Novel ruthenium(II) complexes containing imino- or aminophosphine ligands for catalytic transfer hydrogenation

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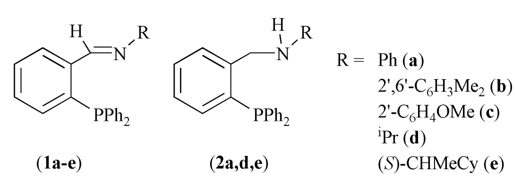
Five- and six-coordinate ruthenium(II) complexes containing imino- and aminophosphines have been prepared by ligand exchange processes. Thus, reactions of $[RuCl_2(PPh_3)_3]$ with 2-$Ph_2PC_6H_4CH{=}NR$ (R = Ph (**1a**); 2′,6′-$C_6H_3Me_2$ (**1b**); 2′-C_6H_4OMe (**1c**)) lead to the chelate iminophosphine complexes $[RuCl_2(\kappa^2$-*P*,*N*-2-$Ph_2PC_6H_4CH{=}NR)(PPh_3)]$ (R = Ph (**3a**); 2′,6′-$C_6H_3Me_2$ (**3b**)) and $[RuCl_2(\kappa^3$-*P*,*N*,*O*-2-$Ph_2PC_6H_4CH{=}N$-2′-$C_6H_4OMe)(PPh_3)]$ (**3c**), respectively. Similarly, reactions with aminophosphine ligands 2-$Ph_2PC_6H_4CH_2NHR$ (R = Ph (**2a**); ^iPr (**2d**); (*S*)-CHMeCy (**2e**)) afford the 16-electron complexes $[RuCl_2(\kappa^2$-*P*,*N*-2-$Ph_2PC_6H_4CH_2NHR)(PPh_3)]$ (R = Ph (**5a**); ^iPr (**5d**); (*S*)-CHMeCy (**5e**)). The iminophosphines 2-$Ph_2PC_6H_4CH{=}NR$ (R = ^iPr (**1d**); (*S*)-CHMeCy (**1e**)) react with $[RuCl_2(DMSO)_4]$ to lead to the bis-iminophosphine complexes $[RuCl_2(\kappa^2$-*P*,*N*-2-$Ph_2PC_6H_4CH{=}NR)_2]$ (R = ^iPr (**4d**); (*S*)-CHMeCy (**4e**)). The crystal structure of **4d** has been determined by X-ray diffraction. Complexes **3a–c**, **4d,e** and **5a,d,e** are active in catalytic transfer hydrogenation of acetophenone. All of them are more efficient than the precursor $[RuCl_2(PPh_3)_3]$.

Introduction

The design of new ligands for promoting high reactivity and selectivity in metal-catalyzed synthesis is a field of constant ongoing research activity. Heteroditopic ligands, bearing phosphorus and nitrogen atoms, have attracted particular attention since they can induce increased selectivity owing to the different electronic properties of the two donor atoms. Thus, they have been successfully used in a great variety of transition metal catalyzed reactions, among others, hydrosilylations of C=O bonds, allylic substitutions and Heck reactions.[1] In particular, many ruthenium(II) complexes bearing bidentate or tridentate P,N ligands such as phosphinooxazolines and pyridylphosphines have proven to be efficient catalysts in transfer hydrogenation of ketones[1–3] with high rates and conversions. In contrast, only a few catalysts containing analogous imino- and aminophosphine ligands have been used to date in this type of catalytic process.[4]

We have recently reported the synthesis of five- and six-coordinate ruthenium(II) complexes containing 2-$Ph_2PC_6H_4CH{=}N^tBu$ and 2-$Ph_2PC_6H_4CH_2NH^tBu$ as chelate ligands.[5] Since these complexes have proved to be very active catalysts in transfer hydrogenation of acetophenone by propan-2-ol, we believe it of interest to extend these studies with a series of imino- and aminophosphine complexes by using analogous P,N ligands in which the imino and amino substituents introduce different steric and/or electronic features. Thus, in this paper we report: (i) the synthesis of new ruthenium(II) complexes containing bidentate 2-$Ph_2PC_6H_4CH{=}NR$ (R = Ph (**1a**); 2′,6′-$C_6H_3Me_2$ (**1b**); ^iPr (**1d**); (*S*)-CHMeCy (**1e**)) and 2-$Ph_2PC_6H_4CH_2NHR$ (R = Ph (**2a**); ^iPr (**2d**); (*S*)-CHMeCy (**2e**)), and the tridentate 2-$Ph_2PC_6H_4CH{=}N$-2′-C_6H_4OMe (**1c**) ligands, (ii) the study of their catalytic activity in transfer hydrogenation of acetophenone.

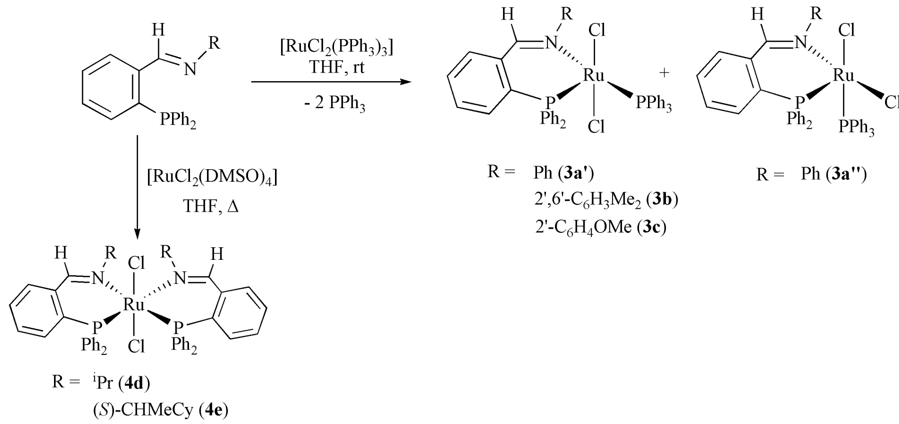


Results and discussion

The new ligands **1c,e** and **2d,e** have been synthesized following classical methodologies.[6] They have been isolated as air-stable solids (**1c**) or oils (**1e**, **2d,e**) in good yields and characterized by IR and $^{31}P\{^1H\}$, ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and mass spectrometry (see Experimental section for details). The most significant features are: (i) $^{31}P\{^1H\}$ NMR: a singlet signal at *ca.* −14 ppm, (ii) ^1H NMR of **1c,e**: a doublet at *ca.* 9 ppm attributed to the iminic proton, and (iii) ^1H NMR of **2d,e**: a resonance at *ca.* 4 ppm corresponding to the CH_2N hydrogen nuclei.

Synthesis of the iminophosphine complexes $[RuCl_2(\kappa^2$-*P*,*N*-2-$Ph_2PC_6H_4CH{=}NR)(PPh_3)]$ (R = Ph (3a); 2′,6′-$C_6H_3Me_2$ (3b)) and $[RuCl_2(\kappa^3$-*P*,*N*,*O*-2-$Ph_2PC_6H_4CH{=}N$-2′-$C_6H_4OMe)(PPh_3)]$ (3c)

As described for the preparation of the complex $[RuCl_2(\kappa^2$-*P*,*N*-2-$Ph_2PC_6H_4CH{=}N^tBu)(PPh_3)]$,[5] the iminophosphines 2-$Ph_2PC_6H_4CH{=}NR$ (R = Ph (**1a**); 2′,6′-$C_6H_3Me_2$ (**1b**)) react



Scheme 1

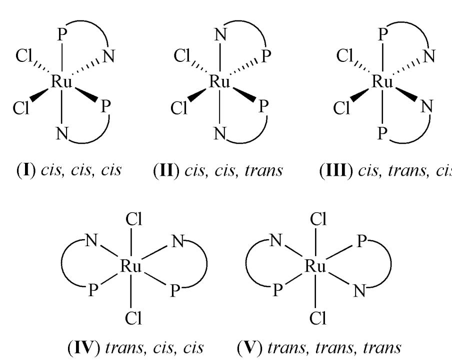
with $[RuCl_2(PPh_3)_3]$, in THF at room temperature, affording complexes $[RuCl_2(\kappa^2\text{-}P,N\text{-}2\text{-}Ph_2PC_6H_4CH{=}NR)(PPh_3)]$ (R = Ph (**3a**); 2′,6′-$C_6H_3Me_2$ (**3b**)). Similarly, the reaction with the tridentate iminophosphine **2c** gives the complex $[RuCl_2(\kappa^3\text{-}P,N,O\text{-}2\text{-}Ph_2PC_6H_4CH{=}N\text{-}2'\text{-}C_6H_4OMe)(PPh_3)]$ (**3c**) (Scheme 1).

