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: Synthesis, Characterization, and Catalytic Activity in Transfer Hydrogenation of Ketones

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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 $[RuCl_2(PPh_3)_3]$ and $[RuCl_2(DMSO)_4]$ with 2-$Ph_2PC_6H_4CH{=}N^tBu$ (**a**) lead to $[RuCl_2(\kappa^2\text{-}P,N\text{-}2\text{-}Ph_2PC_6H_4CH{=}N^tBu)(PPh_3)]$ (**1a**) and *trans*-$[RuCl_2(\kappa^2\text{-}P,N\text{-}2\text{-}Ph_2PC_6H_4CH{=}N^tBu)(DMSO)_2]$ (**2a**), respectively. Similarly, reactions with 2-$Ph_2PC_6H_4CH_2NH^tBu$ (**b**) afford complexes $[RuCl_2(\kappa^2\text{-}P,N\text{-}2\text{-}Ph_2PC_6H_4CH_2NH^tBu)(PPh_3)]$ (**5b**) and $[RuCl_2(\kappa^2\text{-}P,N\text{-}2\text{-}Ph_2PC_6H_4CH_2NH^tBu)(DMSO)]$ (**6b**) in good yield. The crystal structures of **1a** and **5b** have been determined by X-ray diffraction. Compound **2a**, containing two labile DMSO ligands, has been used as a precursor to synthesize the derivatives $[RuCl_2(\kappa^2\text{-}P,N\text{-}2\text{-}Ph_2PC_6H_4CH{=}N^tBu)L]$ [L = PPh_3 (**1a**); PPh_2Me (**3a**); PMe_2Ph (**4a**)]. Complexes **1a**, **2a**, **5b**, and **6b** are active in catalytic transfer hydrogenation of aryl−alkyl and dialkyl ketones in propan-2-ol. The five-coordinate complexes **1a**, **5b**, and **6b** show higher catalytic activity than the octahedral complex **2a**. Complexes **1a** and **5b** are more efficient catalysts than the precursor complex $[RuCl_2(PPh_3)_3]$. For the best catalyst, **1a**, yields up to 91% were obtained and turnover frequencies may be as high as 41 400 h^{-1}.

Introduction

The catalytic hydride transfer reduction of ketones has been largely investigated among those catalytic processes with potential applications. Although phosphines were historically the first type of ligands used in transition metal catalysts,[1] it is now well-established that the use of mixed phosphorus−nitrogen (P−N) ligands has led to an increased activity.[2] In particular, many ruthenium(II) complexes bearing bidentate or tridentate phosphinooxazoline as well as pyridylphosphine ligands have proved to be very efficient catalysts.[2−5] In contrast, to the best of our knowledge very few imino- or aminophosphine ligands have been used for this type of catalytic transformations. The first complexes, recently reported by Noyori and co-workers, contain the tetradentate C_2-diphosphine/diimine and diphosphine/diamine ligands *N*,*N*′-(*S*,*S*)-bis[*o*-(diphenylphosphino)benzylidene]cyclohexane-1,2-diamine (**A**) and *N*,*N*′-(*S*,*S*)-bis[*o*-(diphenylphosphino)benzyl]cyclohexane-1,2-diamine (**B**).[6] Interestingly, marked differences in activity are observed between the sp^2-N and the sp^3-N ligands, the iminophosphine complex being almost inactive in the reduction of acetophenone, whereas the aminophosphine complex leads to a high conversion. The high catalytic activity is attributed to the presence of the amino N−H group in the ligand. Rhodium(I) complexes containing these ligands have also shown a similar behavior, i.e., a higher activity for the complex with the diaminodiphosphine ligand.[7] Moreover, ruthenium(II) complexes containing an analogous tridentate NPN-type ligand, which also bears two secondary amino groups, have also been shown to catalyze the reduction of aryl−alkyl or dialkyl ketones by 2-propanol.[8]

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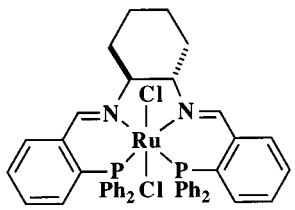
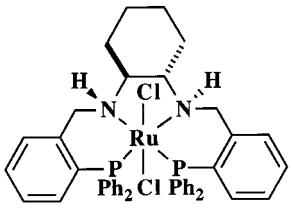
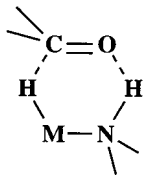


(A)



(B)

In addition to this type of catalyst, other complexes bearing a wide variety of similar ligands such as diamines,[2,3,9] amino alcohols,[2,10] amino acids,[11] bisoxazolines,[2] phenanthrolines,[2] diimines,[2,12] imino alcohols,[10g] aminosulfides,[13] and iminopyridines[2] have also proved to be good catalysts in transfer hydrogenation of ketones. Once again, the presence of an N−H group seems to be crucial to obtain good activity.[2b,9f,10c,g,14] The acceleration effect of primary and secondary amines has been explained on the basis of their ability to deliver the hydrogen atom from the metal-hydride catalysts to the ketones via a six-membered transition structure involving the N−H moiety (structure **C**). This mechanism has been supported by theoretical calculations.[15]



(C)

The importance of the N−H group in catalytic transfer hydrogenations and the scarceness of studies involving related amino- and iminophosphines prompted us to prepare new ruthenium(II) complexes incorporating this type of ligand in order to enable comparative studies on their catalytic activity. Since the iminophosphine **a** and its aminophosphine derivative **b** are readily accessible[16,17] in high yield and can be handled in air, we believed it to be of interest to use them as ligands of ruthenium(II) catalysts. Although a wide series of palladium(II)[18] and other transition metal complexes[19] have been reported, as far as we know, no ruthenium(II) complexes containing bidentate iminophosphine ligands 2-$Ph_2PC_6H_4CH{=}NR$ have been described to date.[20] Only some examples containing related tetradentate diimino/diphosphines $Ph_2PC_6H_4CH{=}N{-}X{-}N{=}CHC_6H_4PPh_2$ (X = C_2H_4, C_3H_6, C_6H_{12}, C_6H_{10}, dimethylbiphenylene, binaphthylene)[6,21] and tridentate anionic $Ph_2PC_6H_4CH{=}N{-}Y$ ($Y{=}C_6H_4O^-$, $CHMeCHPhO^-$)[22] ligands are known.

We report herein (i) the synthesis and characterization of five- and six-coordinate novel ruthenium(II) complexes containing the iminophosphine 2-$Ph_2PC_6H_4CH{=}N^tBu$ (**a**) and the related aminophosphine 2-Ph_2-

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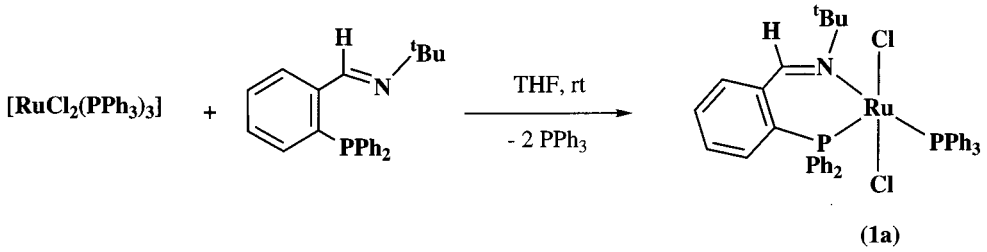
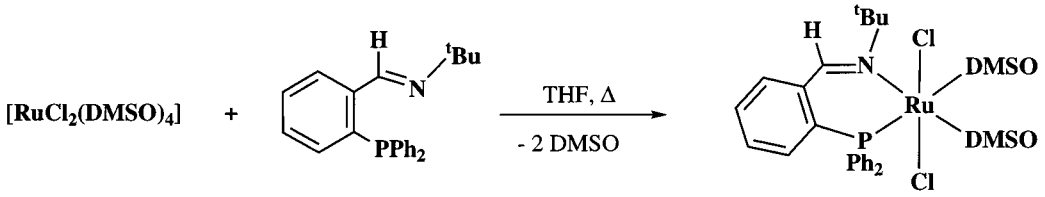
Scheme 1



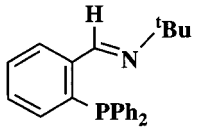
(1a)

Scheme 2



(2a)

$PC_6H_4CH_2NH^tBu$ (**b**) as ligands and (ii) a preliminary study of their catalytic activity in hydrogen transfer reactions to ketones.



