COD)]_2$ respectively (Scheme 1, top). After 3 h stirring at room temperature, the $^{31}P\{^1H\}$ NMR spectra of the reaction mixtures showed the complete disappearance of the signal corresponding to the free ligand and the appearance of a new signal for the expected products. Both complexes were

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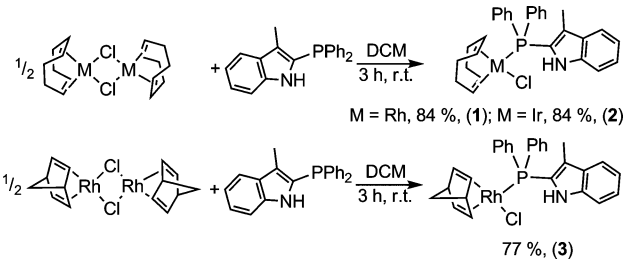
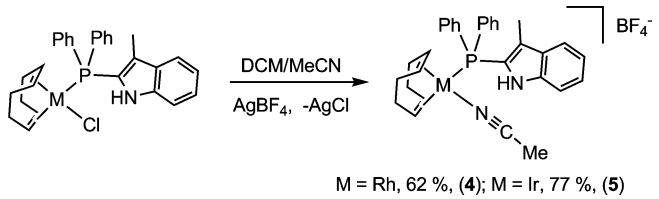


Scheme 1 Synthesis of complexes [RhCl(COD)**L**] (**1**) and [IrCl(COD)**L**] (**2**) (top) and [RhCl(NBD)**L**] (**3**) (bottom).

obtained as analytically pure solids in high yields, following a standard work up procedure (see Experimental section).

The two compounds were fully characterised by spectroscopic and analytical methods. The $^{31}P\{^{1}H\}$ NMR spectra revealed sharp peaks at 14.1 ppm (d, $^{1}J_{PRh}$ = 146 Hz) for **1** and 6.7 ppm (s) for **2** at downfield chemical shifts relative to the free ligand δ = –32.7 ppm.[11] The ^{1}H and $^{13}C\{^{1}H\}$ NMR data for both **1** and **2** were consistent with the formation of [RhCl(COD)**L**] and [IrCl(COD)**L**]. The IR spectra of **1** and **2** showed bands characteristic of the ligand together with sharp bands at 3290 cm^{-1} and 3325 cm^{-1} (powder film) due to the stretching mode of the NH group. Mass spectroscopy and elemental analysis were both consistent with the molecular composition of **1** and **2**. In order to test the effect of a diene with greater ring strain, the corresponding rhodium norbornadiene complex [RhCl(NBD)**L**] (**3**) was also prepared in a good yield. Complex **3** was synthesised and fully characterised by analogous methods as those described for complexes **1** and **2** (Scheme 1, bottom).

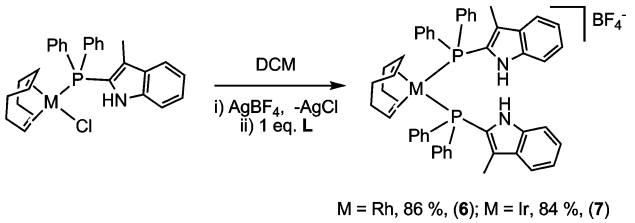
In order to explore this further, complexes containing two phosphine ligands were targeted.[18] Our initial reactions involved the addition of the phosphine ligands to dichloromethane solutions of **1** and **2** followed by addition of $AgBF_4$. The $^{31}P\{^{1}H\}$ NMR spectra of the reaction mixtures were complicated and consistently revealed a broad peak at –10.1 ppm along with signals corresponding to starting material and several other peaks. The broad peak was tentatively assigned as the complex resulting from coordination of **L** to the silver salt. In the following reactions, the silver halide was removed prior to the addition of the second equivalent of **L**. Addition of one equivalent of $AgBF_4$ to a solution of **1** in dichloromethane resulted in the rapid precipitation of AgCl from the mixture (interestingly no decomposition was observed even when non-coordinating solvents were utilized). Following filtration, the $^{31}P\{^{1}H\}$ NMR of the resulting filtrate was recorded which revealed the presence of two new doublet signals at 11.4 ppm (d, $^{1}J_{PRh}$ = 154 Hz, major component) and 9.1 [(d, $^{1}J_{PRh}$ = 142 Hz, minor component, < 15% (estimated from $^{31}P\{^{1}H\}$ integration]. The minor component was later shown to correspond to [Rh(COD)$\mathbf{L}_2$]BF_4 (see below). Despite a number of attempts, we were unable to establish the identity of the major component within this mixture. When the reaction was carried out in the presence of MeCN, (or when MeCN was used as a solvent), a new single broad peak centred at 8.7 ppm ($\Delta\nu_{1/2}$ = 122 Hz) was observed in the $^{31}P\{^{1}H\}$ NMR spectrum. An orange solid was isolated from this reaction mixture in high yield following standard workup (see Experimental section). The ^{1}H and $^{13}C\{^{1}H\}$ NMR data for this compound were consistent with the formation of [Rh(COD)(NCMe)**L**]BF_4 (**4**) (Scheme 2). The corresponding



Scheme 2 Synthesis of complexes [Rh(COD)(NCMe)**L**]BF_4 (**4**) and [Ir(COD)(NCMe)**L**]BF_4 (**5**).

iridium complex, [Ir(COD)(NCMe)**L**]BF_4 (**5**), was also prepared in good yield *via* a similar method to that for complex **4** and was characterised by spectroscopic and analytical methods. Both complexes **4** and **5** showed limited stability in solution and in the solid state even when stored under a nitrogen atmosphere.

The corresponding complexes containing two of the phosphine ligands, [Rh(COD)$\mathbf{L}_2$]BF_4 (**6**) and [Ir(COD)$\mathbf{L}_2$]BF_4 (**7**), were readily prepared by a two step procedure (Scheme 3). The chloride ligand was removed from complexes **1** and **2** by addition of $AgBF_4$ to their dichloromethane solutions. After 1 h the reaction mixtures were filtered to remove the precipitated AgCl, and one equivalent of **L** was added. The $^{31}P\{^{1}H\}$ NMR spectra of the resulting reaction mixtures revealed new signals at 9.1 ppm (d, $^{1}J_{PRh}$ = 142 Hz) and at 2.2 ppm (s), respectively suggesting the formation of the targeted products **6** and **7**. Addition of hexane to these mixtures resulted in the precipitation of these compounds in high yields which were fully characterised. The ^{1}H and $^{13}C\{^{1}H\}$ NMR data for both **6** and **7** were consistent with the formation of [Rh(COD)$\mathbf{L}_2$]BF_4 and [Ir(COD)$\mathbf{L}_2$]BF_4. The IR spectra of **6** and **7** showed bands characteristic of the ligand including bands at 3389 cm^{-1} and 3379 cm^{-1}, corresponding to N–H stretching frequencies together with broad bands at 1058 cm^{-1} and 1056 cm^{-1} for the BF_4 counterions, respectively. The presence of two phosphine ligands in each complex was confirmed by mass spectrometry and elemental analysis.



Scheme 3 Synthesis of complexes [Rh(COD)$\mathbf{L}_2$]BF_4 (**6**) and [Ir(COD)$\mathbf{L}_2$]BF_4 (**7**).