Spectroscopic (IR, Far-IR, $^{31}P\{^1H\}$, ^1H, and $^{13}C\{^1H\}$ NMR) and analytical data confirm the proposed formulations. Complex **3a** has been isolated as a mixture of two non-separable stereoisomers (**3a′** and **3a″**) as inferred by IR and NMR spectroscopy. In particular, the Far-IR spectrum shows ν_{Ru-Cl} absorptions at 320, and at 292 and 245 cm^{-1} which are consistent with the presence of *trans* (**3a′**) and *cis* (**3a″**) dichloride complexes, respectively (Scheme 1).[7] In addition, the $^{31}P\{^1H\}$ NMR spectrum exhibits the expected resonances for two AX spin systems at 87.9 (**3a′**) and 84.2 (**3a″**) (Ph_2P fragment) and 36.2 (**3a′**) and 43.9 ppm (**3a″**) (PPh_3 ligand). The small coupling constant values ($^2J_{PP}$ = 31.3 (**3a′**) and 39.6 (**3a″**) Hz) are in agreement with the *cis*-disposition of the two P-donor groups. In contrast, complexes **3b,c** are obtained stereoselectively as the *trans* dichloride isomers. This is assessed by the Far-IR spectra which display one single ν_{Ru-Cl} stretching absorption at *ca.* 320 cm^{-1}. The $^{31}P\{^1H\}$ NMR spectra of **3b,c** show an AX spin system at 87.5 (**3b**) and 69.7 (**3c**) (PPh_2 group) and 35.7 (**3b**) and 34.7 (**3c**) ppm (PPh_3 ligand) with a small coupling constant ($^2J_{PP}$ = 33.4 (**3b**) and 32.6 (**3c**) Hz) indicative of the *cis*-arrangement of the two phosphorus nuclei. The ^1H NMR spectra of the *cis* and *trans* isomers also show remarkable differences. Thus, the iminic proton resonances of the *trans* complexes **3a′,b,c** show a relatively high $^4J_{PH}$ value (8.8–9.1 Hz) characteristic of a *trans* disposition of the imino group and the PPh_3 ligand.[8] This contrasts with the corresponding resonance of the *cis* complex **3a″** which appears as a singlet in accordance with a *cis* arrangement of these two groups.[5,9] Far-IR and NMR spectroscopic data of *trans* complexes **3a′,b,c** can be compared with those reported for the complex $[RuCl_2(\kappa^2\text{-}P,N\text{-}2\text{-}Ph_2PC_6H_4CH{=}N^tBu)(PPh_3)]$[10] which has also been characterized by X-ray diffraction. In general, the chelate coordination of iminophosphine ligands leads to a downfield shift of the phosphorus as well as the *C*H=N carbon resonances with respect to the free ligands (δ 166.5 (**3a′**), 167.1 (**3a″**), 172.2 (**3b**) and 166.1 (**3c**) *vs.* 158.9 (**1a**), 161.1 (**1b**) and 159.7 (**1c**) ppm). In addition, the downfield shift observed for the O*Me* signal in the $^{13}C\{^1H\}$ NMR spectrum of **3c** with respect to that of the free ligand is attributed to its coordination to ruthenium (δ 63.3 (**3c**) *vs.* 55.8 (**1c**) ppm). This is also in accord with the highfield resonance (69.7 ppm) of the phosphorus nucleus *trans* to the methoxy group. In contrast, the corresponding resonance in the five coordinate complexes **3a′**, **3a″** and **3b** appears at 87.9–84.2 ppm.

Synthesis of the bis-iminophosphine complexes *trans,cis,cis*-$[RuCl_2(\kappa^2\text{-}P,N\text{-}2\text{-}Ph_2PC_6H_4CH{=}NR)_2]$ (R = ^{i}Pr (4d); (*S*)-CHMeCy (4e))

The treatment of $[RuCl_2(PPh_3)_3]$ with one equivalent of $2\text{-}Ph_2PC_6H_4CH{=}NR$ (R = ^{i}Pr (**1d**); (*S*)-CHMeCy (**1e**)) does not afford the expected derivatives $[RuCl_2(\kappa^2\text{-}P,N\text{-}2\text{-}Ph_2PC_6H_4CH{=}NR)(PPh_3)]$, leading instead to an equimolar mixture of the bis-iminophosphine complexes $[RuCl_2(\kappa^2\text{-}P,N\text{-}2\text{-}Ph_2PC_6H_4CH{=}NR)_2]$ (R = ^{i}Pr (**4d**); (*S*)-CHMeCy (**4e**)) and the ruthenium precursor. Complexes **4d,e** were obtained in a quantitative yield by the reaction of two equivalents of **1d,e** with $[RuCl_2(DMSO)_4]$ in refluxing THF (Scheme 1).[11] All attempts to synthesize the bis-iminophosphine complexes $[RuCl_2(\kappa^2\text{-}P,N\text{-}2\text{-}Ph_2PC_6H_4CH{=}NR)_2]$ (R = Ph; 2′,6′-$C_6H_3Me_2$; 2′-C_6H_4OMe) by treatment of either $[RuCl_2(PPh_3)_3]$ or $[RuCl_2(DMSO)_4]$ with a large excess of **1a–c** in refluxing THF failed. Monitoring the reaction by $^{31}P\{^1H\}$ NMR only the formation of **3a–c** is observed.

Complexes **4d,e** have been characterized by elemental analyses, and spectroscopic methods (IR, Far-IR, $^{31}P\{^1H\}$, ^1H, and $^{13}C\{^1H\}$ NMR spectroscopy). Spectroscopic data show that only one stereoisomer is obtained among the five possible for **4d** (I–V) and the eight possible for **4e** (two diastereoisomers for each of structures I–III plus IV and V).



On the basis of $^{31}P\{^1H\}$ and ^1H NMR data, stereoisomers I, III and V can be discarded since the spectra display: (a) only a single phosphorus resonance (δ 48.7 (**4d**) and 48.8(**4e**)), (b) the proton iminic resonance as a filled-in doublet owing to virtual coupling (δ 8.78 (**4e**) and 8.82 (**4d**)). This suggests a small $^2J_{PP}$ value[12] consistent with a *cis*-disposition of the phosphorus nuclei. In order to determine unambiguously the stereochemistry of these compounds an X-ray diffraction study was carried out on **4d**.

