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Preparation of Monocarbonyl Ruthenium Complexes Bearing Bidentate Nitrogen and Phosphine Ligands and their Catalytic Activity in the Carbonyl Compound Reduction

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Abstract

The monocarbonyl complexes $[RuCl_2(CO)(PR_3)(NN)]$ (R = Cy, NN = en **1**, ampy **2**; R = *i*Pr, NN = en **3**) have been prepared in a one pot reaction from $[RuCl_2(CO)(dmf)(PPh_3)_2]$, PR_3 and the NN ligand in CH_2Cl_2. Treatment of the $[Ru(OAc)_2(CO)(PPh_3)_2]$ with NN ligands in methanol gives the cationic derivatives $[Ru(OAc)(CO)(PPh_3)(NN)]OAc$ (NN = en **4**, ampy **5**) in which one acetate acts as bidentate ligand, whereas the other is not coordinated. The diphosphine complexes $[RuCl_2(CO)(PP)(PPh_3)]$ (PP = dppb **6**, dppf **7**, (*R*)-BINAP **8**, (R,S_p)-Josiphos **9** and (*R*,*R*)-Skewphos **10**) have been obtained starting from $[RuCl_2(CO)(dmf)(PPh_3)_2]$ and the PP ligand in $CHCl_3$ or toluene at reflux. Reaction of $[Ru(OAc)_2(CO)(PPh_3)_2]$ with PP in CH_2Cl_2 or toluene affords the fluxional acetate derivatives $[Ru(OAc)_2(CO)(PP)]$ (PP = dppb **11**, dppf **12**, (*R*)-BINAP **13**, and (*R*,*R*)-Skewphos **14**). The cationic diphosphine complexes [RuCl(CO)(PP)(en)]Cl (PP = dppb **15**, dppf **16**) are prepared from $[RuCl_2(CO)(dmf)(PPh_3)_2]$, PP and en in CH_2Cl_2 or, alternatively, from $[RuCl_2(CO)_2]_n$ or the **6**, **7** derivatives. Similarly, $[Ru(OAc)(CO)(PP)(NN)]OAc$ (PP = dppb, NN = en **17**, ampy **18**; PP = dppf, NN = en **19**, ampy **20**) are isolated starting from $[Ru(OAc)_2(CO)(PPh_3)_2]$, PP and NN ligands or from **11**, **12**. The derivatives $[Ru(OAc)_2(CO)(PP)]$ show a fluxional behavior in solution as the result of the flexible coordination of acetate ligands. These complexes are found active in the transfer hydrogenation and hydrogenation of ketones and aldehydes, including furfural derivatives, at S/C up to 10000 and TOF up to 18000 h^{-1}.

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Introduction

Ruthenium complexes have been widely investigated in the last decades on account of their broad catalytic activity for a number of organic transformations. In addition to C-C coupling reactions,[1, 2] the reduction of the C=O bond via hydrogenation (HY)[3-6] and transfer hydrogenation (TH)[7-13] reactions promoted by ruthenium catalysts are extensively accepted in the industry as efficient and environmentally benign way for the preparation of alcohols[14] and only few examples have been demonstrated active in both HY or TH reactions.[15-18] The search of the appropriate set of ligands remains crucial for achieving high selectivity and productivity, which are prerequisites for large-scale applications. Monocarbonyl ruthenium complexes have attracted a great deal of attention in homogeneous catalysis on account of their ability to promote several catalytic transformations, including hydrogenation of carbonyl compounds,[19-23] esters and amides,[24-28] dehydrogenation of alcohols,[29-38] borrowing hydrogen reactions.[39-43] Some relevant examples are shown in Figure 1.

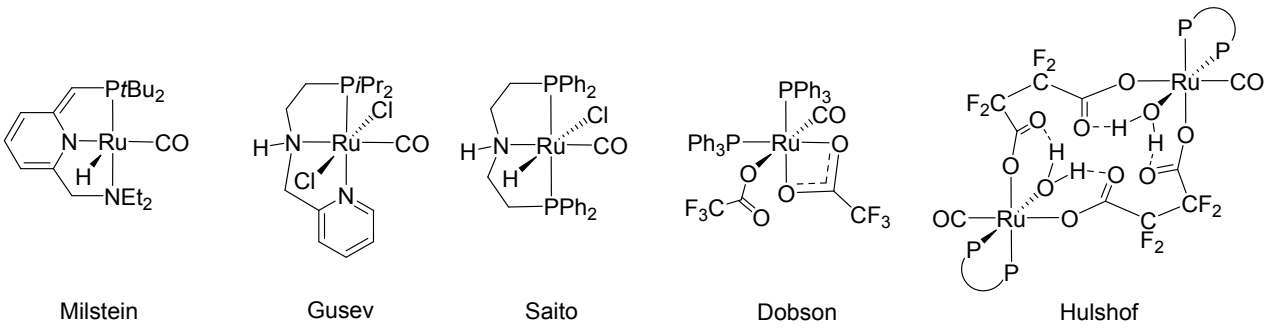

Figure 1. Monocarbonyl ruthenium catalysts.

It is worth noting that a number of dicarbonyl ruthenium complexes employed in catalysis have proven to dissociate one CO, thus resulting in the formation of catalytically active monocarbonyl complexes.[44-48] The presence of a CO ligand on ruthenium may prevent side reactions, such as decarbonylation of the substrates (i.e. aldehydes), which is regarded as a pathway of catalyst deactivation.[49-51] As far as the preparation of monocarbonyl complexes is concerned, $[RuHCl(CO)(XPh_3)_3]$ (X = P, As) and $[RuH_2(CO)(PPh_3)_3]$ are usually employed as suitable precursors via displacement of PPh_3 with strongly coordinating polydentate ligands, or protonation of the hydride. Recently, we reported the isolation of [RuH(CO)(dppp)(NN)]Cl from $[RuHCl(CO)(PPh_3)_3]$ and dppp,[52] a reaction which failed when using the related diphosphines dppb and dppf, thus limiting the scope of this reaction.[53] In addition, Batista et al. described a series of

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monocarbonyl Ru complexes with dppb and bipyridine ligands, from $[RuCl_2(CO)(dppb)]_2(dppb)$, which display antitumor activity,[54, 55] whereas $[RuCl_2(CO)(PP)]_2(PP)$ have been obtained from $[RuCl_2(CO)_2]_n$ and PP ligands.[56] It is to point out that a systematic and simple approach for the synthesis of monocarbonyl ruthenium derivatives with different bidentate PP and NN ligands has been sparingly described in spite of the great interest for PP and NN ruthenium complexes in catalysis and other applications.

In our ongoing interest in the synthesis of carbonyl ruthenium complexes for homogeneous catalysis,[57, 58] we report herein a general entry for the easy preparation of a series of monocarbonyl ruthenium complexes containing bidentate nitrogen and diphosphine ligands through straightforward syntheses starting from $[RuCl_2(CO)(dmf)(PPh_3)_2]$[59] and $[Ru(OAc)_2(CO)(PPh_3)_2]$[60] precursors. The monocarbonyl phosphine ruthenium complexes, in the presence of primary amine ligands (i.e. en and ampy[61]), display catalytic activity in the reduction of ketones and aldehydes at S/C up to 10000.

Results and Discussion

Synthesis of monocarbonyl ruthenium chloride and acetate complexes with NN ligands. Complexes having formula $[RuCl_2(CO)(PR_3)(NN)]$ are easily obtained from $[RuCl_2(CO)(dmf)(PPh_3)_2]$ by reaction with a phosphine and a bidentate dinitrogen ligand, whereas the acetate complexes $[Ru(OAc)(CO)(PPh_3)(NN)]OAc$ are prepared from $[Ru(OAc)_2(CO)(PPh_3)_2]$ and a NN ligand. Accordingly, treatment of $[RuCl_2(CO)(dmf)(PPh_3)_2]$ with PCy_3 in CH_2Cl_2 at RT, followed by reaction with en, affords the complex *trans*-$[RuCl_2(CO)(PCy_3)(en)]$ (**1**), isolated in 89% yield (Scheme 1). The ^1H NMR spectrum of **1** in CD_2Cl_2 displays two multiplets at δ 3.10 and 2.93 ppm for the methylene groups of the en[52] ligand, while the NH_2 moieties appear at δ 3.70 and 3.27 ppm. The $^{13}C\{^1H\}$ NMR doublet at δ 206.0 ppm ($^2J_{CP}$ = 16.8 Hz) is attributable the CO carbon, whereas the doublets at δ 43.5 and 42.3 ppm are for the CH_2 groups of en (Table 1). The low $\nu_{C\equiv O}$ at 1936 cm^{-1} in the IR spectrum of **1** is in agreement with the presence of a *trans* amine and a *cis* PCy_3 ligand.[19, 62] Control $^{31}P\{^1H\}$ NMR experiments carried out after the addition of PCy_3 to $[RuCl_2(CO)(dmf)(PPh_3)_2]$ in CD_2Cl_2 at RT, show the appearance of two doublets at δ 31.9 and 26.1 ppm with a $^2J_{PP}$ = 330 Hz, consistent with the formation of the intermediate **A** by substitution of one PPh_3 with PCy_3 (Scheme 1).

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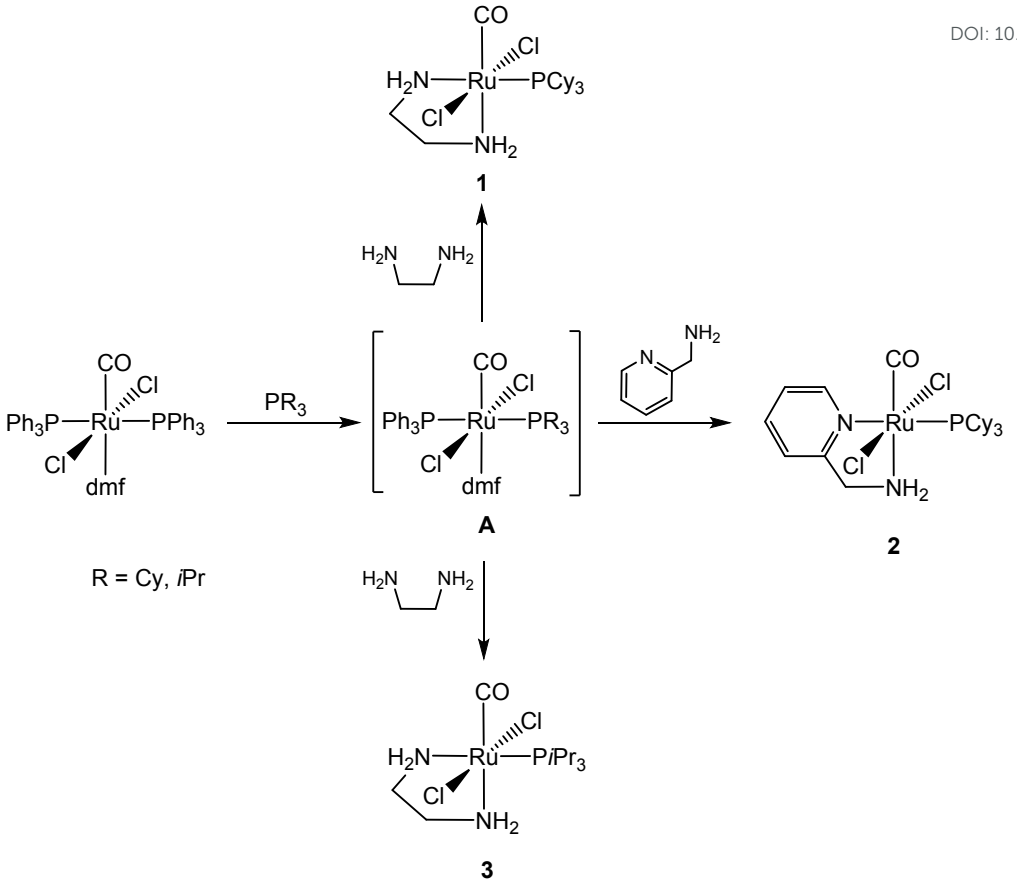
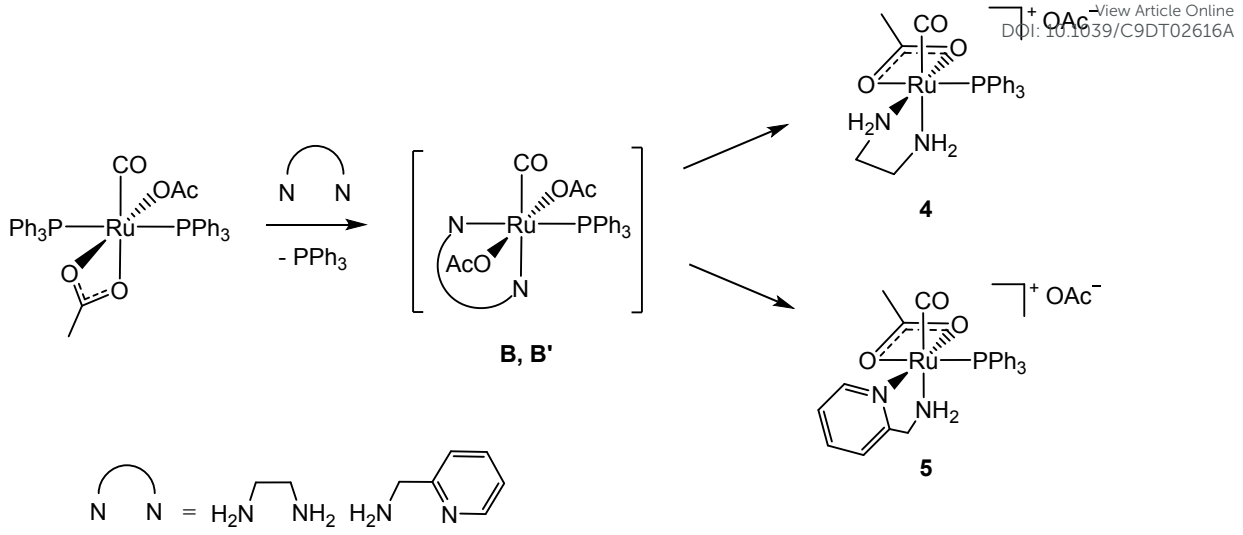


Scheme 1. Synthesis of *trans*-[$RuCl_2(CO)(PR_3)(NN)$] (**1**-**3**).

