2-(Aminomethyl)pyridine−Phosphine Ruthenium(II) Complexes: Novel Highly Active Transfer Hydrogenation Catalysts

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Received October 25, 2004

The complexes *trans,cis*-$RuCl_2(PPh_3)_2$(ampy) (**1**) and *trans*-$RuCl_2[Ph_2P(CH_2)_4PPh_2]$(ampy) (**2**) have been prepared in high yield by reaction of $RuCl_2(PPh_3)_3$ and $RuCl_2(PPh_3)[Ph_2P(CH_2)_4PPh_2]$ with 2-(aminomethyl)pyridine (ampy) at room temperature by PPh_3 displacement. Heating compound **1** in refluxing toluene leads to the isomer *cis,cis*-$RuCl_2(PPh_3)_2$(ampy) (**3**), which has been proven to be a good precursor for the preparation of the complexes *cis*-$RuCl_2$(PP)(ampy) [PP = (*S*,*S*)-Chiraphos, **4**; $Ph_2P(CH_2)_3PPh_2$, **5**; (*S*,*S*)-Skewphos, **6**; $Ph_2P(CH_2)_4PPh_2$, **7**; (*R*,*R*)-Diop, **8**] by displacement of two PPh_3 with the appropriate diphosphine. The derivatives *cis*-$RuCl_2$(PP)(ampy) [PP = (*R*,*S*)-Josiphos, **9**; (*R*,*S*)-^{t}Bu-Josiphos, **10**] have been synthesized from $RuCl_2(PPh_3)_3$ and PP followed by addition of ampy. The chiral complexes **4**, **6**, **8**, **9**, and **10** are formed stereoselectively, as inferred by NMR data in solution. For the derivatives **7** and **9** the molecular structures have been determined by X-ray measurements. The monohydride complex *trans,cis*-$RuHCl(PPh_3)_2$(ampy) (**11**) has been prepared from $RuHCl(PPh_3)_3$ and ampy in heptane by PPh_3 substitution. Compound **11** reacts with sodium isopropoxide in toluene, affording the dihydride derivative *cis,trans*-$Ru(H)_2(PPh_3)_2$(ampy) (**12**) via the alkoxide route. The intermediate species *cis,cis*-$Ru(H)_2(PPh_3)_2$(ampy) (**A**) has been also characterized by NMR in solution. All these complexes have been found to be highly efficient transfer hydrogenation catalysts. With the complexes *cis*-$RuCl_2$(PP)(ampy) a large number of ketones (dialkyl, diaryl, and alkyl-aryl) can be quantitatively reduced to alcohols in 2-propanol and in the presence of NaOH (ketone/Ru/NaOH = 2000/1/40) with remarkably high TOF values (up to 400 000 h^{-1} at 50% conversion). The derivatives containing chiral diphosphines afforded rapid (TOF > 10^5 h^{-1}) and enantioselective (ee up to 94%) reduction of methyl-aryl ketones using low loading of catalysts (0.05−0.01 mol %). In the absence of base the dihydride compound **12** catalyzes the transfer hydrogenation of acetophenone.

Introduction

Ruthenium(II) complexes containing both nitrogen and phosphino ligands are well-known since the pioneering works of Wilkinson on $RuCl_2(PPh_3)_3$,[1] and the research in this area has led to the synthesis of a large number of derivatives[2] with different combinations of P and N donor ligands.[3] The interest in this type of complexes has strongly increased in the last decade following the discovery by Noyori and co-workers that *trans*-$RuCl_2$(PP)(1,2-diamine) (PP = diphosphine) containing chiral phosphine and amine ligands can promote the rapid and highly stereoselective hydrogenation of ketones, and evidence has been provided that the Ru−H/−NH_2 motif is crucial for the activity of these catalysts.[4] It is now well-established that ruthenium complexes bearing phosphorus and nitrogen ligands can also catalyze the transfer hydrogenation of ketones by means of 2-propanol as hydrogen source, a process that is often proposed as an alternative to H_2 use, for small- or medium-scale applications.[5] Thus, catalytically efficient

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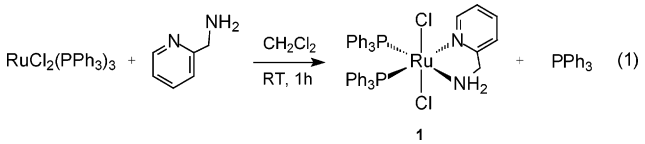
10.1021/om0491701 CCC: $30.25
Publication on Web 02/26/2005

systems have been obtained in situ by reaction of $RuCl_2(PPh_3)_3$ with chiral NN pyridylmethylamine[6] and NNN oxazoline[7] ligands. Conversely, structurally well-defined transfer hydrogenation catalysts are those of general formula $RuCl_2(PR_3)(L)$ (L = bidentate PN oxazolinylferrocenylphosphine[8] and aminophosphine,[9] tridentate PNO pyridine,[10] NPN,[11] and NNN[12] oxazoline ligands), $RuCl_2(PR_3)_2(NN)$[13] (NN = diamine, dipyridine), *trans*-$RuCl_2(PP)$(1,2-diamine),[14] $RuCl_2$(PNNP) with a tetradentate diphosphine/diamine ligand,[14,15] and [RuCl(*p*-cymene)(PN)][BF_4] containing a mixed phosphole−pyridine ligand.[16] Although some of the chiral systems exhibit high enantioselectivity for the reduction of methyl-aryl ketones,[8,12,15] their speed remains lower (TOF $\leq 10^4$ h^{-1}) compared to the most active achiral systems.[10,11,16]

Recently, we have found that commercially available 2-(aminomethyl)pyridine (ampy) shows a particularly high ligand acceleration effect in the transfer hydrogenation catalyzed by ruthenium(II) complexes in 2-propanol. Thus, with the cyclometalated compound RuCl(CO)[(2-CH_2-6-MeC_6H_3)PPh_2](NN) (NN = ethylenediamine) complete conversion of acetophenone is achieved in 0.5 h (ketone/Ru = 1000/1; TOF = 2800 h^{-1}), whereas with NN = ampy the reduction occurs in a few minutes (TOF = 60 000 h^{-1}).[17] With this in mind, we have investigated the ruthenium(II) chemistry of the ampy ligand in combination with various phosphines in view of the potential interest of these systems as catalysts in transfer hydrogenation. We describe here the preparation and characterization of a new series of complexes of formulas $RuCl_2(PPh_3)_2$(ampy) and $RuCl_2$(PP)(ampy) (PP = diphosphine), including a structural analysis by X-ray diffraction of two derivatives. Furthermore, a study of their catalytic activity in transfer hydrogenation from 2-propanol to ketones is also reported. These compounds are extremely active hydrogen transfer catalysts with remarkable high turnover frequency (TOFs up to 400 000 h^{-1}). Quantitative formation of alcohols with high substrate/Ru ratio (2000−10 000) and good to high enantioselectivity (ee up to 94%) is achieved with the derivatives bearing chiral diphosphines. To the best of our knowledge, these structurally well-defined systems are among the most active hydrogen transfer catalysts reported to date. We also report the isolation and catalytic activity of the hydride complexes *trans,cis*-RuHCl$(PPh_3)_2$(ampy) and *cis,trans*-$Ru(H)_2(PPh_3)_2$(ampy).

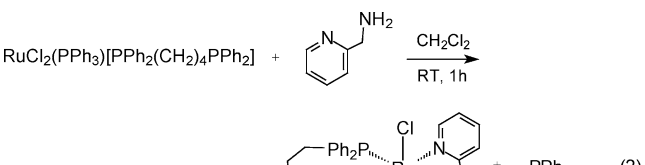
Results and Discussion

Synthesis and Characterization of $RuCl_2(PPh_3)_2$(ampy) and $RuCl_2$(PP)(ampy) (PP = diphosphine). Treatment of $RuCl_2(PPh_3)_3$ with an equimolar amount of ampy in dichloromethane at room temperature promptly affords the complex *trans,cis*-$RuCl_2(PPh_3)_2$(ampy) (**1**) by displacement of one phosphine, as inferred by NMR spectroscopy, and the product has been isolated in high yield (eq 1).



1

The $^{31}P\{^1H\}$ NMR spectrum of **1** shows two relatively close doublets (δ 44.0 and 40.1) with a J(PP) = 32.7 Hz, indicating a *cis* phosphorus arrangement.[18] Furthermore, in the ^1H NMR spectrum the ampy ligand displays a doublet for the *ortho*-pyridine proton shifted downfield at δ 8.53 (J(HH) = 4.2 Hz), whereas the methylene protons appear as a broad singlet at δ 4.46 and those of the NH_2 group are at δ 3.29, suggesting that ampy lies in the RuP_2 plane, with two *trans* chloride atoms. In the $^{13}C\{^1H\}$ NMR spectrum the CH_2 group is at δ 50.8, only slightly shifted downfield with respect to the free ligand (δ 47.8). Similarly to the previous preparation, reaction of the diphosphine ruthenium precursor $RuCl_2(PPh_3)[Ph_2P(CH_2)_4PPh_2]$[19] with ampy easily leads to the *trans*-$RuCl_2[Ph_2P(CH_2)_4PPh_2]$(ampy) (**2**) derivative (eq 2).