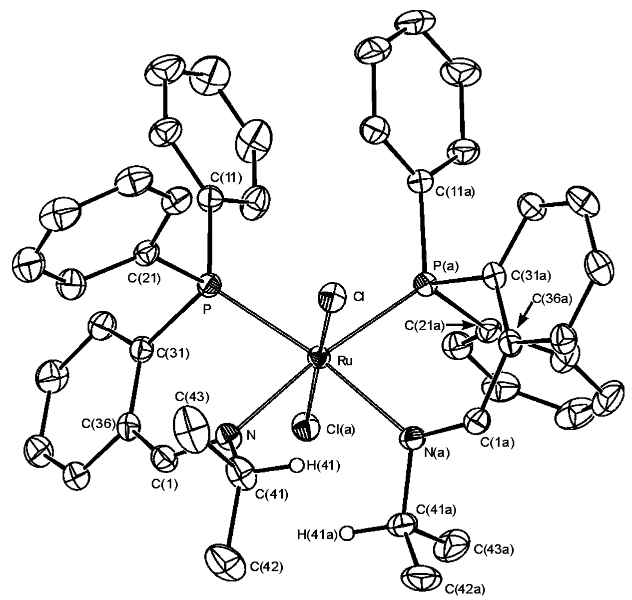


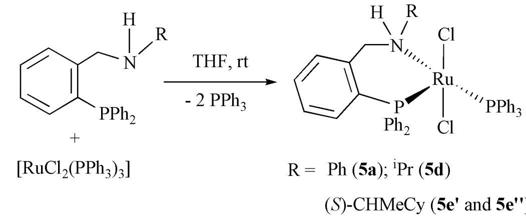
Fig. 1 ORTEP view of the bis-iminophosphine complex **4d**. Thermal ellipsoids are shown at 30% probability. Hydrogen atoms, except those of the NC*H*Me_2 fragment (H(41) and H(41a)), are omitted for clarity.

X-Ray crystal structure of complex 4d

An ORTEP drawing is shown in Fig. 1 (stereoisomer IV). Selected bonds and angles are collected in Table 1. The coordination geometry around the ruthenium atom can be described as an octahedron with two chloride atoms occupying the apical positions [Cl–Ru–Cl_a = 175.58(4)°]. The equatorial plane is formed by the two bidentate 2-$Ph_2PC_6H_4CH$=N^{i}Pr ligands, displaying a bite angle P–Ru–N of 81.30(7)°. The two phosphorus as well as the two nitrogen atoms are in a *cis*-disposition [P–Ru–P_a = 106.10(5); N–Ru–N_a = 91.3(1)°]. The ruthenium atom is contained in the best least-square base plane. The Ru–N and C(1)–N imine bond lengths, 2.183(2) and 1.290(4) Å, are similar to those found in [$RuCl_2$(κ^4-*P,N,N′,P′*-$Ph_2PC_6H_4CH$=NCH_2CH_2N=$CHC_6H_4PPh_2$)] [2.094(9), 2.097(6), and 1.297(9), 1.285(9) Å],[13] [$RuCl_2$(κ^4-*P,N,N′,P′*-(*S,S*)-$Ph_2PC_6H_4CH$=$NC_6H_{10}N$=$CHC_6H_4PPh_2$)] [2.100(5), 2.091(5), and 1.273(8), 1.272(8) Å],[4a] and [$RuCl_2$(κ^2-*P,N*-2-$Ph_2PC_6H_4CH$=N^{t}Bu)(PPh_3)] [2.082(6) and 1.255(9) Å].[5] In contrast with the latter iminophosphine ruthenium complex, the metallacycles deviate strongly from planarity, probably to minimize the interactions between the two isopropyl groups. This is also reflected in the relative disposition of the two $NCHMe_2$ fragments since the hydrogen atoms, H(41) and H(41a), are facing each other.

Table 1 Selected bond lengths (Å) and angles (°) for **4d**

Bond lengths			
Ru–N	2.183(2)	N–C(1)	1.290(4)
Ru–P	2.2957(9)	N–C(41)	1.504(4)
Ru–Cl	2.4164(9)		
Bond angles			
N–Ru–P	81.30(7)	N–Ru–N_a	91.3(1)
N–Ru–P_a	172.54(7)	P–Ru–Cl	94.23(3)
P–Ru–P_a	106.10(5)	P–Ru–Cl_a	88.43(3)
N–Ru–Cl	90.09(7)	Cl–Ru–Cl_a	175.58(4)
Torsion angles			
Ru–P–C(31)–C(36)	43.7(2)	C(36)–C(1)–N–Ru	−11.1(5)
P–C(31)–C(36)–C(1)	1.8(4)	P–Ru–N–C(1)	45.4(3)
C(31)–C(36)–C(1)–N	−24.6(5)	N–Ru–P–C(31)	−52.0(1)



Scheme 2

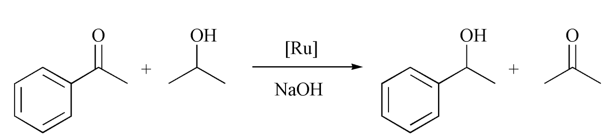
Synthesis of the five-coordinate aminophosphine complexes [$RuCl_2$(κ^2-*P,N*-2-$Ph_2PC_6H_4CH_2NHR$)(PPh_3)] (R = Ph (5a); ^{i}Pr (5d); (*S*)-CHMeCy (5e))

Reactions of the aminophosphines **2a,d,e** with [$RuCl_2(PPh_3)_3$], in THF at room temperature, lead to the formation of the five-coordinate complexes [$RuCl_2$(κ^2-*P,N*-2-$Ph_2PC_6H_4CH_2NHR$)(PPh_3)] (R = Ph (**5a**); ^{i}Pr (**5d**); (*S*)-CHMeCy (**5e**)) (Scheme 2). They have been characterized by elemental analyses and spectroscopic techniques (IR, Far-IR, and ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectroscopy) all data being in agreement with the stoichiometry and a *trans* $RuCl_2$ arrangement. The most significant features, which can be compared to those shown by **3a′**, **3b** and **3c**, are: (i) ^{31}P{^{1}H} NMR: an AX spin system in the range 72.5–77.6 (PPh_2 group) and 40.8–42.0 (PPh_3 ligand) ppm with a small $^2J_{PP}$ coupling constant (34.2–38.1 Hz) in accordance with a *cis*-arrangement of two different P-donor groups, and (ii) Far-IR: an absorption at *ca.* 320 cm^{-1} indicative of a *trans* arrangement of the chloride atoms. In addition, the ^{1}H NMR spectra exhibit a NH signal at *ca.* 4.0–4.5 ppm and the two resonances attributable to the two diastereotopic CH_2N protons in the range 4.0–5.2 ppm. The inequivalence of the methylenic protons arises from the coordination of the amino group which converts the nitrogen atom in a stereogenic center. Complex **5e** incorporating the chiral aminophosphine (*S*)-2-$Ph_2PC_6H_4CH_2NHCHMeCy$ was obtained as a non-separable mixture of two diastereoisomers, **5e′** and **5e″**, in a 20:80 ratio, arising from the *R* and *S* configurations of the nitrogen atom.

Catalytic studies

The catalytic activity in transfer hydrogenation of acetophenone by propan-2-ol of all the novel complexes has been investigated (Scheme 3). In a typical experiment, NaOH was added to a solution of the ruthenium(II) catalyst precursor and acetophenone (0.1 M) in ^{i}PrOH (ketone:Ru:base = 500:1:24) at refluxing temperature, the reaction being monitored by gas chromatography. Selected results are collected in Table 2. For comparative purposes, the catalytic activity of complexes [$RuCl_2$(κ^2-*P,N*-2-$Ph_2PC_6H_4CH$=N^{t}Bu)(PPh_3)] and [$RuCl_2$(κ^2-*P,N*-2-$Ph_2PC_6H_4CH_2NH^t$Bu)(PPh_3)] previously reported by us[5] and that of [$RuCl_2(PPh_3)_3$] used by Bäckvall,[14] have also been examined under the same conditions.