Similarly to **1**, the derivative *trans*-[$RuCl_2(CO)(PCy_3)$(ampy)] (**2**) has been prepared by reaction of [$RuCl_2(CO)(dmf)(PPh_3)_2$] with PCy_3 and ampy[52] (84% yield), while *trans*-[$RuCl_2(CO)(PiPr_3)$(en)] (**3**) has been obtained from the ruthenium precursor using P*i*Pr_3 and en in CH_2Cl_2 at RT (66% yield) (Scheme 1). The $^{31}P\{^1H\}$ NMR spectrum of **2** in CD_2Cl_2 displays a singlet at δ 56.9 ppm, a value very close to that of **1** (δ 55.6 ppm). In the ^1H NMR spectrum of **2** the methylene and the NH_2 protons of ampy appear as two triplets at δ 4.71 and 4.19 ppm, with $^3J_{HH}$ = 6.0 Hz, respectively. The $^{13}C\{^1H\}$ NMR signal of the carbonyl group is observed as a doublet at δ 207.6 ppm (d, $^2J_{CP}$ = 17.8 Hz), while the CO stretching band in the IR spectrum is at 1941 cm^{-1}, values close to those of **1**. Complex **3** shows spectroscopic data related to those of **1** and **2** with an IR CO stretching absorbance at 1921 cm^{-1}. Treatment of the acetate precursor [$Ru(OAc)_2(CO)(PPh_3)_2$] with en in methanol at 70 °C for 2 h, affords the cationic complex [$Ru(OAc)(CO)(PPh_3)$(en)]OAc (**4**), isolated in 73% yield (Scheme 2).



Scheme 2. Synthesis of [Ru(OAc)(CO)(PPh_3)(NN)]OAc (NN = en **4**, ampy **5**) complexes.

The $^{31}P\{^1H\}$ NMR spectrum of **4** in CD_2Cl_2 shows a singlet at δ 47.3 ppm. The en NH protons give four broad signals at δ 6.97, 5.22, 3.13 and 2.66 ppm in the ^1H NMR spectrum, consistent with the presence of an N-H···O hydrogen bond interaction, whereas the acetate methyl groups afford two singlets at δ 1.98 and 1.58 ppm. In the $^{13}C\{^1H\}$ NMR spectrum, the CO appears as a doublet at δ 204.9 ppm ($^2J_{CP}$ = 18.4 Hz), whereas the *C*H_2N appear as doublets at δ 46.7 and 43.9 ppm. The two acetates afford the signals at δ 181.4 and 179.3 ppm for the *C*OMe and at δ 25.2 and 24.3 ppm for the CH_3 corresponding moieties, while the IR ν_{CO} adsorption band of the CO is at 1924 cm^{-1}. Control experiments show that reaction of [Ru$(OAc)_2$(CO)$(PPh_3)_2$] with en in dichloromethane at RT (30 min), leads to the formation of **4** and *trans*-[Ru$(OAc)_2$(CO)(PPh_3)(en)] (**B**) (δ_P 51.6 ppm) in about 2/3 molar ratio. The ^1H NMR spectrum of **B** shows triplets at δ 4.95 and 3.90 ppm attributable to the NH_2CH_2 moiety, respectively, and a singlet at δ 1.62 ppm for the acetate ligand (see ESI, Figures S13 and S14). By refluxing this mixture in methanol for 12 h, complete conversion to **4** is achieved, thus indicating that upon *trans* to *cis* isomerization the thermodynamically most stable complex displays a bidentate acetate, while the second acetate acts as the counterion. Similarly, [Ru(OAc)(CO)(PPh_3)(ampy)]OAc (**5**) has been obtained by reaction of [Ru$(OAc)_2$(CO)$(PPh_3)_2$] with ampy in methanol at reflux for 6 h (Scheme 2). The $^{31}P\{^1H\}$ NMR spectrum reveals a signal at δ 49.8 ppm, while the ampy NH protons give two signals at δ 8.87 and 1.27 ppm in the ^1H NMR spectrum indicating a N-H···O hydrogen bond interaction. In the $^{13}C\{^1H\}$ NMR spectrum the CO appears as a doublet at δ 205.7 ppm ($^2J_{CP}$ = 17.9 Hz), whereas the two acetate groups give two resonances at δ 182.0 and 177.7 ppm for the *C*OMe and δ 25.0 and 24.2 for the CH_3 moieties, likewise to **4**. Finally, the IR stretching bands of CO is at 1923 cm^{-1}. Addition of sodium acetate (0.5 and 3.5 eq.) to **5** in

CD_3OD shows a progressive increase of the signal at δ 1.98 ppm for $CH_3CO_2^-$, confirming that one acetate of **5** is not coordinated to ruthenium (see ESI, Fig. S18).

As for **4**, the intermediate species *trans*-[Ru(OAc)$_2$(CO)(PPh$_3$)(ampy)] (**B'**) was observed in dichloromethane (δ_P 53.8 ppm) which converts quantitatively into **5** in refluxing methanol (see ESI, Figures S19 and S20). Thus, we have demonstrated that the monocarbonyl ruthenium precursors [RuCl$_2$(CO)(dmf)(PPh$_3$)$_2$] and [Ru(OAc)$_2$(CO)(PPh$_3$)$_2$] react with a monodentate phosphine and / or a bidentate NN ligands affording the derivatives *trans*-[RuX$_2$(CO)(PR$_3$)(NN)] (X = Cl, OAc). While the chloride derivatives are stable in solution, the acetate compounds undergo easily isomerization in alcohol media, with the formation of the cationic [Ru(OAc)(CO)(PPh$_3$)(NN)]OAc species in which one acetate acts as bidentate ligand while the other is present as counterion.

Table 1. Selected spectroscopic data of the complexes 1-20 recorded at 20 °C

Complex	$^{31}P\{^1H\}$		$^{13}C\{^1H\}$ (Ru-*C*O)		ν_{CO} (cm^{-1})[a]
	δ_P (ppm)	$^2J_{PP}$ (Hz)	δ_C (ppm)	$^2J_{CP}$ (Hz)	
trans-[RuCl$_2$(CO)(en)(PCy$_3$)] (**1**)	55.6 (s)	-	206.0 (d)	16.8	1936
trans-[RuCl$_2$(CO)(ampy)(PCy$_3$)] (**2**)	56.9 (s)	-	207.6 (d)	17.8	1941
trans-[RuCl$_2$(CO)(P*i*Pr$_3$)(en)] (**3**)	55.9 (s)	-	205.8 (d)	17.0	1921
[Ru(OAc)(CO)(PPh$_3$)(en)]OAc (**4**)	47.3 (s)	-	204.9 (d)	18.4	1924
[Ru(OAc)(CO)(PPh$_3$)(ampy)]OAc (**5**)	49.8 (s)	-	205.7 (d)	17.9	1923
trans-[RuCl$_2$(CO)(dppb)(PPh$_3$)] (**6**)	27.5 (t; 1P) 16.4-14.8 (m; 2P)	25.8	200.1 (dt)	11.9 3.0	1974
trans-[RuCl$_2$(CO)(dppf)(PPh$_3$)] (**7**)	53.8 (m; 1P) 46.4 (m; 2P)	-	199.7 (br t)	16.0	1979
trans-[RuCl$_2$(CO)((*R*)-BINAP)(PPh$_3$)] (**8**)	31.2 (pseudo-t; 1P) 25.8 (dd; 1P) 21.3 (dd; 1P)	24.3 348.7 25.2 348.6 23.3	199.9 (dt)	83.6 15.8	1981
trans-[RuCl$_2$(CO)((*R*,*S$_p$*)-Josiphos)(PPh$_3$)] (**9**)	47.7 (pseudo-t; 1P) 14.3 (dd; 1P) 12.0 (dd; 1P)	23.0 357.2 23.0 357.2 22.7	197.1 (m)	-	1979
trans-[RuCl$_2$(CO)((*R*,*R*)-Skewphos)(PPh$_3$)] (**10**)	several multiplets	-	-	-	1976

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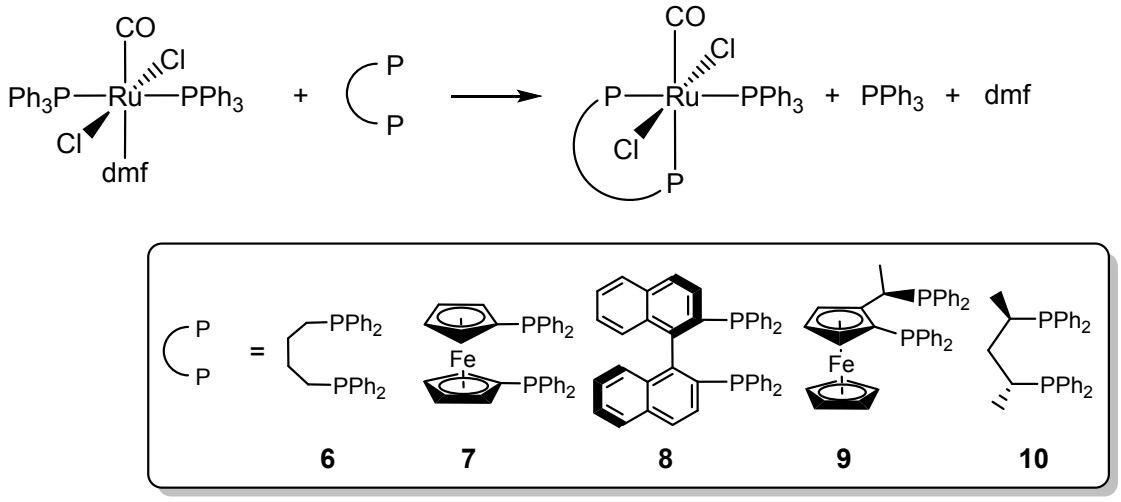
[Ru(OAc)$_2$(CO)(dppb)] (**11**)	48.0 (d)[b] 46.2 (d)[b] major isomer	26.4	204.5 (dd)[b]	21.6 15.8	1954
[Ru(OAc)$_2$(CO)(dppf)] (**12**)	49.8 (d)[c] 45.4 (d)[c] major isomer	30.4	203.3 (t)[c]	16.9	1974
[Ru(OAc)$_2$(CO)((*R*)-BINAP)] (**13**)	49.6 (d)[d] 40.1 (d)[d] major isomer	27.6	205.0 (t)[d]	27.2	1975
[Ru(OAc)$_2$(CO)((*R*,*R*)-Skewphos)] (**14**)	54.3 (d)[d] 48.8 (d)[d] major isomer	38.8	201.8 (t)[d] major isomer	16.9	1958
[RuCl(CO)(dppb)(en)]Cl (**15**)	37.4 (s)	-	199.5 (t)	13.6	1969
[RuCl(CO)(dppf)(en)]Cl (**16**)	39.8 (s)	-	199.9 (t)	14.4	1960
[Ru(OAc)(CO)(dppb)(en)]OAc (**17**)	37.1 (s)	-	203.9 (t)	14.8	1939
[Ru(OAc)(CO)(dppb)(ampy)]OAc (**18**)	46.4 (d) 34.0 (d)	28.8	203.2 (t)	12.7	1944
[Ru(OAc)(CO)(dppf)(en)]OAc (**19**)	40.1 (s)	-	203.2 (t)	15.1	1963
[Ru(OAc)(CO)(dppf)(ampy)]OAc (**20**)	51.2 (d) 40.5 (d)	29.1	210.3 (t)	16.4	1959

[a] nujol mull; [b] at - 80 °C; [c] at - 70 °C; [d] at - 60 °C.

Synthesis of monocarbonyl ruthenium chloride and acetate complexes with PP ligands. The monocarbonyl diphosphine derivatives [RuCl$_2$(CO)(PP)(PPh$_3$)] and [Ru(OAc)$_2$(CO)(PP)] are easily obtained by reaction of the precursors [RuCl$_2$(CO)(dmf)(PPh$_3$)$_2$] and [Ru(OAc)$_2$(CO)(PPh$_3$)$_2$], respectively, with a suitable (chiral) diphosphine. Treatment of [RuCl$_2$(CO)(dmf)(PPh$_3$)$_2$] with dppb in chloroform at 60 °C overnight gives *trans*-[RuCl$_2$(CO)(dppb)(PPh$_3$)] (**6**), which was isolated in 75% yield (Scheme 3).



Scheme 3. Synthesis of *trans*-[RuCl$_2$(CO)(PP)(PPh$_3$)] (**6-10**).

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The $^{31}P\{^{1}H\}$ NMR spectrum of **6** in CD_2Cl_2 at 20 °C exhibits a second-order ABX splitting pattern with a triplet at δ 27.5 ppm ($^{2}J_{PP}$ = 25.8 Hz) for one P atom of dppb and a broad multiplet in the range of δ 16.4-14.8 ppm for PPh_3 and one P atom of the dppb ligand.[63] The NMR spectra of **6** show broad signals for the dppb methylene protons (δ_H 3.3-1.5 ppm) and a resonance at δ_C 200.1 ppm for the CO, whereas the IR CO stretching absorption is at 1974 cm^{-1}. Reaction of $[RuCl_2(CO)(dmf)(PPh_3)_2]$ with the robust dppf[52, 64] in toluene at reflux for 2 h affords *trans*-$[RuCl_2(CO)(dppf)(PPh_3)]$ (**7**), isolated in 39% yield (Scheme 3). This synthesis required higher temperature with respect to that for **6**, possibly due to the higher rigidity and the less basicity of dppf, compared to dppb. Complex **7** displays two resonances at δ_P 53.8 and 46.4 ppm in a 1:2 ratio, with a carbonyl signal at δ_C 199.7 ppm while the IR ν_{CO} band appears at 1979 cm^{-1}. Similarly to **6**, treatment of $[RuCl_2(CO)(dmf)(PPh_3)_2]$ with one equivalent of the chiral (*R*)-BINAP[52] in toluene at reflux for 2 h leads to *trans*-$[RuCl_2(CO)((R)\text{-BINAP})(PPh_3)]$ (**8**), isolated in 88% yield as a single stereoisomer (Scheme 3). The $^{31}P\{^{1}H\}$ NMR spectrum of **8** in C_7D_8 displays an ABX pattern at 293 K, with a pseudo-triplet at δ 31.2 ppm and two doublets of doublets at δ 25.8 and 21.3 ppm, respectively. The upfield signals present a large coupling constant ($^{2}J_{PP}$ = 348.7 Hz) for a PPh_3 and a (*R*)-BINAP phosphorus atoms in trans configuration. The CO ligand gives a doublet of triplets at δ_C 199.9 ppm with a $(^{2}J_{CP})_{trans}$ of 83.6 Hz and a $(^{2}J_{CP})_{cis}$ of 15.8 Hz, in agreement with a planar arrangement of the three P atoms and the CO ligand. Finally, the monocarbonyl derivatives *trans*-$[RuCl_2(CO)((R,S_p)\text{-Josiphos})(PPh_3)]$ (**9**) and *trans*-$[RuCl_2(CO)((R,R)\text{-Skewphos})(PPh_3)]$ (**10**) are obtained by treatment of $[RuCl_2(CO)(dmf)(PPh_3)_2]$ with the corresponding chiral diphosphine in toluene at reflux for 2 h, and isolated in 65 and 87% yield, respectively (Scheme 3). While the (R,S_p)-Josiphos[52] compound **9** was obtained as a single stereoisomer, the (*R*,*R*)-Skewphos[52] complex **10** consists of a mixture of two different stereoisomers, as inferred from ^{1}H and $^{31}P\{^{1}H\}$ NMR measurements.

Treatment of $[Ru(OAc)_2(CO)(PPh_3)_2]$ with dppb in CH_2Cl_2 overnight at RT, affords the diacetate ruthenium monocarbonyl $[Ru(OAc)_2(CO)(dppb)]$ (**11**), isolated in 88% yield, by displacement of both PPh_3 ligands (Scheme 4).