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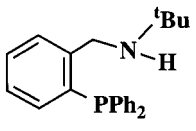

(b)

Results and Discussion

Synthesis of the Iminophosphine Complexes [$RuCl_2$(κ^2-*P*,*N*-2-$Ph_2PC_6H_4CH{=}N^tBu$)L] (L = PPh_3 (1a); PPh_2Me (3a); PMe_2Ph (4a)) and *trans*-[$RuCl_2$-(κ^2-*P*,*N*-2-$Ph_2PC_6H_4CH{=}N^tBu$)$(DMSO)_2$] (2a). The treatment of ruthenium(II) precursors [$RuCl_2(PPh_3)_3$] and [$RuCl_2(DMSO)_4$] with the iminophosphine **a**[16] yields the desired ruthenium(II) complexes via ligand exchange processes. Thus, the reaction of [$RuCl_2(PPh_3)_3$] with 1 equiv of **a** in THF results in the formation of the five-coordinate complex [$RuCl_2$(κ^2-*P*,*N*-2-$Ph_2PC_6H_4CH{=}N^tBu$)(PPh_3)] (**1a**) (Scheme 1).

Similarly the hexacoordinate complex *trans*-[$RuCl_2$-(κ^2-*P*,*N*-2-$Ph_2PC_6H_4CH{=}N^tBu$)$(DMSO)_2$] (**2a**) is obtained from the reaction of [$RuCl_2(DMSO)_4$] with 1 equiv of **a** (Scheme 2). All attempts to synthesize the bis(iminophosphine) complex [$RuCl_2$(κ^2-*P*,*N*-2-$Ph_2PC_6H_4$-$CH{=}N^tBu)_2$] by treatment of either [$RuCl_2(PPh_3)_3$] or [$RuCl_2(DMSO)_4$] with a large excess of 2-$Ph_2PC_6H_4CH{=}N^tBu$ in refluxing THF failed. Monitoring the reaction by $^{31}P\{^1H\}$ NMR the formation of only **1a** or **2a** is observed. This behavior reflects the steric requirements of the iminophosphine ligand **a**.

The stoichiometry of the five- and six-coordinate complexes **1a** and **2a**, respectively, is supported by elemental analysis and IR, $^{31}P\{^1H\}$, ^1H, and $^{13}C\{^1H\}$ NMR spectroscopic data (see Experimental Section for details), which are also consistent with a chelate coordination of the iminophosphine ligand. This is readily assessed by the NMR spectra which show a downfield shifting of the phosphorus resonances as well as those of carbon and proton of the imino group with respect to the free ligand.[23] Similarly, IR spectra show a slight lowering of the ν(C=N) absorption (1634 cm^{-1} (**a**) vs 1629 (**1a**) and 1627 cm^{-1} (**2a**)). The presence of two inequivalent phosphorus nuclei in complex **1a** gives rise to the expected AB pattern which appears at δ 81.6 and 35.7 ($^2J_{PP}$ = 33.4 Hz). The small value of the coupling constant is consistent with a *cis* disposition of the two phosphorus atoms. ^1H and $^{13}C\{^1H\}$ NMR spectra of **2a** show the expected resonances arising from the presence of the iminophosphine and DMSO ligands. They show only two sets of proton and carbon resonances for the methyl groups of the DMSO ligands, which is consistent with a *cis* disposition. Furthermore, the far-infrared (FIR) spectrum, which shows an absorption at 327 cm^{-1} (with a shoulder at 317 cm^{-1}), indicates a *trans* arrangement of the chloride ligands. No absorptions below 300 cm^{-1} are observed. All of these data support the stereochemistry shown in Scheme 2.

To determine unambiguously the stereochemistry of **1a**, an X-ray diffraction study was carried out. An ORTEP drawing of **1a** is shown in Figure 1, and selected bond lengths and angles are collected in Table 1. As for the precursor [$RuCl_2(PPh_3)_3$],[24] the coordination geometry around the ruthenium atom in **1a** can be described as a distorted square pyramid, with the phosphorus atom [P(2)] of the PPh_2 group at the apical position. The base of the pyramid is formed by the two chloride atoms occupying opposite sites [Cl(1)−Ru−Cl(2) = 167.39 (6)°] and by the nitrogen of the imino group in *trans* position to the triphenylphosphine ligand [N−Ru−P(1) = 166.02 (15)°]. The ruthenium atom is 0.2470 Å above the best least-squares base plane. The metallacycle formed by the iminophosphine ligand is almost planar. The deviations from the best plane are −0.00167 (Ru), −0.01597 [P(2)], 0.002009 [C(61)], 0.00220 [C(66)], −0.03356 [C(67)], and 0.02890 (N) Å. The Ru−N and C(67)−N bond lengths, 2.082(6) and 1.255(9) Å, respectively, are similar to those found in [$RuCl_2$(κ^4-*P*,*N*,*N*′,*P*′-$Ph_2PC_6H_4$-$CH{=}NCH_2CH_2N{=}CHC_6H_4PPh_2$)] [2.094(9), 2.097(6) and

(23) For the free ligand, in $CDCl_3$, $\delta CH{=}N$, 8.78 (d, $^4J_{PH}$ = 4.8 Hz); $\delta CH{=}N$, 154.4 (d, $^3J_{PC}$ = 20.3 Hz); $\delta^{31}P\{^1H\}$, −11.7 (s).

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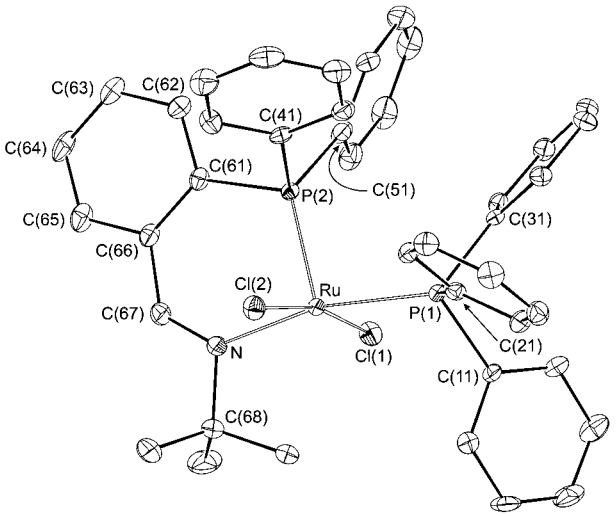


Figure 1. ORTEP view of the iminophosphine complex **1a**. Thermal ellipsoids are shown at 30% probability.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 1a