In order to explore the interactions of substrates with the metal centres further we attempted to synthesise the complex [Rh(COD){N(Me)=C(H)Ph}**L**]BF_4. In a similar procedure to that described above, the halide was abstracted from [RhCl(COD)**L**] with $AgBF_4$ and one equivalent of N(Me)=C(H)Ph was subsequently added to the resulting filtrate. The $^{31}P\{^{1}H\}$ NMR spectrum revealed the presence of a new doublet signal at 6.3 ppm (d, $^{1}J_{PRh}$ = 145 Hz, C_6D_6) suggesting the formation of our target complex. The proton NMR spectrum of the isolated solid was also consistent with the formation of the target product [Rh(COD){N(Me)=C(H)Ph}**L**]BF_4. Our attempts to purify this compound by recrystallisation led to isolation of single crystals which were found to be the unexpected complex

Table 1 Selected bond distances (Å) and angles (°) for **1–4**

	1	**2**	**3**	**4**
Rh(1)–P(1)/Ir(1)–P(1)	2.3077(3)	2.3064(7)	2.2884(5)	2.2981(10)
Rh(1)–Cl(1)/Ir(1)–Cl(1)	2.3766(3)	2.3664(7)	2.3626(5)	—
Rh(1)–N(2)	—	—	—	2.063(3)
Rh(1)–C(22)/Ir(1)–C(22)	2.2312(13)	2.209(3)	2.2181(19)	2.214(4)
Rh(1)–C(23)/Ir(1)–C(23)	2.2193(13)	2.196(3)	2.2177(19)	2.242(3)
Rh(1)–C(26)/Ir(1)–C(26)	2.1326(12)	2.121(3)	2.104(2)	2.132(4)
Rh(1)–C(27)/Ir(1)–C(27)	2.1156(12)	2.104(3)	2.103(2)	2.140(4)
C(22)–C(23)	1.3816(19)	1.395(4)	1.372(3)	1.376(5)
C(26)–C(27)	1.409(2)	1.411(4)	1.408(3)	1.383(6)
P(1)–C(1)	1.8032(13)	1.808(3)	1.807(2)	1.796(4)
P(1)–Rh(1)–Cl(1)/P(1)–Ir(1)–Cl(1)	90.726(12)	91.33(3)	94.034(18)	—
P(1)–Rh(1)–N(2)	—	—	—	91.06(9)
C(1)–P(1)–Rh(1)/C(1)–P(1)–Ir(1)	115.61(4)	115.54(10)	114.51(6)	113.40(13)
Rh(1)–Cl(1)–H(1)–N(1)/Ir(1)–Cl(1)–H(1)–N(1)	92.24	91.89	81.21	—

$[Rh_2(COD)_2\{N(Me)=C(H)Ph\}\{PPh_2(C_9H_8N)\}][BF_4]_2$ (**8**). Details of this complex are presented in the following section.

X-Ray crystal structures of complexes 1, 2, 3, 4 and 8

The coordination of diphenyl-2-(3-methyl)indolylphosphine to the rhodium and iridium centres was further confirmed by single crystal X-ray diffraction studies for complexes **1–4** and **8**. Single crystals were obtained by layering a dichloromethane solution of **1** with hexane (Fig. 2) and upon layering a chloroform solution of **2** with diethyl ether (Fig. 3). Single crystals of **3** were obtained by layering a chloroform solution of the complex with hexane. The molecular structure of **3** is shown in Fig. 4. Single crystals of **4** were grown by layering a THF solution with diethyl ether (Fig. 5). Finally, single crystals of **8** were grown by layering a dichloromethane solution with hexane and the molecular structure is shown in Fig. 6. Selected bond lengths and distances and crystallographic parameters for complexes **1–4** and **8** are highlighted in Tables 1, 2 and 3.

Complexes **1** and **2** are isostructural (and their crystals are isomorphous). The metals adopt a square planar geometry with one COD ligand, one chloride ligand and the diphenyl-2-(3-methyl)indolylphosphine coordinated to the metal centre *via* the phosphorus atom. The M–P bond distances in **1** and **2** are 2.3077(3) Å and 2.3064(7) Å, respectively. The indolyl N–H functional group is orientated so that it points in the direction of the chloride ligand. The indolyl ring is twisted with a torsion angle defined by M (Rh or Ir), Cl(1), H(1) and N(1), of 92.24° (**1**) and 91.89° (**2**). The positioning of this group is perhaps governed by steric factors and also by a hydrogen bond interaction of the

Table 2 Selected bond distances (Å) and angles (°) for **8**

Rh(1)–P(1)	2.3192(9)
Rh(1)–N(1)	2.098(3)
Rh(1)–C(1)	2.160(4)
Rh(1)–C(2)	2.151(4)
Rh(1)–C(5)	2.247(4)
Rh(1)–C(6)	2.233(4)
C(1)–C(2)	1.389(5)
C(5)–C(6)	1.383(6)
N(1)=C(10)	1.284(5)
P(1)–C(29)	1.807(4)
Rh(1)–N(1)=C(10)	129.2(3)
P(1)–Rh(1)–N(1)	91.40(9)
C(29)–P(1)–Rh(1)	110.41(12)
Rh(1)–P(1)–C(29)–N(2)	–4.7(3)

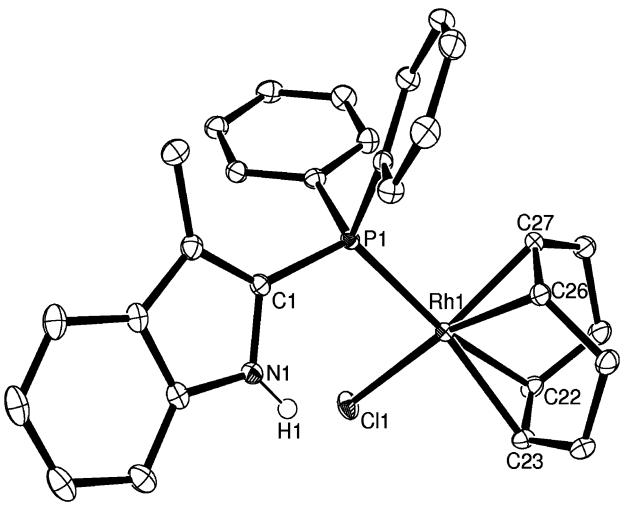


Fig. 2 Molecular structure of [RhCl(COD)**L**] (**1**), [hydrogen atoms {except for H(1)} have been omitted for clarity (thermal ellipsoids drawn at the 50% level)].

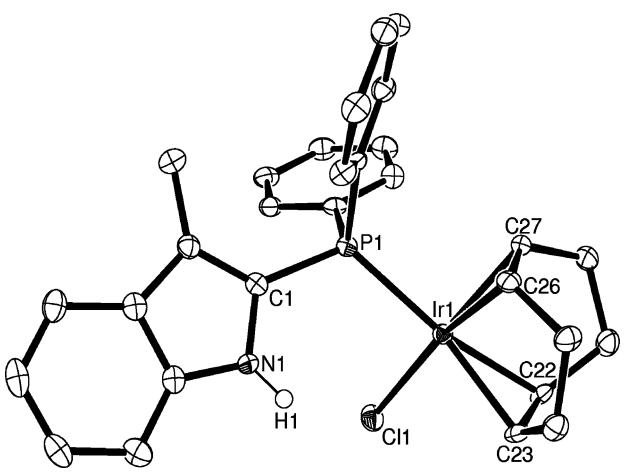


Fig. 3 Molecular structure of [IrCl(COD)**L**] (**2**), [hydrogen atoms {except for H(1)} have been omitted for clarity (thermal ellipsoids drawn at the 50% level)].

Table 3 Crystallographic parameters for complexes **1–4** and **8**

Complex	**1**	**2**	**3**	**4**	**8**
Chemical formula	$C_{29}H_{30}ClNPRh$	$C_{29}H_{30}ClIrNP$	$C_{28}H_{26}ClNPRh$	$C_{35}H_{41}BF_4N_2OPRh$	$C_{45}H_{51}B_2F_8N_2PRh_2$
Formula weight	561.87	651.16	545.83	726.39	1030.29
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a/Å	10.3430(3)	10.3316(3)	10.3647(2)	9.5738(2)	11.0623(4)
b/Å	15.0230(4)	15.0241(5)	13.1993(3)	18.7089(4)	11.2983(4)
c/Å	16.3236(5)	16.3586(5)	17.0825(4)	18.5897(4)	19.1151(7)
β (°)	105.2310(10)	105.5230(10)	97.6650(10)	91.6770(10)	98.481(2)
Z	4	4	4	4	2
T/K	100(2)	100(2)	100(2)	100(2)	100(2)
μ/mm^{-1}	0.891	5.650	0.939	0.614	0.809
No. of data collected	56256	22523	24809	29947	32973
No. of unique data	7494	5635	5298	7630	10602
Goodness of fit on F^2	1.076	1.063	1.033	1.018	1.076
R_{int}.	0.0230	0.0333	0.0318	0.0812	0.0326
Final $R_{indices}$ for ($I > 2\sigma$I)	0.0209	0.0211	0.0248	0.0478	0.0439
Final $R_{indices}$ for all data	0.0240	0.0266	0.0320	0.0876	0.0594

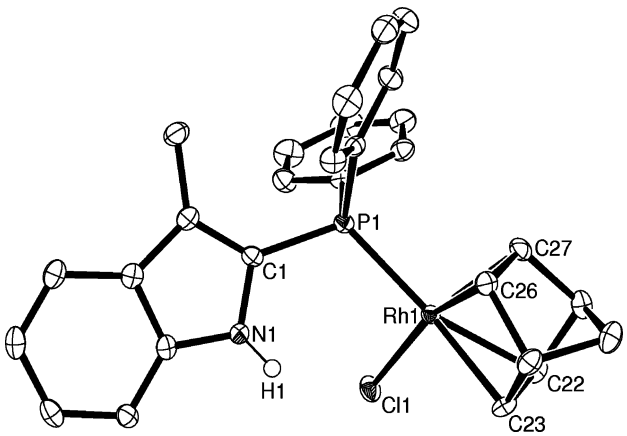


Fig. 4 Molecular structure of [RhCl(NBD)**L**] (**3**) [hydrogen atoms {except for H(1)} have been omitted for clarity (thermal ellipsoids drawn at the 50% level)].