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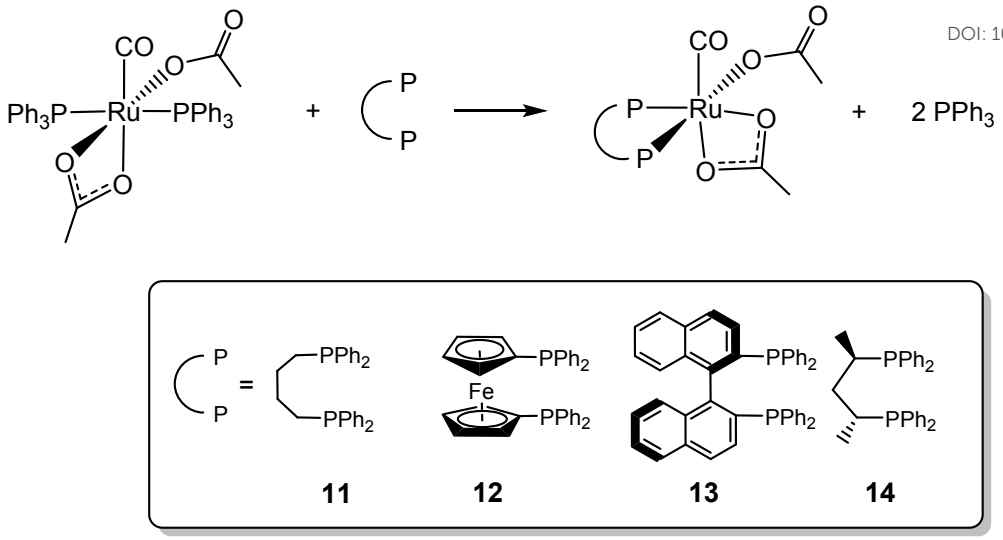

Scheme 4. Synthesis of $[Ru(OAc)_2(CO)(PP)]$ (**11-14**).

The $^{31}P\{^1H\}$ NMR spectrum of **11** in CD_2Cl_2 at RT displays a broad signal at δ 46.8 ppm , while upon cooling two doublets at δ 48.0 and 46.2 ppm with $^2J_{PP}$ = 26.4 Hz and two broad signals in the range δ 45.2-34.0 ppm appear at 193 K, indicating the presence of two species in about 3:1 ratio (see ESI, Fig. S38). The ^1H and $^{13}C\{^1H\}$ NMR spectra for the methyl groups at RT show broad singlets at δ_H 1.42 and δ_C 23.7 ppm, respectively, whereas at low temperature the spectra reveal the presence of two species, in agreement with the $^{31}P\{^1H\}$ NMR data, with an IR CO stretching band at 1954 cm^{-1}. The fluxionality of **11** is likely due to the rapid intramolecular exchange of the monodentate and bidentate acetate groups, a well-known behavior observed for the analogous trifluoroacetate $[Ru(CF_3CO_2)_2(CO)(PPh_3)_2]$.[37, 38, 65] It is likely that the presence of different species at low temperature is due to the different coordination modes of the acetate groups and the conformers of the diphosphine ligand. The complex $[Ru(OAc)_2(CO)(dppf)]$ (**12**) is easily obtained by reaction of $[Ru(OAc)_2(CO)(PPh_3)_2]$ with dppf in toluene at reflux for 2 h and isolated in 67% yield (Scheme 4). At RT the $^{31}P\{^1H\}$ NMR spectrum of **12** in CD_2Cl_2 shows a broad singlet at δ 50.7 ppm, while upon cooling at 203 K three species appear (7:2:1 ratio), with the major isomer displaying two doublets at δ 49.8 and 45.4 ppm with $^2J_{PP}$ of 30.4 Hz. In the ^1H NMR spectrum, the broad signal at δ 1.56 ppm is for the two acetates, while at low temperature three isomers containing two non-equivalent acetates (δ 1.73-1.33 ppm) are observed, in agreement with the $^{31}P\{^1H\}$ measurements (see ESI, Fig. S45). The IR ν_{CO} of **12** is at 1974 cm^{-1}, shifted at higher wavenumber compared to **11** and $[Ru(OAc)_2(CO)(dippf)]$[52, 66] (1939 cm^{-1}), due to the low basicity of dppf.[67-71] Similarly to **12**, the chiral complexes **13** and **14** are obtained from $[Ru(OAc)_2(CO)(PPh_3)_2]$ and the suitable diphosphine, namely (*R*)-BINAP and (*R*,*R*)-Skewphos, in toluene at reflux and isolated in good yield (71-93%, Scheme 4). $^{31}P\{^1H\}$ and ^1H NMR spectra of **13-14** display at RT broad peaks due to the fluxional

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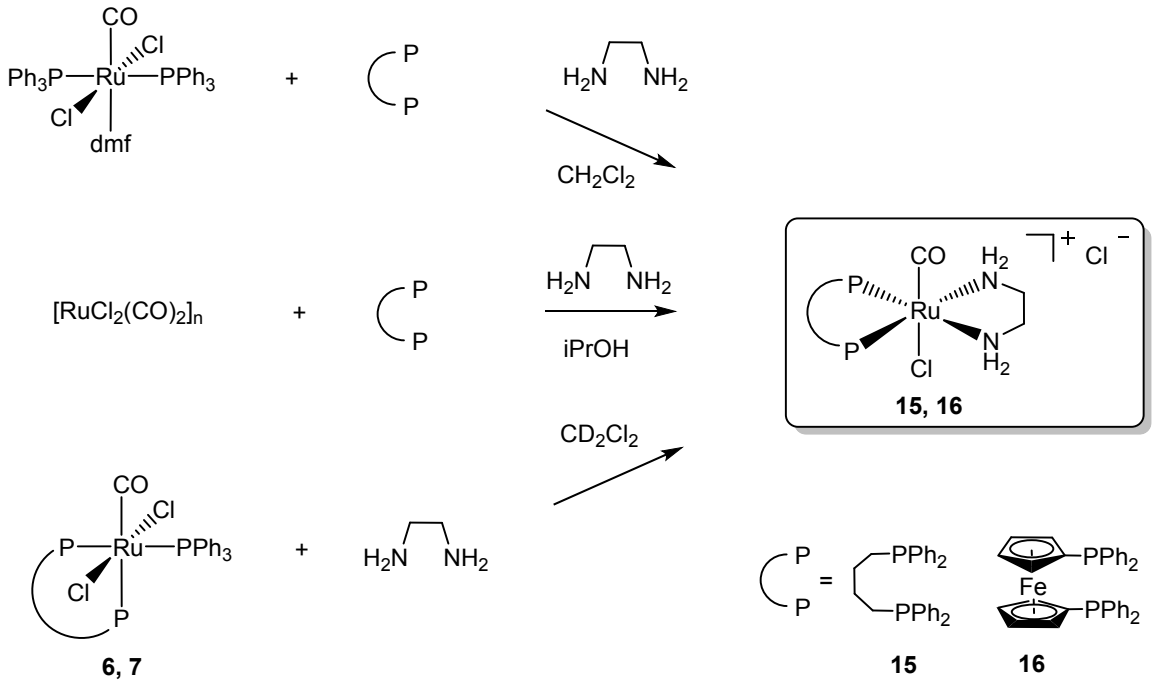
behavior of these complexes, whereas at low temperature several isomers appear in the NMR spectra (see ESI, Fig. S50-S59). Thus, by difference to the monocarbonyl ruthenium diphosphine complexes with chloride ligands, the corresponding acetate derivatives do not contain an additional PPh_3, on account of the ability of the carboxylate to act as bidentate ligand.

Synthesis of the monocarbonyl ruthenium chloride and acetate complexes with NN and PP ligands. The ruthenium complexes [RuX(CO)(PP)(NN)]X (X = Cl, OAc) can be obtained by reactions of the precursors $[RuX_2(CO)(dmf)_n(PPh_3)_2]$ (X = Cl, n = 1; X = OAc, n = 0), $[RuCl_2(CO)_2]_n$[72] and the above reported derivatives $[RuX_2(CO)(PP)(PPh_3)_n]$ (X = Cl, n = 1; X = OAc, n = 0) with PP and / or NN ligands. Treatment of $[RuCl_2(CO)(dmf)(PPh_3)_2]$ with dppb in CH_2Cl_2, followed by addition of en at RT, leads to the cationic derivative [RuCl(CO)(dppb)(en)]Cl (**15**) isolated in 87% yield (Scheme 5).

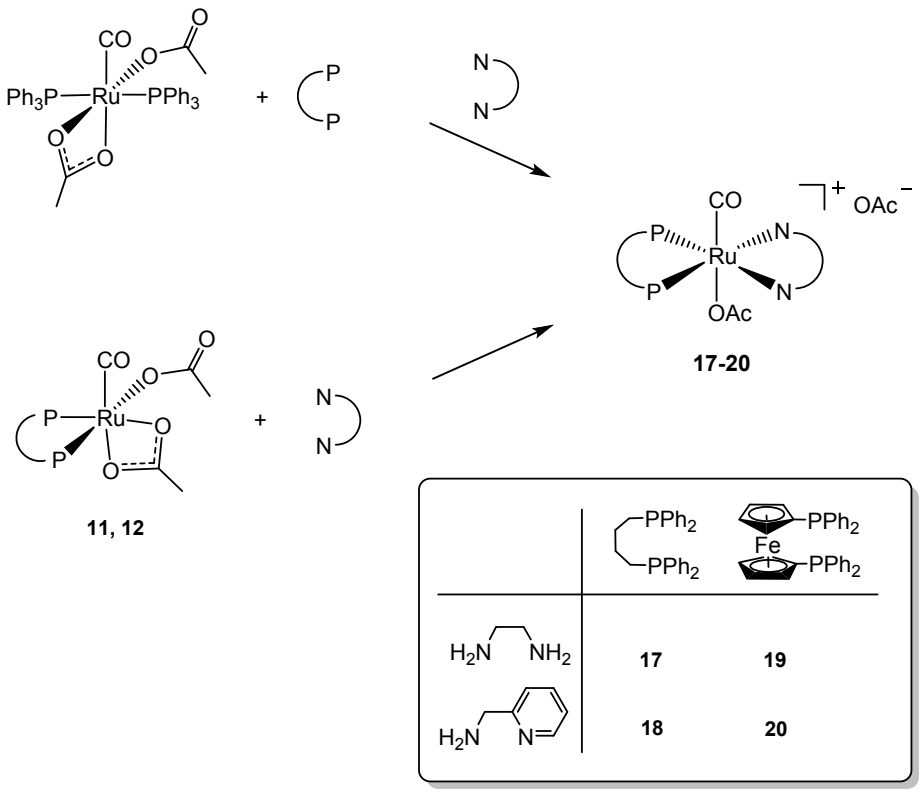


Scheme 5. Synthesis of the cationic [RuCl(CO)(PP)(en)]Cl complexes **15** and **16**.

Alternatively, **15** can be prepared in a more advantageous way (93% yield) by reaction of $[RuCl_2(CO)_2]_n$ with dppb in 2-propanol, followed by treatment with en at reflux for 2 h via decarbonylation (Scheme 5). The $^{31}P\{^1H\}$ NMR spectrum of **15** in CD_2Cl_2 displays a singlet at δ 37.4 ppm, whereas the $^{13}C\{^1H\}$ NMR measurements give a triplet at δ 199.5 ppm ($^2J_{CP}$ = 13.6 Hz) for the CO and a singlet at δ 45.9 ppm for the en ligand. The IR CO stretching absorbance of **15** appears at 1969 cm^{-1}.[53] Employment of dppf with $[RuCl_2(CO)(dmf)(PPh_3)_2]$ affords the complex

[RuCl(CO)(dppf)(en)]Cl (**16**) which is isolated in 88% yield. Complexes **16** shows similar spectroscopic data observed for **15**, with a $^{31}P\{^{1}H\}$ NMR singlet at δ 39.8 ppm and IR ν_{CO} at 1960 cm^{-1}. In addition, complexes **15** and **16** are quantitatively formed by reaction of **6** and **7** with en at RT (2 h), as inferred from NMR measurements in CD_2Cl_2 (Scheme 5).

The acetate complex [Ru(OAc)(CO)(dppb)(en)]OAc (**17**) is obtained through a one-pot reaction from $[Ru(OAc)_2(CO)(PPh_3)_2]$, dppb and en in CH_2Cl_2 and isolated in 97% yield (Scheme 6).



Scheme 6. Synthesis of the acetate complexes [Ru(OAc)(CO)(PP)(NN)]OAc.

Likewise the analogous chloride complex **15**, the acetate derivative **17** displays in the $^{31}P\{^{1}H\}$ NMR spectrum (CD_3OD) one singlet at δ 37.1 ppm, while the CO gives a triplet at δ_C 203.8 ppm ($^{2}J_{CP}$ = 14.8 Hz). The doublet at δ 46.6 ppm ($^{3}J_{CP}$ = 11.0 Hz) and the singlet at δ 44.9 ppm are ascribed to the en *C*H_2 moieties, whereas the two acetate ligands display the signals at δ 182.8 and 182.5 ppm for the *C*OMe and at δ 25.7 and 24.1 ppm for the methyl groups. Interestingly, the ^{1}H NMR spectrum of **17** exhibits four different N-H protons, with one NH_2 group showing a signal at δ 7.27 ppm, suggesting an NH···O hydrogen bond interaction with one acetate,[62] and the other at δ 1.24 ppm, as inferred from ^{15}N-^{1}H HSQC 2D NMR analysis (see ESI, Fig. S69), while the infrared stretching band at 1939 cm^{-1} is for CO ligand. Conversely, **17** can also be obtained from **11** and en in CD_2Cl_2 at RT. Reaction of **11** with ampy in toluene at RT (30 min) leads to the cationic complex

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[Ru(OAc)(CO)(dppb)(ampy)]OAc (**18**), isolated in 87% yield (Scheme 6). $^{31}P\{^{1}H\}$ NMR spectrum of **18** in C_7D_8 displays two doublets at δ 46.4 and 34.0 ppm with a $^{2}J_{PP}$ = 28.8 Hz, whereas the diastereotopic methylene protons of the ampy give in the ^{1}H NMR spectrum two signals at δ 4.22 and 3.21 ppm with $^{2}J_{HH}$ = 12.4 Hz and $^{3}J_{HH}$ = 10.2 and 10.7 Hz. The ^{15}N-^{1}H HSQC 2D NMR analysis reveals that the NH_2 signals are at δ 6.21 and 1.67 ppm, which is consistent with the presence of a NH···O hydrogen bond interaction, as observed for **17**. The $^{13}C\{^{1}H\}$ NMR signal of CO is a triplet at δ 203.2 ppm with $^{2}J_{CP}$ = 16.7 Hz, while the IR ν_{CO} is at 1944 cm^{-1}, similarly to en derivative **17**. Complex [Ru(OAc)(CO)(dppf)(en)]OAc (**19**) was synthesized from **12** by reaction with en in toluene and isolated in 88% yield (Scheme 6). Complex **19** shows similar spectroscopic data observed for **17**, with the $^{31}P\{^{1}H\}$ NMR singlet at δ 40.1 ppm in CD_2Cl_2, whereas the $^{13}C\{^{1}H\}$ NMR CO signal appears as a triplet at δ 203.2 ppm ($^{2}J_{CP}$ = 15.1 Hz). The acetate carbonyl resonances appear as a singlet at δ 181.4 ppm for the free acetate, and a doublet of doublets at δ 176.6 ppm ($^{3}J_{CP}$ = 12.1 Hz, $^{3}J_{CP}$ = 5.6 Hz) for the coordinated ligand. Finally, the IR spectra of **19** exhibits a ν_{CO} band at 1963 cm^{-1}, whereas the stretching bands at 1617 and 1569 cm^{-1} can be attributed to the acetate groups. In addition, treatment of **12** with ampy in toluene at RT leads to [Ru(OAc)(CO)(dppf)(ampy)]OAc (**20**), which has been isolated in 87% yield (Scheme 6). The spectroscopic data of **20** resembles that of the analogue ampy derivative **18**, with the two ^{1}H NMR signals at δ 4.84 and 2.55 ppm for the diastereotopic CH_2N protons, whereas the NH_2 resonances are found at δ 6.07, and 2.33 ppm. The $^{31}P\{^{1}H\}$ NMR spectrum of **20** displays two doublets at δ 51.2 and 40.5 ppm with a $^{2}J_{PP}$ = 29.1 Hz, whereas the $^{13}C\{^{1}H\}$ NMR CO signal is a triplet at δ 210.3 ppm ($^{2}J_{CP}$ = 16.4 Hz); the IR CO stretching band is at 1959 cm^{-1}. Thus, according to procedure a series of PP and NN monocarbonyl complexes with different stereoelectronic properties bearing chloride and acetate ligands have been easily isolated and characterized.