2

Compounds **1** and **2** are structurally related to the thermally stable *trans*-$RuCl_2$(PP)(diamine)[4a] and *trans*-$RuCl_2(PP)(Py)_2$[20] that catalyze the hydrogenation of ketones.

At room temperature complex **1** is relatively stable in solution, but upon heating, it isomerizes to the thermodynamically favored *cis,cis*-$RuCl_2(PPh_3)_2$(ampy)

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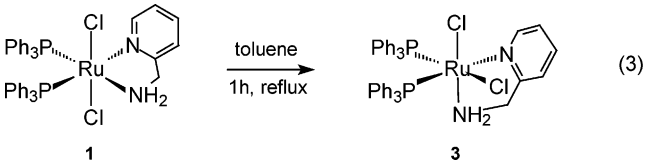
(**3**) compound, which can be quantitatively obtained by refluxing a suspension of **1** in toluene (eq 3).

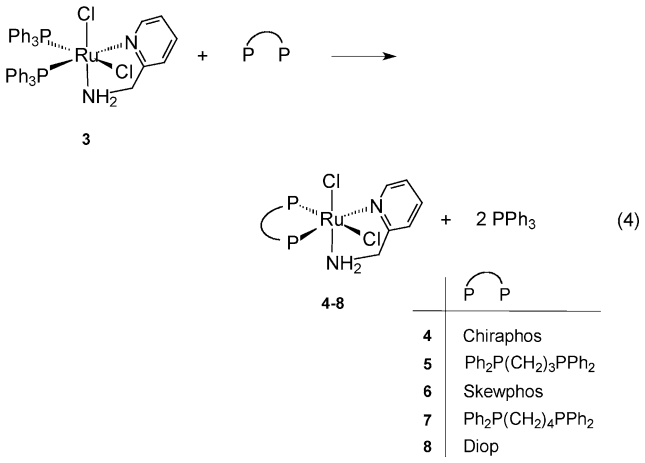


1 **3** (3)

Alternatively, complex **3** can also be prepared in a one-pot reaction from $RuCl_2(PPh_3)_3$ and ampy in toluene at reflux. The $^{31}P\{^1H\}$ NMR doublets for **3** are at δ 50.5 and 43.8 (J(PP) = 33.4 Hz), while in the ^1H NMR the CH_2NH_2 moiety displays three signals at δ 3.65, 3.00, and 1.42 in a 2/1/1 ratio, suggesting that the ampy ligand lies out of the RuP_2 plane and the complex shows a *cis* arrangement of the chlorides. In basic solution the amino protons undergo fast H/D exchange. Thus, addition of a D_2O solution of NaOH to **3** in $CDCl_3$ results in the disappearance of the NH_2 signals, while the nonequivalent geminal protons of the CH_2 group appear as two doublets at δ 3.65 and 3.00 (J(HH) = 15.8 Hz). It is worth pointing out that the *trans*/*cis* isomerization of the diphosphino complexes $RuCl_2[Ph_2P(CH_2)_4PPh_2](NN)$ has been observed by James and co-workers when NN is a dipyridine type ligand, whereas with ethylenediamine or with pyridine the *trans* derivatives are thermodynamically favored.[21] Conversely, Lindner et al. described structurally related derivatives with $Ph_2P(CH_2)_3PPh_2$ or $Ph_2PCH_2CH_2OCH_3$ and diamines in which the *trans*-$RuCl_2$ configuration is preferred in solution, whereas in the solid state both *trans* and *cis* isomers have been found.[22]

Compound **3** is a useful precursor that easily reacts with bidentate phosphines, leading to the *cis*-$RuCl_2$(PP)(ampy) derivatives via substitution of two PPh_3, as shown in eq 4.

Treatment of **3** in refluxing toluene with an equimolar amount of the diphosphine (*S*,*S*)-(−)-Chiraphos, showing a C_2 backbone, affords the derivative *cis*-$RuCl_2$[(*S*,*S*)-Chiraphos](ampy) (**4**) in high yield, as established by $^{31}P\{^1H\}$ NMR (δ = 89.0, 73.9 and J(PP) = 30.9 Hz). By contrast, with 1,2-bis(diphenylphosphino)ethane both PPh_3 and ampy ligands are displaced, resulting in the formation of the complex *trans*-$RuCl_2[Ph_2P(CH_2)_2PPh_2]_2$,[19] and this may be due to the fewer steric requirements of the achiral diphosphine.[23] When diphosphines with a higher chelate bite angle[24] are employed, clean formation of the *cis* derivatives is observed with no substitution of ampy. According to eq 4, the complexes *cis*-$RuCl_2[Ph_2P(CH_2)_3PPh_2]$(ampy) (**5**) and *cis*-$RuCl_2$[(*S*,*S*)-Skewphos](ampy) (**6**) containing C_3 backbone diphosphines have been obtained by reaction of **3** with $Ph_2P(CH_2)_3PPh_2$ and the C_2 symmetry phosphine (*S*,*S*)-(−)-$Ph_2P(CHMeCH_2CHMe)PPh_2$ (Skewphos), respectively. In the $^{31}P\{^1H\}$ NMR compound **5** exhibits two doublets at δ 53.2 and 37.2 (J(PP) = 46.2 Hz), while the signals for **6** are at δ 64.8 and 45.3 (J(PP) = 44.7 Hz). The low-field $^{31}P\{^1H\}$ NMR resonances for **4** compared to **5** and **6** are consistent with the ring contribution to the coordination chemical shift of phosphorus.[25] It is worth pointing out that the $^{31}P\{^1H\}$ NMR spectra of **4**−**6** display only one set of signals for each compound, indicating that **4** and **6** are formed as single stereoisomers with chirality at the metal center, while **5** is present as a racemate.[4a,26] Similarly to **5**, treatment of **3** with $Ph_2P(CH_2)_4PPh_2$ afforded the complex *cis*-$RuCl_2[Ph_2P(CH_2)_4PPh_2]$(ampy) (**7**) (eq 4), which can be easily prepared also through different routes. Thus, $RuCl_2(PPh_3)_3$ cleanly reacts in toluene at reflux with ampy and the diphosphine in a one-pot reaction leading to compound **7**. Alternatively, the latter can also be prepared from the precursor $RuCl_2(PPh_3)[Ph_2P(CH_2)_4PPh_2]$ and ampy via formation of the *trans* derivative **2**, which subsequently isomerizes to **7**. The $^{31}P\{^1H\}$ NMR spectrum exhibits two doublets at δ 54.9 and 40.1 (J(PP) = 37.0 Hz). Addition of a basic (NaOH) D_2O solution to **7** in $CDCl_3$ affords fast N−H/D exchange and allowed assignment of the ^1H NMR signals at δ 3.74 and 3.22 to the diasterotopic geminal NCH_2 protons (J(HH) = 15.0 Hz). The X-ray analysis of **7** shows that the ruthenium is in an octahedral environment with a *cis* arrangement of the chloride ligands, the pyridine nitrogen *trans* to one phosphorus and the NH_2 group *trans* to one chloride (see Figure 1 and Table 1).



(4)

In compound **7** the Ru−Cl1 bond length is 2.4415(5) Å, whereas the Ru−Cl2 bond *trans* to the phosphorus displays a slightly longer distance (2.4899(5) Å), as observed for *cis*-$RuCl_2[Ph_2P(CH_2)_4PPh_2](NN)$ (NN = 2,2′-bipyridine, 1,10-phenantroline).[21] The angle N1−Ru−N2 for ampy is 76.98(7)°, whereas the angles Cl1−Ru−N1 and Cl2−Ru−N1 are 166.23(6)° and 81.22(6)°,

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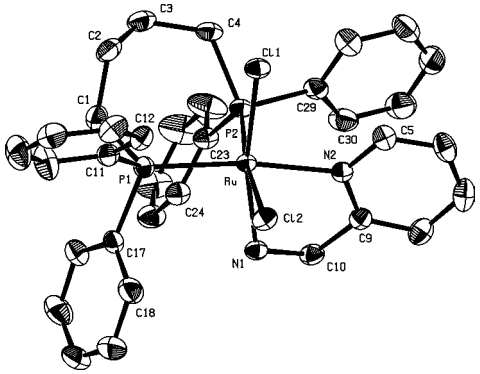


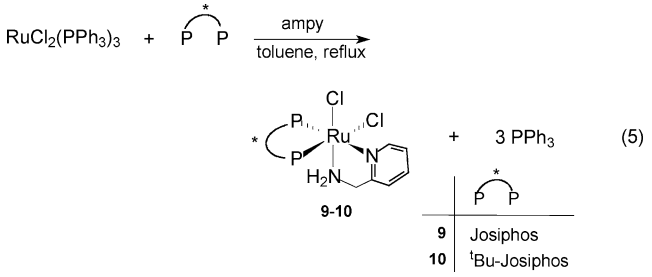
Figure 1. ORTEP representation of compound **7** in the solid state of **7**·CH_2Cl_2.[27] Thermal ellipsoids are at the 50% probability level; hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Distances (Å) and Angles (deg) for 7·CH_2Cl_2 and 9·2$CHCl_3$