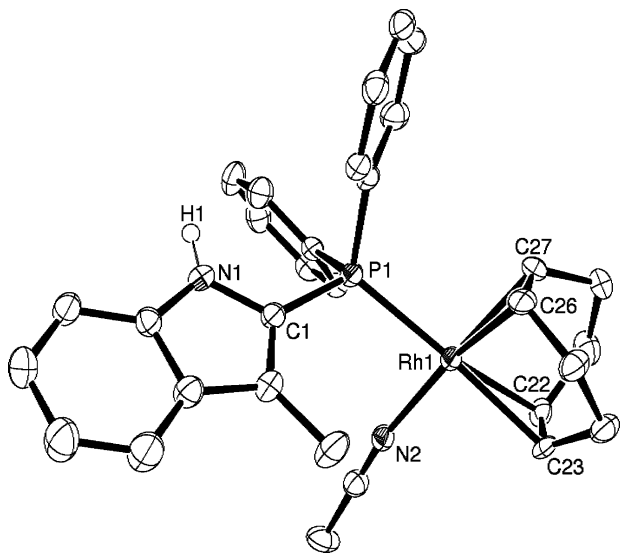


Fig. 5 Crystal structure of complex **4**·C_4H_8O [the non-coordinating solvent molecule, anion and hydrogen atoms {except for H(1)} have been omitted for clarity (thermal ellipsoids drawn at the 50% level)].

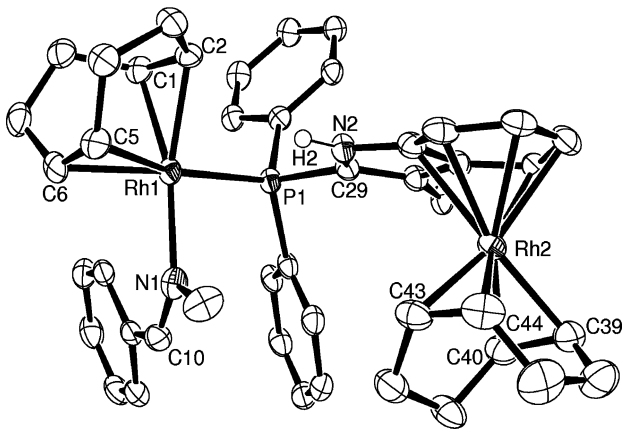


Fig. 6 Crystal structure of complex **8** [the two BF_4 counterions and hydrogen atoms {except for H(2)} have been omitted for clarity (thermal ellipsoids drawn at the 50% level)].

NH group with the chlorine. The H(1)–Cl(1) distances are 2.522 Å and 2.551 Å for complexes **1** and **2**, respectively.

The norbornadiene based complex, **3**, has a similar structure to the cyclooctadiene based complexes. The Rh–P bond distance is 2.2884(5) Å. The indolyl ring is twisted with a torsion angle defined by M (Rh or Ir), Cl(1), H(1) and N(1), of 81.21°. The H(1)–Cl(1) distance (2.450 Å) is slightly shorter than found in complexes **1** and **2**. The angle defined by the atoms P(1), Rh(1) and Cl(1) provides an indication of the ring strain of the diene ligands. The greater strain associated with NBD complex (**3**) gives an angle of 94.034(18)° while the corresponding angle in the COD based complex (**1**) is 90.726(12)°.

The rhodium centre in complex **4** adopts a square planar geometry with one COD ligand, one acetonitrile ligand and the diphenyl-2-(3-methyl)indolylphosphine coordinated to the metal centre *via* the phosphorus atom. The Rh–P bond distance is 2.2981(10) Å. The indolyl N–H functional group is orientated so that it points away from the metal centre.

In the case of complex **8**, an additional '[Rh(COD)]' fragment was bound to the expected structure [Rh{N(Me)=C(H)Ph)}(COD)**L**] which was coordinated to

the aromatic ring of the indolyl group in a η^6 mode. To the best of our knowledge, this is the first example of the indolylphosphine ligand adopting a η^6 coordination mode. These six indole carbon atoms are not all equally separated from this metal atom. The rhodium centre is furthest away from the quaternary carbon atoms of indolyl [2.398(4) Å and 2.393(4) Å compared to the range 2.254–2.293 Å for the four other carbon atoms]. This has been observed in previous examples involving indole coordination[19] and exhibits some distortion towards a η^4 coordination mode involving a 16-electron species (Fig. 7). The structure reveals a Rh(1)–P(1) bond length of 2.3192(9) Å [*c.f.* 2.3077(3) Å for **1**]. The Rh(1)–N(1) and N(1)=C(10) distances are 2.098(3) Å and 1.284(5) Å, respectively, comparable to other complexes of the type Rh–{N(R)=C(H)Ph}.[20] The phenyl group of the imine ligand is in close proximity with one phenyl groups of phosphine ligand with a distance between the two centroids of 3.780 Å and the distance between the two closest atoms of 3.442 Å.

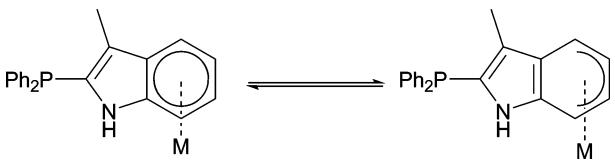


Fig. 7 η^6 and η^4 coordination modes for diphenyl-2-(3-methyl)-indolylphosphine.

Comparison of complexes 1–7

A comparison of selected NMR and IR spectroscopic data for complexes **1–7** is shown in Table 4. The $^{31}P\{^1H\}$ NMR spectra of these complexes consists of a single resonance for each complex. The positively charged complexes (**4**, **5**, **6** and **7**) give signals with upfield chemical shifts compared to the chloro-substituted complexes (**1** and **2**). The spectra for the rhodium complexes showed a doublet signals for each of the corresponding products with $^1J_{RhP}$ coupling constants ranging between 145–167 Hz, with the exception of complex **4**, where the signal was too broad to allow for the measurement of the coupling constant ($\Delta\nu_{1/2} = 124$ Hz).