Reduction of aldehydes and ketones via TH and HY catalyzed by monocarbonyl ruthenium complexes. The catalytic activity of the monocarbonyl ruthenium complexes has been investigated in the reduction of acetophenone **a** via both TH, with 2-propanol in the presence of NaO*i*Pr and HY with H_2 (30 bar) in ethanol with KO*t*Bu (Scheme 7). The *in situ* addition of NN ligands to the ruthenium phosphine derivatives has proven to accelerate the catalytic reactions. Complexes **1**, **2** and **3** (S/C = 1000), bearing the en and ampy ligands in combination with the strongly coordinating alkyl monophosphine PCy_3 or P*i*Pr_3, display poor activity in the TH of **a** (27-54% conv.), in 2-propanol at reflux after 60-90 min (Table 2, entries 1-3). A higher activity is observed for the cationic acetate derivatives **4** and **5** in the presence of the less basic PPh_3, (81 and 95% conv., respectively) after 90 min (entries 4-5). The results obtained with **1-5** are in agreement with the higher

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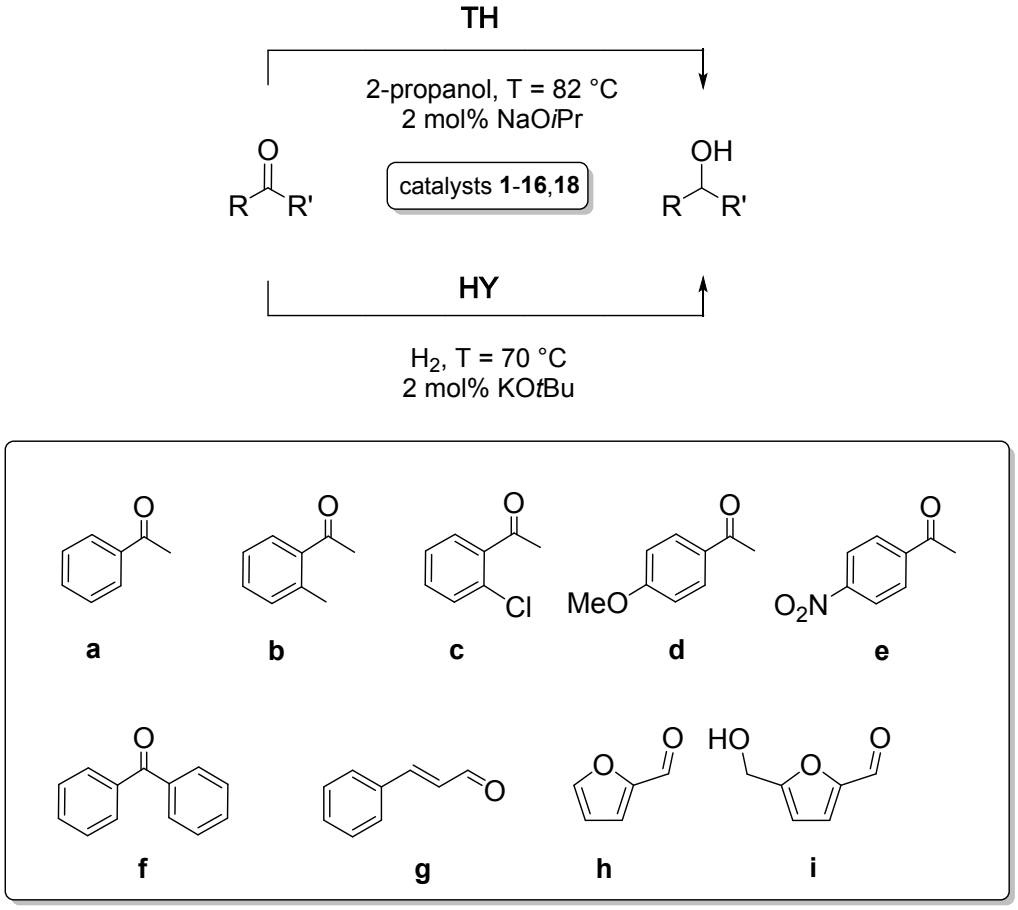
trans influence[73, 74] of PPh_3 vs Cl, allowing a shorter induction time for the formation of the catalytically active Ru hydride species. The complexes $[RuCl_2(CO)(PP)(PPh_3)]$ (PP = dppb, **6**; PP = dppf, **7**) show poor activity (10% in 120 min and 98% in 48 h), while the addition of ampy and displacement of PPh_3 (*vide infra*) leads to an increase of activity, as observed for **7** (90% conv.; entries 6-8). Employment of the chiral (*R*)-BINAP complex **8** in the presence of (*R*,*R*)-DPEN[52] affords high conversion (97%) with TOF of 8400 h^{-1}, respectively, but accompanied by poor *ee* (entry 9). The rate of the TH of **a** with the (R,S_p)-Josiphos derivative **9** is low and increases by addition of (*R*,*R*)-DPEN, (*S*)-1-phenylethanol is obtained in 59% *ee* (entries 10-11).



Scheme 7. Reduction of carbonyl compounds via TH and HY, catalyzed by complexes **1-16, 18**.

Complex **10** bearing the (*R*,*R*)-Skewphos in combination with (±)-*i*Pr-ampy[52] affords the (*R*) alcohol with 67% *ee* (TOF = 5800 h^{-1}) (entry 12). The acetate dppb **11** and dppf **12** derivatives are poorly active and the *in situ* addition of ampy leads to 93 and 72% conversion in 2 h, respectively, with TOF 7400 and 6900 h^{-1}, showing a faster rate compared to their corresponding chlorides **6** and **7** complexes, which require displacement of a PPh_3 by the NN ligand (entries 13-15). With the (*R*)-BINAP **13** and (*R*,*R*)-Skewphos **14** complexes in combination with ampy, (±)-*i*Pr-ampy and (*R*,*R*)-

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DPEN a considerable increase of the reaction rate is observed, with 90-97% conversion in 5-30 min (TOF = 10000-18000 h^{-1}), but low enantioselectivity has been attained (up to 39%) (entries 16-20). Finally, the dppb and dppf complexes **15**, **16** and **18** bearing en and ampy afford the TH of **a** with better performances with respect to those observed with the *in situ* reactions of **6**, **7**, **11** with the nitrogen ligands (entries 21-23).

Table 2. **Catalytic TH of acetophenone (0.1 M) with complexes 1-16, 18 (S/C = 1000) and NaO*i*Pr (2 mol%) in 2-propanol at 82 °C**.

Entry	Complex	Ligand (5 equiv.)	Time [min]	Conv.[a] [%]	TOF[b] [h^{-1}]	e.e. (%)
1	**1**	-	90	54	-	-
2	**2**	-	60	42	-	-
3	**3**	-	90	27	-	-
4	**4**	-	90	81	-	-
5	**5**	-	90	95	-	-
6	**6**	-	120	10	-	-
7	**6**	ampy	120	38	-	-
8	**7**	ampy	120	90	3500	-
9	**8**	(*R*,*R*)-DPEN	120	94	8400	32 (*S*)
10	**9**	-	8 h	97	180	5 (S)
11	**9**	(*R*,*R*)-DPEN	120	96	1200	59 (*S*)
12	**10**	(±)-*i*Pr-ampy[c]	60	95	5800	67 (*R*)
13	**11**	-	120	31	-	-
14	**11**	ampy	120	93	7400	-
15	**12**	ampy	120	72	6900	-
16	**13**	ampy	5	95	18000	23 (*S*)
17	**13**	(*R*,*R*)-DPEN	5	97	15000	30 (*S*)
18	**14**	-	120	81	6400	25 (*R*)
19	**14**	ampy	30	95	10000	25 (*R*)
20	**14**	(±)-*i*Pr-ampy[c]	5	90	15000	39 (*R*)
21	**15**	-	90	94	2100	-
22	**16**	-	90	88	3900	-
23	**18**	-	90	91	7100	-

[a] The conversion has been determined by GC analysis. [b] Turnover frequency (moles of ketone converted to alcohol per mole of catalyst per hour) at 50% conversion. [c] 2 eq. with respect to the diphosphine precursors.

The monocarbonyl derivatives have been investigated in the TH of ketones and aldehydes. Thus, the ampy-derivative **5** (S/C = 1000) catalyzes the quantitative reduction of benzophenone **f** to benzhydrol

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in 0.5 h (Table 3, entry 1). Interestingly, complex **1** bearing en and PCy_3 affords the TH of *trans*-cinnamaldehyde **g**, furfural **h** and 5-(hydroxymethyl)furfural (5-HMF) **i**, which belong to the lignocellulosic biomass platform aldehydes, in 16-60 h (entries 2-4). It is worth pointing out that aldehydes are substrates that are not easily reduced on account of incoming side reactions, which may lead to catalyst deactivation.[75, 76] A higher activity has been observed with complex **18** bearing ampy and dppb for **g** and **h**, affording 98 and 99% conversion after 12 and 1 h, respectively, and without hydrogenation of C=C bond under these catalytic conditions (entries 5-6).

Table 3. **Catalytic TH of aldehydes and ketones (0.1 M) to alcohols with complexes 1, 5 and 18 (S/C = 1000) and NaO*i*Pr (2 mol%) as base in 2-propanol at 82 °C.**

Entry	Complex	substrate	Time [h]	Conv.[a] [%]
1	**5**	**f**	0.5	94
2	**1**[b]	**g**	16	97
3	**1**	**h**	16	92
4	**1**	**i**	60	96
5	**18**[b]	**g**	12	98
6	**18**	**h**	1	99

[a]The conversion has been determined by GC analysis.
[b]Using K_2CO_3 5 mol% as base.

The catalytic results obtained with **1**-**18** indicate that the chloride and the acetate monocarbonyl phosphine complexes without nitrogen ligands display poor activity in TH reactions and their performances increase by addition of primary amine ligands, facilitating the formation of the catalytically active Ru–H species.[77, 78] NMR studies in solution show that reaction of **18** with NaOiPr (2 equiv.) in 2-propanol at RT affords a monohydride species with the hydride ligand (δ - 5.58 ppm) *trans* to a phosphorus atom ($(^2J_{HP})_{trans}$ = 115.6 Hz and $(^2J_{HP})_{cis}$ = 19.8 Hz), in agreement with the results observed for [RuCl(CO)(dppp)(ampy)]Cl complex[53] (see ESI, Fig. S73). The low enantioselectivity observed for the BINAP **8** and **13** compounds, by difference to the Noyori *trans*-$[RuCl_2(BINAP)(NN)]$ system,[79, 80] it is possibly due to the formation of a *trans* H-Ru-P species.

The monocarbonyl amine complexes are also found active in the HY of **a** in ethanol at 70 °C at 30 bar of H_2 pressure. The HY reactions have been carried out both in a catalyst screening system (8 vessels Endeavor™ Biotage system), that allows parallel reactions to be performed, and in a stainless steel autoclave following the single process. The PCy_3 and P*i*Pr_3 **1**-**3** and the dppb **15** complexes (S/C = 2000) give full hydrogenation of **a** (2.0 M) within 16 h in the presence of KO*t*Bu (2 mol%) (Table 4, entries 1-4).

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Table 4. **Catalytic HY of acetophenone (a) (2.0 M) with complexes 1-3, 15 (S/C = 2000) (30 bar) of H_2 and KO*t*Bu (2 mol%) in EtOH at 70 °C.**

Entry	Complex	Time [h]	Conv.[a] [%]
1	**1**	16	99
2	**2**	16	99
3	**3**	16	98
4	**15**	16	99

[a] The conversion has been determined by GC analysis.

In addition, complexes **2** and **15** (S/C = 1000-10000) have been found active in the HY of several ketones. 2'-Methylacetophenone **b**, 2'-choloracetophenone **c** and 4'-methoxyacetophenone **d** are quantitatively reduced to the corresponding alcohols with **2**, whereas 4'-nitroacetophenone **e** leads to poor conversion (10%) (Table 5, entries 1-4). In the HY of **c** and **f**, complex **15** displays much of the same activity of **2**, affording complete conversion, while the reduction of **d** leads to 75% conversion (Table 5, entries 5-8). Therefore, the monocarbonyl ruthenium complexes with a monophosphine or a diphosphine in combination with en and ampy have proven to catalyze the ketone HY with high productivity.

Table 5. **Catalytic HY (30 bar) of ketones (2.0 M) to alcohols with complexes 2, 15 and KO*t*Bu (2 mol%) as base in EtOH at 70 °C**.

Entry	Complex	Substrate	S/C	Time [h]	Conv.[a] [%]
1	**2**	**b**	10000	16	99
2	**2**	**c**	10000	16	99
3	**2**	**d**	1000	5	99
4	**2**	**e**	10000	16	10
5	**2**	**f**	1000	5	98
6	**15**	**c**	10000	16	98
7	**15**	**d**	1000	5	75
8	**15**	**f**	1000	5	99

[a] The conversion has been determined by GC analysis.

Conclusions

In summary, we have described a general approach for the straightforward preparation of a series of monocarbonyl ruthenium complexes, containing bidentate NN and/or PP ligands with chloride and acetate, starting from the precursors $[RuCl_2(CO)(PPh_3)_2(dmf)]$ and $[Ru(OAc)_2(CO)(PPh_3)_2]$. The

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acetate complexes show a fluxional behavior in solution on account of the tendency of the acetate to switch from the mono to bidentate mode of coordination. The reported complexes containing the Ru(CO)(P)(NN) and Ru(CO)(PP)(NN) motifs show good to high catalytic activity in the transfer hydrogenation and hydrogenation of a number of carbonyl compounds. These results will be helpful for the designing of novel monocarbonyl ruthenium complexes containing chelate ligands. Studies are in progress to extend this protocol for the preparation of new derivatives with pincer ligands and expand the use of ruthenium carbonyl complexes in catalytic C-H activation reactions.