7·CH_2Cl_2		**9**·2$CHCl_3$	
Ru−Cl1	2.4415(5)	Ru−Cl2	2.4360(7)
Ru−Cl2	2.4899(5)	Ru−Cl1	2.4981(7)
Ru−P1	2.2874(6)	Ru−P1	2.2813(7)
Ru−P2	2.2825(6)	Ru−P2	2.3142(7)
Ru−N1	2.116(2)	Ru−N2	2.104(3)
Ru−N2	2.148(2)	Ru−N1	2.138(2)
Cl1−Ru−Cl2	89.75(2)	Cl1−Ru−Cl2	89.27(2)
Cl1−Ru−P1	94.98(2)	Cl2−Ru−P1	93.79(3)
Cl1−Ru−P2	87.81(2)	Cl2−Ru−P2	88.75(3)
Cl1−Ru−N1	166.23(6)	Cl2−Ru−N2	168.23(8)
Cl1−Ru−N2	91.65(5)	Cl2−Ru−N1	93.35(7)
Cl2−Ru−P1	93.45(2)	Cl1−Ru−P1	90.38(3)
Cl2−Ru−P2	173.36(2)	Cl1−Ru−P2	175.99(3)
Cl2−Ru−N1	81.22(6)	Cl1−Ru−N2	82.66(8)
Cl2−Ru−N2	82.78(5)	Cl1−Ru−N1	82.65(7)
P1−Ru−P2	92.92(2)	P1−Ru−P2	93.24(3)
P1−Ru−N1	95.92(5)	P1−Ru−N2	94.80(8)
P1−Ru−N2	172.36(5)	P1−Ru−N1	169.95(7)
P2−Ru−N1	100.00(6)	P2−Ru−N2	98.76(8)
P2−Ru−N2	91.11(5)	P2−Ru−N1	93.98(7)
N1−Ru−N2	76.98(7)	N1−Ru−N2	77.19(10)

leading to a rather distorted octahedral geometry. Treatment of **3** with an equimolar amount of (*R*,*R*)-(−)-Diop in dichloromethane leads to the complex *cis*-$RuCl_2$[(*R*,*R*)-Diop](ampy) (**8**) (eq 4), whose $^{31}P\{^1H\}$ NMR spectrum reveals two doublets at δ 48.7 and 31.8 (J(PP) = 36.6 Hz), attributable to the formation of a single stereoisomer.

When bulkier diphosphines are employed, such as those of the Josiphos type, the *cis* derivatives can be prepared by reaction of $RuCl_2(PPh_3)_3$ with the phosphorus ligand, followed by addition of ampy (eq 5).



(5)

According to this procedure, the complexes *cis*-$RuCl_2$-[(*R*,*S*)-Josiphos](ampy) (**9**) and *cis*-$RuCl_2$[(*R*,*S*)-^{t}Bu-Josiphos](ampy) (**10**) have been obtained in good yield from the corresponding C_1 symmetry diphosphines in

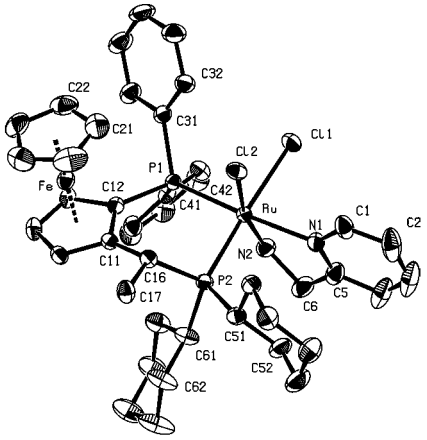
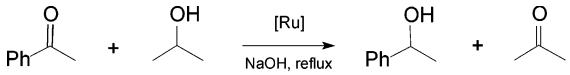


Figure 2. ORTEP representation of compound **9** in the solid state of **9**·2$CHCl_3$. Thermal ellipsoids are at the 50% probability level; hydrogen atoms are omitted for clarity.

toluene at reflux. The $^{31}P\{^1H\}$ NMR spectrum of **9** shows two doublets at δ 60.8 and 39.7 (J(PP) = 40.9 Hz), whereas for **10** the signals are at δ 82.4 and 36.9 (J(PP) = 33.3 Hz), indicating that these complexes are formed stereoselectively. Also in the $^{13}C\{^1H\}$ NMR spectra the CH_2 groups appear as single resonances at δ 53.4 and 52.8, respectively, in the range of all *cis*-$RuCl_2$(PP)(ampy) compounds (δ from 51.5 to 53.5). An ORTEP drawing of compound **9**, obtained from an X-ray diffraction measurement carried out at 173 K, is reported in Figure 2.

Similarly to **7**, the ruthenium is in a distorted octahedral environment with a *cis* arrangement of the two chloride ligands. The Ru−Cl1 bond length for the chloride *trans* to phosphorus of the PCy_2 moiety is 2.4981(7) Å and is slightly longer compared to that of Ru−Cl2 (2.4360(7) Å) (Table 1). Furthermore, the ampy ligand shows a small N1−Ru−N2 angle (77.19(10)°) with the amino group opposite the ferrocenyl moiety.

Catalytic Transfer Hydrogenation of Ketones. The new ruthenium complexes $RuCl_2(PPh_3)_2$(ampy) and $RuCl_2$(PP)(ampy) efficiently catalyze the reduction of acetophenone to 1-phenylethanol in 2-propanol via transfer hydrogenation (eq 6).



(6)

The catalytic reactions were carried out using a 0.1 M solution of ketone in the presence of 0.05 mol % of ruthenium complex and 2 mol % of NaOH under reflux conditions. As we can see from Table 2 the derivatives **3** and **7** displaying a *cis* chloride arrangement show a higher catalytic activity compared to the *trans* analogues **1** and **2**, respectively.

Furthermore, complexes **2** and **7** bearing the diphosphine $Ph_2P(CH_2)_4PPh_2$ show a significantly higher activity compared to **1** and **3**, with two PPh_3 ligands, leading to an increase of up to 10^2 in TOF values. Complete conversion within 1 min is also observed with complex **5** (TOF = 220 000 h^{-1}), indicating that the derivatives of formula *cis*-$RuCl_2$(PP)(ampy) show the highest activity. Notably, a TOF value of 300 000 h^{-1} observed for **7** is one of the highest values reported in

Table 2. Catalytic Transfer Hydrogenation of Acetophenone Using the Ampy Ruthenium Complexes[a]

complex	conversion % (min)[b]	TOF (h^{-1})[c]
1	83 (90)	2400
2	98 (10)	35 000
3	98 (70)	5200
5	97 (1)	220 000
7	97 (1)	300 000
11	98 (10)	28 000
12	92 (30)	11 000

[a] Conditions: reactions were carried out at 82 °C, acetophenone 0.1 M in 2-propanol, ketone/Ru/NaOH = 2000/1/40. [b] The conversion was determined by GC analysis. [c] Turnover frequency (moles of ketone converted to alcohol per mole of catalyst per hour) at 50% conversion.

the literature,[10,11,28] and is lower only than that of the [RuCl(*p*-cymene)(PN)][BF_4] system[16] (1.2×10^6 h^{-1}), which catalyzes the reduction of acetophenone in refluxing 2-propanol under more basic conditions (50 mol % of KOH) and which requires 60 h. In this regard we want to point out that Le Page and James reported that even in the absence of a transition metal complex acetophenone is quantitatively reduced within 24 h in refluxing 2-propanol containing NaOH (34 mol %).[29] High catalytic activity has also been observed when **7** is prepared in situ by reacting $RuCl_2(PPh_3)[Ph_2P(CH_2)_4PPh_2]$ with ampy (1/2 molar ratio), leading to 96% conversion of the ketone in 1 min (TOF = 250 000 h^{-1}). It should be noted that Yamagishi et al. and Brunner et al. reported asymmetric transfer hydrogenation of aryl-alkyl ketones using catalysts generated in situ from $RuCl_2(PPh_3)_3$ and chiral ligands related to ampy,[6] but no isolated complexes have been described.

Catalyst **7** can be used for the reduction of different ketones such as cyclic, dialkyl, and diaryl substrates, and the corresponding alcohols are formed quantitatively in few minutes with remarkably high TOF values in the range 80 000−400 000 h^{-1} (Table 3).