The ^{1}H NMR spectra of these compounds revealed single broad peaks for the N*H* functional groups over a wide range between 9.02–10.86 ppm (*cf.* 7.8 ppm for the free ligand). The N*H* resonances within the chloro-substituted complexes **1** and **2** were located at 10.78 ppm and 10.44 ppm, respectively. The complexes containing two of the phosphine ligands gave N*H* resonances at 9.61 ppm (**6**) and 9.52 ppm (**7**). The N*H* resonances of the acetonitrile-substituent complexes were located at 9.02 ppm (**4**) and 9.09 ppm (**5**). The chemical shift of this group appears to be related to its orientation and interactions with neighbouring groups. The downfield chemical shifts, in the case of the chloride complexes (**1** and **2**), are consistent with hydrogen bonding interactions between the NH group and the halide.[10] The chemical shifts of the corresponding protons on the methyl group of the ligand are observed between 1.78 and 2.73 ppm. The signals corresponding to the methyl groups in both complexes **4** and **5** are found at downfield chemical shifts relative to the other complexes. The solid state structure of complex **4** reveals that the methyl group is orientated so that it points towards an axial site on the rhodium centre [Rh–C_{methyl} distance 3.385(4) Å] indicating a Rh···H–C interaction. Such interactions are supported by a number of previous examples where a similar downfield shift has been recorded.[21]

The olefin protons of the coordinated 1,5-cyclooctadiene ligand were found at 3.22 ppm and 5.58 ppm for **1**, while in complex **2** they were found at 2.81 ppm and 5.21 ppm. The downfield signals were assigned as those protons which are *trans* to the phosphine on the basis of the assignment of related complexes.[18c,22] This was confirmed by a HMQC correlation experiment since their corresponding carbon signals coupled to the phosphorus *trans* to them. In the case of the acetonitrile complexes **4** and **5**, only one particularly broad signal (integrating for 4 protons) corresponding to the olefin protons of the coordinated 1,5-cyclooctadiene ligands was observed [4.56 ppm (**4**) and 4.33 ppm (**5**)]. This suggests that there is some fluxional behaviour in these complexes, resulting from rapid loss and re-coordination of the solvent molecule.[23] The ^{1}H NMR spectra of the bis-phosphine complexes also revealed one chemical environment for the olefin protons as expected. The signals corresponding to the coordinated 1,5-cyclooctadiene, suggesting a more symmetric environment and only one broad signal integrating for four protons, was observed for the olefin protons in each case (4.74 ppm for **6** and 4.40 ppm for **7**).

The IR spectra of these complexes display a characteristic N–H stretching frequency of indole group – with reduced frequency relative to the free ligand (3445 cm^{-1}). The ESI$^+$ mass spectra of **1–7** showed molecular ion peaks for the expected cationic complexes with the exception of the acetonitrile complex **4** which showed signs of decomposition during the analysis (see Experimental section). The molecular composition of the complexes was further confirmed by elemental analysis.

Table 4 A comparison of the NMR and IR spectroscopic data for complexes **1–7**

	$^{31}P\{^1H\}^a$		$^1H^a$ (N*H*)	$^1H^a$ (CH_3)	IR^b (N–H stretch)
Complex	δ (ppm)	$^1J_{PRh}$/Hz	δ (ppm)	δ (ppm)	cm^{-1}
[RhCl(COD)**L**] (**1**)	14.1	146	10.78[c]	1.78	3290
[Rh(COD)$\mathbf{L}_2$]BF_4 (**6**)	9.1	142	9.61	1.81	3389
[RhCl(NBD)**L**] (**3**)	15.8	167	10.86	1.82	3267
[Rh(COD)(MeCN)**L**]BF_4 (**4**)	8.7[e]	u.r[d,e]	9.02[e]	2.73[e]	3372
[IrCl(COD)**L**] (**2**)	6.7	—	10.44	1.79	3325
[Ir(COD)$\mathbf{L}_2$]BF_4 (**7**)	2.2	—	9.52	1.80	3379
[Ir(COD)(MeCN)**L**] BF_4 (**5**)	0.3[e]	—	9.09[e]	2.65[e]	3364

[a] Recorded in $CDCl_3$ unless otherwise stated. [b] Powder film. [c] The N*H* signal of **1** was observed at 10.45 ppm in CD_3CN. [d] Unresolved. [e] Recorded in CD_3CN.

Catalytic studies

Complexes **1–3** and **6** and **7** were tested for their activities in the transfer hydrogenation of ketones using standard literature procedures.[24] Complexes **4** and **5** gave irreproducible results, presumably due to their instability and so they have not been included. The results of our preliminary investigations are summarized in Tables 5–7. The reactions were carried out at 84 °C and the resulting conversions were recorded at 1 h, 3 h and 24 h intervals and were determined by the relative integration of the substrates against products in their ^{1}H NMR spectra (see Experimental section for details). Our initial catalytic reactions (runs 1–12) were performed using 10 mL of 0.2 M solution of KOH in ^{i}PrOH (Table 5). As shown, complexes **1**, **2**, **6** and **7** are active catalyst for the transfer hydrogenation of acetophenone (**A**), benzophenone (**B**) and cyclohexanone (**C**). Table 5 reveals that the rhodium and iridium complexes **1**, **2**, **6** and **7** exhibit similar activities and hydrogenate cyclohexanone more readily than the aryl ketones, acetophenone and benzophenone. The conversion to the respective alcohols is essentially complete within a 24 h period for all substrates. The bis-phosphine iridium complex (**7**) provides the best activity for the conversion of cyclohexanone to cyclohexanol which is essentially complete within 3 h with a 65% conversion within 1 h.

Table 5 Transfer hydrogenation of ketones using complexes **1**, **2**, **6** and **7** with 0.2 M KOH in ^{i}PrOH

			Conversion (%)[c]		
Run	Complex[a]	Substrate[b]	1 h	3 h	24 h
1	**1**	**A**	15	30	86
2	**2**	**A**	10	31	94
3	**6**	**A**	11	27	79
4	**7**	**A**	21	45	92
5	**1**	**B**	14	27	78
6	**2**	**B**	7	22	82
7	**6**	**B**	24	44	76
8	**7**	**B**	39	46	90
9	**1**	**C**	44	69	99
10	**2**	**C**	54	69	99
11	**6**	**C**	42	57	99
12	**7**	**C**	65	89	> 99

[a] 10 mL of 0.2 M KOH in ^{i}PrOH, 0.1 mol% catalyst loading, 2 mmol of substrate, 84 °C. [b] **A** – acetophenone, **B** – benzophenone, **C** – cyclohexanone. [c] Measured by NMR integration.

Table 6 A comparison of the effect of base concentration upon the transfer hydrogenation of ketones

			Conversion (%)[c]		
Run	Conditions[a]	Substrate[b]	1 h	3 h	24 h
14	0.1% L/no base	**C**	—	—	—
15	0.2M KOH/^{i}PrOH	**C**	23	48	99
16	0.02 M KOH/^{i}PrOH	**C**	trace	10	50
17	0.1% L/0.2 M KOH/^{i}PrOH	**C**	14	39	94
18	0.1% L/0.02 M KOH/^{i}PrOH	**C**	trace	12	44
19	0.1% L/0.2 M KOH/^{i}PrOH	**A**	7	21	80
20	0.1% 1/0.2 M KOH/^{i}PrOH	**C**	44	69	99
21	0.1% 1/0.02 M KOH/^{i}PrOH	**C**	39	65	98
22	0.1% 1/0.002 M KOH/^{i}PrOH	**C**	18	34	33

[a] 10 mL of KOH in ^{i}PrOH, 2 mmol of substrate, 84 °C. [b] **A** – acetophenone, **C** – cyclohexanone. [c] Measured by NMR integration.

Table 7 A comparison of the activities of the COD and NBD complexes under 0.02 M KOH in ^{i}PrOH conditions

			Conversion (%)[c]		
Run	Complex[a]	Substrate[b]	1 h	3 h	24 h
23	**1**	**A**	8	24	56
24	**2**	**A**	11	24	76
25	**3**	**A**	51	63	90
26	**6**	**A**	4	16	35
27	**7**	**A**	17	26	73
28	**1**	**B**	12	21	53
29	**2**	**B**	7	14	58
30	**3**	**B**	26	43	74
31	**6**	**B**	4	14	50
32	**7**	**B**	6	10	48
33	**2**	**C**	13	17	79
34	**3**	**C**	60	94	99
35	**6**	**C**	19	51	88
36	**7**	**C**	34	73	99

[a] 10 mL of 0.02 M KOH in ^{i}PrOH, 0.1 mol% catalyst loading, 2 mmol of substrate, 84 °C. [b] **A** – acetophenone, **B** – benzophenone, **C** – cyclohexanone. [c] Measured by NMR integration.

The role of the base within transfer hydrogenation has previously been noted (although only in a small number of cases)[25] and so the catalytic reactions were carried out under various concentrations of KOH in ^{i}PrOH. Runs 14–22, shown in Table 6, show that there is indeed a strong dependence of the base concentration on the observed activities. Our observations confirm those previously reported[25] which show that the base catalyses the reaction even in the absence of a transition metal catalyst.[26] A comparison of catalytic runs 15 and 16 reveals that under 0.2 M KOH/^{i}PrOH conditions the conversion of cyclohexanone to cyclohexanol was essentially complete after 24 h while under 0.02 M KOH/^{i}PrOH conditions the conversion was 50% after the same period. A similar result is observed when the reactions were carried out in the presence of 0.1 mol% of **L** [*cf.* 94% (0.2 mol% KOH) *vs.* 44% (0.02 mol% KOH) after 24 h (runs 17 and 18, respectively)]. Run 21 shows that in the presence of 0.1 mol% of complex **1** the corresponding conversion was 65% after 3 h compared to only 10% in its absence (run 16). In order to lower the background effect of the activity of the base, subsequent runs were performed at lower base concentrations (0.02 M in ^{i}PrOH).