Bond Lengths			
Ru−N	2.082(6)	Ru−Cl(1)	2.398(4)
Ru−P(1)	2.362(4)	Ru−Cl(2)	2.401(4)
Ru−P(2)	2.203(3)	C(67)−N	1.255(9)
Bond Angles			
N−Ru−P(1)	166.02(15)	N−Ru−Cl(2)	85.8(2)
N−Ru−P(2)	94.53(18)	P(2)−Ru-Cl(1)	98.05(11)
P(2)−Ru-P(1)	99.17(10)	P(2)−Ru-Cl(2)	92.82(11)
N−Ru−Cl(1)	87.0(2)	Cl(1)−Ru-Cl(2)	167.39(6)
Torsion Angles			
N−Ru−P(2)−C(61)	−0.6(3)	C(66)−C(67)−N−Ru	7.8(12)
Ru−P(2)−C(61)−C(66)	2.6(6)	P(2)−Ru−N−C(67)	−4.3(7)
C(61)−C(66)−C(67)−N	−4.9(12)		

1.297(9), 1.285(9) Å],[21a] [$RuCl_2$(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],[6] and [Ru(κ^3-*P,N,O*-(*S,R*)-$Ph_2PC_6H_4CH{=}NCHMeCHPhO)_2$] [2.059(5) and 1.303(8) Å].[22]

The lability of DMSO ligands in complex **2a** allows their substitution by phosphines with relatively small cone angles. Thus, the reaction of **2a** with 1 equiv of PPh_3, in toluene at room temperature, leads to the displacement of both DMSO ligands to afford **1a**. Similarly, PPh_2Me and PMe_2Ph react with **2a** to afford the related complexes [$RuCl_2$(κ^2-*P,N*-2-$Ph_2PC_6H_4CH{=}N^tBu$)(PPh_2Me)] (**3a,** 88%) and [$RuCl_2$(κ^2-*P,N*-2-$Ph_2PC_6H_4CH{=}N^tBu$)(PMe_2Ph)] (**4a**, 89%), respectively (Scheme 3). In contrast no reaction is observed when the bulkier phosphine P^iPr_3 is used.

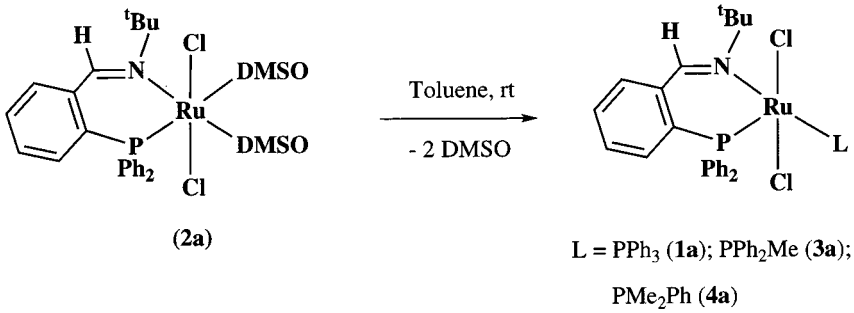
Complexes **3a** and **4a** are fully characterized by elemental analyses and spectroscopic methods (IR, ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR). The following features from the NMR spectra are noteworthy: (a) the $^{31}P\{^1H\}$ NMR spectra show resonances of an AB system [86.3 and 24.7 (**3a**); 86.2 and 19.3 (**4a**) ppm]. The small $^2J_{PP}$ value (36.7 Hz) is consistent with the *cis* disposition of both P-donor fragments. (b) The C*H*=N resonance in the ^1H NMR spectra appears as a doublet with an appreciable coupling to the phosphorus nuclei of PPh_2-Me or PMe_2Ph ($^4J_{PH}$ = 9.7 Hz), as confirmed by heteronuclear $^1H-^{31}P$ NMR correlation. This coupling constant suggests that the CH=N group is *trans* to the phosphine. Similar coupling constant values are found for **1a** and in a series of palladium(II)[18f,n] and iridium(I)[19f] complexes in which the imino group is also located *trans* to a phosphorus.[25]

Synthesis of the Aminophosphine Complexes [$RuCl_2$(κ^2-P,N-2-$Ph_2PC_6H_4CH_2NH^tBu$)L] (L = PPh_3 (5b); DMSO (6b)). Reactions of 1 equiv of the aminophosphine **b**[17] with [$RuCl_2(PPh_3)_3$] and [$RuCl_2(DMSO)_4$] in THF lead to the formation of the five-coordinate complexes [$RuCl_2$(κ^2-*P,N*-2-$Ph_2PC_6H_4CH_2NH^tBu$)(PPh_3)] (**5b**, 85%) and [$RuCl_2$(κ^2-*P,N*-2-$Ph_2PC_6H_4CH_2NH^tBu$)-(DMSO)] (**6b**, 92%), respectively (Schemes 4 and 5). Complexes **5b** and **6b** have been characterized by elemental analysis, IR, and $^{31}P\{^1H\}$, ^1H, and $^{13}C\{^1H\}$ NMR spectroscopy. In particular, the ^1H NMR spectra show the NH resonance at δ 4.71 (**5b**) and 4.46 (**6b**) ppm and two signals at δ 4.46 and 4.00 (**5b**) ppm, and 4.38 and 4.06 (**6b**) ppm attributable to the two diastereotopic CH_2N protons. The inequivalence of the methylene protons arises from the coordination of the amino group, which converts the nitrogen atom in a stereogenic center. Therefore no cleavage of the Ru−N bond, which would lead to an inversion of the configuration around the N atom, is taking place on the NMR time scale. The X-ray crystal structure determination of **5b** confirms the presence of a pair of enantiomers (see below). The $^{31}P-\{^1H\}$ NMR spectrum of **5b** exhibits as for the analogous complex **1a** an AB pattern at δ 73.4 and 40.1 ($^2J_{PP}$ = 37.3 Hz) indicating a *cis* arrangement of the two phosphorus atoms. Although the spectroscopic data of complex **6b** do not allow us to assess unambiguously its stereochemistry, an analogous *trans* arrangement for both chloride ligands and DMSO-amine group is proposed.

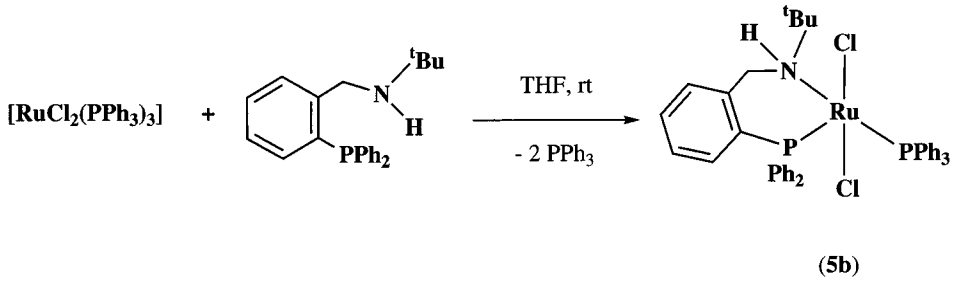
The structure of complex **5b** was confirmed by X-ray diffraction. An ORTEP drawing of **5b** is shown in Figure 2, and selected bond lengths and angles are collected in Table 2. Similarly to **1a**, the coordination geometry around the ruthenium atom in **5b** can be described as a distorted square pyramid, with the phosphorus atom [P(2)] of the PPh_2 group at the apical position. The base of the pyramid is formed by the two chloride atoms occupying opposite sites [Cl(2)−Ru−Cl(1) = 164.61(3)°] and by the nitrogen in *trans* position to the triphenylphosphine ligand [N−Ru−P(1) = 169.87(6)°]. The deviations from the best plane are −0.0317 [P(1)], 0.0349 [Cl(1)], 0.0354 [Cl(2)], and −0.0386 (N) Å. The ruthenium atom is −0.2356 Å above this plane. The Ru−N bond length, 2.225(2) Å, which is longer than that of the imino complex **1a**, is similar to those found in [$RuCl_2$(κ^3-*P,N,N′*-(*S,S*)-$Ph_2PC_6H_4CH_2NHC_6H_{10}NH$-$CH_2C_6H_4PPh_2$)] [2.157(9) and 2.231(8) Å],[21d] [$RuCl_2$ (κ^4-*P,N,N′,P′*-$Ph_2PC_6H_4CH_2NHC_2H_4NHCH_2C_6H_4$-$PPh_2$)] [2.177(1) and 2.16(1) Å],[21b] and [$RuCl_2$(κ^4-*P,N, N′,P′*-(*S,S*)-$Ph_2PC_6H_4CH_2NHC_6H_{10}NHCH_2C_6H_4$-$PPh_2$)].[6] As expected, the planarity of the metallacycle found in complex **1a** is no longer observed in complex **5b** due to the transformation of the sp^2-N imino to sp^3-N amino group. It is worth drawing attention to the very short Cl(1)···HN distance of 2.43(3) Å (expected van der Waals separation, 3.0 Å), which is ascribed to an

(25) $^4J_{PH}$ values for *cis* arrangement in the range 0−4.9 Hz. For references see for example 19c,e, 20g, and 22.