Experimental

General

All reactions were carried out under an argon atmosphere using standard Schlenk techniques. Unless stated otherwise, the solvents were carefully dried by standard methods and distilled under argon before use. The ruthenium compounds $[RuCl_2(CO)(dmf)(PPh_3)_2]$,[59] $[RuCl_2(CO)_2]_n$,[72] and $[Ru(OAc)_2(CO)(PPh_3)_2]$[60] 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 and Avance III HD NMR 400 spectrometers. Chemical shifts (ppm) are relative to TMS for ^1H and $^{13}C\{^1H\}$, whereas H_3PO_4 was used for $^{31}P\{^1H\}$. Elemental analyses (C, H, N) were carried out with a Carlo Erba 1106 analyzer, whereas GC analyses were performed with a Varian CP-3380 gas chromatograph equipped with a 25 m length MEGADEX-ETTBDMS-β chiral column with hydrogen (5 psi) as the carrier gas and flame ionization detector (FID). The injector and detector temperature was 250 °C, with initial T = 95 °C ramped to 140 °C at 3 °C/min rate and then to 210 °C at 20 °C/min, for a total of 20 min of analysis.

Synthesis of *trans*-$[RuCl_2(CO)(PCy_3)(en)]$ (1)

$[RuCl_2(CO)(dmf)(PPh_3)_2]$ (250 mg, 0.31 mmol) was suspended in dichloromethane (5 mL) and reacted with PCy_3 (175 mg, 0.62 mmol, 2 equiv.) stirring the mixture for 3 h at RT. En (25 μL, 0.37 mmol, 1.2 equiv) was added and the resulting solution was stirred for 3 h at RT. The solvent was reduced to about half volume by evaporation under reduced pressure, and the addition of *n*-pentane (5 mL) afforded the precipitation of the product. The solid was filtered, washed with diethyl ether (2x10 mL) and dried under reduced pressure. Yield: 149 mg (89%). Elemental analysis calcd (%) for $C_{21}H_{41}Cl_2N_2OPRu$ (540.52): C 46.66, H 7.65, N 5.18; found: C 46.59, H 7.58, N 5.26. ^1H NMR (200.1 MHz, CD_2Cl_2, 20 °C): δ = 3.70 (pseudo-t, J_{HH} = 5.0 Hz, 2H; NH_2), 3.27 (m, 2H; NH_2), 3.10

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(m, 2H; CH_2N), 2.93 (m, 2H; CH_2N), 2.20 (dd, $^3J_{HH}$ = 23.4 Hz, $^3J_{HH}$ = 12.3 Hz, 3H; PCH), 2.14-1.08 ppm (m, 30H; CH_2 (Cy)). $^{13}C\{^1H\}$, NMR (50.3 MHz, CD_2Cl_2, 20 °C): δ = 206.0 (d, $^2J_{CP}$ = 16.8 Hz; CO), 43.5 (d, $^3J_{CP}$ = 2.8 Hz; *C*H_2N), 42.3 (d, $^3J_{CP}$ = 1.5 Hz; *C*H_2N), 35.3 (d, $^1J_{CP}$ = 21.0 Hz; P*C*H), 29.7 (d, $^3J_{CP}$ = 1.3 Hz; PCHCH$_2$*C*H$_2$), 28.2 (d, $^2J_{CP}$ = 10.0 Hz; PCH*C*H$_2$), 27.0 ppm (d, $^4J_{CP}$ = 1.0 Hz; CH_2). $^{31}P\{^1H\}$ NMR (81.0 MHz, CD_2Cl_2, 20 °C): δ = 55.6 ppm (s). IR (Nujol): $\tilde{\nu}$ = 1936 (s) (C≡O) cm^{-1}.

Synthesis of *trans*-[$RuCl_2(CO)(PCy_3)$(ampy)] (2)

Complex **2** was prepared following the procedure used for **1**, with ampy (39 µL, 0.38 mmol, 1.2 equiv.) in place of en. Yield: 153 mg (84%). Elemental analysis calcd (%) for $C_{25}H_{41}Cl_2N_2OPRu$ (588.56): C 51.02, H 7.02, N 4.76; found: C 51.06, H 7.10, N 4.67. ^1H NMR (200.1 MHz, CD_2Cl_2, 20 °C): δ = 9.11 (d, $^3J_{HH}$ = 5.3 Hz, 1H; ortho-C*H* of C_5H_4N), 7.76 (m, 1 H; para-C*H* of C_5H_4N), 7.50-7.28 (m, 2H; meta-C*H* of C_5H_4N), 4.71 (t, $^3J_{HH}$ = 6.0 Hz, 2H; CH_2), 4.19 (t, $^3J_{HH}$ = 6.0 Hz, 2H; NH_2), 2.34 (qt, $^3J_{HH}$ = 12.1 Hz, $^4J_{HH}$ = 2,5 Hz, 3H; PCH), 2.18-1.09 ppm (m, 30H; CH_2 (Cy)). $^{13}C\{^1H\}$ NMR (50.3 MHz, CD_2Cl_2, 20 °C): δ = 207.6 (d, $^2J_{CP}$ = 17.8 Hz; CO), 160.1 (s; N*C*CH$_2$), 152.6 (d, $^2J_{CP}$ = 1.2 Hz; ortho-*C*H of C_5H_4N), 137.6 (s; para-*C*H of C_5H_4N), 124.5 (d, $^4J_{CP}$ = 2.3 Hz; meta-*C*H of C_5H_4N), 121.7 (d, $^4J_{CP}$ = 1.8 Hz; meta-*C*H of C_5H_4N), 50.6 (d, $^3J_{CP}$ = 2.2 Hz; *C*H_2N), 34.5 (d, $^1J_{CP}$ = 21.1 Hz; P*C*H), 29.6 (d, $^3J_{CP}$ = 1.3 Hz; PCHCH$_2$*C*H$_2$), 28.1 (d, $^2J_{CP}$ = 10.0 Hz; PCH*C*H$_2$), 27.0 ppm (s, CH_2). $^{31}P\{^1H\}$ NMR (81.0 MHz, CD_2Cl_2, 20 °C): δ = 56.9 ppm (s). IR (Nujol): $\tilde{\nu}$ = 1941 (s) (C≡O) cm^{-1}.

Synthesis of *trans*-[$RuCl_2(CO)(P$*i*$Pr_3)$(en)] (3)

Complex **3** was prepared following the procedure used for **1**, with P*i*Pr_3 (77 µL, 0.40 mmol, 1.3 equiv.) in place of PCy_3. Yield: 86 mg (66%). Elemental analysis calcd (%) for $C_{12}H_{29}Cl_2N_2OPRu$ (420.32): C 34.29, H 6.95, N 6.66; found: C 34.20, H 7.01, N 6.60. ^1H NMR (200.1 MHz, CD_2Cl_2, 20 °C): δ = 3.62 (m, 2H; NH_2), 3.31 (m, 2H; NH_2), 3.09 (m, 2H; CH_2N), 2.94 (m, 2H; CH_2N), 2.52 (m, 3H; P*C*H(CH$_3$)$_2$), 1.33 ppm (dd, $^3J_{HP}$ = 13.1 Hz, $^3J_{HH}$ = 7.3 Hz, 18H; CH(C*H*$_3$)$_2$). $^{13}C\{^1H\}$ NMR (50.3 MHz, CD_2Cl_2, 20 °C): δ = 205.8 (d, $^2J_{CP}$ = 17.0 Hz; CO), 43.5 (d, $^3J_{CP}$ = 2.9 Hz; CH_2N), 42.2 (d, $^3J_{CP}$ = 1.5 Hz; CH_2N), 25.1 (d, $^1J_{CP}$ = 22.3 Hz; P*C*H(CH$_3$)$_2$), 19.6 ppm (d, $^2J_{CP}$ = 0.7 Hz; CH(C*H*$_3$)$_2$). $^{31}P\{^1H\}$ NMR (81.0 MHz, CD_2Cl_2, 20 °C): δ = 55.9 ppm (s). IR (Nujol): $\tilde{\nu}$ = 1921 (s) (C≡O) cm^{-1}.

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Synthesis of [Ru(OAc)(CO)(PPh_3)(en)]OAc (4)

$[Ru(OAc)_2(CO)(PPh_3)_2]$ (200 mg, 0.26 mmol) was suspended in methanol (5 mL) and reacted with en (22.5 µl, 0.34 mmol, 1.3 equiv), stirring the mixture for 15 h at reflux. The solvent was removed from the obtained solution by evaporation under reduced pressure. The residue was dissolved in dichloromethane (2 mL) and the product was precipitated by addition of *n*-heptane (10 mL). The solid was filtered, washed with diethyl ether (3x4 mL), and *n*-pentane (2x5 mL) and finally dried under reduced pressure. Yield: 108 mg (73%). Elemental analysis calcd (%) for $C_{25}H_{29}N_2O_5PRu$ (569.56): C 52.72, H 5.13, N 4.92; found: C 52.80, H 5.07, N 4.94. ^{1}H NMR (200.1 MHz, CD_2Cl_2, 20 °C): δ = 7.72 (m, 4H; aromatic protons), 7.62-7.30 (m, 11H; aromatic protons), 6.97 (m, 1H; NH_2), 5.22 (m, 1H; NH_2), 3.13 (m, 1H; NH_2), 2.89 (m, 1H; NCH_2), 2.81 (m, 1H; NCH_2), 2.66 (m, 1H; NH_2), 2.49 (m, 1H; NCH_2), 2.53 (m, 1H; NCH_2), 1.98 (s, 3H; CH_3CO), 1.58 ppm (s, 3H; CH_3CO). ^{13}C{^{1}H} NMR (50.3 MHz, CD_2Cl_2, 20 °C): δ = 204.9 (d, $^2J_{CP}$ = 18.4 Hz; CO), 181.4 (s; CH_3CO), 179.3 (s; CH_3CO), 134.3-128.4 (aromatic carbon atoms), 46.7 (d, $^3J_{CP}$ = 3.1 Hz; NCH_2), 44.3 (d, $^3J_{CP}$ = 2.3 Hz; NCH_2), 25.2 (s; CH_3CO), 24.3 ppm (s; CH_3CO). ^{31}P{^{1}H} NMR (81.0 MHz, CD_2Cl_2, 20 °C): δ = 47.3 ppm (s). IR (Nujol): $\tilde{\nu}$ = 1924 (s) (C≡O), 1582 (C=O) cm^{-1}.

Synthesis of [Ru(OAc)(CO)(PPh_3)(ampy)]OAc (5)

Complex **5** was prepared following the procedure used for **4** employing ampy (35 µl, 0.34 mmol, 1.3 equiv.) in place of en. Yield: 106 mg (66%). Elemental analysis calcd (%) for $C_{29}H_{29}N_2O_5PRu$ (617.60): C 56.40, H 4.73, N 4.54; found: C 56.45, H 4.69, N 4.48. ^{1}H NMR (200.1 MHz, CD_2Cl_2, 20 °C): δ = 8.87 (m, 1H; NH_2), 8.54 (m, 1H; ortho-C*H* of C_5H_4N), 7.81 (td, $^3J_{HH}$ = 7.6 Hz, $^3J_{HH}$ = 1.6 Hz, 1H; para-C*H* of C_5H_4N), 7.77-7.67 (m, 5H; aromatic protons), 7.48-7.38 (m, 11H; aromatic protons), 7.32 (d, $^3J_{HH}$ = 7.7 Hz, 1H; meta-C*H* of C_5H_4N), 4.09 (dd, $^2J_{HH}$ = 16.0 Hz, $^3J_{HH}$ = 5.0 Hz, 1H; NCH_2), 3.87 (ddd, $^2J_{HH}$ = 16.0 Hz, $^3J_{HH}$ = 10.0 Hz, $^3J_{HH}$ = 5.0 Hz, 1H; NCH_2), 2.02 (s, 3H; CH_3CO), 1.33 (s, 3H; CH_3CO), 1.27 ppm (m, 1H; NH_2). ^{13}C{^{1}H} NMR (50.3 MHz, CD_2Cl_2, 20 °C): δ = 205.7 (d, $^2J_{CP}$ = 17.9 Hz; CO), 182.0 (s; CH_3CO), 177.7 (s; CH_3CO), 161.2 (d, $^3J_{CP}$ = 1.8 Hz; $NCCH_2$), 150.2 (s; ortho-*C*H of C_5H_4N), 138.4 (s; para-*C*H of C_5H_4N), 134.9-120.9 (m; aromatic carbon atoms), 52.9 (d, $^3J_{CP}$ = 2.3 Hz; NCH_2), 25.0 (s; CH_3CO), 24.2 ppm (s; CH_3CO). ^{31}P{^{1}H} NMR (81.0 MHz, CD_2Cl_2, 20 °C): δ = 49.8 ppm (s). IR (Nujol): $\tilde{\nu}$ = 1923 (s) (C≡O), 1579 (C=O) cm^{-1}.

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Synthesis of *trans*-[$RuCl_2(CO)(dppb)(PPh_3)$] (6)

[$RuCl_2(CO)(dmf)(PPh_3)_2$] (104 mg, 0.13 mmol) was suspended in $CHCl_3$ (5 mL) and reacted with dppb (55.4 mg, 0.13 mmol, 1 equiv.) stirring the mixture at 60 °C overnight. The obtained solution was concentrated to about 1 mL, and the complex precipitated by addition of *n*-heptane (10 mL). The solid was filtered, washed with of *n*-heptane (3x4 mL), diethyl ether (3x3 mL) and dried under reduced pressure. Yield: 87 mg (75%). Elemental analysis calcd (%) for $C_{47}H_{43}Cl_2OP_3Ru$ (888.76): C 63.52, H 4.88; found: C 63.56, H 4.94. ^{1}H NMR (200.1 MHz, CD_2Cl_2, 20 °C): δ = 7.77 (m, 4H; aromatic protons), 7.66-6.97 (m, 28H; aromatic protons), 6.82 (m, 3H; aromatic protons), 3.06 (m, 1H; CH_2), 2.72-2.10 (m, 4H; CH_2), 1.63 ppm (m, 3H; CH_2). ^{13}C{^{1}H} NMR (50.3 MHz, CD_2Cl_2, 20 °C): δ = 200.1 (dt, $^2J_{CP}$ = 11.9 Hz, $^2J_{CP}$ = 3.0 Hz; CO), 139.5-125.3 (m; aromatic carbon atoms), 33.0 (m; P*C*H_2), 30.6 (m; P*C*H_2), 25.4 (br s; *C*H_2), 22.2 ppm (br s; *C*H_2). ^{31}P{^{1}H} NMR (81.0 MHz, CD_2Cl_2, 20 °C): δ = 27.5 (t, $^2J_{PP}$ = 25.8 Hz, 1P), 16.4-14.8 ppm (m, 2P). IR (Nujol): $\tilde{\nu}$ = 1974 (s) (C≡O) cm^{-1}.