Table 7 shows the activities of complexes **1–3**, **6** and **7** for the transfer hydrogenation of substrates **A**, **B** and **C** under the lower base concentrations. A comparison of the activities of the related cyclooctadiene and norbornadiene complexes **1** and **3** is also shown. Runs 23–36 show a decrease in activity for the cyclooctadiene complexes (**1**, **2**, **6** and **7**) under the lower base concentrations and that, in each case, the norbornadiene complex (**3**) outperformed the cyclooctadiene complexes. Complex **3** provided conversions of 90%, 74% and 99% for acetophenone, benzophenone and cyclohexanone, respectively, after a period of 24 h. This has been attributed to the greater strain of the former diene resulting in facile generation of the active species. A similar observation has recently been recorded by Pugin and Pfaltz *et al.*[27] and by Heller.[28]

Conclusions

In summary, we have reported the synthesis and characterisation of a range of group 9 complexes containing the ligand diphenyl-2-(3-methyl)indolylphosphine (**L**). For complex **8**, a second rhodium metal centre coordinates to the indolyl moiety of the ligand through a η^6 coordination mode. This is the first example of such a coordination mode for this ligand. After optimisation, it was found that the isolated complexes were active catalysts for the transfer hydrogenation in acetophenone, benzophenone and cyclohexanone at even at low catalyst loading and low base concentration (0.1 mol% catalyst, 0.02M KOH in ^{i}PrOH). Complex **3**, which is the only complex to contain the NBD ligand, shows the highest activities while the other complexes show moderate activities. Nevertheless, the activities are comparable to other rhodium and iridium systems containing bidentate *N*-heterocyclic carbene,[3a] mixed *N*-heterocyclic carbene-nitrogen,[29] bidentate nitrogen[30] and bidentate phosphine[31] ligands at low catalyst loadings (0.1 mol%).

Experimental

General remarks

All manipulations were performed in a Braun glovebox with an O_2 and H_2O atmosphere of below 5 ppm or by using standard Schlenk techniques. Solvents (CH_2Cl_2, THF, Et_2O, MeCN and hexane) were dried using a Grubbs' alumina system, and were kept in Young's ampoules under N_2 over molecular sieves (4 Å). Dry n-pentane (<0.05 ppm H_2O) was purchased from Fluka and was stored in a Young's ampoule under N_2 over molecular sieves (4 Å). The ligand, **L**,[11] and the complexes, $[RhCl(COD)]_2$,[32] and $[IrCl(COD)]_2$,[33] were synthesised according to standard literature procedures. $[RhCl(NBD)]_2$ was purchased from STREM and used as received. The deuterated solvents, $CDCl_3$ and CD_3CN, were degassed by three freeze-thaw cycles, stirred over 4 Å molecular sieves then vacuum distilled and stored in Young's ampoules over 4 Å molecular sieves under N_2. ^{1}H NMR, ^{31}P{^{1}H} NMR spectra were recorded on a JEOL Lambda 300 spectrometer operating at 300 MHz (^{1}H), a JEOL ECP300 spectrometer operating at 300 MHz (^{1}H), a JEOL ECP 400 spectrometer operating at 400 MHz (^{1}H) or a Varian VNMR S500 instrument operating at 500 MHz (^{1}H). ^{13}C{^{1}H} NMR, DEPT-135, and hetero-nuclear correlation experiments spectra were recorded on a JEOL ECP400 spectrometer operating at 400 MHz (^{1}H), or a Varian 400-MR spectrometer operating at 400 MHz (^{1}H). The spectra were referenced internally, to the residual protic solvent (^{1}H) or the signals of the solvent (^{13}C). ^{31}P{^{1}H} NMR spectra are referenced relative to high frequency of 85% H_3PO_4. Mass spectra were recorded on a Bruker Daltonics Apex (7.0 Tesla) FT-ICR-MS mass spectrometer using ESI$^+$ ionization. Elemental analyses were performed at the microanalytical laboratory of the School of Chemistry at the University of Bristol. Infrared spectra were recorded on a Perkin-Elmer Spectrum 100 FT-IR spectrometer (solid state, neat) from 4000 cm^{-1} to 650 cm^{-1}. Fig. 8 shows the numbering scheme used for assignment of the signals related to **L**.

[RhCl(COD)L] (1). A Schlenk flask was charged with $[RhCl(COD)]_2$ (100.0 mg, 0.202 mmol) and **L** (127.4 mg, 0.404 mmol). CH_2Cl_2 (20 mL) was subsequently added to the mixture with stirring. The resulting yellow solution was stirred at room temperature for 3 h after which time the mixture was concentrated to approximately 3 mL. A yellow powder was precipitated when hexane (20 mL) was added. The product was isolated by filtration and dried under vacuum. Yield: 190.0 mg (84%). Crystals suitable for a single-crystal X-ray diffraction study were grown from layering hexane upon CH_2Cl_2 solution. Anal. Calcd. for $C_{29}H_{30}ClNPRh$ (561.89): C, 61.99; H, 5.38; N, 2.49. Found: C, 61.84; H, 5.42; N, 2.56. ^{1}H NMR ($CDCl_3$, 400.2 MHz) δ [ppm] = 1.78 (d, $^4J_{PH}$ = 1.5 Hz, 3H, $^{indole}CH_3$), 1.92–2.02 (m, 2H, $^{COD}CH_2$), 2.06–2.17 (m, 2H, $^{COD}CH_2$), 2.38–2.54 (m, 4H, $^{COD}CH_2$), 3.22 (br, 2H, ^{COD}CH *trans* to Cl), 5.58 (br, 2H, ^{COD}CH *trans* to P), 7.13 (ddd, $^3J_{HH}$ = 8.0 Hz, $^3J_{HH}$ = 6.9 Hz, $^4J_{HH}$ = 1.0 Hz, 1H, $^{indole}C^6H$), 7.28 (ddd, $^3J_{HH}$ = 8.0 Hz, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1.2 Hz, 1H, $^{indole}C^7H$), 7.37–7.47 (m, 6H, *o,p*-^{PPh2}CH), 7.49 (ddd, $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 0.9 Hz, $^4J_{HH}$ = 0.9 Hz, 1H, $^{indole}C^5H$), 7.57 (dd, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 0.7 Hz, 1H, $^{indole}C^8H$), 7.59–7.66 (m, 4H, *m*-^{PPh2}CH), 10.78 (br, 1H, N*H*). ^{31}P{^{1}H} NMR ($CDCl_3$, 121.4 MHz) δ [ppm] = 14.1 (d, $^1J_{PRh}$ = 146 Hz, *P*Ph$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz) δ [ppm] = 11.2 (s, $^{indole}CH_3$), 28.9 (d, J_{RhC} = 1.5 Hz, $^{COD}CH_2$), 33.0 (d, J_{RhC} = 3.1 Hz, $^{COD}CH_2$), 71.6 (d, J_{RhC} = 13.8 Hz, ^{COD}CH *trans* to Cl), 105.6 (dd, J_{RhC} = 11.5 Hz, J_{PC} = 6.9 Hz, ^{COD}CH *trans* to P), 112.1 (s, $^{indole}C^5$H), 119.1 (s, $^{indole}C^8$H), 119.3 (s, $^{indole}C^6$H), 120.0 (d, $^1J_{CP}$ = 1.5 Hz, $^{indole}C$PPh$_2$), 120.8 (s,$^{indole}CCH_3$), 123.8 (s, $^{indole}C^7$H), 128.5 (d, $^2J_{CP}$ = 10.8 Hz, *o*-^{PPh2}CH), 129.4 (d, $^3J_{CP}$ = 7.7 Hz,$^{indole}C^4$), 130.2 (d, $^4J_{CP}$ = 2.3 Hz, *p*-^{PPh2}CH), 130.6 (s, $^{PPh2}C_{ipso}$), 133.2 (d, $^3J_{CP}$ = 11.5 Hz, *m*-^{PPh2}CH), 137.7 (d, $^3J_{CP}$ = 9.2 Hz, $^{indole}C^9$). IR: 3289.9 cm^{-1} (υ_{N-H}). MS *m*/*z* (ESI)$^+$: 526.11 [M–Cl$^-$]$^+$ (100%).