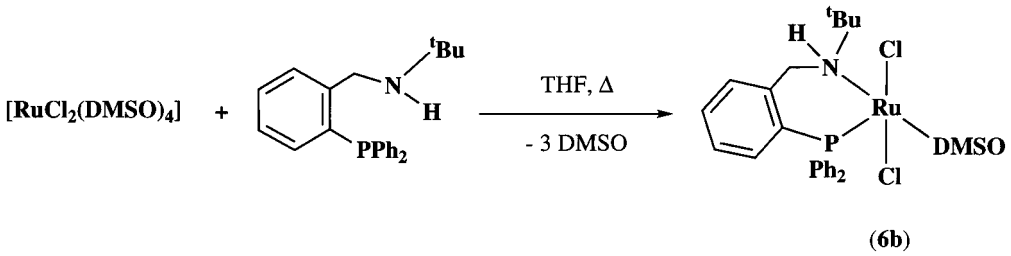
Scheme 3



Scheme 4



Scheme 5



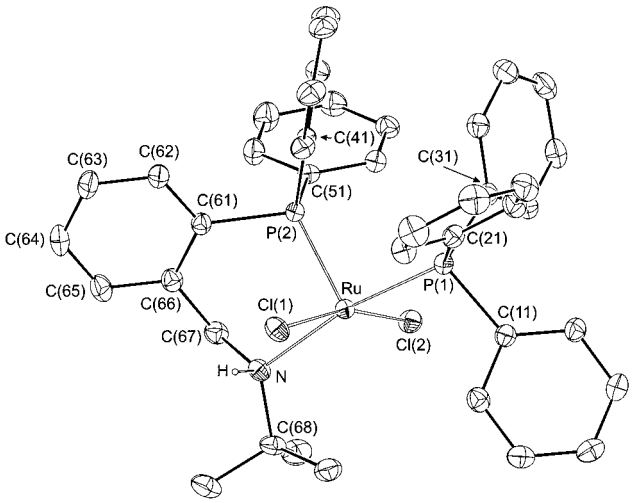


Figure 2. ORTEP view of the aminophosphine complex **5b**. Hydrogen atoms except NH have been omitted for clarity. Thermal ellipsoids are shown at 30% probability.

intramolecular hydrogen bond.[26] Another indication of the bonding interaction between the hydrogen and the chlorine is the fact that the amine hydrogen lies in the plane of N, Cl(1), and Ru, thus minimizing the NH··· Cl(1) distance [Cl(1)−Ru−N−H = 5.88 (2.23)°].

(26) (a) Fryzuk, M. D.; Montgomery, C. D.; Rettig, S. J. *Organometallics* **1991**, *10*, 467. (b) Haack, K.-J.; Hashiguchi, S.; Fujii, A.; Ikariya, T.; Noyori, R. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 285.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 5b

Bond Lengths			
Ru−N	2.225(2)	Ru−Cl(1)	2.4020(7)
Ru−P(1)	2.3318(7)	Ru−Cl(2)	2.3727(7)
Ru−P(2)	2.1943(7)	N−H	0.86(3)
Bond Angles			
N−Ru−P(1)	169.87(6)	N−Ru−Cl(2)	90.48(7)
NRu−P(2)	91.94(6)	P(2)−Ru-Cl(1)	95.38(3)
P(2)−Ru-P(1)	98.16(3)	P(2)−Ru-Cl(2)	97.19(2)
N−Ru−Cl(1)	80.22(7)	Cl(1)−Ru-Cl(2)	164.61(3)
Torsion Angles			
N−Ru−P(2)−C(61)	29.95(1)	C(66)−C(67)−N−Ru	−71.5(3)
Ru−P(2)−C(61)−C(66)	−47.5(2)	P(2)−Ru−N−C(67)	−155.1(3)
C(61)−C(66)−C(67)−N	65.4(3)		

The formation of the aminophosphine five-coordinate complex [$RuCl_2$(κ^2-*P*,*N*-2-$Ph_2PC_6H_4CH_2NH^tBu$)(DMSO)] (**6b**) containing only one DMSO ligand contrasts with that of the six-coordinate complex [$RuCl_2$(κ^2-*P*,*N*-2-$Ph_2PC_6H_4CH{=}N^tBu$)$(DMSO)_2$] (**1a**), probably reflecting the higher steric hindrance induced by the aminophosphine **b**.

Catalytic Transfer Hydrogenation of Ketones. Preliminary catalytic studies on the transfer hydrogenation of C=O bonds by propan-2-ol using the complexes **1a**, **2a**, **5b**, and **6b** as catalysts have been performed. The coordination of the chelate imino- and aminophosphine ligands in the identical ruthenium moiety [$RuCl_2$-(PPh_3)] allows comparative studies. In a typical experiment, the ruthenium(II) catalyst precursor (0.2 mol %)

Table 3. Transfer Hydrogenation of Acetophenone[a,b]

entry	catalyst	*T* [°C]	yield [%][c]	time [min]	TOF[d]
1	**1a**	90	81.1 (91.4)	5 (30)	5070 (910)
2	**5b**	90	79.4 (91.4)	5 (30)	4960 (910)
3	**2a**	90	25.8 (64.2)	10 (450)	760 (40)
4	**6b**	90	27.5 (87.9)	10 (450)	810 (60)
5	$[RuCl_2(PPh_3)_3]$	90	27.0 (89.9)	5 (115)	1690 (230)
6	**1a**	70	33.6 (80.1)	5 (200)	2100 (120)
7	**5b**	70	23.9 (72.9)	5 (285)	1500(80)
8	**1a**	50	17.5 (30.8)	10 (120)	520 (80)
9	**5b**	50	10.1 (26.4)	10 (330)	300 (20)

[a] Conditions: reactions were carried out in a sealed tube at the indicated temperature using 7 mL of propan-2-ol, 5 mmol of acetophenone, 0.2 mol % of catalyst precursor, and 0.5 mol % of NaOH. [b] Values in parentheses refer to results obtained after prolonged reaction time. [c] Yield of 1-phenylethanol, GC determined. [d] Turnover frequency: moles of product per mole of catalyst per hour, in h^{-1}.

and base (NaOH, 0.5 mol %) were added to a 0.71 M solution of the ketone in ^{i}PrOH, the reaction being monitored by gas chromatography. Selected results for the reduction of acetophenone at different temperatures are reported in Table 3. For comparative purposes the catalytic activity of the complex $[RuCl_2(PPh_3)_3]$, which has been previously studied by Bäckvall and co-workers,[27] has been also examined under the same conditions. The substitution in $[RuCl_2(PPh_3)_3]$ of two PPh_3 ligands by one P−N chelate iminophosphine (**a)** or aminophosphine ligand (**b**) in complexes **1a** and **5b**, respectively, induces an increase of the catalytic activity: 81.1% and 79.4% vs 27.0% of conversion in 5 min (entries 1, 2, and 5) at 90 °C. On the basis of Noyori's results,[6,15a] a marked increase in activity should be expected for the aminophosphine complex **5b**, with respect to the iminophosphine derivative **1a**. Nevertheless, the rates observed at 90 °C for **1a** and **5b** are similar. Moreover, complex **1a** becomes more efficient than **5b** when the reaction is carried out at lower temperature (70 or 50 °C): TOF value of 520 h^{-1} vs 300 h^{-1} after 10 min at 50 °C. As far as we know, this is the first example where an imino complex proves to be more active than the corresponding amino derivative. These results seem to indicate that the NH group does not participate in the interaction with the ketone throughout the catalytic cycle.