Synthesis of *trans*-[$RuCl_2(CO)(dppf)(PPh_3)$] (7)

[$RuCl_2(CO)(dmf)(PPh_3)_2$] (199 mg, 0.25 mmol) suspended in toluene (5 mL), was reacted with dppf (139 mg, 0.25 mmol, 1 equiv.) stirring the mixture at 110 °C for 2 h. The obtained solution was concentrated to about 1 mL, *n*-heptane (10 mL) was added and the suspension was stirred at room temperature for 1 h. The precipitate was filtered, washed with *n*-heptane (3x4 mL), diethyl ether (3x3 mL) and dried under reduced pressure. Yield: 99 mg (39%). Elemental analysis calcd (%) for $C_{53}H_{43}Cl_2FeOP_3Ru$ (1016.67): C 62.61, H 4.26; found: C 62.65, H 4.33. ^{1}H NMR (200.1 MHz, CD_2Cl_2, 20 °C): δ = 7.88-7.07 (m, 35H; aromatic protons), 4.53 (br s, 2H; C_5H_4), 4.44 (br s, 2H; C_5H_4), 4.30 (br s, 2H; C_5H_4), 4.16 ppm (br s, 2H; C_5H_4). ^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2, 20 °C): δ = 199.7 (br t, $^2J_{CP}$ = 16.0 Hz; CO), 135.2-125.0 (m; aromatic carbon atoms), 78.6 (d, $^1J_{CP}$ = 56.0 Hz; *ipso*-C_5H_4), 77.2 (d, $^1J_{CP}$ = 60.6 Hz; *ipso*-C_5H_4), 76.6 (d, $^2J_{CP}$ = 9.3 Hz; *C*H of C_5H_4), 75.7 (d, $^2J_{CP}$ = 9.8 Hz; *C*H of C_5H_4), 75.6 (d, $^2J_{CP}$ = 11.0 Hz; *C*H of C_5H_4), 74.8 (d, $^3J_{CP}$ = 7.2 Hz; *C*H of C_5H_4), 74.2 (d, $^3J_{CP}$ = 7.0 Hz; *C*H of C_5H_4), 72.6 (d, $^3J_{CP}$ = 6.0 Hz; *C*H of C_5H_4), 72.1 ppm (d, $^3J_{CP}$ = 6.4 Hz; *C*H of C_5H_4). ^{31}P{^{1}H} NMR (81.0 MHz, CD_2Cl_2, 20 °C): δ = 53.8 (m; 1P), 46.4 (m; 2P). IR (Nujol): $\tilde{\nu}$ = 1979 (s) (C≡O) cm^{-1}.

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Synthesis of *trans*-[$RuCl_2(CO)$((*R*)-BINAP)(PPh_3)] (8)

Complex **8** was prepared following the procedure used for **7**, with (*R*)-BINAP (156 mg, 0.25 mmol, 1 equiv.) in place of dppf. Yield: 239 mg (88%). Elemental analysis calcd (%) for $C_{63}H_{47}Cl_2OP_3Ru$ (1084.96): C 69.74, H 4.37; found: C 69.77, H 4.40. ^{1}H NMR (400.1 MHz, C_7D_8, 20 °C): δ = 8.73 (t, $^3J_{HH}$ = 8.6 Hz, 1H; aromatic proton), 8.14 (t, $^3J_{HH}$ = 8.8 Hz, 1H; aromatic proton), 7.77-7.68 (m, 1H; aromatic proton), 7.36-7.27 (m, 1H; aromatic proton), 7.24 (t, $^3J_{HH}$ = 8.8 Hz, 1H; aromatic proton), 7.13-6.93 (m, 20H; aromatic protons), 6.81-6.74 (m, 1H; aromatic proton), 6.70-6.63 (m, 2H; aromatic protons), 6.60-6.53 (m, 1H; aromatic proton), 6.49-6.38 (m, 2H; aromatic protons), 6.27 ppm (t, $^3J_{HH}$ = 6.0 Hz, 1H; aromatic proton). ^{13}C{^{1}H} NMR (100.6 MHz, C_7D_8, 20 °C): δ = 199.9 (dt, $^2J_{CP}$ = 83.6 Hz, $^2J_{CP}$ = 15.8 Hz; CO), 138.3-124.2 ppm (m; aromatic carbon atoms). ^{31}P{^{1}H} NMR (162.0 MHz, C_7D_8, 20 °C): δ = 31.2 (pseudo-t, $^2J_{PP}$ = 24.3 Hz, 1P; Ar*P*Ph_2), 25.8 (dd, $^2J_{PP}$ = 348.7 Hz, $^2J_{PP}$ = 25.2 Hz, 1P; *P*Ph_3), 21.3 ppm (dd, $^2J_{PP}$ = 348.6 Hz, $^2J_{PP}$ = 23.3 Hz, 1P; Ar*P*Ph_2). IR (Nujol): $\tilde{\nu}$ = 1981 (s) (C≡O) cm^{-1}.

Synthesis of *trans*-[$RuCl_2(CO)$((*R*,S_p)-Josiphos)(PPh_3)] (9)

Complex **9** was prepared following the procedure used for **7**, with (*R*,S_p)-Josiphos (146 mg, 0.25 mmol, 1 equiv.) in place of dppf. Yield: 227 mg (87%). Elemental analysis calcd (%) for $C_{55}H_{47}Cl_2FeOP_3Ru$ (1044.72): C 63.23, H 4.53; found: C 63.16, H 4.47. ^{1}H NMR (200.1 MHz, C_7D_8, 20 °C): δ = 8.66 (br s, 2H; aromatic protons), 8.07 (m, 2H; aromatic protons), 7.73 (m, 4H; aromatic protons), 7.32 (m, 3H; aromatic protons), 7.25-6.80 (m, 18H; aromatic protons), 6.74 (m, 4H; aromatic protons), 6.38 (m, 1H; aromatic proton), 5.84 (m, 1H; aromatic proton), 3.96 (br s, 5H; C_5H_5), 3.79 (br s, 1H; C_5H_3), 3.73 (br s, 1H; C_5H_3), 3.64 (br s, 1H; C_5H_3), 1.34 (m, 1H; C*H*CH_3), 1.13-0.96 ppm (m, 3H; CHC*H*$_3$). ^{13}C{^{1}H} NMR (100.6 MHz, C_7D_8, 20 °C): δ = 197.1 (m; CO), 142.8-124.2 (m; aromatic carbon atoms), 94.9 (dd, $^1J_{CP}$ = 18.7 Hz, $^3J_{CP}$ = 4.1 Hz; *ipso*-C_5H_3), 77.1 (dd, $^1J_{CP}$ = 40.4 Hz, $^3J_{CP}$ = 5.6; *ipso*-C_5H_3), 71.8 (s; C_5H_3), 71.6 (s; C_5H_3), 71.5 (s; C_5H_3), 69.7 (s; C_5H_5), 37.2 (d, $^1J_{CP}$ = 21.3 Hz; P*C*HCH$_3$), 13.8 ppm (d, $^2J_{CP}$ = 5.7 Hz; PCH*C*H$_3$). ^{31}P{^{1}H} NMR (81.0 MHz, C_7D_8, 20 °C): δ = 47.7 (pseudo-t, $^2J_{PP}$ = 23.0 Hz; 1P), 14.3 (dd, $^2J_{PP}$ = 357.2 Hz, $^2J_{PP}$ = 23.0 Hz; 1P), 12.0 ppm (dd, $^2J_{PP}$ = 357.2 Hz, $^2J_{PP}$ = 22.7 Hz; 1P). IR (Nujol): $\tilde{\nu}$ = 1979 (s) (C≡O) cm^{-1};

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Synthesis of *trans*-[$RuCl_2(CO)$((*R*,*R*)-Skewphos)(PPh_3)] (10)

Complex **10** was prepared following the procedure used for **7**, with (*R*,*R*)-Skewphos (110 mg, 0.25 mmol, 1 equiv.) in place of dppf. Yield: 147 mg (65%) as a mixture of two diastereoisomers. Elemental analysis calcd (%) for $C_{48}H_{45}Cl_2OP_3Ru$ (902.78): C 63.86, H 5.02; found: C 63.79, H 4.97. ^{1}H NMR (200.1 MHz, CD_2Cl_2, 20 °C): δ = 8.48 (m, 1H; aromatic proton), 8.04 (m, 4H; aromatic protons), 7.71-7.17 (m, 21H; aromatic protons), 7.15-6.92 (m, 8H; aromatic protons), 6.19 (m, 1H; aromatic proton), 4.07-3.81 (m, 1H; CH_2), 3.69-3.29 (m, 1H; CH_2), 3.14-2.87 (m, 1H; CH_2), 2.86-2.60 (m, 1H; CH_2), 2.34-1.66 (m, 2H; C*H*CH_3), 1.16 (dd, $^3J_{HP}$ = 13.7 Hz, $^3J_{HH}$ = 7.2 Hz; CHC*H*$_3$), 1.05 (dd, $^3J_{HP}$ = 11.7 Hz, $^3J_{HH}$ = 6.6 Hz; CHC*H*$_3$), 0.68 (dd, $^3J_{HP}$ = 11.5 Hz, $^3J_{HH}$ = 6.4 Hz; CHC*H*$_3$), 0.55 ppm (dd, $^3J_{HP}$ = 12.3 Hz, $^3J_{HH}$ = 7.2 Hz; CHC*H*$_3$). ^{31}P{^{1}H} NMR (81.0 MHz, CD_2Cl_2, 20 °C): δ = 28.6 (d, $^2J_{PP}$ = 29.3 Hz, 1P), 24.4 (d, $^2J_{PP}$ = 29.3 Hz, 2P), 22.6 (dd, $^2J_{PP}$ = 29.1 Hz, $^2J_{PP}$ = 20.9 Hz, 3P), 17.2 ppm (d, $^2J_{PP}$ = 20.4 Hz, 1P). IR (Nujol): $\tilde{\nu}$ = 1976 (s) (C≡O) cm^{-1}.

Synthesis of [$Ru(OAc)_2(CO)$(dppb)] (11)

[$Ru(OAc)_2(CO)(PPh_3)_2$] (300 mg, 0.39 mmol) was suspended in CH_2Cl_2 (5 mL) and reacted with dppb (166 mg, 0.39 mmol, 1 equiv.), stirring the mixture at RT overnight. The obtained solution was concentrated to about 0.5 ml evaporating the solvent under reduced pressure. The complex was precipitated by addition of *n*-heptane (10 mL), filtered, washed with *n*-heptane (3x4 mL) and diethyl ether (3x3 mL), and finally dried under reduced pressure. Yield: 231 mg (88%) as mixture of two isomers in a ratio of 3:1 at - 60 °C that interchanges at RT. Elemental analysis calcd (%) for $C_{33}H_{34}O_5P_2Ru$ (673.65): C 58.84, H 5.09; found: C 58.80, H 5.10. ^{1}H NMR (200.1 MHz, CD_2Cl_2, 20 °C): δ = 7.85-7.23 (m, 20H; aromatic protons), 2.84 (m, 2H; PCH_2), 2.45 (m, 2H; PCH_2), 1.98-1.66 (m, 4H; CH_2CH_2), 1.42 ppm (s, 6H; CH_3CO). ^{1}H NMR (200.1 MHz, CD_2Cl_2, - 80 °C): δ = 8.05-7.74 (m, 3H; aromatic protons), 7.72-7.20 (m, 15H; aromatic protons), 7.03 (t, $^3J_{HH}$ = 8.3 Hz, 2H; aromatic protons), 3.30-2.36 (m, 3H; CH_2), 2.29-1.38 (m, 5H; CH_2), 1.56 (s, 3H; CH_3CO minor isomer), 1.42 (s, 3H; CH_3CO minor isomer), 1.34 (s, 3H; CH_3CO major isomer), 1.14 ppm (s, 3H; CH_3CO major isomer). ^{13}C{^{1}H} NMR (50.3 MHz, CD_2Cl_2, 20 °C): δ = 204.8 (m; CO), 135.1-128.6 (m; aromatic carbon atoms), 30.3 (br s; *C*H_2), 29.7 (br s; *C*H_2), 23.7 (br s; *C*H_3CO), 23.6 ppm (br s; *C*H_2). ^{13}C{^{1}H} NMR (50.3 MHz, CD_2Cl_2, - 80 °C): δ = 204.5 (dd, $^2J_{CP}$ = 21.6 Hz, $^2J_{CP}$ = 15.8 Hz; CO), 202.6 (t, $^2J_{CP}$ = 17.0 Hz; CO), 189.1 (s; CH_3*C*O), 182.4 (t, $^3J_{CP}$ = 38.5 Hz; CH_3*C*O), 175.3 (d, $^3J_{CP}$ = 2.6 Hz; CH_3*C*O), 137.3-122.7 (m; aromatic carbon atoms), 29.9 (d, $^1J_{CP}$ = 35.3 Hz; P*C*H_2), 27.7 (d, $^1J_{CP}$ = 32.7 Hz; P*C*H_2), 25.2 (br s; *C*H_2), 24.4 (s; *C*H_3CO), 21.9 (d, $^4J_{CP}$ = 4.3 Hz; *C*H_3CO), 20.5 ppm (br s;

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CH_2). $^{31}P\{^1H\}$ NMR (81.0 MHz, CD_2Cl_2, 20 °C): δ = 46.8 ppm (br s). $^{31}P\{^1H\}$ NMR (81.0 MHz, CD_2Cl_2, - 60 °C): δ = 48.2 (d, $^2J_{PP}$ = 27.0 Hz, major isomer), 46.1 (d, $^2J_{PP}$ = 27.0 Hz, major isomer), 43.3 ppm (br s, minor isomer). $^{31}P\{^1H\}$ NMR (81.0 MHz, CD_2Cl_2, - 80 °C): δ = 48.0 (d, $^2J_{PP}$ = 26.4 Hz, major isomer), 46.2 (d, $^2J_{PP}$ = 26.4 Hz, major isomer), 45.2-34.0 ppm (br m; minor isomer). IR (Nujol): $\tilde{\nu}$ = 1954 (s) (C≡O), 1614 (s), 1571 (s) (C=O) cm^{-1}.