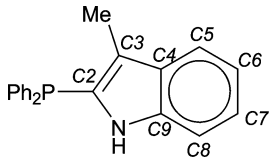


Fig. 8 Numbering scheme for **L**.

[IrCl(COD)L] (2). A Schlenk flask was charged with $[IrCl(COD)]_2$ (100.0 mg, 0.148 mmol) and **L** (93.7 mg, 0.297 mmol). CH_2Cl_2 (20 mL) was subsequently added to the mixture. The resulting orange solution was stirred at room temperature for 3 h after which time the mixture was concentrated to approximately 2 mL. A yellow-orange powder was precipitated when hexane (20 mL) was added. The product was isolated by filtration and dried under vacuum. Yield: 163.7 mg (84%). Crystals suitable for single-crystal X-ray diffraction study were grown from layering Et_2O upon $CDCl_3$ solution. Anal. Calcd. for $C_{29}H_{30}ClNIrP$ (651.20): C, 53.49; H, 4.64; N, 2.15. Found: C, 53.61; H, 4.75; N, 2.69. ^{1}H NMR ($CDCl_3$, 300.5 MHz) δ [ppm] = 1.55–1.74 (m, 2H, $^{COD}CH_2$), 1.79 (d, $^4J_{PH}$ = 0.9 Hz, 3H, $^{indole}CH_3$), 1.85–2.00 (m, 2H, $^{COD}CH_2$), 2.15–2.41 (m, 4H, $^{COD}CH_2$), 2.81 (br, 2H, ^{COD}CH *trans* to Cl), 5.21 (br, 2H, ^{COD}CH *trans* to P), 7.14 (ddd, $^3J_{HH}$ = 7.9 Hz, $^3J_{HH}$ = 6.9 Hz, $^4J_{HH}$ = 1.4 Hz, 1H, $^{indole}C^6H$), 7.29 (ddd, $^3J_{HH}$ = 7.5 Hz, $^3J_{HH}$ = 7.0 Hz, $^4J_{HH}$ = 1.1 Hz, 1H, $^{indole}C^7H$), 7.38–7.46 (m, 6H, *o,p*-^{PPh2}CH), 7.49 (dd, $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 0.6 Hz, 1H, $^{indole}C^5H$), 7.54–7.65 (m, 5H, *m*-^{PPh2}CH &$^{indole}C^8H$), 10.44 (br, 1H, N*H*). ^{31}P{^{1}H} NMR ($CDCl_3$, 121.7 MHz) δ [ppm] = 6.70 (s, *P*Ph$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.5 MHz) δ [ppm] = 11.3 (s, $^{indole}CH_3$), 29.5 (d, J_{PC} = 1.6 Hz, $^{COD}CH_2$), 33.4 (d, J_{PC} = 3.1 Hz,

$^{COD}CH_2$), 54.6 (s, ^{COD}CH *trans* to Cl), 94.7 (d, J_{PC} = 14.0 Hz, ^{COD}CH *trans* to P), 112.1 (s, $^{indole}C^5H$), 119.2 (s, $^{indole}C^8H$), 119.4 (s, $^{indole}C^6H$), 120.6 (d, $^1J_{CP}$ = 3.1 Hz, $^{indole}CPPh_2$), 121.7 (s, $^{indole}CCH_3$), 123.9 (s, $^{indole}C^7H$), 128.4 (d, $^2J_{CP}$ = 10.9 Hz, *o*-^{PPh2}CH), 129.1 (s, $^{indole}C^4$), 129.6 (s, $^{PPh2}C_{ipso}$), 130.4 (d, $^4J_{CP}$ = 2.3 Hz, *p*-^{PPh2}CH), 133.5 (d, $^3J_{CP}$ = 11.7 Hz, *m*-^{PPh2}CH), 137.4 (d, $^3J_{CP}$ = 8.6 Hz, $^{indole}C^9$). IR: 3324.5 cm^{-1} (υ_{N-H}). MS *m*/*z* (ESI)$^+$: 616.18 [M–Cl$^-$]$^+$ (68%), 674.14 [M+Na$^+$]$^+$ (100%).

[RhCl(NBD)L] (3). A Schlenk flask was charged with [RhCl(NBD)]$_2$ (50.0 mg, 0.108 mmol) and **L** (68.1 mg, 0.216 mmol). CH_2Cl_2 (10 mL) was subsequently added to the mixture. The resulting yellow solution was stirred at room temperature for 3 h after which time the mixture was concentrated to approximately 2 mL. A bright yellow powder was precipitated when hexane (10 mL) was added. The product was isolated by filtration and dried under vacuum. Yield: 91.5 mg (77%). Crystals suitable for single-crystal X-ray diffraction study were grown from layering hexane upon $CDCl_3$ solution. Anal. Calcd. for $C_{28}H_{26}ClNPRh$ (545.85): C, 61.61; H, 4.80; N, 2.57. Found: C, 61.40; H, 4.93; N, 2.79. ^{1}H NMR ($CDCl_3$, 400.2 MHz) δ [ppm] = 1.34–1.47 (m, 2H, $^{NBD}CH_2$), 1.82 (d, $^4J_{PH}$ = 1.3 Hz, 3H, $^{indole}CH_3$), 3.06 (br, 2H, ^{NBD}CH=CH *trans* to Cl), 3.78–3.82 (m, 2H, ^{NBD}CH), 5.34 (br, 2H, ^{NBD}CH=CH *trans* to P), 7.10 (ddd, $^3J_{HH}$ = 8.0 Hz, $^3J_{HH}$ = 7.0 Hz, $^4J_{HH}$ = 1.0 Hz, 1H, $^{indole}C^6H$), 7.25 (ddd, $^3J_{HH}$ = 8.1 Hz, $^3J_{HH}$ = 6.9 Hz, $^4J_{HH}$ = 0.8 Hz, 1H, $^{indole}C^7H$), 7.40–7.44 (m, 6H, *o*,*p*-^{PPh2}CH), 7.49 (ddd, $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 0.9 Hz, $^4J_{HH}$ = 0.9 Hz, 1H, $^{indole}C^5H$), 7.55 (dd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 0.8 Hz, 1H, $^{indole}C^8H$), 7.57–7.64 (m, 4H, *m*-^{PPh2}CH), 10.86 (br, 1H, NH). ^{31}P {^{1}H} NMR ($CDCl_3$, 121.4 MHz) δ [ppm] = 15.8 (d, $^1J_{PRh}$ = 167 Hz, PPh_2). ^{13}C {^{1}H} NMR ($CDCl_3$, 100.6 MHz) δ [ppm] = 11.0 (s, $^{indole}CH_3$), 50.6 (d, J_{RhC} = 2.3 Hz, ^{NBD}CH), 52.2 (d, J_{RhC} = 11.5 Hz, ^{NBD}CH *trans* to Cl), 63.8 (d, J_{RhC} = 6.2 Hz, $^{NBD}CH_2$), 85.4 (dd, J_{RhC} = 11.5 Hz, J_{PC} = 5.5 Hz, ^{NBD}CH *trans* to P), 112.1 (s, $^{indole}C^5H$), 119.0 (s, $^{indole}C^8H$), 119.1 (s, $^{indole}CPPh_2$), 119.3 (s, $^{indole}C^6H$), 122.0 (s, $^{indole}CCH_3$), 123.7 (s, $^{indole}C^7H$), 128.6 (d, $^2J_{CP}$ = 10.8 Hz, *o*-^{PPh2}CH), 129.2 (d, $^3J_{CP}$ = 6.9 Hz, $^{indole}C^4$), 130.3 (d, $^4J_{CP}$ = 2.3 Hz, *p*-^{PPh2}CH), 130.4 (s, $^{PPh2}C_{ipso}$), 133.1 (d, $^3J_{CP}$ = 11.5 Hz, *m*-^{PPh2}CH), 137.7 (d, $^3J_{CP}$ = 10.0 Hz, $^{indole}C^9$). IR: 3266.7 cm^{-1} (υ_{N-H}). MS *m*/*z* (ESI)$^+$: 510.09 [M–Cl]$^+$ (100%).