All the complexes **3a–c**, **4d,e** and **5a,d,e** are more active catalysts than the precursor [$RuCl_2(PPh_3)_3$] (entries 1–10 *vs.* entry 11), and afford almost quantitative yields of 1-phenylethanol within 4 hours. The highest rate is observed for **3a** (as a mixture of **3a′** and **3a″**), the turnover frequency being 5220 h^{-1} at 50% of conversion (entry 2). The chiral six coordinate complex **4e** leads to a moderate enantiomeric excess (44%; entry 6). In contrast, no chiral induction is observed when the mixture



Scheme 3

Table 2 Transfer hydrogenation of acetophenone[a]

Entry	Catalyst	Yield (%)[b]	Time/h	TOF_{50}[c]	ee (%)[d]
Complexes [RuCl$_2$(PPh$_3$)(2-Ph$_2$PC$_6$H$_4$CH=NR)]					
1	R = ^{t}Bu[5]	97	2	1650	—
2	R = Ph, **3a**	98	1	5220	—
3	R = 2′,6′-$C_6H_3Me_2$, **3b**	98	3	590	—
4	R = 2′-C_6H_4OMe, **3c**	98	4	730	—
Complexes [RuCl$_2$(2-Ph$_2$PC$_6$H$_4$CH=NR)$_2$]					
5	R = ^{i}Pr, **4d**	97	1	1030	—
6	R = (*S*)-CHMeCy, **4e**	97	1	820	44 (R)
Complexes [RuCl$_2$(PPh$_3$)(2-Ph$_2$PC$_6$H$_4$CH$_2$NHR)]					
7	R = ^{t}Bu[5]	97	2	1610	—
8	R = Ph, **5a**	96	2	1680	—
9	R = ^{i}Pr, **5d**	96	2	1040	—
10	R = (*S*)-CHMeCy, **5e**	98	1	2500	0
11	$[RuCl_2(PPh_3)_3]$	91	5	220	—

[a] Conditions: reactions were carried out in a Schlenk tube fitted with a condenser at 82 °C using 50 mL of propan-2-ol, 5 mmol of acetophenone, 0.2 mol% of catalyst precursor and 4.8 mol% of NaOH. [b] Yield of 1-phenylethanol, GC determined. [c] Turnover frequency = ((mol product/mol catalyst)/time) at 50% conversion, in h^{-1}. [d] Enantiomeric excess, GC determined. Absolute configuration in parenthesis, determined on the basis of the sign of optical rotation.

of diastereoisomers of the five-coordinate complex **5e** is used (entry 10) even at temperatures lower than 82 °C.

The evolution of the conversion as a function of the reaction time was investigated. In contrast with 16-electron complexes **3a,b** and **5a,d,e**, the saturated derivatives [RuCl$_2$(κ^3-*P*,*N*,*O*-2-Ph$_2$PC$_6$H$_4$CH=N-2′-C$_6$H$_4$OMe)(PPh$_3$)] (**3c**), [RuCl$_2$(κ^2-*P*,*N*-2-Ph$_2$PC$_6$H$_4$CH=N^{i}Pr)$_2$] (**4d**) and [RuCl$_2$(κ^2-*P*,*N*-(*S*)-2-Ph$_2$PC$_6$H$_4$CH=NCHMeCy)$_2$] (**4e**) present, before the fast reaction of acetophenone, an induction period (of 5, 20 and 30 min respectively). In addition, during the first thirty minutes, the enantiomeric excess observed for **4e** increases from 16 to 46% and then remains almost constant. This is indicative of an evolution of the active species. In order to find out how the chiral catalyst **4e** changes as a function of time, the following experiments were carried out: (i) the catalyst and NaOH were refluxed for 30 min, and then acetophenone was added, and (ii) the catalyst, NaOH and a small quantity of acetophenone (Ru:acetophenone = 1:10) were refluxed for 30 min, and then the rest of acetophenone was added, (iii) the catalyst, NaOH and a small quantity of racemic 1-phenylethanol (Ru:1-phenylethanol = 1:10) were refluxed for 30 min, and then acetophenone was added. In the two former cases the induction time, the conversion and the enantiomeric excess are not affected. In the latter case no induction period is observed but the enantiomeric excess drops dramatically to 2%. This seems to indicate that the initial active species formed from the precursor and the base reacts with the 1-phenylethanol. When the 1-phenylethanol is enantiomerically enriched the enantiomeric excess increases with the conversion. A similar effect has been described previously in hydrogen transfer reaction of isopropyl phenyl ketone catalyzed by $[Ir(COD)Cl]_2$ associated with a salen type ligand.[15]

Conclusions

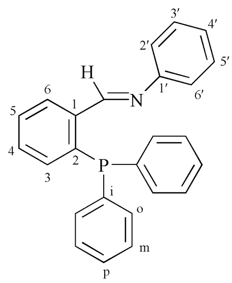
In this work new five (**3a–b**) and six coordinate (**3c,4c–d**) iminophosphine ruthenium(II) complexes are reported. The stoichiometry seems to depend on the steric hindrance of the ligands. Thus the bulky iminophosphines **1a–c** bearing iminic aryl groups give rise only to the five coordinate complexes (**3a–b**), while the ligands **1d,e**, bearing a -C*H*RR′ substituent on the nitrogen, lead to the six-coordinate bis-iminophosphine derivatives (**4d,e**). In contrast, aminophosphines **2a,d,e** only form five coordinate 16-electron complexes (**5a,d,e**) reflecting the higher steric hindrance of these ligands in comparison with the related iminophosphines. The steric properties also seem to govern the stereoselectivity of the five coordinate iminophosphine complexes **3a,b** since, for the bulkier xylyl group, the *trans* stereoisomer *vs.* the mixture of *cis* and *trans* for the phenyl substituted iminophosphine, is obtained.

All the complexes **3–5** are efficient catalysts in transfer hydrogenation of ketones. The catalytic activity can be compared to that observed for analogous ruthenium(II) complexes bearing other chelating P,N ligands.[3] It is interesting to note that the mixture of the *trans* and *cis* isomers of complex [RuCl$_2$(κ^2-*P*,*N*-2-Ph$_2$PC$_6$H$_4$CH=NPh)(PPh$_3$)] (**3a′** and **3a″** respectively) has been found to be by far the most efficient catalyst precursor. Since similar five-coordinate *cis*-dichloride complexes [RuCl$_2$(PPh$_3$)(oxazolinylferrocenylphosphine)] have proved to be particularly active in transfer hydrogenation of acetophenone[3c,d,f] we propose that the increased catalytic activity observed for **3a** is probably due to the presence of the *cis*-isomer. However, the catalytic results for **3–5** do not allow us to determine clearly the influence of the steric and electronic properties of the different ligands on the catalytic activity.