Complexes **2a** and **6b**, containing DMSO ligands, are less efficient than $[RuCl_2(PPh_3)_3]$ and afford only 25.8% and 27.5% yield after 10 min (entries 3 and 4), the rate observed for the aminophosphine complex **6b** being slightly higher than that for the iminophosphine derivative **2a**. However this difference is most probably due to the presence of a free coordination site in complex **6b** rather than an effect of the NH group. Since the coordination of the substrate on the ruthenium catalyst is generally proposed during the catalytic cycle, it is not surprising that the five-coordinate complexes **1a**, **5b**, **6b**, and $[RuCl_2(PPh_3)_3]$ are all more efficient than the six-coordinate complex **2a**.Complexes **1a** and **5b** also show good catalytic activity in the transfer hydrogenation of 2-methoxyacetophenone, ethyl methyl ketone, and cyclohexanone, as shown in Table 4. The conversions can be compared to those found for acetophenone at 90 °C (Table 3).

(27) Chowdhury, R. L.; Bäckvall, J.-E. *J. Chem. Soc., Chem. Commun.* **1991**, 1063.

Since the nature of the base induces in some cases a change in the catalytic activity of the system,[28] we have investigated the transfer hydrogenation of acetophenone in the presence of different bases (no reduction of the ketone is observed in the absence of base). Selected results are summarized in Table 5. Addition of inorganic bases, like NaOH, K_2CO_3, or $NaCO_2H$, leads to similar final conversions (entries 15−17), but the highest rate is observed when sodium hydroxide is employed. In contrast, the use of an organic base such as Et_3N leads to only very low conversions even when a high concentration is used.

Conclusions

We have prepared the first ruthenium(II) complexes containing non-oxazoline bidentate iminophosphines $[RuCl_2(\kappa^2\text{-}P,N\text{-}2\text{-}Ph_2PC_6H_4CH{=}N^tBu)L]$ (L = PPh_3 (**1a**); PPh_2Me (**3a**); PMe_2Ph (**4a**)) and the related aminophosphine derivatives $[RuCl_2(\kappa^2\text{-}P,N\text{-}2\text{-}Ph_2PC_6H_4CH_2NH^tBu)L]$ (L = PPh_3 (**5b**); DMSO (**6b**)). The steric hindrance of the bidentate ligands 2-$Ph_2PC_6H_4CH{=}N^tBu$ (**a**) and 2-$Ph_2PC_6H_4CH_2NH^tBu$ (**b**) seems to govern the stoichiometry of the resulting complexes, giving rise preferentially to five-coordinate complexes. Only one six-coordinate derivative *trans*-$[RuCl_2(\kappa^2\text{-}P,N\text{-}2\text{-}Ph_2PC_6H_4CH{=}N^tBu)(DMSO)_2]$ (**2a**) is obtained with the less sterically demanding iminophosphine ligand. The following features are noteworthy in these complexes: (i) All the five-coordinate complexes $[RuCl_2(\kappa^2\text{-}P{-}N)L]$ have been obtained stereoselectively with the monodentate ligand in *trans* position to the imino or amino group. (ii) These complexes provide a series of related imino- and aminophosphine complexes active in transfer hydrogen reactions of ketones. They are unusual examples where the influence of the imino −CH=NR and amino $-CH_2-NHR$ groups on the catalytic activity can be directly compared.

Complexes **1a**, **2a**, **5b**, and **6b** in the presence of base are active catalysts in transfer hydrogenation of ketones. In particular the catalytic activity of **1a** and **5b** is higher than that found for the phosphine complex $[RuCl_2(PPh_3)_3]$,[27] and the observed conversions can be compared to those found for other octahedral and five-coordinate ruthenium(II) complexes with analogous tridentate ligands.[4a,5a,29] As expected, the iminophosphine complex **1a** and the related aminophosphine derivative **5b** exhibit different catalytic activity. Nevertheless, as far as we know, this is the first example where an imino complex proves to be more efficient than the corresponding amino derivative. Indeed, previous comparative studies between imino- and aminophosphine,[6] or imino and amino alcohol,[10g] have both concluded that amino ligands lead to better activity. Further enantioselective transfer hydrogen reactions using chiral imino- and aminophosphines are currently under investigation.

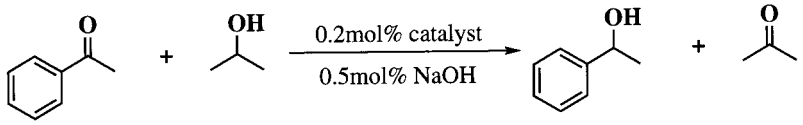
Experimental Section

The manipulations were performed under an atmosphere of dry nitrogen using vacuum-line and standard Schlenk

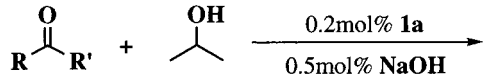
(28) Carmona, D.; Lahoz, F. J.; Atencio, R.; Oro, L. A.; Lamata, M. P.; Viguri, F.; San, José, E.; Vege, C.; Reyes, J.; Joó, F.; Kathó, A. *Chem. Eur. J.* **1999**, *5*, 1544.

(29) Dani, P.; Karlen, T.; Gossage, R. A.; Gladiani, S.; van Koten, G. *Angew. Chem., Int. Ed.* **2000**, *39*, 743.

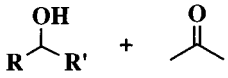
Scheme 6



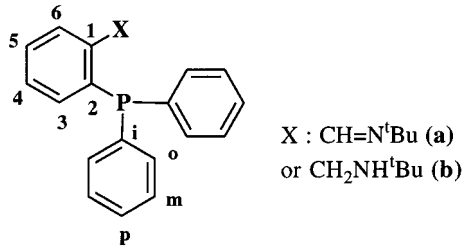
Scheme 7



R = Me; R = *o*-C_6H_4OMe
R = Me; R' = Et
RR'CO = cyclohexanone



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 $[RuCl_2(PPh_3)_3]$,[30] $[RuCl_2(DMSO)_4]$,[31] 2-$Ph_2PC_6H_4CH{=}NH^tBu$,[16] and 2-$Ph_2PC_6H_4CH_2NH^tBu$[17] were prepared by following the methods previously reported. Since only the hydrochloride salt of 2-$Ph_2PC_6H_4CH_2NH^tBu$ is spectroscopically described in the literature,[17] we report herein the full characterization. Gas chromatographic measurements were made on Hewlett-Packard HP6890 equipment. A HP-INNOWAX cross-linked poly(ethylene glycol) column (30 m, 250 μm) was used. Infrared spectra were recorded on a Perkin-Elmer 1720-XFT or a Perkin-Elmer 599 IR spectrometer. The C, H, and N analyses were carried out with a Perkin-Elmer 240-B microanalyzer. NMR spectra were recorded on a Bruker AC300 or 300DPX instrument at 300 MHz (^{1}H), 121.5 MHz (^{31}P), or 75.4 MHz (^{13}C) using $SiMe_4$ or 85% H_3PO_4 as standard. DEPT experiments have been carried out for all the compounds. Coupling constants *J* are given in hertz. Abbreviations used: Ar, aromatic; s, singlet; d, doublet; vt, virtual triplet; m, multiplet. Numbering used for the ligands:



X : CH=N^{t}Bu **(a)**
or CH_2NH^tBu **(b)**

Spectroscopic Data of 2-$Ph_2PC_6H_4CH_2NH^tBu$ (b). ^{31}P{^{1}H} NMR, $CDCl_3$, δ: −15.2 (s). ^{1}H NMR, $CDCl_3$, δ: 7.51−6.83 (m, 14 H, ArH), 3.91 (s br, 2 H, NCH_2), 1.02 (s, 9 H, ^{t}Bu), the NH proton is not observed. ^{13}C{^{1}H} NMR, C_6D_6, δ: 146.6 (d, $^1J_{PC}$ = 23.4, C-2), 138.0 (d, $^1J_{PC}$ = 11.3, C−i), 136.3 (d, $^2J_{PC}$ = 14.3, C-1), 134.4 (d, $^2J_{PC}$ = 20.4, C-o), 133.8 (s, C-4, 5, or 6), 130.0 (d, $^2J_{PC}$ = 5.3, C-3), 129.2 (s, C-4, 5, or 6), 128.9 (d, $^3J_{PC}$ = 6.8, C-m), 128.8 (s, C-p), 127.3 (s, C-4, 5, or 6), 50.6 (s, *C*Me_3), 46.1 (d, $^3J_{PC}$ = 22.7, *C*H_2N), 29.1 (s, C*Me*$_3$). IR (Nujol, cm^{-1}), ν_{N-H}: 3312. HRMS *m/z* calcd. for $C_{23}H_{26}NP$ (found): M^+ = 347.18028 (347.18011).

Synthesis of [$RuCl_2$(κ^2-*P,N*-2-$Ph_2PC_6H_4CH{=}N^tBu$)(PPh_3)] (1a). A solution of $[RuCl_2(PPh_3)_3]$ (1.127 g, 1.18 mmol) and 2-$Ph_2PC_6H_4CH{=}N^tBu$ (0.435 g, 1.27 mmol) in THF (100 mL) was stirred for 2 h at room temperature. After evaporation to dryness, the resulting residue was washed 3 times with 10 mL of a mixture of hexane and ether (1:1) to afford a dark red solid. Yield: 0.86 g (93%). Anal. Found (calcd for $C_{41}H_{39}Cl_2NP_2Ru$): C, 63.01 (63.16); H, 5.27 (5.04); N, 1.65 (1.80). ^{31}P{^{1}H} NMR, $CDCl_3$, δ: 81.6 (d, $^2J_{PP}$ = 33.4, PPh_2), 35.7 (d, $^2J_{PP}$ = 33.4, PPh_3). ^{1}H NMR, $CDCl_3$, δ: 8.99 (d, 1 H, $^4J_{PH}$ = 9.7,[32] C*H*=N), 7.65−7.05 (m, 29 H, ArH), 1.55 (s, 9 H, ^{t}Bu). ^{13}C{^{1}H} NMR, $CDCl_3$, δ: 162.8 (d, $^3J_{PC}$ = 4.5, *C*H=N), 135.1 (d, $^2J_{PC}$ = 9.9, C-o, PPh_3), 129.1 (s, C-p, PPh_3), 127.4 (d, $^3J_{PC}$ = 9.9, C-m, PPh_3), 137.1−125.2 (other aromatic carbons), 68.2 (s, *C*Me_3), 28.3 (s, C*Me*$_3$). IR (Nujol, cm^{-1}), $\nu_{C=N}$: 1629.

Synthesis of [$RuCl_2$(κ^2-*P,N*-2-$Ph_2PC_6H_4CH{=}N^tBu$)(DMSO)$_2$] (2a). A mixture of $[RuCl_2(DMSO)_4]$ (0.126 g, 0.26 mmol) and 2-$Ph_2PC_6H_4CH{=}N^tBu$ (0.108 g, 0.31 mmol) in 30 mL of THF was refluxed for 5 h. The resulting dark red solution was evaporated to dryness and the residue washed twice with 10 mL of a mixture of hexane and ether (1:1) to afford a red solid. Yield: 0.150 g (86%). Anal. Found (calcd for $C_{27}H_{36}Cl_2NO_2PRuS_2$): C, 48.01 (48.14); H, 5.28 (5.39); N, 1.97 (2.08). ^{31}P{^{1}H} NMR, $CDCl_3$, δ: 80.3 (s). ^{1}H NMR, $CDCl_3$, δ: 8.88 (s br, 1 H, C*H*=N), 8.10−6.98 (m, 14 H, ArH), 2.97 (s, 6 H, Me), 2.62 (s, 6 H, Me), 1.70 (s, 9 H, ^{t}Bu). ^{13}C{^{1}H} NMR, $CDCl_3$, δ: 164.2 (d, $^3J_{PC}$ = 5.3, CH=N), 137.8 (d, $^2J_{PC}$ = 14.4, C-1), 137.0 (d, $^2J_{PC}$ = 9.1, C-3), 134.9 (s, C-4, 5, or 6), 134.4 (d, $^2J_{PC}$ = 9.8, C-o), 132.7 (d, $^1J_{PC}$ = 58.2, C-i), 131.6 (s, C-4, 5, or 6), 131.5 (d, J_{PC} = 7.6, C-4 or 6), 130.2 (d, $^4J_{PC}$ = 2.3, C-p), 127.6 (d, $^3J_{PC}$ = 11.3, C-m), 123.9 (d, $^1J_{PC}$ = 50.6, C-2), 70.3 (s, *C*Me_3), 44.4 (s, *Me*$_2$SO), 41.0 (s, *Me*$_2$SO),27.6 (s, C*Me*$_3$). IR (Nujol, cm^{-1}): $\nu_{C=N}$ 1627; ν_{RuCl} 327 (with shoulder at 217).