[Rh(COD)L(NCMe)]BF$_4$ (4). A Schlenk flask was charged with [RhCl(COD)**L**] (**1**) (50.0 mg, 0.089 mmol). MeCN (10 mL) was added and then CH_2Cl_2 (15 mL). $AgBF_4$ (25.9 mg, 0.133 mmol) was added to the flask in one portion and the flask was subsequently covered with aluminium foil. The yellow cloudy solution was filtered. All volatiles were subsequently removed under reduced pressure to provide a yellow solid. Yield: 36.0 mg (62%). Crystals suitable for single-crystal X-ray diffraction study were grown from layering Et_2O upon THF solution. ^{1}H NMR (CD_3CN, 300.5 MHz) δ [ppm] = 1.96 (s, 3H, $^{coordinated}NCCH_3$), 2.04–2.15 (m, 4H, $^{COD}CH_2$), 2.37–2.55 (m, 4H, $^{COD}CH_2$), 2.73 (br, 3H, $^{indole}CH_3$), 4.56 (br, 4H, ^{COD}CH), 7.15 (ddd, $^3J_{HH}$ = 8.1 Hz, $^3J_{HH}$ = 7.0 Hz, $^4J_{HH}$ = 1.1 Hz, 1H, $^{indole}C^6H$), 7.26 (ddd, $^3J_{HH}$ = 8.2 Hz, $^3J_{HH}$ = 7.0 Hz, $^4J_{HH}$ = 1.1 Hz, 1H, $^{indole}C^7H$), 7.41 (d, $^3J_{HH}$ = 8.3 Hz, 1H, $^{indole}C^5H$), 7.46–7.63 (m, 10H, PC_6H_5), 7.69 (d, $^3J_{HH}$ = 8.3 Hz, 1H, $^{indole}C^8H$), 9.02 (br, 1H, NH). ^{31}P{^{1}H} NMR (CD_3CN, 121.6 MHz) δ [ppm] = 8.7 (br, $\Delta\nu_{1/2}$ = 122 Hz, PPh_2). IR: 3371.5 (υ_{N-H}), 1015.6 (υ_{B-F}) cm^{-1}.[34,35]

[Ir(COD)L(NCMe)]BF$_4$ (5). A Schlenk flask was charged with [IrCl(COD)**L**] (**2**) (50.0 mg, 0.076 mmol). MeCN (10 mL) was added and then CH_2Cl_2 (15 mL). $AgBF_4$ (22.4 mg, 0.115 mmol) was added to the flask in one portion and the flask was subsequently covered with aluminium foil. The orange cloudy solution was filtered, hexane (10 mL) was added and all volatiles were subsequently removed under reduced pressure to provide a bright orange solid. Yield: 44.0 mg (77%). ^{1}H NMR (CD_3CN, 499.9 MHz) δ [ppm] = 1.96 (s, 3H, $^{coordinated}NCCH_3$), 1.97–2.03 (m, 4H, $^{COD}CH_2$), 2.23–2.35 (m, 4H, $^{COD}CH_2$), 2.65 (br, 3H, $^{indole}CH_3$), 4.33 (br, 4H, ^{COD}CH), 7.17 (dd, $^3J_{HH}$ = 7.5 Hz, $^3J_{HH}$ = 7.0 Hz, 1H, $^{indole}C^6H$), 7.29 (dd, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 7.2 Hz, 1H, $^{indole}C^7H$), 7.46 (d, $^3J_{HH}$ = 8.2 Hz, 1H, $^{indole}C^5H$), 7.50–7.65 (m, 10H, PC_6H_5), 7.71 (d, $^3J_{HH}$ = 7.9 Hz, 1H, $^{indole}C^8H$), 9.09 (br, 1H, NH). ^{31}P {^{1}H} NMR (CD_3CN, 121.6 MHz) δ [ppm] = 0.3 (s, PPh_2). ^{13}C {^{1}H} NMR[36] (CD_3CN, 100.5 MHz) δ [ppm] = 1.6 ($^{coordinated}CH_3CN$), 11.7 ($^{indole}CH_3$), 31.9 (s, $^{COD}CH_2$), 80.9 (d, J_{PC} = 6.2 Hz, ^{COD}CH), 113.0 (s, $^{indole}C^5H$), 118.5 ($^{coordinated}MeCN$), 120.1 ($^{indole}CPPh_2$), 120.6 (s, $^{indole}C^8H$), 120.9 (s, $^{indole}C^6H$), 124.8 ($^{indole}CCH_3$), 125.6 (s, $^{indole}C^7H$), 128.5 ($^{PPh2}C_{ipso}$), 130.0 ($^{indole}C^4$), 130.2 (d, $^2J_{CP}$ = 10.9 Hz, *o*-^{PPh2}CH), 132.5 (d, $^4J_{CP}$ = 2.3 Hz, *p*-^{PPh2}CH), 134.5 (d, $^3J_{CP}$ = 11.7 Hz, *m*-^{PPh2}CH), 136.3 ($^{indole}C^9$). IR: 3363.6 (υ_{N-H}), 1054.5 (υ_{B-F}) cm^{-1}. MS *m*/*z* (ESI)$^+$ 616.17 [M$^+$–MeCN]$^+$ (100%), 657.20 [M]$^+$ (25%), 931.28 [M+**L**]$^+$ (40%).[34]

[Rh(COD)L$_2$]BF$_4$ (6). A Schlenk flask was charged with [RhCl(COD)**L**] (**1**) (50.0 mg, 0.089 mmol) and CH_2Cl_2 (10 mL). After stirring well and covering flask with foil, $AgBF_4$ (20.8 mg, 0.106 mmol) was added to the Schlenk in one portion. The yellow solution was filtrated after 1 h of stirring in room temperature. The colour became yellow-orange initial after addition of **L** (28.1 mg, 0.089 mmol). After 1 h further of stirring at room temperature, a yellow powder was precipitated when hexane (20 mL) was added. The product was isolated by filtration and dried under vacuum. Yield: 71.0 mg (86%). Anal. Calcd. for $C_{50}H_{48}BF_4N_2P_2Rh{\cdot}2H_2O$[38] (1911.22): C, 62.84; H, 5.38; N, 2.93. Found: C, 62.36; H, 5.60; N, 2.99. ^{1}H NMR ($CDCl_3$, 300.5 MHz) δ [ppm] = 1.81 (s, 6H, $^{indole}CH_3$), 2.19–2.30 (m, 4H, $^{COD}CH_2$), 2.61–2.74 (m, 4H, $^{COD}CH_2$), 4.74 (br, 4H, ^{COD}CH), 7.10–7.23 (m, 10H, *o*-^{PPh2}CH & $^{indole}C^6H$), 7.28–7.41 (m, 14H, *m*,*p*-^{PPh2}CH & $^{indole}C^7H$), 7.54 (d, $^3J_{HH}$ = 8.4 Hz, 2H, $^{indole}C^8H$), 7.74 (d, $^3J_{HH}$ = 8.0 Hz, 2H, $^{indole}C^5H$), 9.61 (s, 2H, NH). ^{31}P {^{1}H} NMR ($CDCl_3$, 121.6 MHz) δ [ppm] = 9.1 (d, $^1J_{PRh}$ = 142 Hz, PPh_2). ^{13}C {^{1}H} NMR ($CDCl_3$, 100.6 MHz) δ [ppm] = 11.9 (s, $^{indole}CH_3$), 30.7 (s, $^{COD}CH_2$), 101.2 (dd, J_{RhC} = 7.7 Hz, J_{PC} = 4.6 Hz, ^{COD}CH), 113.4 (s, $^{indole}C^5H$), 118.8 (s, $^{indole}C^8H$), 119.8 (s, $^{indole}CPPh_2$), 120.2 (s, $^{indole}C^6H$), 122.0 (virtual t, $^2J_{CP}$ = 2.3 Hz, $^{indole}CCH_3$), 125.0 (s, $^{indole}C^7H$), 128.7 (virtual t, $^2J_{CP}$ = 5.4 Hz, *o*-^{PPh2}CH),[37] 129.0 (virtual t, $^3J_{CP}$ = 3.8 Hz, $^{indole}C^4$),[37] 129.6 (s, $^{PPh2}C_{ipso}$), 130.3 (s, *p*-^{PPh2}CH), 132.7 (virtual t, $^3J_{CP}$ = 5.8 Hz, *m*-^{PPh2}CH),[37] 138.5 (virtual t, $^3J_{CP}$ = 4.6 Hz, $^{indole}C^9$).[37] IR: 3388.9 (υ_{N-H}), 1058.4 (υ_{B-F}) cm^{-1}. MS *m*/*z* (ESI)$^+$: 526.11 [M$^+$–**L**]$^+$ (95%), 841.24 [M]$^+$ (100%).[39]