Experimental

General

The manipulations were performed under an atmosphere of dry nitrogen using vacuum-line and standard Schlenk techniques. All reagents were obtained from commercial suppliers and used without further purification. Solvents were dried by standard methods and distilled under nitrogen before use. The compounds $[RuCl_2(PPh_3)_3]$,[16] $[RuCl_2(DMSO)_4]$,[17] 2-Ph$_2$PC$_6$H$_4$CH=NR (R = Ph,[18] -2′,6′-C$_6$H$_3$Me$_2$,[19] ^{i}Pr[20]) and 2-Ph$_2$PC$_6$H$_4$CH$_2$NHPh[21] were prepared following the methods previously reported. Gas chromatographic measurements were made on a Hewlett Packard HP6890 equipment. A HP-INNOWAX cross-linked polyethyleneglycol (30 m, 250 μm) or a Supelco Beta-Dex™ 120 (30 m, 250 μm) columns were used. Infrared spectra were recorded on a Perkin-Elmer 1720-XFT or a Perkin Elmer FT-IR 1000 spectrometer. The C, H and N analyses were carried out with a Perkin-Elmer 2400 microanalyzer. NMR spectra were recorded on Bruker AC300 or 300DPX instruments at 300 (^{1}H), 121.5 (^{31}P) or 75.4 MHz (^{13}C) using $SiMe_4$ or 85% H_3PO_4 as standards. DEPT experiments have been carried out for all the compounds. Coupling constants J are given in Hertz. Abbreviations used: FIR, Far-infrared; Ar, aromatic; s, singlet; d, doublet; d_f, filled-in doublet; sept, septuplet; m, multiplet. Numbering used for the ligands:



Synthesis and product characterization

2-$Ph_2PC_6H_4CH$=N-2′-C_6H_4OMe, 1c. A solution of 2-(diphenylphosphino)benzaldehyde (0.248 g, 0.85 mmol) and 2-anisidine (0.105 g, 0.85 mmol) in a mixture of methanol (40 mL) and dichloromethane (20 mL) was stirred overnight at room temperature. After evaporation to dryness, the residue was washed twice with 5 mL of a mixture of hexane–diethyl ether (9:1) to afford a pale yellow solid. Yield: 0.321 g (96%). Found (calc. for $C_{26}H_{22}NOP$): C, 79.03 (78.97); H, 5.74 (5.61); N, 3.49 (3.54)%. $^{31}P\{^1H\}$ NMR, $CDCl_3$, δ: −13.9 (s). ^1H NMR, $CDCl_3$, δ: 9.18 (d, 1 H, $^4J_{PH}$ = 5.4 Hz, CH=N), 8.33 (m, 1 H, H-6), 7.72–6.60 (m, 17 H, ArH), 3.78 (s, 3 H, OMe). $^{13}C\{^1H\}$ NMR, $CDCl_3$, δ: 159.7 (d, $^3J_{PC}$ = 25.6, CH=N), 152.3 (s, C-2′), 141.4 (s, C-1′), 139.5 (d, $^2J_{PC}$ = 16.9, C-1), 138.4 (d, $^1J_{PC}$ = 19.8, C-2), 136.2 (d, $^1J_{PC}$ = 9.9, C-*i*), 134.1 (d, $^2J_{PC}$ = 19.8, C-*o*), 133.4 (s, C-4, 5 or 6), 130.9 (s, C-4, 5 or 6), 129.0 (s, C-4, 5 or 6), 128.9 (s, C-*p*), 128.7 (d, $^3J_{PC}$ = 7.0, C-*m*), 127.8 (d, $^2J_{PC}$ = 4.1, C-3), 126.7, 120.9, 120.7 and 111.5 (all s, C-3′, 4′, 5′ and 6′), 55.8 (s, OMe). IR (Nujol, cm^{-1}), $\nu_{C=N}$: 1607.

Synthesis of (*S*)-2-$Ph_2PC_6H_4CH$=NCHMeCy, 1e. Following the same procedure **1e** was prepared as a colorless oil, using 0.272 g (0.94 mmol) of 2-(diphenylphosphino)benzaldehyde and 0.2 mL (1.35 mmol) of (*S*)-(+)-cyclohexylethylamine. Yield: 0.365 g (97%). $^{31}P\{^1H\}$ NMR, $CDCl_3$, δ: −12.9 (s). ^1H NMR, $CDCl_3$, δ: 8.81 (d, 1 H, $^4J_{PH}$ = 4.8 Hz, C*H*=N), 7.99 (m, 1 H, H-6), 7.60–7.14 (m, 12 H, ArH), 6.86 (m, 1 H, H-3), 2.89 (m, 1 H, C*H*Me), 1.70–0.60 (m, 11 H, Cy), 1.03 (d, 3 H, $^3J_{HH}$ = 6.3 Hz, CH*Me*). $^{13}C\{^1H\}$ NMR, $CDCl_3$, δ: 157.3 (d, $^3J_{PC}$ = 21.2 Hz, *C*H = N), 139.7 (d, $^2J_{PC}$ = 16.6 Hz, C-1), 137.1 (d, $^1J_{PC}$ = 18.9 Hz, C-2), 136.5 (d, $^1J_{PC}$ = 9.8 Hz, C-*i*), 136.4 (d, $^1J_{PC}$ = 9.1 Hz, C-*i*), 134.2 (d, $^2J_{PC}$ = 20.4 Hz, C-*o*), 134.1 (d, $^2J_{PC}$ = 20.4 Hz, C-*o*), 132.8 (s, C-4, 5, or 6), 129.8 (s, C-4, 5 or 6), 128.8 (s, 2 C, C-*p*), 128.5 (d, 4 C, $^3J_{PC}$ = 6.8 Hz, C-*m*), 128.3 (s, C-4, 5 or 6), 127.7 (d, $^2J_{PC}$ = 4.5 Hz, C-3), 71.9 (s, N*C*H), 43.4 (s, CH of Cy), 29.6, 26.5, 26.3 and 26.2 (all s, CH_2 of Cy), 19.7 (s, Me). IR (Nujol, cm^{-1}), $\nu_{C=N}$: 1638. HRMS m/z calc. for $C_{27}H_{30}NP$ (found): M^+ = 399.21120 (399.21139).

Synthesis of 2-$Ph_2PC_6H_4CH_2NH^iPr$, 2d. A solution of 2-$Ph_2PC_6H_4CH$=N^iPr (0.410 g, 1.24 mmol) in 30 mL of methanol was treated by $NaBH_4$ (0.180 g, 4.76 mmol) at 0 °C. After stirring 15 min the reaction was quenched with aqueous NaOH (5 mL, 1 M). The organic layer was extracted with dichloromethane (3 × 15 mL) and the combined phases were dried over $MgSO_4$. The solvents were removed to afford a pale yellow oil which was used without further purification. Yield: 0.390 g (94%). $^{31}P\{^1H\}$ NMR, $CDCl_3$, δ: −15.6 (s). ^1H NMR, $CDCl_3$, δ: 7.48 (m, 1 H, H-6), 7.36–7.14 (m, 12 H, ArH), 6.89 (ddd, $^3J_{HH}$ = 7.3, $^3J_{PH}$ = 4.6, $^4J_{HH}$ = 1.1, 1 H, H-3), 3.99 (s broad, 2 H, CH_2N), 2.70 (sept, 1 H, $^3J_{HH}$ = 6.2, C*H*Me_2), 0.93 (d, 6 H, $^3J_{HH}$ = 6.2, CH*Me*$_2$), the NH proton is not observed. $^{13}C\{^1H\}$ NMR, $CDCl_3$, δ: 144.2 (d, $^1J_{PC}$ = 23.5, C-2), 136.5 (d, $^1J_{PC}$ = 10.2, C-*i*), 137.7, (d, $^2J_{PC}$ = 13.4, C-1), 133.8 (d, $^2J_{PC}$ = 20.3, C-*o*), 133.6 (s, C-4, 5 or 6), 129.6 (d, $^2J_{PC}$ = 5.1, C-3), 129.0 (s, C-4, 5 or 6), 128.7 (s, C-*p*), 128.5 (d, $^3J_{PC}$ = 7.0, C-*m*), 127.3 (s, C-4, 5 or 6), 50.0 (d, $^3J_{PC}$ = 21.0, CH_2N), 48.0 (s, *C*HMe_2), 22.4 (s, CH*Me*$_2$). IR (Neat, cm^{-1}), ν_{N-H}: 3312. HRMS m/z calc. for $C_{22}H_{24}NP$ (found): M^+ = 333.16463 (333.16471).