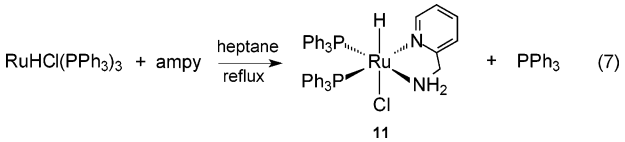
It is noteworthy that hydrogen transfer to the unsaturated ketone 5-hexen-2-one leaves the C=C double bond entirely intact. In addition, benzhydrol, which is an important pharmaceutical intermediate, can be quickly prepared using low loading of achiral catalyst (i.e., benzophenone/**7** = 5000; isolated yield 1.70 g, 88%) with hydrogen transfer instead of using dihydrogen.[30] In this regard, increasing activity and productivity of achiral catalysts already has considerable industrial potential, because transfer hydrogenation can conveniently replace reductions by means of traditional hydride reagents (i.e., $LiAlH_4$, $NaBH_4$), which require a lengthy workup.[31]

Employment of catalysts **6** and **9**, bearing diphosphines with chiral C_3 backbones, afforded enantioselective reduction of methyl-aryl ketones within a few minutes with TOF values up to 300 000 h^{-1} and ee in the range 83−94% (Table 4).

Thus, acetophenone is reduced at 82 °C to (*S*)-1-phenylethanol with **6**, whereas catalyst **9** gives the *R* enantiomer (ee = 85 and 83%, respectively). Notably, fast and quantitative conversion of acetophenone has also been observed with higher substrate/catalyst ratio (10 000) without erosion of enantioselectivity (Table 4). With catalyst **6**, *ortho*-substituted ketones are quickly reduced to the corresponding *S* enantiomers with higher ee values (up to 94%). Furthermore, pyridyl alcohols such as (*S*)-phenyl(2-pyridyl)methanol (ee = 90%) can be easily obtained from the corresponding pyridyl ketones.[32] The high performance of *cis*-$RuCl_2$(PP)(ampy) catalysts provides their use for preparative scope. Thus, 1.24 g of (*S*)-2′-methoxy-1-phenylethanol has been isolated in 80% yield (ee = 94%) starting from 1.53 g of 2-methoxyacetophenone (0.1 M in 2-propanol) and 1.4 mg of **6** (ketone/Ru/NaOH = 5000/1/100) by refluxing the solution for 30 min.

As regards the activity of ruthenium complexes containing P and N ligands, it is interesting to note that ampy generally gives systems that appear to be more active than the 1,2-diamine analogues in catalytic transfer hydrogenation reactions. As a matter of fact, we have observed that with cyclometalated ruthenium complexes RuCl(CO)[(2-CH_2-6-MeC_6H_3)PPh_2](NN) [NN = ampy, en] the ampy ligand leads to a significantly more active hydrogen transfer system compared to the ethylenediamine (en) system.[17] We now have found that *trans*-$RuCl_2[Ph_2P(CH_2)_4PPh_2]$(en)[21] catalyzes the transfer hydrogenation of acetophenone in refluxing 2-propanol with a TOF = 1000 h^{-1}, which is a value lower than the related complex *trans*-$RuCl_2[Ph_2P(CH_2)_4PPh_2]$-(ampy) (**2**) (35 000 h^{-1}). This result agrees with the data reported by Lindner's group and Morris' group on the *trans*-$RuCl_2$(PP)(1,2-diamine) complexes, which show moderate activity in transfer hydrogenation.[13,14]

Synthesis and Catalytic Activity of $RuH_nCl_{2-n}(PPh_3)_2$(ampy) (n = 1, 2). Since ruthenium hydride complexes are commonly proposed as key species involved in transfer hydrogenation reactions, our attention has been devoted to the preparation of hydride derivatives bearing ampy and PPh_3 ligands. A mono- and a dihydride species have been isolated and characterized, whereas a second dihydride complex has been detected in solution. Thus, the compound *trans,cis*-$RuHCl(PPh_3)_2$(ampy) (**11**) can be cleanly prepared from $RuHCl(PPh_3)_3$[33] and ampy in refluxing heptane by displacement of PPh_3 (eq 7).[34]



11

The $^{31}P\{^1H\}$ NMR spectrum of **11** displays two signals at δ 73.7 and 68.9 strongly shifted downfield compared

(27) The depicted structure is for one enantiomer of the racemic mixture of **7**.

(28) (a) Dani, P.; Karlen, T.; Gossage, R. A.; Gladiali, S.; van Koten, G. *Angew. Chem., Int. Ed.* **2000**, *39*, 743. (b) Albrecht, M.; Kocks, B. M.; Spek, A. L.; van Koten, G. *J. Organomet. Chem.* **2001**, *624*, 271. (c) Amoroso, D.; Jabri, A.; Yap, G. P. A.; Gusev, D. G.; dos Santos, E. N.; Fogg, D. E. *Organometallics* **2004**, *23*, 4047.

(29) Le Page, M. D.; James, B. R. *Chem. Commun.* **2000**, 1647.

(30) Ohkuma, T.; Koizumi, M.; Ikehira, H.; Yokozawa, T.; Noyori, R. *Org. Lett*. **2000**, *2*, 659.

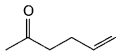
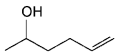
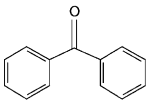
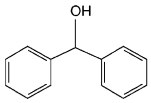
(31) Blaser, H. U.; Studer, M. *Chirality* **1999**, *11*, 459.

(32) Okano, K.; Murata, K.; Ikariya, T. *Tetrahedron Lett.* **2000**, *41*, 9277.

(33) Amoroso, D.; Snelgrove, J. L.; Conrad, J. C.; Drouin, S. D.; Yap, G. P. A.; Fogg, D. E. *Adv. Synth. Catal.* **2002**, *344*, 757.

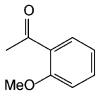
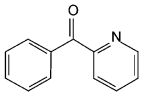
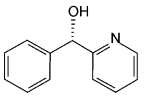
(34) We recently learned that some of this hydride-ruthenium aminomethylpyridine chemistry was done independently by another research group: Morris, R. H. Private communication.

Table 3. Catalytic Transfer Hydrogenation of Ketones Using Complex 7[a]

Ketone	Alcohol	Conversion %(min)[b]	TOF (h^{-1})[c]
		97 (5)	88000
		99 (1)	400000
		94 (10)	280000
		98 (10)	80000

[a] Conditions: reactions were carried out at 82 °C, ketone 0.1 M in 2-propanol, ketone/Ru/NaOH = 2000/1/40. [b] The conversion was determined by GC or ^{1}H NMR analysis. [c] Turnover frequency (moles of ketone converted to alcohol per mole of catalyst per hour) at 50% conversion.

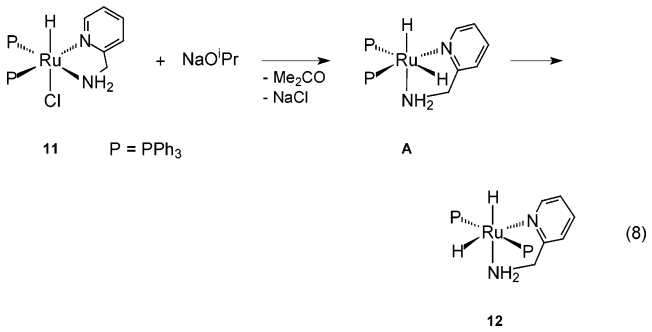
Table 4. Catalytic Enantioselective Transfer Hydrogenation of Methyl-Aryl Ketones Using Complexes 6 and 9[a]

Complex	Ketone	Alcohol	Conversion %(min)[b]	TOF (h^{-1})[c]	*ee* (%)[b]
6			96 (1)	300000	85 *S*
6[d]			95 (5)	270000	85 *S*
9			97 (2)	230000	83 *R*
6			96 (1)	290000	89 *S*
6			96 (2)	250000	94 *S*
6			98 (5)[e]	150000	90 *S*[e]

[a] Conditions: reactions were carried out at 82 °C, ketone 0.1 M in 2-propanol, ketone/Ru/NaOH = 2000/1/40. [b] The conversion and ee were determined by GC analysis; absolute configuration was determined by comparing optical rotations with literature values. [c] Turnover frequency (moles of ketone converted to alcohol per mole of catalyst per hour) at 50% conversion. [d] Ru: 0.01 mol %. [e] The conversion was determined by ^{1}H NMR, and ee was determined on the ester of (*R*)-(−)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride by ^{19}F NMR measurements.

to those of **1**, with a J(PP) = 37.0 Hz, in agreement with a *cis* phosphine arrangement.[18] In the ^{1}H NMR spectrum the hydride appears as a doublet of a doublet at δ −17.70 (H *trans* to Cl)[35] with J(HP) = 23.5 and 29.7 Hz, indicating a *fac* geometry for the $RuHP_2$ moiety, whereas the CH_2NH_2 protons appear as four signals in the range δ 4.30−2.20. Compound **11** dissolved in CD_2Cl_2 reacts promptly with aqueous HCl, leading to **3**, as inferred by NMR measurements. Note that Morris and co-workers have reported that the reaction of $RuHCl(PPh_3)_3$ with diamines leads to the derivatives *trans,cis*-$RuHCl(PPh_3)_2$(diamine).[35] When compound **11** is treated with an equimolar amount of sodium isopropoxide in toluene, the derivative *cis,trans*-$Ru(H)_2(PPh_3)_2$(ampy) (**12**), which shows two *trans* phosphorus atoms, is formed at 30 °C within a few hours via the alkoxide route[36] (eq 8).