Synthesis of [$RuCl_2$(κ^2-*P,N*-2-$Ph_2PC_6H_4CH{=}N^tBu$)L] [L = PPh_3 (1a); PPh_2Me (3a); PMe_2Ph (4a)] from 2a. 1a: A solution of **2a** (0.085 g, 0.13 mmol) in 10 mL of toluene was treated with a solution of triphenylphosphine in toluene (0.07 M, 1.8 mL, 0.13 mmol) and stirred at room temperature for 8 h. After evaporation to dryness, the residue was washed twice with 4 mL of a mixture of hexane/ether (1:1) and vacuum-dried. Yield: 0.088 g (87%). **3a**: Following the same procedure using 0.097 g (0.14 mmol) of **2a** and PPh_2Me (26 μL, 0.14 mmol). Reaction time: 1 h. Yield: 0.088 g (88%). Anal. Found (calcd for $C_{36}H_{37}Cl_2NP_2Ru$): C, 60.31 (60.25); H, 5.14 (5.20); N, 2.00 (1.95). ^{31}P{^{1}H} NMR, C_6D_6, δ: 86.3 (d, $^2J_{PP}$ = 36.7, PPh_2), 24.7 (d, $^2J_{PP}$ = 36.7, PPh_2Me). ^{1}H NMR, C_6D_6, δ: 8.64 (d, 1 H, $^4J_{PH}$ = 9.7,[32] C*H*=N), 8.07−6.75 (m, 24 H, ArH), 1.62 (d, 3 H, $^2J_{PH}$ = 8.8, PPh_2*Me*), 1.50 (s, 9 H, ^{t}Bu). ^{13}C{^{1}H} NMR, $CDCl_3$, δ: 162.4 (d, $^3J_{PC}$ = 4.7, CH=N), 137.7 (d, $^1J_{PC}$ = 12.8, C-1), 136.7 (d, $^2J_{PC}$ = 9.3, C-3), 135.9 (d, $^1J_{PC}$ = 37.3, C-2), 134.8 (d, $^1J_{PC}$ = 55.3, C-i), 134.5 (s, C-4, 5, or 6), 133.9 (d, $^2J_{PC}$ = 9.3, C-o), 132.7 (d, $^2J_{PC}$ = 8.7, C-o), 130.9 (s, C-4, 5, or 6), 130.8 (s, C-4, 5, or 6), 129.4 (d, $^4J_{PC}$ = 2.3, C-p), 129.1 (s, C-p), 127.9 (d, $^3J_{PC}$ = 8.2, C-m), 127.3 (d, $^3J_{PC}$ = 11.1, C-m), 125.5 (d, $^1J_{PC}$ = 46.6, C-i), 68.5 (s, *C*Me_3), 28.0 (s, C*Me*$_3$), 9.57 (d, $^1J_{PC}$ = 31.4, PMe). IR (Nujol, cm^{-1}), $\nu_{C=N}$: 1623. **4a**: Following the same procedure using 0.100 g (0.15 mmol) of **2a** and 21 μL (0.15 mmol) of PMe_2Ph. Reaction time: 1 h. Yield: 0.088 g (89%). Anal. Found (calcd for $C_{31}H_{35}Cl_2NP_2Ru$): C, 58.73 (58.80); H, 5.29 (5.38); N, 1.97 (2.14). ^{31}P{^{1}H} NMR, $CDCl_3$, δ: 86.2 (d, $^2J_{PP}$ = 36.7, PPh_2), 19.3 (d, $^2J_{PP}$ = 36.7, PMe_2Ph). ^{1}H NMR, $CDCl_3$, δ: 8.89 (d, 1 H, $^4J_{PH}$ = 9.7,[32] C*H*=N), 7.72−6.96 (m, 19 H, ArH), 1.51 (d, 6 H, $^2J_{PH}$ = 9.1, P*Me*$_2$Ph), 1.44 (s, 9 H,

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Table 4. Transfer Hydrogenation of Ketones RR′C=O[a,b]

entry	R, R′	catalyst	yield [%]	time [min]	TOF
10	2-$MeOC_6H_4$, Me	**1a**	73.7 (98.1)	10 (90)	2170 (330)
11	2-$MeOC_6H_4$, Me	**5b**	63.7 (97.7)	10 (60)	1870 (490)
12	Et, Me	**1a**	70.3 (94.7)	10 (45)	2070 (630)
13	cyclohexanone	**1a**	69.0 (99.4)	0.5 (5)	41400 (6230)

[a] Conditions: reactions were carried out in a sealed tube at 90 °C using 7 mL of propan-2-ol, 5 mmol of substrate, 0.2 mol % of catalyst precursor, and 0.5 mol % of NaOH. [b] Values in parentheses refer to results obtained after prolonged reaction time.

Table 5. Transfer Hydrogenation of Acetophenone in the Presence of Different Bases[a,b]

entry	base	yield [%]	time [min]	TOF
14	without	0	240	
15	NaOH	81.1 (91.4)	5 (30)	5070 (910)
16	K_2CO_3	1.5 (92.4)	30 (210)	20 (130)
17	$NaCO_2H$	2.7 (92.5)	10 (195)	80 (140)
18	NEt_3	0.5 (6.4)	5 (240)	30 (10)

[a] Conditions: reactions were carried out at 90 °C with 5 mmol of acetophenone, 0.2 mol % of **1a**, and 0.5 mol % of base. [b] Values in parentheses refer to results obtained after prolonged reaction time.

^{t}Bu). $^{13}C\{^1H\}$ NMR, $CDCl_3$, δ: 162.0 (d, $^3J_{PC}$ = 4.1, CH=N), 143.0−126.2 (m, aromatic carbons), 68.5 (s, *C*Me_3), 27.9 (s, C*Me*$_3$), 11.9 (d, $^1J_{PC}$ = 28.5, PMe_2). IR (Nujol, cm^{-1}), $\nu_{C=N}$: 1621.

Synthesis of [$RuCl_2$(κ^2-*P,N*-2-$Ph_2PC_6H_4CH_2NH^tBu$)(PPh_3)] (5b). Following the same procedure as for **1a**, **5b** was prepared as a green solid, using [$RuCl_2(PPh_3)_3$] (0.392 g, 0.41 mmol) and 2-$Ph_2PC_6H_4CH_2NH^tBu$ (0.263 g, 0.76 mmol) in 40 mL of THF. Yield: 0.208 g (85%). Anal. Found (calcd for $C_{41}H_{41}Cl_2NP_2Ru$): C, 62.87 (63.00); H, 5.42 (5.29); N, 1.77 (1.79). $^{31}P\{^1H\}$ NMR, $CDCl_3$, δ: 73.4 (d, $^2J_{PP}$ = 37.3, PPh_2), 40.1 (d, $^2J_{PP}$ = 37.3, PPh_3). ^1H NMR, $CDCl_3$, δ: 7.64−6.54 (m, 29 H, ArH), 4.71 (br s, 1 H, NH), 4.46 (vt, 1 H, $^2J_{HH} = {}^3J_{HH}$ = 10.1, NCH_2), 4.00 (dd, 1 H, $^3J_{HH}$ = 10.1, $^2J_{HH}$ = 2.0, NCH_2), 1.41 (s, 9 H, ^{t}Bu). $^{13}C\{^1H\}$ NMR, $CDCl_3$, δ: 141.9 (d, $^1J_{PC}$ = 12.8, C-1), 135.0 (d, $^2J_{PC}$ = 9.8, C-o, PPh_3), 131.7 (d, J_{PC} = 3.8, C-4, 5, or 6), 131.4 (d, J_{PC} = 2.3, C-4, 5, or 6), 130.5 (d, J_{PC} = 2.3, C-p PPh_2), 130.1 (d, J_{PC} = 2.3, C-p PPh_2), 129.6 (d, $^4J_{PC}$ = 1.5, C-p, PPh_3), 128.5 (d, $^2J_{PC}$ = 7.8, C-3), 128.0 (d, $^3J_{PC}$ = 9.1, C-m, PPh_3), 127.3 (d, $^3J_{PC}$ = 10.6, C-m, PPh_2), 135.5−129.2 (m, other aromatic carbons), 59.2 (s, *C*Me_3), 52.6 (d, $^3J_{PC}$ = 6.8, CH_2N), 28.9 (s, C*Me*$_3$). IR (Nujol, cm^{-1}), ν_{N-H}: 3192.