Synthesis of (*S*)-2-$Ph_2PC_6H_4CH_2$NHCHMeCy, 2e. Following the same procedure **2e** was obtained as a pale yellow oil using (*S*)-2-$Ph_2PC_6H_4CH$=NCHMeCy (0.200 g, 0.50 mmol) and $NaBH_4$ (0.081 g, 2.14 mmol). Yield: 0.193 g (96%). $^{31}P\{^1H\}$ NMR, $CDCl_3$, δ:−15.7 (s). ^1H NMR, $CDCl_3$, δ: 7.55–7.15 (m, 13 H, ArH), 6.92 (m, 1 H, H-3), 4.05 (part A of AB system, 1 H, $^2J_{HH}$ = 19.7, NC*H*$_2$), 3.95 (part B of AB system, 1 H, $^2J_{HH}$ = 19.7, NC*H*$_2$), 2.42 (m, 1 H, C*H*Me), 1.80–0.78 (m, 11 H, Cy), 0.93 (d, 3 H, $^3J_{HH}$ = 6.3 Hz, CH*Me*), the NH proton is not observed. $^{13}C\{^1H\}$ NMR, $CDCl_3$, δ: 145.1 (d, $^1J_{PC}$ = 24.1, C-2), 136.8 (d, $^1J_{PC}$ = 9.9, C-*i*), 135.6 (d, $^2J_{PC}$ = 12.8, C-1), 133.8 (d, $^2J_{PC}$ = 19.2, C-*o*), 133.7 (d, $^2J_{PC}$ = 19.2, C-*o*), 133.6 (s, C-4, 5 or 6), 129.5 (d, $^2J_{PC}$ = 5.7, C-3), 129.0 (s, C-4, 5 or 6), 128.6 (d, $^4J_{PC}$ = 2.1, C-*p*), 128.5 (d, $^3J_{PC}$ = 7.1, C-*m*), 127.1 (s, C-4, 5 or 6), 57.0 (s, N*C*HMe), 50.2 (d, $^3J_{PC}$ = 21.3, CH_2N), 42.6 (s, CH, Cy), 29.7, 27.6, 26.7, 26.6 and 26.4 (all s, CH, Cy), 16.3 (s, Me). IR (Nujol, cm^{-1}), ν_{N-H}: 3315. HRMS m/z calc. for $C_{27}H_{32}NP$ (found): M^+ = 401.22722 (401.22729).

Synthesis of [$RuCl_2$(κ^2-*P*,*N*-2-$Ph_2PC_6H_4CH$=NPh)(PPh_3)], 3a′ and 3a″. A solution of [$RuCl_2(PPh_3)_3$] (0.200 g, 0.21 mmol) and 2-$Ph_2PC_6H_4CH$=NPh (0.116 g, 0.32 mmol) in 30 mL of THF was stirred for 2 hours at room temperature. After evaporation to dryness, the resulting residue was washed 3 times with 10 mL of a mixture of hexane and diethyl ether (1:1) to afford a red solid. A mixture of two non-separable isomers, **3a′** and **3a″**, is obtained in a 60:40 ratio. Yield: 0.151 g (90%). Found (calc. for $C_{43}H_{35}Cl_2NP_2Ru$): C, 64.55 (64.58); H, 4.38 (4.41); N, 1.73 (1.75). $^{31}P\{^1H\}$ NMR, $CDCl_3$, δ: **3a′** 87.9 (d, $^2J_{PP}$ = 31.3, PPh_2), 36.2 (d, $^2J_{PP}$ = 31.3, PPh_3); **3a″** 84.2 (d, $^2J_{PP}$ = 39.6, PPh_2), 43.9 (d, $^2J_{PP}$ = 39.6, PPh_3). ^1H NMR, $CDCl_3$, δ: **3a′** 9.00 (d, 1 H, $^4J_{PH}$ = 9.1, C*H* = N), 8.07–6.67 (m, 34 H, ArH); **3a″** 8.72 (s, 1 H, C*H* = N), 8.07–6.67 (m, 34 H, ArH). $^{13}C\{^1H\}$ NMR, $CDCl_3$, δ: **3a′** 166.5 (d, $^3J_{PC}$ = 4.5, CH=N), 150.9 (s, C-1′), 136.7–123.1 (m, Ar); **3a″** 167.1 (d, $^3J_{PC}$ = 6.0, CH=N), 151.9 (s, C-1′), 136.7–123.1 (m, aromatic). IR and FIR (Nujol, cm^{-1}), $\nu_{C=N}$: 1608, 1588; $\nu_{Cl-Ru-Cl}$: 323, 292, 245.

Synthesis of [$RuCl_2$(κ^2-*P*,*N*-2-$Ph_2PC_6H_4CH$=N-2′,6′-$C_6H_3Me_2$)(PPh_3)], 3b. Following the same procedure **3b** was prepared as a purple solid using [$RuCl_2(PPh_3)_3$] (0.200 g, 0.21 mmol), 2-$Ph_2PC_6H_4CH$=N-2′,6′-$C_6H_3Me_2$ (0.116 g, 0.29 mmol) and 20 mL of THF. Yield: 0.132 g (76%). Found (calc. for $C_{45}H_{39}Cl_2NP_2Ru$): C, 65.15 (65.30); H, 4.74 (4.75); N, 1.72 (1.69). $^{31}P\{^1H\}$ NMR, CD_2Cl_2, δ: 87.5 (d, $^2J_{PP}$ = 33.4, PPh_2), 35.7 (d, $^2J_{PP}$ = 33.4, PPh_3). ^1H NMR, CD_2Cl_2, δ: 8.80 (d, 1 H, $^4J_{PH}$ = 8.8, C*H* = N), 7.76–6.66 (m, 32 H, ArH), 6.66 (dd, 1 H, $^3J_{PH}$ = 10.5, $^3J_{HH}$ = 7.7, H-3), 1.86 (s, 6 H, Me). $^{13}C\{^1H\}$ NMR, CD_2Cl_2, δ: 172.2 (d, $^3J_{PC}$ = 4.1, CH=N), 153.2 (s, C-1′), 137.3 (d, $^1J_{PC}$ = 12.2, C-2), 134.9 (d, J_{PC} = 9.9, C-*o*, PPh_3), 133.4 (d, $^1J_{PC}$ = 55.3, C-*i*, PPh_3), 125.7 (s, C-4′), 137.4–126.7 (m, Ar), 20.4 (s, Me). IR and FIR (Nujol, cm^{-1}), $\nu_{C=N}$: 1598; $\nu_{Cl-Ru-Cl}$: 318.

Synthesis of [$RuCl_2$(κ^3-*P*,*N*,*O*-2-$Ph_2PC_6H_4CH$=N-2′-C_6H_4OMe)(PPh_3)], 3c. Following the same procedure **3c** was prepared as a red solid, using [$RuCl_2(PPh_3)_3$] (0.181 g, 0.19

mmol) and 2-$Ph_2PC_6H_4CH$=N-2′-C_6H_4OMe (0.090 g, 0.23 mmol) in 40 mL of THF. Yield: 0.139 g (88%). Found (calc. for $C_{44}H_{37}Cl_2NOP_2Ru$): C, 63.81 (63.70); H, 4.48 (4.50); N, 1.67 (1.70). $^{31}P\{^1H\}$ NMR, CD_2Cl_2, δ: 69.7 (d, $^2J_{PP}$ = 32.6, PPh_2), 34.7 (d, $^2J_{PP}$ = 32.6, PPh_3). ^1H NMR, CD_2Cl_2, δ: 9.03 (d, 1 H, $^4J_{PH}$ = 8.8, *CH* = N), 7.77–6.72 (m, 33 H, ArH), 3.41(s, 3 H, OMe). $^{13}C\{^1H\}$ NMR, CD_2Cl_2, δ: 166.1 (d, $^3J_{PC}$ = 3.2, CH=N), 156.1 (s, C-2′), 145.7 (s, C-1′), 137.7 (d, $^2J_{PC}$ = 12.7, C-1), 137.5 (d, $^2J_{PC}$ = 8.3, C-3), 127.7 (d, $^3J_{PC}$ = 8.9, C-*m*, PPh_3), 127.5 (d, $^3J_{PC}$ = 10.2, C-*m*, PPh_2), 124.2, 119.2 and 117.6 (all s, 3 C of C-3′, 4′, 5′ and 6′), 135.8–128.9 (m, Ar), 63.3 (s, OMe). IR and FIR (Nujol, cm^{-1}), $\nu_{C=N}$: 1608; $\nu_{Cl-Ru-Cl}$: 319.