(35) (a) Abdur-Rashid, K.; Lough, A. J.; Morris, R. H. *Organometallics* **2000**, *19*, 2655. (b) Abdur-Rashid, K.; Lough, A. J.; Morris, R. H. *Organometallics* **2001**, *20*, 1047.



(8)

Compound **12** in C_6D_6 affords a $^{31}P\{^1H\}$ NMR spectrum with a single resonance at δ 67.2, which is consistent with a *trans* RuP_2 arrangement. In the hydride region, the ^1H NMR spectrum shows two triplets of doublets at δ −16.31 and −18.24, with J(HP) = 27.5 and 27.7 Hz, respectively, and a J(HH) = 6.7 Hz, indicating a *cis* RuH_2 geometry, in agreement with the related dihydride compound *cis*,*trans*-$Ru(H)_2(PPh_3)_2$(cydn) (cydn = cyclohexyldiamine).[35a] Furthermore, two triplets at δ 2.76 and 1.67 with J(HH) = 6.1 Hz are for the geminal CH_2 and NH_2 protons, respectively. NMR experiments carried out at room temperature on a C_6D_6 solution of **11** with either sodium isopropoxide or sodium methoxide (1/1 molar ratio) revealed formation of the intermediate species *cis*,*cis*-$Ru(H)_2(PPh_3)_2$(ampy) (**A**) with a hydride ligand *trans* to one PPh_3, which slowly isomerizes to **12**. Thus, the $^{31}P\{^1H\}$ NMR spectrum of the solution displays two signals at δ 82.7 and 57.2 with a relatively small J(PP) = 14.0 Hz, indicating a *cis* geometry for the two PPh_3 ligands. A ^1H-coupled ^{31}P NMR measurement shows that the latter resonance is a doublet with a large ^2J(PH) = 95 Hz, for the phosphorus atom *trans* to one hydride ligand.[36d] The ^1H NMR spectrum exhibits two RuH hydride signals, specifically a doublet of a doublet at δ −5.16 with J(HP) = 95.5 and 36.5 Hz attributable to the hydride *trans* to the phosphorus, and a triplet at −14.85 with a J(HP) = 24.5 Hz, in agreement with the aforementioned proposed structure. Thus, the complex **A**, which is formed from **11** by displacement of the chloride with a hydride via a ruthenium alkoxide and subsequent β-elimination, is thermally unstable, and in solution it slowly undergoes an isomerization process in which one hydride and one PPh_3 are exchanged. Therefore, when the catalytic precursors **1** and **3** are treated with NaOH in 2-propanol, several hydride species with different geometry may be formed in solution, and they could be relevant for the transfer hydrogenation.

Under the usual experimental conditions (ketone/Ru/NaOH = 2000/1/40) the hydride derivatives **11** and **12** have been shown to be capable of reducing acetophenone with 2-propanol. Thus, the monohydride **11** exhibits a significantly higher speed in the reduction of acetophenone (TOF = 28 000 h^{-1}) compared to the dichloride **1** (Table 2). Surprisingly, the dihydride **12**, in which the two PPh_3 ligands present a *trans* arrangement, affords a TOF value of 11 000 h^{-1}, which is a value between those of **1** and **11**. It is possible that the highest activity of **11**, compared to that of **12**, may arise from the presence in solution of the intermediate **A**, which presents a hydride *trans* to a phosphorus atom, a better ligand arrangement for catalysis. The transfer hydrogenation of acetophenone (0.1 M) in 2-propanol has also been carried out using **11** and **12** in the absence of base. With a molar ratio ketone/Ru = 2000, complex **11** is inactive, whereas **12** leads to 38% conversion after 1 h. At higher ruthenium concentration (ketone/Ru = 200, i.e., 0.5 mol %) complex **11** affords about 1% conversion in 10 min, whereas with **12** the reduction of acetophenone is quantitative (TOF = 5500 h^{-1}). Therefore, it is likely that during catalysis the chloride precursors **1**−**10** lead to dihydride species via metal alkoxide intermediates and β-elimination. This agrees with the results reported by Bäckvall et al. for $RuCl_2(PPh_3)_3$[36a,37] and more recently by Cadierno et al. for the $RuCl_2(CNR)_2$(PP) systems (R = alkyl, aryl; PP = 1,1′-bis(diphenylphosphino)ferrocene).[38] However, the activity of **12** is notably higher when the catalysis is carried out in the presence of additional base, and this suggests that the catalytic cycle may be somehow different from that proposed by Bäckvall; the presence of the NH_2 amino group of ampy may lead to a different catalytic route.[37a]

Concluding Remarks

In summary, we have shown that the new derivatives of the type $RuCl_2(PPh_3)_2$(ampy) and $RuCl_2$(PP)(ampy) can be easily prepared from $RuCl_2(PPh_3)_3$ ampy and a diphosphine. With the mixed pyridine-amine ligand ampy, the complexes with a *cis* chloride arrangement are thermodynamically favored compared to the *trans* analogues which show a geometry currently found for the corresponding diamine complexes. The compounds *cis*-$RuCl_2$(PP)(ampy) represent new highly active precatalysts for the reduction of manifold ketones with 2-propanol in the presence of NaOH. The derivatives bearing chiral diphosphines allowed both fast and enantioselective transfer hydrogenation at low catalyst loading. These complexes, which can be obtained on a gram scale from commercially available compounds through one- or two-step reactions, hold promise for a broad application in reduction of carbonyl compounds. The related ruthenium hydride complexes *trans*,*cis*-$RuHCl(PPh_3)_2$(ampy) and *cis*,*trans*-$Ru(H)_2(PPh_3)_2$(ampy) have been isolated and characterized, and the latter catalyzes the transfer hydrogenation also in absence of base. Work is in progress to gain further mechanistic insight to understand the particularly high ligand acceleration effect of ampy in the transfer hydrogenation and to extend this chemistry to other functionalized ampy ligands for the exploitation of other catalytic reactions.

Experimental Section

General Methods. All reactions were carried out under an argon atmosphere using standard Schlenk techniques. The solvents were carefully dried by standard methods and dis-

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(37) (a) Pàmies, O.; Bäckvall, J. E. *Chem. Eur. J.* **2001**, *7*, 5052. (b) Chowdhury, R. L.; Bäckvall, J. E. *J. Chem. Soc., Chem. Commun*. **1991**, 1063.

(38) Cadierno, V.; Crochet, P.; Díez, J.; García-Garrido, S. E.; Gimeno, J.; *Organometallics* **2004**, *23*, 4836.

tilled under argon before use. The ruthenium complexes $RuCl_2(PPh_3)_3$,[1b] $RuHCl(PPh_3)$,[33] and $RuCl_2(PPh_3)[Ph_2P(CH_2)_4PPh_2]$[19] were prepared according to literature procedures, whereas all other chemicals were purchased from Aldrich and Strem and used without further purification. NMR measurements were recorded on a Bruker AC 200 spectrometer. Chemical shifts, in ppm, are relative to TMS for ^1H and ^{13}C, whereas H_3PO_4 was used for ^{31}P. Elemental analyses (C, H, N) were carried out with a Carlo Erba 1106 elemental analyzer.

Synthesis of *trans,cis*-$RuCl_2(PPh_3)_2$(ampy) (1). $RuCl_2(PPh_3)_3$ (400 mg, 0.417 mmol) was suspended in 5 mL of dichloromethane, and ampy (45 μL, 0.436 mmol) was added. The mixture was stirred at room temperature for 1 h and concentrated, and addition of pentane afforded a yellow precipitate. After filtration the product was washed with ether and dried under reduced pressure. Yield: 250 mg (75%). Anal. Calcd for $C_{42}H_{38}Cl_2N_2P_2Ru$: C, 62.69; H, 4.76; N, 3.48. Found: C, 62.85; H, 4.80; N, 3.54. ^1H NMR (200.1 MHz, $CDCl_3$, 20 °C): δ 8.53 (d, J(HH) = 4.2 Hz, 1H; *o*-C_5H_4N), 7.60−6.50 (m, 33H; aromatic protons), 4.46 (s br, 2H; CH_2), 3.29 (s br, 2H; NH_2). $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$, 20 °C): δ 162.8 (s; $NCCH_2$), 157.6 (s; NCH of C_5H_4N), 136.6−120.1 (m; aromatic carbons), 50.8 (s; CH_2). $^{31}P\{^1H\}$ NMR (81.0 MHz, $CDCl_3$, 20 °C): δ 44.0 (d, J(PP) = 32.7 Hz), 40.1 (d, J(PP) = 32.7 Hz).