Synthesis of [Ru(OAc)$_2$(CO)(dppf)] (12)

[Ru(OAc)$_2$(CO)(PPh_3)$_2$] (200 mg, 0.26 mmol) suspended in toluene (5 mL), was added of dppf (144 mg, 0.26 mmol, 1 equiv.) and the mixture was stirred at reflux for 2 h. The resulting solution was concentrated to about 1 mL evaporating the solvent under reduced pressure, and the complex was precipitated by addition of *n*-heptane (10 mL). The solid was filtered, washed with *n*-heptane (3x4 mL) and diethyl ether (3x3 mL), and dried under reduced pressure. Yield: 140 mg (67%) as mixture of 3 isomers in a 7:2:1 ratio at - 70 °C that interchanges at RT. Elemental analysis calcd (%) for $C_{39}H_{34}FeO_5P_2Ru$ (801.56): C 58.44, H 4.28; found: C 58.38, H 4.30. ^1H NMR (200.1 MHz, CD_2Cl_2, 20 °C): δ = 7.91-7.11 (br m, 20 H; aromatic protons), 4.80-4.06 (br m, 8H; C_5H_4), 1.56 ppm (br s, 6H; CH_3CO). ^1H NMR (200.1 MHz, CD_2Cl_2, - 70 °C): δ = 7.94 (t, $^3J_{HH}$ = 9.0 Hz; aromatic protons), 7.74 (t, $^3J_{HH}$ = 8.6 Hz; aromatic protons), 7.63-7.23 (m, aromatic protons), 4.97-3.97 (m; C_5H_4), 1.73 (s; CH_3CO major isomer), 1.61 (s; CH_3CO major isomer), 1.46 (s; CH_3CO), 1.38 (s; CH_3CO), 1.33 ppm (s; CH_3CO). $^{13}C\{^1H\}$ NMR (50.3 MHz, CD_2Cl_2, 20 °C): δ = 134.6-127.2 (m; aromatic carbon atoms), 75.6 (dd, $^2J_{CP}$ = 37.0 Hz, $^4J_{CP}$ = 4.3 Hz; C_5H_4), 73.1 (br m; C_5H_4), 72.6 (br m; C_5H_4), 24.2 ppm (br s; *C*H_3CO). $^{13}C\{^1H\}$ NMR (50.3 MHz, CD_2Cl_2, - 70 °C): δ = 203.3 (t, $^2J_{CP}$ = 16.9 Hz; CO), 188.9 (s; CH_3*C*O), 182.8 (s; CH_3*C*O major isomer), 182.0 (br s; CH_3*C*O major isomer), 175.7 (s; CH_3*C*O), 135.0-126.1 (m; aromatic carbon atoms), 79.0-76.1 (m; ipso-C_5H_4), 76.0 (d, J_{CP} = 5.4 Hz; C_5H_4), 75.4 (d, J_{CP} = 7.3 Hz; C_5H_4), 75.0 (d, J_{CP} = 7.4 Hz; C_5H_4), 74.4 (d, J_{CP} = 8.9 Hz; C_5H_4 major isomer), 72.7 (d, J_{CP} = 6.1 Hz; C_5H_4 major isomer), 71.8 (d, J_{CP} = 5.4 Hz; C_5H_4), 71.1 (d, J_{CP} = 5.4 Hz; C_5H_4), 25.4 (s; *C*H_3CO major isomer), 24.5 (d, $^4J_{CP}$ = 4.8 Hz; *C*H_3CO), 23.8 ppm (s; *C*H_3CO major isomer). $^{31}P\{^1H\}$ NMR (81.0 MHz, CD_2Cl_2, 20 °C): δ = 50.7 ppm (br s). $^{31}P\{^1H\}$ NMR (81.0 MHz, CD_2Cl_2, - 70 °C): δ = 53.1 (d, $^2J_{PP}$ = 26.8 Hz), 52.0 (d, $^2J_{PP}$ = 27.5 Hz), 50.4 (d, $^2J_{PP}$ = 27.5 Hz), 49.8 (d, $^2J_{PP}$ = 30.4 Hz; major isomer), 45.4 (d, $^2J_{PP}$ = 30.4 Hz; major isomer), 43.5 ppm (d, $^2J_{PP}$ = 26.8 Hz). IR (Nujol): $\tilde{\nu}$ = 1974 (s) (C≡O), 1613 (s), 1569 (s) (C=O) cm^{-1}.

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Synthesis of [Ru(OAc)$_2$(CO)((*R*)-BINAP)] (13)

Complex **13** was prepared following the procedure used for **12** employing (*R*)-BINAP (162 mg, 0.26 mmol, 1 equiv.) in place of dppf. Yield: 210 mg (93%) as mixture of a predominant species (60%) and several other isomers at - 60 °C that interchanges at RT. Elemental analysis calcd (%) for $C_{49}H_{38}O_5P_2Ru$ (869.86): C 67.66, H 4.40; found: C 67.70, H 4.32. ^{1}H NMR (200.1 MHz, CD_2Cl_2, 20 °C): δ = 7.90 (m, 2H; aromatic protons), 7.71-7.24 (m, 20H; aromatic protons), 7.23-6.97 (m, 2H; aromatic protons), 6.87 (d, $^3J_{HH}$ = 8.4 Hz, 2H; aromatic protons), 6.79 (d, $^3J_{HH}$ = 6.6 Hz, 2H; aromatic protons), 6.69 (d, $^3J_{HH}$ = 8.4 Hz, 2H; aromatic protons), 6.60 (d, $^3J_{HH}$ = 6.5 Hz, 2H; aromatic protons), 1.29 ppm (br s, 6H; CH_3CO). ^{1}H NMR (200.1 MHz, CD_2Cl_2, - 60 °C): δ = 8.02-5.94 (m, 32H; aromatic protons), 1.91 (s, 3H; CH_3CO major isomer), 1.19 ppm (s, 3H; CH_3CO major isomer). ^{13}C{^{1}H} NMR (50.3 MHz, CD_2Cl_2, - 60 °C): δ = 205.0 (t, $^2J_{CP}$ = 27.2 Hz; CO), 189.1 (d, $^3J_{CP}$ = 3.6 Hz; CH_3CO major isomer), 183.2 (s; CH_3CO), 182.2 (s; CH_3CO), 181.0 (s; CH_3CO), 176.0 (d, $^3J_{CP}$ = 4.3 Hz; CH_3CO major isomer), 139.40-124.62 (m; aromatic carbon atoms), 25.9 (s; CH_3CO), 24.5 (s; CH_3CO major isomer), 23.8 (d, $^4J_{CP}$ = 7.3 Hz; CH_3CO), 22.3 (d, $^4J_{CP}$ =7.4 Hz; CH_3CO major isomer), 21.1 ppm (s; CH_3CO). ^{31}P{^{1}H} NMR (81.0 MHz, CD_2Cl_2, 20 °C): δ = 50.5 (d, $^2J_{PP}$ = 25.3 Hz), 43.4 ppm (br s). ^{31}P{^{1}H} NMR (81.0 MHz, CD_2Cl_2, - 60 °C): δ = 49.6 (d, $^2J_{PP}$ = 27.6 Hz; major isomer), 40.1 ppm (d, $^2J_{PP}$ = 27.6 Hz; major isomer). IR (Nujol): $\tilde{\nu}$ = 1975 (s) (C≡O), 1616 (s), 1505 (s) (C=O) cm^{-1}.

Synthesis of [Ru(OAc)$_2$(CO)((*R*,*R*)-Skewphos)] (14)

Complex **14** was prepared following the procedure used for **12** employing (*R*,*R*)-Skewphos (115 mg, 0.26 mmol, 1 equiv.) in place of dppf. Yield: 127 mg (71%) as mixture of several isomers at - 60 °C that interchanges at RT. Elemental analysis calcd (%) for $C_{34}H_{36}O_5P_2Ru$ (687.67): C 59.38, H 5.28; found: C 59.29, H 5.21. ^{1}H NMR (200.1 MHz, CD_2Cl_2, 20 °C): δ = 7.77-7.47 (m, 13H; aromatic protons), 7.46-7.33 (m, 3H; aromatic protons),7.32-7.08 (m, 4H; aromatic protons), 3.15 (m, 1H; PC*H*CH_3), 2.73 (m, 1H; PC*H*CH_3), 2.37-2.01 (m, 1H; CHC*H*$_2$), 1.99-1.68 (m, 1H; CHC*H*$_2$), 1.58 (br s, 6H; CH_3CO), 1.01 (dd, $^3J_{HP}$ = 15.6 Hz, $^3J_{HH}$ = 7.5 Hz, 3H; CHC*H*$_3$), 0.89 ppm (dd, $^3J_{HP}$ = 12.5 Hz, $^3J_{HH}$ = 7.0 Hz, 3H; CHC*H*$_3$). ^{1}H NMR (200.1 MHz, CD_2Cl_2, - 60 °C): δ = 9.46 (m; aromatic proton), 7.72 (t, ^3J(H,H) = 9.2 Hz; aromatic proton), 7.65-7.20 (m; aromatic protons), 7.07 (m; aromatic proton), 6.92 (t, $^3J_{HH}$ = 9.2 Hz; aromatic proton), 3.10 (m; PC*H*CH_3), 2.83 (m; PC*H*CH_3), 2.68 (m; PC*H*CH_3), 2.32-1.81 (m, 1H; CHC*H*$_2$), 1.75 (br s; CH_3CO), 1.66 (s; CH_3CO), 1.56-1.46 (m, 1H; CHC*H*$_2$), 1.25 (br s; CH_3CO), 0.90 (dd, $^3J_{HP}$ = 15.2 Hz, $^3J_{HH}$ = 6.6 Hz; CHC*H*$_3$), 0.75 ppm (dd, $^3J_{HP}$

= 12.2 Hz, $^3J_{HH}$ = 6.4 Hz; CHC*H*$_3$). $^{13}C\{^1H\}$ NMR (50.3 MHz, CD_2Cl_2, - 60 °C): δ = 203.4 (m; CO), 201.80 (t, $^2J_{CP}$ = 16.9 Hz; CO major isomer), 189.0 (s; CH_3CO), 187.4 (s; CH_3CO), 183.1 (s; CH_3CO), 182.6 (s; CH_3CO), 181.9 (s; CH_3CO major isomer), 180.8 (s; CH_3CO), 176.4 (s; CH_3CO), 174.8 (s; CH_3CO), 136.8-122.4 (m; aromatic carbon atoms), 36.2 (br s; $CHCH_2$), 35.5 (br s; $CHCH_2$), 35.0 (br s; $CHCH_2$ major isomer), 34.5 (br s; $CHCH_2$), 31.0 (d, $^1J_{CP}$ = 31.6 Hz; P*C*H), 30.0 (d, $^1J_{CP}$ = 35.0 Hz; P*C*H major isomer), 25.2 (s; *C*H$_3$CO major isomer), 24.9 (d, $^4J_{CP}$ = 2.1 Hz; *C*H$_3$CO), 24.7 (s; *C*H$_3$CO), 23.7 (s; *C*H$_3$CO), 23.1 (d, $^4J_{CP}$ = 4.6 Hz; *C*H$_3$CO), 21.7 (s; *C*H$_3$CO), 21.0 (s; *C*H$_3$CO), 18.3-17.7 (m; P*C*H), 15.8 (s; CH*C*H$_3$), 15.2 (s; CH*C*H$_3$ major isomer), 15.0 (s; CH*C*H$_3$), 14.7 ppm (s; CH*C*H$_3$). $^{31}P\{^1H\}$ NMR (81.0 MHz, CD_2Cl_2, 20 °C): δ = 55.0 (br s), 50.6 ppm (br s). $^{31}P\{^1H\}$ NMR (81.0 MHz, CD_2Cl_2, - 60 °C): δ = 59.5 (d, $^2J_{PP}$ = 35.1 Hz), 58.6 (d, $^2J_{PP}$ = 33.8 Hz), 56.7 (d, $^2J_{PP}$ = 34.2 Hz), 54.3 (d, $^2J_{PP}$ = 38.8 Hz; major isomer), 52.3 (d, $^2J_{PP}$ = 38.7 Hz), 51.6 (d, $^2J_{PP}$ = 36.5 Hz), 48.8 (d, $^2J_{PP}$ = 38.8 Hz; major isomer), 48.1 (d, $^2J_{PP}$ = 34.6 Hz), 48.0 (d, $^2J_{PP}$ = 36.5 Hz), 47.0 (d, $^2J_{PP}$ = 28.2 Hz), 46.1 ppm (d, $^2J_{PP}$ = 33.8 Hz). IR (Nujol): $\tilde{\nu}$ = 1958 (s) (C≡O), 1568 (s) (C=O) cm^{-1}.

Synthesis of [RuCl(CO)(dppb)(en)]Cl (15)

Method A: $[RuCl_2(CO)(dmf)(PPh_3)_2]$ (200 mg, 0.25 mmol) was dissolved in CH_2Cl_2 (5 mL) and reacted with dppb (124 mg, 0.29 mmol, 1.2 equiv.), stirring the mixture for 2 h at RT. En (25 µL, 0.37 mmol, 1.5 equiv) was then added and the slurry was stirred at RT for other 2 h. The resulting solution was concentrated to about 0.5 mL by evaporation of the solvent under reduced pressure and the complex was precipitated by addition of *n*-heptane (10 mL). The solid was filtered, washed with diethyl ether (4x3 mL) and dried under reduced pressure. Yield: 149 mg (87%). Elemental analysis calcd (%) for $C_{31}H_{36}Cl_2N_2OP_2Ru$ (686.56): C 54.23, H 5.29, N 4.08; found: C 54.18, H 5.22, N 4.10. ^1H NMR (200.1 MHz, $CDCl_3$, 20 °C): δ = 7.62-7.48 (m, 4H; aromatic protons), 7.44-7.35 (m, 16H; aromatic protons), 4.94 (m, 2H; NH_2), 3.60 (m, 2H; NH_2), 2.96-2.38 (m, 4H; CH_2 and CH_2N), 2.35-1.65 ppm (m, 8H; CH_2 and CH_2N). $^{13}C\{^1H\}$ NMR (50.3 MHz, CD_2Cl_2, 20 °C): δ = 199.5 (t, $^2J_{CP}$ = 13.6 Hz; CO), 136.9-128.6 (aromatic carbon atoms), 45.9 (s; *C*H$_2$N), 25.5 (t, $^1J_{CP}$ = 14.8 Hz; P*C*H$_2$), 22.1 ppm (s; PCH$_2$*C*H$_2$). $^{31}P\{^1H\}$ NMR (81.0 MHz, CD_2Cl_2, 20 °C): δ = 37.4 ppm (s). IR (Nujol): $\tilde{\nu}$ = 1969 (s) (C≡O) cm^{-1}.

Method B: $[RuCl_2(CO)_2]_n$ (50 mg, 0.22 mmol) was suspended in 2-propanol (5 mL) and reacted with dppb (94 mg, 0.22 mmol, 1 equiv.) stirring the mixture for 2 h at 90 °C. En (15 µL, 0.22 mmol, 1 equiv.) was added and the obtained solution was stirred for other 2 h at 90 °C, and then evaporated under reduced pressure. The residue was dissolved in $CHCl_3$ (3 mL) and stirred for 3 h at RT. The

volume was reduced by half, and the product was precipitated by addition of *n*-pentane (5 mL). The solid was filtered, washed with diethyl ether (2x10 mL) and dried under reduced pressure. Yield: 140 mg (93%).