Synthesis of *trans,cis,cis*-[$RuCl_2$(κ²-*P,N*-2-$Ph_2PC_6H_4CH$=N$^iPr)_2$], 4d. A suspension of [$RuCl_2(DMSO)_4$] (0.500 g, 1.03 mmol) and 2-$Ph_2PC_6H_4CH$=N^{i}Pr (0.821 g, 2.48 mmol) in 60 mL of THF was refluxed for 6 hours. The resulting red solution was filtered through kieselguhr and the filtrate was evaporated to dryness. The residue was washed 3 times with 10 mL of a mixture of hexane–diethyl ether (4:1) to afford a red-brownish solid. Yield: 0.645 g (75%). Found (calc. for $C_{44}H_{44}Cl_2N_2P_2Ru$): C, 63.27 (63.31); H, 5.42 (5.31); N, 3.27 (3.36)%. $^{31}P\{^1H\}$ NMR, $CDCl_3$, δ: 48.7 (s). ^1H NMR, $CDCl_3$, δ: 8.78 (d_f, 2 H, $^4J_{PH}$ = 6.5, CH=N), 7.71–6.31 (m, 28 H, ArH), 4.57 (m, 2 H, C*H*Me_2), 1.51 (d, 6 H, $^3J_{HH}$ = 6.5, Me), 0.73 (d, 6 H, $^3J_{HH}$ = 6.0, Me). $^{13}C\{^1H\}$ NMR, CD_2Cl_2, δ: 167.4 (broad s, CH=N), 139.5–127.2 (m, Ar), 61.7 (s, *C*HMe_2), 28.3 (s, CH*Me*), 24.1 (s, CH*Me*). IR and FIR (Nujol, cm^{-1}), $\nu_{C=N}$: 1616; $\nu_{Cl-Ru-Cl}$: 341.

Synthesis of *trans,cis,cis*-[$RuCl_2$(κ²-*P,N*-(*S*)-2-$Ph_2PC_6H_4CH$=NCHMeCy)$_2$], 4e. Following the same procedure **4e** was prepared as a red-brownish solid using [$RuCl_2(DMSO)_4$] (0.480 g, 0.99 mmol), (*S*)-2-$Ph_2PC_6H_4CH$=NCHMeCy (0.950 g, 2.38 mmol) and 60 mL of THF. Yield: 0.640 g (67%). Found (calc. for $C_{54}H_{60}Cl_2N_2P_2Ru$): C, 66.73 (66.80); H, 6.31 (6.23); N, 2.93 (2.88)%. $^{31}P\{^1H\}$ NMR, $CDCl_3$, δ: 48.8 (s). ^1H NMR, $CDCl_3$, δ: 8.82 (d_f, 2 H, $^4J_{PH}$ = 6.7, CH=N), 7.71–6.31 (m, 28 H, ArH), 2.42 (m, 1 H, C*H*Me), 1.80–0.78 (m, 11 H, Cy), 0.93 (d, 3 H, $^3J_{HH}$ = 6.3 Hz, CH*Me*). $^{13}C\{^1H\}$ NMR, CD_2Cl_2, δ: 167.0 (s, CH=N), 140.2–127.5 (m, Ar), 69.4 (s, CHN), 40.9 (s, CH, Cy), 31.2, 26.7, 26.6, 25.6 and 23.7 (all s, CH_2, Cy), 14.9 (s, Me). IR and FIR (Nujol, cm^{-1}), $\nu_{C=N}$: 1616.; $\nu_{Cl-Ru-Cl}$: 335.

Synthesis of [$RuCl_2$(κ²-*P,N*-2-$Ph_2PC_6H_4CH_2NHPh$)(PPh_3)], 5a. A solution of [$RuCl_2(PPh_3)_3$] (0.228 g, 0.24 mmol) and 2-$Ph_2PC_6H_4CH_2NHPh$ (0.105 g, 0.29 mmol) in 30 mL of THF was stirred at room temperature for 2 hours. After evaporation to dryness, the resulting residue was washed 3 times with 10 mL of a mixture of hexane and diethyl ether (1:1) to afford a green solid. Yield: 0.182 g (95%). Found (calc. for $C_{43}H_{37}Cl_2NP_2Ru$): C, 64.03 (64.42); H, 4.87 (4.65); N, 1.80 (1.75)%. $^{31}P\{^1H\}$ NMR, $CDCl_3$, δ: 77.6 (d, $^2J_{PP}$ = 38.1, PPh_2), 40.8 (d, $^2J_{PP}$ = 38.1, PPh_3). ^1H NMR, $CDCl_3$, δ: 7.67–6.35 (m, 34 H, ArH), 5.19 (dd, 1 H, *J* = 11.5, $^2J_{HH}$ = 11.5, CH_2N), 4.50* (broad d, 1 H, $^3J_{HH}$ = 3.8, NH), 4.32 (dd, 1 H, $^2J_{HH}$ = 11.5, $^3J_{HH}$ = 3.8, CH_2N).* This signal disappears when D_2O is added. $^{13}C\{^1H\}$ NMR, CD_2Cl_2, δ: 146.9 (s, C-1′), 140.1 (d, $^1J_{PC}$ = 13.6, C-2), 135.0 (d, $^1J_{PC}$ = 41.8, C-*i*, PPh_3), 135.1 (d, J_{PC} = 10.2, C-*o* or -*m*, PPh_2), 134.7 (d, J_{PC} = 10.2, C-*o* or -*m*, PPh_2), 134.6 (d, J_{PC} = 10.2, C-*o* or -*m*, PPh_3), 133.5 (d, $^1J_{PC}$ = 47.5, C-*i*, PPh_2), 132.5–132.1 (m, Ar), 132.0 (d, J_{PC} = 3.7, C-3,4,5 or 6), 131.4 (d, J_{PC} = 2.4, C-3,4,5 or 6), 130.8 (d, $^1J_{PC}$ = 54.3, C-*i*, PPh_2), 130.6 (d, $^4J_{PC}$ = 2.4, C-*p*, PPh_2), 130.3 (d, $^4J_{PC}$ = 2.4, C-*p*, PPh_2), 129.8 (s, C-*p*, PPh_3), 129.0 (s, C-3′,5′), 128.2 (d, J_{PC} = 10.2, C-*o* or -*m*, PPh_2), 128.1 (d, J_{PC} = 9.0, C-*o* or -*m*, PPh_3), 127.4 (d, J_{PC} = 10.2, C-*o* or -*m*, PPh_2), 125.5 (s, C-4′), 121.3 (s, C-2′,6′), 56.6 (d, J_{PC} = 5.6, 5.6, CH_2N). IR and FIR (Nujol, cm^{-1}), ν_{N-H}: 3225; $\nu_{Cl-Ru-Cl}$: 319.