Synthesis of *trans*-$RuCl_2[Ph_2P(CH_2)_4PPh_2]$(ampy) (2). The synthesis of **2** was carried out as described for **1**, but using the complex $RuCl_2(PPh_3)[Ph_2P(CH_2)_4PPh_2]$ (256 mg, 0.297 mmol), in place of $RuCl_2(PPh_3)_3$, and ampy (31 μL, 0.301 mmol). Yield 170 mg (81%). Anal. Calcd for $C_{34}H_{36}Cl_2N_2P_2Ru$: C, 57.79; H, 5.14; N, 3.96. Found: C, 57.40; H, 5.02; N, 3.72. ^1H NMR (200.1 MHz, $CDCl_3$, 20 °C): δ 8.86 (d, J(HH) = 5.2 Hz, 1H; o-C_5H_4N,), 7.86−6.71 (m, 23H; aromatic protons), 4.31 (pseudo t, J(HH) = 5.0 Hz, 2H; NCH_2), 3.23 (m, 2H; PCH_2), 2.99 (m, 2H; NH_2), 2.48 (m, 2H; PCH_2), 1.78−1.65 (m, 4H; CH_2-CH_2CH_2). $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$, 20 °C): δ 163.2 (s; $NCCH_2$), 155.3 (s; NCH), 138.6−120.6 (m; aromatic carbons), 50.3 (s; CH_2N), 32.4 (d, J(CP) = 35.1 Hz; CH_2P), 26.1 (s; CH_2CH_2P) 24.1 (d, J(CP) = 25.7 Hz; CH_2P), 19.6 (s; CH_2-CH_2P). $^{31}P\{^1H\}$ NMR (81.0 MHz, $CDCl_3$, 20 °C): δ 42.5 (d, J(PP) = 38.0 Hz), 41.5 (d, J(PP) = 38.0 Hz).

Synthesis of *cis,cis*-$RuCl_2(PPh_3)_2$(ampy) (3). Method 1. Complex **1** (300 mg, 0.373 mmol) was added to 3 mL of toluene, and the suspension was refluxed for 1.5 h. After filtration the product was washed with ether and dried under reduced pressure. Yield: 260 mg (87%). Anal. Calcd for $C_{42}H_{38}Cl_2N_2P_2Ru$: C, 62.69; H, 4.76; N, 3.48. Found: C, 62.31; H, 4.87; N, 3.60. ^1H NMR (200.1 MHz, CD_2Cl_2, 20 °C): δ 9.16 (d, J(HH) = 5.7 Hz, 1H; o-C_5H_4N), 7.70−6.89 (m, 33H; aromatic protons), 3.65 (m, 2H; CH_2 and NH_2), 3.00 (m, 1H; CH_2), 1.42 (m, 1H; NH_2). $^{31}P\{^1H\}$ NMR (81.0 MHz, CD_2Cl_2, 20 °C): δ 50.5 (d, J(PP) = 33.4 Hz), 43.8 (d, J(PP) = 33.4 Hz).

Method 2. $RuCl_2(PPh_3)_3$ (1.34 g, 1.40 mmol) was suspended in 10 mL of toluene, and ampy (0.160 mL, 1.55 mmol) was added. The mixture was refluxed for 2 h and concentrated, and addition of pentane afforded a yellow precipitate. The complex was then filtered, washed with ether, and dried under reduced pressure. Yield: 755 mg (67%).

Synthesis of *cis*-$RuCl_2$[(*S,S*)-Chiraphos](ampy) (4). Complex **3** (200 mg, 0.249 mmol) and (*S,S*)-(−)-Chiraphos (106 mg, 0.249 mmol) were refluxed in toluene (5 mL) for 5 h. The mixture was concentrated, and addition of pentane afforded a yellow precipitate. After filtration the product was washed with ether and dried under reduced pressure. Yield: 104 mg (59%). Anal. Calcd for $C_{34}H_{36}N_2Cl_2P_2Ru$: C, 57.79; H, 5.14; N, 3.96. Found: C, 57.41; H, 5.02; N, 3.80. ^1H NMR (200.1 MHz, $CDCl_3$, 20 °C): δ 9.03 (m, 1H; o-C_5H_4N), 8.10−6.82 (m, 23H; aromatic protons), 4.13 (pseudo t, J = 10.0 Hz; 1H; PCH), 3.85 (dd, J(H,H) = 3.5, 15.4 Hz, 1H; CH_2), 3.37 (m, 1H; CH_2), 3.07 (m, 1H; NH_2), 2.33 (m, 1H; PCH), 1.25 (m, 1H; NH_2), 1.16 (dd, J = 7.0, 11.8 Hz, 3H, CH_3), 0.76 (dd, J = 7.0, 12.2 Hz, 3H, CH_3). $^{31}P\{^1H\}$ NMR (81.0 MHz, $CDCl_3$, 20 °C): δ 89.0 (d, J(PP) = 30.9 Hz), 73.9 (d, J(PP) = 30.9 Hz).

Synthesis of *cis*-$RuCl_2[Ph_2P(CH_2)_3PPh_2]$(ampy) (5). Complex **3** (683 mg, 0.85 mmol) was suspended in 20 mL of toluene, $Ph_2P(CH_2)_3PPh_2$ (350 mg, 0.85 mmol) was added, and the mixture was refluxed for 20 h. The suspension was concentrated, and addition of pentane afforded a yellow precipitate. After filtration the product was washed with ether and dried under reduced pressure. Yield: 466 mg (79%). Anal. Calcd for $C_{33}H_{34}Cl_2N_2P_2Ru$: C, 57.23; H, 4.95; N, 4.04. Found: C, 57.01; H 4.98; N, 4.06. ^1H NMR (200.1 MHz, $CDCl_3$, 20 °C): δ 8.91 (m, 1H; o-C_5H_4N), 7.98−6.73 (m, 23H; aromatic protons), 4.55 (m, 1H; NH_2), 3.82 (dd, J(HH) = 3.8, 15.9 Hz, 1H; NCH_2), 3.41 (m, 1H; PCH_2), 3.03 (pseudo t, J(HH) = 15.0 Hz, 1H; NCH_2), 2.63−1.65 (m, 5H; PCH_2CH_2), 0.50 (m, 1H; NH_2). $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$, 20 °C): δ 155.1 (s; $NCCH_2$), 150.1 (s; NCH), 135.7−119.3 (m; aromatic carbons), 52.3 (s; CH_2N), 29.0 (d, J(CP) = 26.4 Hz; CH_2P), 26.3 (d, J(CP) = 35.5 Hz; CH_2P), 20.2 (s; CH_2). $^{31}P\{^1H\}$ NMR (81.0 MHz, $CDCl_3$, 20 °C): δ 53.2 (d, J(PP) = 46.2 Hz), 37.2 (d, J(PP) = 46.2 Hz).

Synthesis of *cis*-$RuCl_2$[(*S,S*)-Skewphos](ampy) (6). The synthesis of **6** was carried out as described for the corresponding complex **5**, but using the phosphine (*S,S*)-(−)-Skewphos in place of $Ph_2P(CH_2)_3PPh_2$. Yield: 453 mg (74%). Anal. Calcd for $C_{35}H_{38}Cl_2N_2P_2Ru$: C, 58.34; H, 5.32; N, 3.89. Found: C, 58.06; H, 5.17; N, 3.73. ^1H NMR (200.1 MHz, $CDCl_3$, 20 °C): δ 8.78 (d, J(HH) = 3.1 Hz, 1H; o-C_5H_4N), 7.95−6.69 (m, 23H; aromatic protons), 4.20 (s br, 1H; NH), 3.61 (d, J(HH) = 15.6 Hz, 1H; CHN), 3.37 (m, 1H; PCH), 3.07 (m, 1H; PCH), 2.81 (s, br 1H; CHN), 2.33−1.63 (m, 2H; CH_2), 1.25 (s br, 1H; NH), 1.16 (dd, J(HP), J(HH) = 7.2, 13.6 Hz, 3H; CH_3), 0.76 (dd, J(HP), J(HH) = 7.0, 11.6 Hz, 3H; CH_3). $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$, 20 °C): δ 158.4 (s; $NCCH_2$), 149.6 (s; NCH), 139.8−119.3 (m, aromatic carbons), 51.5 (s; CH_2N), 37.8 (s; CH_2), 33.5 (d, J(CP) = 27.2 Hz; CHP), 20.3 (d, J(CP) = 32.1 Hz; CHP), 18.9 (d, J(CP) = 6.6 Hz; CH_3), 17.7 (d, J(CP) = 1.6 Hz; CH_3). $^{31}P\{^1H\}$ NMR (81.0 MHz, $CDCl_3$, 20 °C): δ 64.8 (d, J(PP) = 44.7 Hz), 45.3 (d, J(PP) = 44.7 Hz).