[Ir(COD)L$_2$]BF$_4$ (7). A Schlenk flask was charged with [IrCl(COD)**L**] (**2**) (100.0 mg, 0.153 mmol) and CH_2Cl_2 (20 mL). After stirring well and covering flask with foil, $AgBF_4$ (35.8 mg, 0.184 mmol) was added to the Schlenk in one portion. The wine-red solution was filtrated after 1 h of stirring in room temperature. The colour became brighter initial after addition of **L** (48.4 mg, 0.153 mmol). After 1 h further of stirring at room temperature,

a red powder was precipitated when hexane (20 mL) was added. The product was isolated by filtration and dried under vacuum. Yield: 131.1 mg (84%). Anal. Calcd. for $C_{50}H_{48}BF_4IrN_2P_2 \cdot 3H_2O$[38] (1071.94): C, 56.02; H, 5.08; N, 2.61. Found: C, 56.12; H, 5.02; N, 2.66. ^{1}H NMR ($CDCl_3$, 300.5 MHz) δ [ppm] = 1.80 (s, 6H, $^{indole}CH_3$), 1.92–2.10 (m, 4H, $^{COD}CH_2$), 2.42–2.62 (m, 4H, $^{COD}CH_2$), 4.40 (br, 4H, ^{COD}CH), 7.11–7.23 (m, 10H, *o*-^{PPh2}CH &$^{indole}C^6H$), 7.26–7.42 (m, 14H, *m,p*-^{PPh2}CH &$^{indole}C^7H$), 7.55 (d, $^3J_{HH}$ = 8.0 Hz, 2H, $^{indole}C^8H$), 7.73 (d, $^3J_{HH}$ = 8.3 Hz, 2H, $^{indole}C^5H$), 9.52 (s, 2H, N*H*). ^{31}P {^{1}H} NMR ($CDCl_3$, 121.7 MHz) δ [ppm] = 2.2 (s, PPh_2). ^{13}C {^{1}H} NMR ($CDCl_3$, 100.5 MHz) δ [ppm] = 12.0 (s, $^{indole}CH_3$), 31.1 (s, $^{COD}CH_2$), 89.5 (virtual t, J_{PC} = 5.5 Hz, ^{COD}CH),[37] 113.2 (s, $^{indole}C^5H$), 118.5 (s, $^{indole}CPPh_2$), 118.9 (s, $^{indole}C^8H$), 120.2 (s, $^{indole}C^6H$), 122.4 (virtual t, $^2J_{CP}$ = 3.1 Hz, $^{indole}CCH_3$),[37] 125.0 (s, $^{indole}C^7H$), 128.2 (s, $^{PPh2}C_{ipso}$), 128.6 (virtual t, $^2J_{CP}$ = 5.5 Hz, *o*-^{PPh2}CH),[37] 128.9 (virtual t, $^3J_{CP}$ = 3.9 Hz, $^{indole}C^4$),[37] 130.7 (s, *p*-^{PPh2}CH), 132.9 (virtual t, $^3J_{CP}$ = 4.7 Hz, *m*-^{PPh2}CH),[37] 138.2 (virtual t, $^3J_{CP}$ = 4.3 Hz, $^{indole}C^9$).[37] IR: 3379.2 (υ_{N-H}), 1056.0 (υ_{B-F}) cm^{-1}. MS *m/z* (ESI)$^+$: 616.18 [M$^+$–**L**]$^+$ (70%), 931.29 [M]$^+$ (100%).

Synthesis of [Rh(COD){N(Me)=C(H)Ph}L]BF_4 and [Rh_2(COD)$_2${N(Me)=C(H)Ph}L][BF_4]$_2$ (8). To a solution of **1** (50.0 mg, 0.089 mmol) in CH_2Cl_2 (10 mL), silver tetrafluoroborate (20.8 mg, 0.106 mmol) was added. The yellow mixture was filtrated after 1 h of stirring in room temperature before adding N-benzylidenemethylamine (11.03 μL, 0.089 mmol). After stirring at room temperature overnight, a yellow powder was precipitated when Et_2O (20 mL) was added. A yellow solid was isolated by filtration and then dried under vacuum (32.6 mg, 0.032 mmol, 71%, based on the target product, [Rh(COD){N(Me)=C(H)Ph}L]BF_4). Selected data: NMR of isolated solid ^{31}P{^{1}H} (C_6D_6, 121.4 MHz) δ [ppm] = 6.3 (d, $^1J_{PRh}$ = 145 Hz, PPh_2). ^{1}H NMR (C_6D_6, 300.5 MHz) δ [ppm] = 1.19–2.26 (m, 8H, $^{COD}CH_2$), 1.59 (d, 3H, $^1J_{PH}$ = 1.1 Hz,$^{indole}CH_3$), 3.15 (br m, 1H, ^{COD}CH), 3.60 (br m, 1H, ^{COD}CH), 3.86 [s, 3H, C=N(CH_3)], 4.33 (br, m, 1H, ^{COD}CH), 6.00 (br, m, 1H, ^{COD}CH), 6.68 (m, 1H, $^{indole}CH$), 6.81 (m, 1H, $^{indole}CH$) 6.87–7.07 (m, 5H, ^{Ph}CH &$^{indole}CH$), 7.10–7.26 (m, 3H, ^{Ph}CH), 7.31–7.45 (m, 5H, ^{Ph}CH), 7.55 (d, $^3J_{HH}$ = 8.3 Hz, 1H, $^{indole}CH$), 7.89 (br, m 1H, ^{Ph}CH), 8.77–8.83 (m, 2H, ^{Ph}CH), 9.02 (d, $^3J_{RhH}$ = 8.4 Hz, 1H, N=C*H*), 11.15 (s, 1H, N*H*).

Selected data for **8**: Crystals for X-ray diffraction study were grown from layering hexane upon CH_2Cl_2 solution under a nitrogen atmosphere. MS (ESI)$^+$ of crystals: *m/z* 526.12 [M^{2+}–imine–Rh$^+$(COD)] (100%), 645.20 [M^{2+}–Rh (COD)] (25%), 736.12 [M^{2+}–imine–H$^+$] (15%), 857.24 [M^{2+}–H$^+$] (30%).

Catalyst screening

This was performed in a Radleys carousel as follows: a CH_2Cl_2 solution containing 0.5 mol% of catalyst was transferred to a Teflon screw top tube which was connected to a Schlenk line. The solvent was then evaporated under reduced pressure. 2 mmol of substrate (acetophenone, 157 μL; benzophenone, 364 mg; cyclohexanone, 207 μL) was added, followed by 10 mL of a 0.2 M (high base condition) or a 0.02 M (low base condition) solution of KOH in ^{i}PrOH *via* a syringe and the mixture was heated to 84 °C. The reaction was sampled at 1 h, 3 h and 24 h, the portion was added into NMR tube without evaporation or filtration. 3 drops of D_2O was added into NMR tube and the residue analyzed by ^{1}H NMR in $CDCl_3$ (with a reaction mixture: $CDCl_3$ ratio of 2 : 3 by volume). The percentage conversions were determined by relative integration of characteristic resonances of the both the products and the starting materials.

X-Ray crystallography

X-Ray diffraction experiments on **1**, **2**, **3**, **4** and **8** were carried out at 100 K on a Bruker APEX II diffractometer using Mo-Kα radiation (λ = 0.71073 Å) source. Data collections were performed using a CCD area detector from a single crystal mounted on a glass fibre. Intensities were integrated[40] from several series of exposures measuring 0.5° in ω or φ. Absorption corrections were based on equivalent reflections using SADABS.[41] Structures were solved using SHELXS and refined against all F_o^2 data with hydrogen atoms riding in calculated positions using SHELXTL.[42] Crystal structure and refinement data are given in Table 3.

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