Synthesis of $RuCl_2$(κ^2-*P,N*-2-$Ph_2PC_6H_4CH_2NH^tBu$)(DMSO) (6b). Following the same procedure as for **2a**, **6b** was prepared as a purple solid (green in solution), using $RuCl_2(DMSO)_4$ (0.186 g, 0.38 mmol) and 2-$Ph_2PC_6H_4CH_2NH^tBu$ (0.210 g, 0.60 mmol) in 40 mL of THF. Yield: 0.204 g (92 %). Anal. Found (calcd for $C_{25}H_{32}Cl_2NOPRuS$): C, 51.42 (51.46); H, 5.62 (5.53); N, 2.51 (2.40). $^{31}P\{^1H\}$ NMR, CD_2Cl_2, δ: 73.7 (s). ^1H NMR, CD_2Cl_2, δ: 7.65−6.89 (m, 14 H, ArH), 4.46 (d, 1 H, $^3J_{HH}$ = 11.2, NH), 4.38 (vt, 1 H, $^2J_{HH} = {}^3J_{HH}$ = 11.2, CH_2N), 4.06 (d, 1 H, $^2J_{HH}$ = 11.2, CH_2N), 3.33 (s, 3 H, Me_2SO), 2.56 (s, 3 H, Me_2SO), 1.41 (s, 9 H, ^{t}Bu). $^{13}C\{^1H\}$ NMR, CD_2Cl_2, δ: 142.4 (d, $^1J_{PC}$ = 12.8, C-1), 135.0 (d, $^2J_{PC}$ = 9.8, C-o), 133.2 (d, $^1J_{PC}$ = 58.2, C-i), 133.0 (d, J_{PC} = 3.0, C-4, 5, or 6), 132.2 (d, $^4J_{PC}$ = 2.3, C-p), 131.9 (d, $^2J_{PC}$ = 9.8, C-3), 131.2 (d, $^4J_{PC}$ = 2.3, C-p), 130.7 (d, J_{PC} = 3.0, C-4, 5, or 6), 130.0 (d, $^1J_{PC}$ = 49.1, C-2), 129.3 (d, $^1J_{PC}$ = 56.6, C-i), 129.1 (d, J_{PC} = 8.3, C-4, 5, or 6), 128.5 (d, $^3J_{PC}$ = 11.3, C-m), 127.7 (d, $^3J_{PC}$ = 11.3, C-m), 61.3 (s, *C*Me_3), 58.8 (d, $^3J_{PC}$ = 6.8, CH_2N), 46.6 (s, Me_2SO), 44.5 (s, Me_2SO), 27.8 (s, C*Me*$_3$). IR (Nujol, cm^{-1}), ν_{N-H}: 3166.

General Procedure for Ruthenium(II)-Catalyzed Hydrogen Transfer Reactions. Under inert atmosphere the ketone (5 mmol), the ruthenium catalyst precursor (0.01 mmol, 0.2 mol %), and 6 mL of propan-2-ol are introduced in a sealed tube and heated at working temperature for 20 min. Then the base, NaOH unless otherwise specified, is added (1 mL of a 0.025 M solution in propan-2-ol, 0.5 mol %) and the reaction is monitored by gas chromatography. Corresponding alcohol and acetone are the only products detected in all cases.

X-ray Diffraction Studies of 1a and 5b. Crystals suitable for X-ray diffraction analyses were obtained by slow diffusion of hexane into a concentrated solution of the complexes in toluene. Data collection, crystal, and refinement parameters are collected in Table 6. The structures were solved by DIRDIF-99.2[33] (Patterson methods and phase expansion). An empirical absorption correction was applied using XABS2.[34] Full-matrix least-squares refinement on F_o^2 using SHELX97[35] was performed. During the final stages of the refinement, the positional parameters and the anisotropic thermal parameters of the non-H atoms were refined. Atomic scattering factors were taken from International Tables for X-ray Crystallography (1974).[36] Geometrical calculations were made with PARST97.[37] The crystallographic plots were made with PLATON.[38] All calculations were made at the University of Oviedo on the X-ray group computers. This work was partially supported by CICYT (BQU2000-0219).

Crystal Data for 1a. Data collection was performed on a Nonius CAD-4 single-crystal diffractometer. Data were collected with the $\omega-2\theta$ scan technique and a variable scan rate, with a maximum scan time of 60 s per reflection. The final drift correction factors were between 0.97 and 1.06. On all reflections, profile analysis[39,40] was performed. Lorentz and polarization corrections were applied, and the data were reduced to F_o^2 values. The unit cell parameters were obtained from the least-squares fit of 25 reflections (with θ between 15° and 19°). H atoms were geometrically placed riding on their parent atoms with isotropic displacement parameters set to 1.2 times the U_{eq} of the atoms to which they are attached (1.5 for methyl groups).

The function minimized was $[\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (0.2000P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$ with $\sigma^2(F_o^2)$ from counting statistics. The maximum shift-to-esd ratio in the last full-matrix least-squares cycle was 0.000.

Crystal Data for 5b. Data collection was performed on a Nonius KappaCCD single-crystal diffractometer. Crystal−detector distance was fixed at 29 mm, and a total of 1078 images were collected using the oscillation method (φ and ω scans), with 2° oscillation and 40 s exposure time per image. Data collection strategy was calculated with the program COLLECT.[41] Data reduction and cell refinement were performed with the programs HKL DENZO and SCALEPACK.[42] Unit cell dimensions were determined from 6493 reflections

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Table 6. Crystal Data and Structure Refinement for 1a and 5b

	1a	5b
empirical formula	$C_{41}H_{39}Cl_2NP_2Ru \cdot C_7H_8$	$C_{41}H_{41}Cl_2NP_2Ru$
fw	871.78	781.66
temperature	200 (2) K	200 (2) K
wavelength	0.71073 Å	1.5418 Å
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
unit cell dimens	$a = 10.55$ (1) Å $b = 10.66$ (1) Å $c = 19.17$ (3) Å $\alpha = 104.8$ (1)° $\beta = 92.54$ (8)° $\gamma = 98.02$ (9)°	$a = 10.5799$ (3) Å $b = 13.2989$ (3) Å $c = 13.8899$ (3) Å $\alpha = 107.635$ (2)° $\beta = 93.764$ (1)° $\gamma = 91.728$ (2)°
volume	2058 (5) Å^3	1855.89 (8) Å^3
Z	2	2
density (calcd)	1.407 Mg m^{-3}	1.399 Mg m^{-3}
abs coeff	0.624 mm^{-1}	5.779 mm^{-1}
F(000)	900	804
cryst size	0.40 × 0.16 × 0.13 mm	0.17 × 0.12 × 0.12 mm
θ range for data collection	1.10 → 26.0	3.35 → 69.81
index ranges	$-12 \le h \le 12$, $-13 \le k \le 12$, $0 \le l \le 23$	$-12 \le h \le 12$, $-16 \le k \le 15$, $0 \le l \le 16$
no. of reflns collected	8484	32 322
no. of ind reflns	7632 [R(int) = 0.0600]	6945 [R(int) = 0.0360]
completeness to θ	26.00°, 94.4%	69.81°, 99.0%
abs corr	empirical	empirical
max. and min. transmn	0.686 and 1.000	0.515 and 1.000
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
no. of data/restraints/params	7632/0/487	6945/0/436
goodness-of-fit on F^2	1.128	1.161
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0660$, $wR_2 = 0.1925$	$R_1 = 0.0328$, $wR_2 = 0.0925$
R indices (all data)	$R_1 = 0.0999$, $wR_2 = 0.2583$	$R_1 = 0.0349$, $wR_2 = 0.0938$
largest diff peak and hole	2.185 and −3.208 e Å^{-3}	0.547 and −0.567 e Å^{-3}

between $\theta = 1.000°$ and 70.000°. Final mosaicity was 0.389(3)°. All data completeness was 99.0%. Intensity−error ratio for all reflections was 299.5:8.8. H atoms (except H, H67A, and H67B, which were detected by difference Fourier synthesis and isotropically refined with an independent thermal parameter) were geometrically placed riding on their parent atoms with isotropic displacement parameters set to 1.2 times the U_{eq} of the atoms to which they are attached (1.5 for methyl groups).

The function minimized was $[\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (0.0434P)^2 + 1.6695P]$, where $P = (F_o^2 + 2F_c^2)/3$ with $\sigma^2(F_o^2)$ from counting statistics. The maximum shift-to-esd ratio in the last full-matrix least-squares cycle was 0.001.

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Supporting Information Available: Crystal structure data for **1a** and **5b** including tables of atomic parameters, anisotropic thermal parameters, bond distances, and bond angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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