Synthesis of *cis*-$RuCl_2[Ph_2P(CH_2)_4PPh_2]$(ampy) (7). Method 1. The synthesis of **7** was carried out as described for the corresponding complex **5**, but using $Ph_2P(CH_2)_4PPh_2$ in place of $Ph_2P(CH_2)_3PPh_2$. Yield: 475 mg (79%). Anal. Calcd for $C_{34}H_{36}Cl_2N_2P_2Ru$: C, 57.79; H, 5.14; N, 3.96. Found: C, 57.48; H, 5.27; N, 3.70. ^1H NMR (200.1 MHz, $CDCl_3$, 20 °C): δ 9.36 (m, 1H; o-C_4H_5N), 8.23−6.62 (m, 23H; aromatic protons), 4.13 (m, 1H; CHHP), 3.74 (m, 2H; CHHN, NHH), 3.22 (m, 1H; CHHN), 2.82 (m, 1H; CHHP), 2.34−0.90 (m, 7H; $P(CH_2)_4P$, NHH). $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$, 20 °C): δ 158.0 (s; $NCCH_2$), 151.1 (s; NCH), 136.5−119.8 (m; aromatic carbons), 53.5 (s; CH_2N), 34.8 (d, J(CP) = 27.0 Hz; CH_2P), 29.7 (d, J(CP) = 29.9 Hz; CH_2P), 27.6 (s; CH_2), 19.7 (s; CH_2). $^{31}P\{^1H\}$ NMR (81.0 MHz, $CDCl_3$, 20 °C): δ 54.9 (d, J(PP) = 37.0 Hz), 40.1 (d, J(PP) = 37.0 Hz).

Method 2. $RuCl_2(PPh_3)_3$ (1.95 g, 2.03 mmol) was suspended in 30 mL of toluene, and ampy (0.250 mL, 2.43 mmol) was added. The mixture was refluxed for 1 h, $Ph_2P(CH_2)_4PPh_2$ (853 mg, 2.00 mmol) was added, and the suspension was refluxed for 20 h. Addition of pentane afforded a yellow precipitate, which was filtered, washed with ether, and dried under reduced pressure. Yield: 1.25 g (87%).

Method 3. $RuCl_2(PPh_3)[Ph_2P(CH_2)_4PPh_2]$ (202 mg, 0.235 mmol) was suspended in 5 mL of toluene, and ampy (27 μL, 0.262 mmol) was added. The mixture was refluxed for 20 h, and addition of pentane afforded a yellow precipitate, which was filtered, washed with ether, and dried under reduced pressure. Yield: 126 mg (76%).

Synthesis of *cis*-$RuCl_2$[(*R,R*)-Diop](ampy) (8). Complex **3** (356 mg, 0.442 mmol) was suspended in dichloromethane (5 mL), and the phosphine (*R,R*)-(−)-Diop (220 mg, 0.441 mmol) was added. The mixture was refluxed at 40 °C for 1 day and

concentrated, and addition of pentane afforded a yellow precipitate, which was filtered, washed with ether, and dried under reduced pressure. Yield: 170 mg (50%). Anal. Calcd for $C_{37}H_{40}N_2Cl_2O_2P_2Ru$: C, 57.07; H, 5.18; N, 3.60. Found: C, 56.80; H, 5.10; N, 3.40. ^{1}H NMR (200.1 MHz, $CDCl_3$, 20 °C): δ 9.21 (m, 1H; o-C_5H_4N), 8.26−6.60 (m, 23H; aromatic protons), 4.36 (d, J(HH) = 8.9 Hz, 1H; CHO), 4.17 (td, J(HH) = 11.9 Hz, J(HH) = 5.2 Hz; 1H, CHO), 3.68 (m, 2H; CHHN, NHH), 3.11 (m, 1H; CHHN), 2.84 (pseudo t, J(HH) = 14.1 Hz; 2H, PCH_2), 2.54 (m, 2H; PCH_2), 1.97 (s, 1H; NH), 1.19 (s, 3H; CH_3), 1.15 (s, 3H; CH_3). ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$, 20 °C): δ 157.2 (s; $NCCH_2$), 150.9 (s; NCH), 138.8−119.5 (m, aromatic carbons), 108.0 (s, CMe_2), 80.4 (d; J(CP) = 8.5 Hz, OCH), 73.7 (d; J(CP) = 14.7 Hz, OCH), 53.0 (s; CH_2N), 35.3 (d, J(CP) = 23.1 Hz; CH_2P), 30.3 (d, J(CP) = 29.9 Hz; CH_2P), 27.0 (s, CH_3), 26.4 (s, CH_3). ^{31}P{^{1}H} NMR (81.0 MHz, $CDCl_3$, 20 °C): δ 48.7 (d, J(PP) = 36.6 Hz), 31.8 (J(PP) = 36.6 Hz).

Synthesis of *cis*-RuCl$_2$[(*R*,*S*)-Josiphos](ampy) (9). $RuCl_2(PPh_3)_3$ (228 mg, 0.238 mmol) was added to a solution of (*R*,*S*)-(−)-Josiphos (141 mg, 0.237 mmol) dissolved in 10 mL of toluene, and the suspension was refluxed for 30 min. Ampy (26 μL, 0.252 mmol) was added, and the mixture was refluxed for 4 h. Addition of pentane afforded a yellow precipitate, which was filtered, washed with ether, and dried under reduced pressure. Yield: 182 mg (88%). Anal. Calcd for $C_{42}H_{52}Cl_2FeN_2P_2Ru$: C, 57.68; H, 5.99; N, 3.20. Found: C, 57.47; H, 5.80; N, 3.25. ^{1}H NMR (200.1 MHz, $CDCl_3$, 20 °C): δ 10.25 (s, 1H; o-C_5H_4N), 8.39−7.15 (m, 13H; aromatic protons), 5.10 (m, 1H; $CHCH_3$), 4.47 (m, 1H; C_5H_3), 4.30 (m, 1H; C_5H_3), 3.84−3.34 (m, 5H; C_5H_3, CH_2NH_2) 3.66 (s, 5H; C_5H_5), 2.20−0.52 (m, 25H; CH_3, Cy). ^{13}C{^{1}H} NMR (50.3 MHz, CD_2Cl_2, 20 °C): δ 160.3 (s; $NCCH_2$), 152.8 (s; NCH), 136.9−120.6 (m; aromatic carbons), 73.6 (s; FeCH), 71.2 (s; FeC_5H_5), 69.2 (s; FeCH), 69.1 (s; FeCH), 53.4 (s; CH_2N), 40.0 (d, J(CP) = 18.0 Hz; CH of Cy), 37.8 (d, J(CP) = 16.7 Hz; CH of Cy), 31.7−30.8 (m, CH_2 of Cy), 29.9 (d, J(CP) = 20.4 Hz; PCHMe), 29.6−26.4 (m, CH_2 of Cy), 15.5 (d, J(CP) = 7.1 Hz; CH_3). ^{31}P{^{1}H} NMR (81.0 MHz, $CDCl_3$, 20 °C): δ 60.8 (d, J(PP) = 40.9 Hz), 39.7 (d, J(PP) = 40.9 Hz).

Synthesis of *cis*-RuCl$_2$[(*R*,*S*)-^{t}Bu-Josiphos](ampy) (10). $RuCl_2(PPh_3)_3$ (125 mg, 0.130 mmol) was added to a solution of (*R*,*S*)-(−)-^{t}Bu-Josiphos (71 mg, 0.131 mmol) in toluene (5 mL), and the mixture was refluxed for 1 h. Ampy (15 μL, 0.146 mmol) was added, and the solution was refluxed for 3 h and concentrated. Addition of pentane afforded a yellow precipitate. After filtration the product was washed with ether and dried under reduced pressure. Yield: 70 mg (65%). Anal. Calcd for $C_{38}H_{48}Cl_2FeN_2P_2Ru$: C, 55.49; H, 5.88; N, 3.41. Found: C, 55.62; H, 5.71; N, 3.25. ^{1}H NMR (200.1 MHz, $CDCl_3$, 20 °C): δ 10.2 (m, 1H; o-C_5H_4N), 7.66−6.86 (m, 13H; aromatic protons), 5.51 (m, 1H; CHMe), 4.65 (s, 1H; Cp), 4.48 (s, 1H; Cp), 4.42 (s, 1H; Cp), 3.90−358 (m, 3H; CH_2NH_2), 3.60 (s, 5H; Cp), 1.87 (pseudo t, J = 8.5 Hz; 3H; $CHCH_3$), 1.64 (s br, 1H; NH_2), 1.53 (s br, 9H; CCH_3), 0.97 (d, J(HP) = 10.8 Hz; 9H; CCH_3). ^{13}C-{^{1}H} NMR (50.3 MHz, $CDCl_3$, 20°C): δ 160.4 (s; $NCCH_2$), 152.1 (s; NCH), 136.0−120.5 (m; aromatic carbons), 72.9 (s; FeCH), 71.0 (s; FeC_5H_5), 70.0 (s; FeCH), 68.7 (s; FeCH), 52.8 (s; CH_2N), 33.7 (d, J(CP) = 2.4 Hz; Me of ^{t}Bu), 33.5 (d, J(CP) = 10.0 Hz; PCHMe), 32.4 (br s; Me of ^{t}Bu), 18.3 (d, J(CP) = 7.5 Hz; CH_3). ^{31}P{^{1}H} NMR (81.0 MHz, $CDCl_3$, 20 °C): δ 82.4 (d, J(PP) = 33.3 Hz), 36.9 (J(PP) = 33.3 Hz).