Synthesis of [$RuCl_2$(κ²-*P,N*-2-$Ph_2PC_6H_4CH_2NH^iPr$)(PPh_3)], 5d. Following the same procedure [$RuCl_2$(κ²-*P,N*-2-$Ph_2PC_6H_4CH_2NH^iPr$)(PPh_3)] was prepared as a green solid, using [$RuCl_2(PPh_3)_3$] (0.500 g, 0.52 mmol) and 2-$Ph_2PC_6H_4CH_2NH^iPr$ (0.210 g, 0.63 mmol) in 30 mL of THF. Yield: 0.375 g (94%). Found (calc. for $C_{40}H_{39}Cl_2NP_2Ru$): C, 62.63 (62.58); H, 5.10 (5.12); N, 1.85 (1.82)%. $^{31}P\{^1H\}$ NMR, $CDCl_3$, δ: 74.1 (d, $^2J_{PP}$ = 37.3, PPh_2), 41.6 (d, $^2J_{PP}$ = 37.3, PPh_3). ^1H NMR, $CDCl_3$, δ: 7.62–6.67 (m, 29 H, ArH), 4.51 (ddd, 1 H, $^2J_{HH}$ = 11.3, $^4J_{PH}$ = 11.3, *J* = 2.0, CH_2N), 4.01 (m, 2 H, CH_2N and NH), 3.86 (m, 1 H, C*H*Me_2), 1.40 (d, 3 H, $^3J_{HH}$ = 6.3, CH*Me*), 0.89 (d, 3 H, $^3J_{HH}$ = 6.2, CH*Me*). $^{13}C\{^1H\}$ NMR, $CDCl_3$, δ: 140.2 (d, $^2J_{PC}$ = 12.7, C-1), 134.7 (d, $^2J_{PC}$ = 10.2, C-*o*, PPh_3), 134.6 (d, $^1J_{PC}$ = 39.4, C-*i*, PPh_3), 134.5 (d, $^2J_{PC}$ = 9.5, 9.5, C-*o*, PPh_2), 134.4 (d, $^2J_{PC}$ = 10.2, C-*o*, PPh_2), 129.9 (d, $^4J_{PC}$ = 2.5, C-*p*, PPh_2), 129.7 (d, $^4J_{PC}$ = 2.5, C-*p*, PPh_2), 129.1 (d, $^4J_{PC}$ = 1.9, C-*p*, PPh_3), 127.5 (d, $^3J_{PC}$ = 9.5, C-*m*, PPh_3), 127.5 (d, $^3J_{PC}$ = 11.0, C-*m*, PPh_2), 126.9 (d, $^3J_{PC}$ = 11.0, C-*m*, PPh_2), 131.9–129.0 (m, Ar), 53.9 (dd, $^3J_{PC}$ = 7.6, $^3J_{PC}$ = 1.9, CH_2N), 51.3 (s, *C*HMe_2), 23.9 (d, $^4J_{PC}$ = 3.2, CH*Me*), 21.5 (d, $^4J_{PC}$ = 1.9, CH*Me*). IR and FIR (Nujol, cm^{-1}), ν_{N-H}: 3197; $\nu_{Cl-Ru-Cl}$: 317.

Synthesis of [$RuCl_2$(κ²-*P,N*-(*S*)-2-$Ph_2PC_6H_4CH_2$NHCHMeCy)(PPh_3)], 5e′ and 5e″. Prepared following the same procedure as a green solid, using $RuCl_2(PPh_3)_3$ (0.420 g, 0.44 mmol) and (*S*)-2-$Ph_2PC_6H_4CH_2$NHCHMeCy (0.210 g, 0.52 mmol) in 30 mL of THF. Compound **5e** is obtained as a mixture of two non-separable diastereoisomers, **5e′** and **5e″**, in a 20:80 ratio. Yield: 0.384 g (90%). Found (calc. for $C_{44}H_{47}Cl_2NP_2Ru$): C, 64.09 (64.15); H, 5.82 (5.75); N, 1.71 (1.70)%. $^{31}P\{^1H\}$ NMR, $CDCl_3$, δ: **5e′** 72.8 (d, $^2J_{PP}$ = 37.3, PPh_2), 42.0 (d, $^2J_{PP}$ = 37.3, PPh_3), **5e″** 72.5 (d, $^2J_{PP}$ = 34.2, PPh_2), 41.7 (d, $^2J_{PP}$ = 34.2, PPh_3). ^1H NMR, $CDCl_3$, δ: **5e′** 7.62–6.65 (m, 29 H, ArH), 4.54 (dd, 1 H, $^3J_{HH}$ = 10.4, $^2J_{HH}$ = 10.4, CH_2N), 4.43 (ddd, 1 H, $^3J_{HH}$ = 10.4, $^3J_{HH}$ = 10.4, $^3J_{PH}$ = 3.9, NH), 4.02 (dd, 1 H, $^2J_{HH}$ = 10.4, $^4J_{PH}$ = 4.3, CH_2N), 3.66 (m, 1 H, C*H*Me), 2.10–0.87 (m, 11 H, Cy), 0.68 (d, 3 H, $^3J_{HH}$ = 6.8, CHMe). **5e″** 7.62–6.65 (m, 29 H, ArH), 4.28 (m, 2 H, CH_2N and NH), 4.08 (m, 1 H, CH_2N), 3.87 (m, 1 H, C*H*Me), 2.10–0.87 (m, 11 H, Cy), 1.31 (d, 3 H, $^3J_{HH}$ = 6.3, Me). Attribution confirmed by ^1H–^1H Cosy. $^{13}C\{^1H\}$ NMR, $CDCl_3$, δ: **5e′** 140.7–126.9 (m, Ar), 59.8 (s, NCH), 53.1 (d, $^3J_{PC}$ = 5.8, NCH_2), 38.2 (s, CH, Cy), 30.3, 26.8, 26.6, 26.3 and 25.2 (all s, CH_2, Cy), 15.9 (d, $^4J_{PC}$ = 4.6, Me). **5e″** 139.5–127.4 (m, Ar), 58.4 (s, NCH), 52.4 (d, $^3J_{PC}$ = 5.8, NCH_2), 43.8 (s, CH, Cy), 31.5, 29.9, 26.1, 25.6 and 25.3 (all s, CH_2, Cy), 14.7 (d, $^4J_{PC}$ = 2.3, Me). IR and FIR (Nujol, cm^{-1}), ν_{N-H}: 3209; ν_{Ru-Cl}: 320, 315.

General procedure for catalytic transfer hydrogenation of acetophenone

Under an inert atmosphere, acetophenone (5 mmol), the ruthenium catalyst precursor (0.01 mmol, 0.2 mol%), and 45 mL of propan-2-ol were introduced in a Schlenk tube fitted with a condenser and heated at 82 °C for 15 min. Then NaOH was added (5 mL of a 0.048 M solution in propan-2-ol, 4.8 mol%) and the reaction was monitored by gas chromatography. 1-Phenylethanol and acetone were the only products detected in all cases.

X-ray diffraction study of 4d

Suitable single crystals of [$RuCl_2(\kappa^2$-*P*,*N*-2-$Ph_2PC_6H_4CH$=$N^iPr)_2$]·toluene for X-ray diffraction analyses were obtained by slow diffusion of hexane into a concentrated solution of **4d** in toluene. Data were collected on a Nonius CAD-4 single crystal diffractometer. The crystal data and structure refinement are: $C_{51}H_{52}Cl_2N_2P_2Ru$, $M = 926.26$, monoclinic, $a = 14.816(3)$, $b = 17.296(4)$, $c = 18.660(5)$ Å, $\beta = 106.21(3)°$, $U = 4591(2)$ Å^3, $T = 293$ K, space group $C2/c$, $Z = 4$, λ(Mo-K$_\alpha$) = 0.564 mm^{-1}. 4952 reflections measured, 4499 unique ($R_{int} = 0.041$) which were used in all calculations. The final $wR(F^2)$ was 0.117 (all data).

CCDC reference number 199894. See http://www.rsc.org/suppdata/nj/b2/b206119h/ for crystallographic data in CIF or other electronic format.

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