Synthesis of *trans,cis*-RuHCl(PPh$_3$)$_2$(ampy) (11). $RuHCl(PPh_3)_3$ (211 mg, 0.228 mmol) and ampy (24 μL, 0.233 mmol) were suspended in 10 mL of heptane, and the mixture was refluxed for 1 h. The yellow product was filtered, washed with heptane, and dried under reduced pressure. Yield: 118 mg (67%). Anal. Calcd for $C_{42}H_{39}ClN_2P_2Ru$: C, 65.49; H, 5.10; N, 3.64. Found: C, 65.23; H, 5.03; N, 3.43. ^{1}H NMR (200.1 MHz, CD_2Cl_2, 20 °C): δ 8.20 (s, 1H; o-C_5H_4N), 7.70−6.40 (m, 33H; aromatic protons), 4.30 (pseudo t, J(HH) = 14.1 Hz, 1H; CH_2), 4.07 (d, J(HH) = 14.3 Hz, 1H; CH_2), 2.87 (pseudo t, J(HH) = 10 Hz, 1H; NH_2), 2.20 (pseudo d, J(HH) = 10 Hz, 1H; NH_2), −17.70 (dd, J(HP) = 23.5, 29.7 Hz). ^{13}C{^{1}H} NMR (50.3 MHz, CD_2Cl_2, 20 °C): δ 159.7 (s; $NCCH_2$), 155.6 (d, J(CP) = 4.0 Hz; NCH), 138.8−118.7 (m; aromatic carbons), 53.4 (s; CH_2). ^{31}P{^{1}H} NMR (81.0 MHz, CD_2Cl_2, 20 °C): δ 73.7 (d, J(PP) = 37.0 Hz), 68.9 (d, J(PP) = 37.0 Hz).

Synthesis of *cis,trans*-Ru(H)$_2$(PPh$_3$)$_2$(ampy) (12). A 0.2 M solution of sodium isopropoxide in 2-propanol (1.4 mL, 0.280 mmol) was evaporated, and the complex **11** (211 mg, 0.274 mmol) and toluene (12 mL) were added. The resulting suspension was stirred at 30 °C for 3 h, and after filtration, the solution was concentrated. Addition of pentane afforded a yellow precipitate, which was filtered and dried under reduced pressure. Yield: 131 mg (65%). Anal. Calcd for $C_{42}H_{40}N_2P_2Ru$: C, 68.56; H, 5.48; N, 3.81. Found: C, 68.30; H, 5.33; N, 3.62. ^{1}H NMR (200.1 MHz, C_6D_6, 20 °C): δ 7.93−5.73 (m, 34H; aromatic protons), 2.76 (t, J(HH) = 6.1 Hz, 2H; CH_2), 1.67 (t, J(HH) = 6.1 Hz, 2H; NH_2), −16.31 (td, J(HP) = 27.5 Hz, J(HH) = 6.7 Hz, 1H; RuH), −18.24 (td, J(HP) = 27.7 Hz, J(HH) = 6.7 Hz, 1H; RuH). ^{13}C{^{1}H} NMR (50.3 MHz, C_6D_6, 20 °C): δ 158.7 (s; $NCCH_2$), 155.8 (s; NCH), 142.0−118.0 (m; aromatic carbons), 51.4 (s; CH_2). ^{31}P{^{1}H} NMR (81.0 MHz, C_6D_6, 20 °C): δ 67.2.

General Procedure for the Catalytic Transfer Hydrogenation. The samples were typically prepared as follows: the ruthenium complex (5 μmol) was suspended in 3 mL of 2-propanol, and 2 mL of a solution of NaOH (0.1 M in 2-propanol) was added. The ketone (2 mmol) was dissolved in 19 mL of 2-propanol, and the system was refluxed. On addition of 1 mL of the solution of the catalyst, the reaction starts immediately, and the yield and the enantiomeric excess were determined by gas chromatography using a MEGADEX-ETTBDMS-β chiral column.

Single-Crystal X-ray Structure Determination of Compounds 7·CH$_2$Cl$_2$ and 9·2(CHCl$_3$).[39] Crystal data and details of the structure determination are presented in Table 5. Suitable single crystals for the X-ray diffraction study were grown from CH_2Cl_2 ($CHCl_3$). A clear red prism (orange fragment) was stored under perfluorinated ether, transferred in a Lindemann capillary, fixed, and sealed. Preliminary examination and data collection were carried out on an area detecting system (NONIUS, MACH3, κ-CCD) at the window of a rotating anode (NONIUS, FR951) with graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The unit cell parameters were obtained by full-matrix least-squares refinement of 6553 (4587) reflections. Data collection was performed at 173 K (Oxford Cryosystems) within a θ-range of 1.71° < θ < 25.35° (1.45° < θ < 25.38°), measured each with nine data sets in rotation scan mode with $\Delta\varphi/\Delta\omega$ = 1.0° (1.0°). A total of 76 320 (57 988) intensities were integrated. Raw data were corrected for Lorentz, polarization, and, arising from the scaling procedure, latent decay and absorption effects. After merging [R_{int} = 0.047 (0.044)] a sum of 6282 (8805) (all data) and 5445 (8384) [$I > 2\sigma(I)$], respectively, remained, and all data were used. The structures were solved by a combination of direct methods and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic displacement parameters. **7**·CH_2Cl_2: all hydrogen atoms were found and refined with individual isotropic displacement parameters. The hydrogen atoms of the disordered solvent molecule CH_2Cl_2 were placed in ideal positions (riding model). **9**·2($CHCl_3$): all hydrogen atoms were placed in ideal positions (riding model). Full-matrix least-squares refinements with 560 (560) parameters were carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$ with the SHELXL-97 weighting scheme and stopped at shift/err < 0.002 (0.001). The final residual electron density maps showed no remarkable features. Neutral atom scattering factors for all

(39) Compound **9** crystallizes with CH_2Cl_2 as solvent isomorphous to the $CHCl_3$ adduct. **9**·2(CH_2Cl_2): monoclinic, $C2$ (No. 5), a = 23.6455(2) Å, b = 14.2636(1) Å, c = 14.5111(1) Å, β = 106.8682(4)°.

Table 5. Crystallographic Data for 7·CH_2Cl_2 and 9·2$CHCl_3$

	7·CH_2Cl_2	**9**·2$CHCl_3$
formula	$C_{35}H_{38}Cl_4N_2P_2Ru$	$C_{44}H_{54}Cl_8FeN_2P_2Ru$
fw	791.48	1113.35
color/habit	red/prism	orange/fragment
cryst dimens (mm^3)	0.15 × 0.23 × 0.25	0.13 × 0.23 × 0.28
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$ (no. 14)	$C2$ (no. 5)
a, Å	11.6223(1)	23.2361(2)
b, Å	14.8735(1)	14.6588(1)
c, Å	20.0255(1)	14.6304(1)
β, deg	96.9260(2)	105.7930(3)
V, $Å^3$	3436.43(4)	4795.20(6)
Z	4	4
T, K	173	173
D_{calcd}, g cm^{-3}	1.530	1.542
μ, mm^{-1}	0.889	1.164
$F(000)$	1616	2272
θ range, deg	1.71−25.35	1.45−25.38
index ranges (h, k, l)	±14, ±17, ±24	±28, ±17, ±17
no. of rflns collected	76 320	57 988
no. of indep rflns/R_{int}	6282/0.047	8805/0.044
no. of obsd rflns ($I>2\sigma(I)$)	5445	8384
no. of data/restraints/params	6282/0/560	8805/1 /560
Flack's parameter		$\epsilon = -0.03(1)$
R1/wR2 ($I>2\sigma(I)$)[a]	0.0247/0.0550	0.0248/0.0565
R1/wR2 (all data)[a]	0.0326/0.0578	0.0274/0.0576
GOF (on F^2)[a]	1.046	1.067
largest diff peak and hole (e $Å^{-3}$)	+0.52/−0.38	+0.49/−0.39

[a] $R1 = \sum(||F_o| - |F_c||)/\sum|F_o|$; $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; $GOF = \{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$.

atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from *International Tables for Crystallography*. All calculations were performed on an Intel Pentium II PC, with the STRUX-V system, including the programs PLATON, SIR92, and SHELXL-97.[40] **7**·CH_2Cl_2: a disorder [0.63(3)/0.37(3)] of the solvent molecule CH_2Cl_2 could be resolved clearly. **9**·2($CHCl_3$): a disorder [0.619(3)/0.381(3)] of one of the two solvent molecules $CHCl_3$ could be resolved clearly. The correct enantiomer is proved by synthesis and by Flack's parameter $\epsilon = -0.03(1)$. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-241075 [**7**·(CH_2Cl_2)] and CCDC-241076 [**9**·2($CHCl_3$)]. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgment. This work was supported by the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (MURST). The authors thank P. Polese for the elemental analyses and Dr. P. Martinuzzi for assistance in NMR measurements.

Supporting Information Available: Tables of crystal and data collection parameters, atomic coordinates, bond lengths, bond angles, and thermal displacement parameters for **7** and **9** in cif format. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0491701

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