Synthesis of [RuCl(CO)(dppf)(en)]Cl (16)

Complex **16** was prepared following the procedure used for **15** (method A) employing dppf (160 mg, 0.29 mmol, 1.2 equiv.) in place of dppb. Yield: 179 mg (88%). Elemental analysis calcd (%) for $C_{37}H_{36}Cl_2FeN_2OP_2Ru$ (814.48): C 54.56, H 4.46, N 3.44; found: C 54.50, H 4.51, N 3.47. ^{1}H NMR (200.1 MHz, CD_2Cl_2, 20 °C): δ = 7.80-7.35 (m, 20H; aromatic protons), 5.59 (br s, 2H; C_5H_4), 5.05 (m, 1H; NH_2), 4.53 (br s, 2H; C_5H_4), 4.20 (br s, 2H; C_5H_4), 3.97 (br s, 2H; C_5H_4), 3.53 (br s, 1H; NH_2), 3.12-2.62 (m, 4H; CH_2N), 2.51 (br s, 1H; NH_2), 1.98 ppm (br s, 1H; NH_2). ^{13}C{^{1}H} NMR (50.3 MHz, CD_2Cl_2, 20 °C): δ = 199.9 (t, $^2J_{CP}$ = 14.4 Hz; CO), 135.9-128.4 (m; aromatic carbon atoms), 89.7 (d, $^1J_{CP}$ = 55.1 Hz; *ipso*-C_5H_4), 89.0 (d, $^1J_{CP}$ = 52.4 Hz; *ipso*-C_5H_4), 77.9 (t, J_{CP} = 4.9 Hz; C_5H_4), 75.8 (t, J_{CP} = 3.1 Hz; C_5H_4), 73.6 (t, J_{CP} = 3.3 Hz; C_5H_4), 71.4 (t, J_{CP} = 3.0 Hz; C_5H_4), 45.8 ppm (s; CH_2N). ^{31}P{^{1}H} NMR (81.0 MHz, CD_2Cl_2, 20 °C): δ = 39.8 ppm (s). IR (Nujol): $\tilde{\nu}$ = 1960 (s) (C≡O) cm^{-1}.

Synthesis of [Ru(OAc)(CO)(dppb)(en)]OAc (17)

[$Ru(OAc)_2(CO)(PPh_3)_2$] (200 mg, 0.26 mmol) was suspended in CH_2Cl_2 (2 mL) and reacted with dppb (122 mg, 0.29 mmol, 1.1 equiv.) stirring the mixture at RT for 6 h. En (25 µL, 0.37 mmol, 1.4 equiv.) was added to the resulting solution that was stirred at RT for further 2 h. The solvent was reduced by evaporation under reduced pressure to about 0.5 mL and the product was precipitated by addition of *n*-heptane (10 mL). The obtained solid was filtered, washed with diethyl ether (4x3 mL) and dried under reduced pressure. Yield: 185 mg (97%). Elemental analysis calcd (%) for $C_{35}H_{42}N_2O_5P_2Ru$ (733.75): C 57.29, H 5.77, N 3.82; found: C 57.33, H 5.80, N 3.80. ^{1}H NMR (200.1 MHz, CD_3OD, 20 °C): δ = 7.68-7.29 (m, 20H; aromatic protons), 7.27 (br s, 1H; NH_2), 4.72 (m, 1H; NH_2), 4.22 (m, 1H; NH_2), 4.03 (m, 1H; NCH_2), 2.94-2.41 (m, 6H; PCH_2 + CH_2N), 2.55 (br s, 4H; CH_2CH_2), 1.86 (s, 3H; CH_3CO), 1.58 (s, 3H; CH_3CO), 1.24 ppm (br s, 1H; NH_2). ^{13}C{^{1}H} NMR (50.3 MHz, CD_3OD, 20 °C): δ = 203.9 (t, $^2J_{CP}$ = 14.8 Hz; CO), 182.8 (s; CH_3CO), 182.5 (s; CH_3CO), 137.8-129.1 (m; aromatic carbon atoms), 46.6 (d, $^3J_{CP}$ = 11.0 Hz; CH_2N), 44.9 (br s; CH_2N), 33.1 (br s; CH_2), 30.0 (d, $^1J_{CP}$ = 21.5 Hz; PCH_2), 29.8 (d, $^1J_{CP}$ = 28.9 Hz; PCH_2), 25.6 (s; CH_3CO), 24.1 (s;

*C*H$_3$CO), 23.5 ppm (br s; *C*H$_2$). ^{31}P{^{1}H} NMR (81.0 MHz, CD$_3$OD, 20 °C): δ = 37.1 ppm (s). IR (Nujol): $\tilde{\nu}$ = 1939 (s) (C≡O), 1558 (s) (C=O) cm^{-1}.

Synthesis of [Ru(OAc)(CO)(dppb)(ampy)]OAc (18)

Complex **11** (124 mg, 0.184 mmol) was suspended in of toluene (3 mL) and reacted with ampy (19 µL, 0.184 mmol, 1 equiv.), stirring the mixture at RT for 30 min. The resulting solution was concentrated to about 1 mL and the product was precipitated by addition of *n*-heptane (5 mL). The obtained solid was filtered and washed with diethyl ether (4x5 mL) and dried under reduced pressure. Yield: 125 mg (87%). Elemental analysis calcd (%) for C$_{39}$H$_{42}$N$_2$O$_5$P$_2$Ru (781.79): C 59.92, H 5.41, N 3.58; found: C 60.03, H 5.50, N 3.50. ^{1}H NMR (200.1 MHz, C$_7$D$_8$, 20 °C): δ = 8.15 (m, 1H; ortho-C*H* of C$_5$H$_4$N), 7.62-6.81 (m, 22H; aromatic protons), 6.61 (d, $^3J_{HH}$ = 7.7 Hz, 1H; meta-C*H* of C$_5$H$_4$N), 6.21 (pseudo-t, J_{HH} = 8.8 Hz, 1H; NH$_2$), 4.22 (dd, $^2J_{HH}$ = 12.4 Hz, $^3J_{HH}$ = 10.2 Hz, 1H; CH$_2$N), 3.21 (dd, $^2J_{HH}$ = 12.4 Hz, $^3J_{HH}$ = 10.7 Hz, 1H; CH$_2$N), 3.02 (m, 1H; PCH$_2$), 2.56 (m, 1H; PCH$_2$), 2.04 (s, 3H; CH$_3$CO), 1.94 (s, 3H; CH$_3$CO), 1.67 (m, 2H; PCH$_2$ + NH$_2$), 1.49-1.14 ppm (m, 5H; PCH$_2$CH$_2$). ^{13}C{^{1}H} NMR (50.3 MHz, C$_7$D$_8$, 20 °C): δ = 203.2 (t, $^2J_{CP}$ = 12.7 Hz; CO), 187.6 (s; CH$_3$*C*O), 177.0 (s; CH$_3$*C*O), 159.8 (d, $^3J_{CP}$ = 3.8 Hz; N*C*CH$_2$), 149.1 (d, $^3J_{CP}$ = 22.9 Hz; ortho-*C*H of C$_5$H$_4$N), 135.7-120.8 (m; aromatic carbon atoms), 50.4 (s; *C*H$_2$N), 30.2 (d, $^1J_{CP}$ = 33.5 Hz; P*C*H$_2$), 29.8 (d, $^1J_{CP}$ = 36.1 Hz; P*C*H$_2$), 26.1 (d, $^2J_{CP}$ = 2.7 Hz; *C*H$_2$), 25.8 (s; *C*H$_3$CO), 24.6 ppm (d, $^4J_{CP}$ = 4.8 Hz; *C*H$_3$CO). ^{31}P{^{1}H} NMR (81.0 MHz, C$_7$D$_8$, 20 °C): δ = 46.4 (d, $^2J_{PP}$ = 28.8 Hz), 34.0 ppm (d, $^2J_{PP}$ = 28.8 Hz). IR (Nujol): $\tilde{\nu}$ = 1944 (s) (C≡O), 1608 (s), 1586 (s) (C=O) cm^{-1}.

Synthesis of [Ru(OAc)(CO)(dppf)(en)]OAc (19)

Complex **12** (128 mg, 0.159 mmol), was suspended in toluene (3 mL) and reacted with en (12 µL, 0.179 mmol, 1.1 equiv), heating the mixture at 90 °C for 3 h under vigorous stirring. Addition of *n*-heptane (10 mL) afforded the precipitation of the product that was filtered, washed with diethyl ether (3x5 mL) and finally dried under reduced pressure. Yield: 121 mg (88%). Elemental analysis calcd (%) for C$_{41}$H$_{42}$FeN$_2$O$_5$P$_2$Ru (861.66): C 57.15, H 4.91, N 3.25; found: C 57.10, H 4.90, N 3.21. ^{1}H NMR (200.1 MHz, CD$_2$Cl$_2$, 20 °C): δ = 7.90-7.61 (m, 8H; aromatic protons), 7.60-7.22 (m, 12H; aromatic protons), 5.27 (br s partially overlapped with solvent peak, 1H; NH$_2$), 4.55 (br s, 1H; C$_5$H$_4$), 4.42 (br s, 5H; C$_5$H$_4$), 4.16 (br s, 2H; C$_5$H$_4$), 2.87 (br s, 4H; CH$_2$N), 2.62 (br s, 2H; NH$_2$), 1.79 (br s, 6H; CH$_3$CO), 1.27 ppm (br s. 1H; NH$_2$). ^{13}C{^{1}H} NMR (50.3 MHz, CD$_2$Cl$_2$, 20 °C): δ = 203.2 (t, $^2J_{CP}$ = 15.1 Hz; *C*O), 181.4 (s; CH$_3$*C*O), 176.6 (dd, $^3J_{CP}$ = 12.1 Hz, $^3J_{CP}$ = 5.6 Hz; CH$_3$*C*O), 135.5-

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128.5 (m; aromatic carbon atoms), 79.6 (dd, $^{1}J_{CP}$ = 65.8 Hz, $^{3}J_{CP}$ = 9.6 Hz; ipso-C_5H_4), 75.7 (dt, J_{CP} = 18.9 Hz, J_{CP} = 4.3 Hz; C_5H_4), 73.0 (dt, J_{CP} = 14.6 Hz, J_{CP} = 2.9 Hz; C_5H_4), 45.7 (s; CH_2N), 26.1 ppm (s; CH_3CO). $^{31}P\{^{1}H\}$ NMR (81.0 MHz, CD_2Cl_2, 20 °C): δ = 40.1 ppm (s). IR (Nujol): $\tilde{\nu}$ = 1963 (s) (C≡O), 1617 (s), 1569 (s) (C=O) cm^{-1}.

Synthesis of [Ru(OAc)(CO)(dppf)(ampy)]OAc (20)

Complex **20** was prepared following the procedure used for **18** employing the precursor **12** (120 mg, 0.150 mmol) in place of **11**. Yield: 119 mg (87%). Elemental analysis calcd (%) for $C_{45}H_{42}FeN_2O_5P_2Ru$ (909.70): C 59.41, H 4.65, N 3.08; found: C 59.33, H 4.60, N 3.02. ^{1}H NMR (200.1 MHz, C_7D_8, 20 °C): δ = 8.68 (d, $^{3}J_{HH}$ = 4.9 Hz, 1H; ortho-C*H* of C_5H_4N), 8.00 (dd, $^{3}J_{HH}$ = 7.9 Hz, $^{4}J_{HH}$ = 1.5 Hz, 1H; para-C*H* of C_5H_4N), 7.46-6.79 (m, 21H; aromatic protons), 6.61 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H; meta-C*H* of C_5H_4N), 6.07 (pseudo-t, J_{HH} = 9.2 Hz, 1H; NH_2), 4.84 (m, 1H; CH_2N), 4.77 (s, 1H; C_5H_4), 4.22 (s, 1H; C_5H_4), 3.91 (s, 1H; C_5H_4), 3.72 (br s, 4H; C_5H_4), 3.42 (s, 1H; C_5H_4), 2.55 (t, $^{3}J_{HH}$ = 13.5 Hz, 1H; CH_2N), 2.33 (m, 1H; NH_2), 1.85 (s, 3H; CH_3CO), 1.67 ppm (s, 3H; CH_3CO). $^{13}C\{^{1}H\}$ NMR (50.3 MHz, C_7D_8, 20 °C): δ = 210.3 (t, $^{2}J_{CP}$ = 16.4 Hz; CO), 178.4 (s; CH_3CO), 177.0 (d, $^{3}J_{CP}$ = 2.7 Hz; CH_3CO), 160.1 (d, $^{2}J_{CP}$ = 3.7 Hz; $NCCH_2$), 149.1 (s; ortho-*C*H of C_5H_4N), 137.1-121.2 (m; aromatic carbon atoms), 81.5 (d, $^{1}J_{CP}$ = 51.0 Hz; ipso-C_5H_4), 81.4 (d, $^{1}J_{CP}$ = 49.3 Hz; ipso-C_5H_4), 77.0 (d, J_{CP} = 4.0 Hz; C_5H_4), 76.5 (d, J_{CP} = 7.3 Hz; C_5H_4), 75.3 (d, J_{CP} = 7.3 Hz; C_5H_4), 75.0 (d, J_{CP} = 5.2 Hz; C_5H_4), 74.8 (s; C_5H_4), 71.3 (d, J_{CP} = 5.2 Hz; C_5H_4), 70.3 (d, J_{CP} = 5.7 Hz; C_5H_4), 50.4 (s; CH_2N), 26.1 (s; CH_3CO), 24.6 ppm (d, $^{4}J_{CP}$ = 4.9 Hz; CH_3CO). $^{31}P\{^{1}H\}$ NMR (81.0 MHz, C_7D_8, 20 °C): δ = 51.2 (d, $^{2}J_{PP}$ = 29.1 Hz), 40.5 ppm (d, $^{2}J_{PP}$ = 29.1 Hz). IR (Nujol): $\tilde{\nu}$ = 1959 (s) (C≡O), 1609 (s), 1586 (s) (C=O) cm^{-1}.

Procedure for the TH of ketones and aldehydes

The ruthenium catalyst solution used for TH was prepared by dissolving the ruthenium complexes **1-16**, **18** (0.02 mmol) in 5 mL of 2-propanol. A 0.1 M solution of NaO*i*Pr (200 μL, 20 μmol) in 2-propanol and the catalyst solution (250 μL, 1.0 μmol) were added to the ketone or aldehyde solution (1.0 mmol) in 2-propanol (final volume 10 mL) and the resulting mixture was heated under reflux. The reaction was sampled by removing an aliquot of the reaction mixture (0.5 mL), which was quenched by addition of diethyl ether (1:1 v/v), filtered over a short silica pad, and submitted to GC analysis. The addition of the Ru complex was considered as the start time of the reaction. The S/C molar ratio was 1000/1, whereas the base concentration was 2 mol% respect to the substrate (0.1 M).

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Typical procedure for TH of acetophenone with *in situ* prepared catalysts from 6-14

The catalyst solutions were prepared by adding 2-propanol (5 mL) to the complexes **6-14** (0.02 mmol) and the corresponding NN bidentate ligand (0.04 mmol). The mixtures were stirred for 30 min at reflux. The solutions of the *in situ* formed catalyst were used in the TH reactions as described above.

Procedure for the HY of ketones with catalysts 1-3, 15

The HY reactions were performed in an 8 vessels Endeavor Biotage apparatus. The vessels were charged with the ruthenium catalysts (2.5 μmol), loaded with 5 bar of N_2 and slowly vented (five times). The ketones (5 mmol) and the KO*t*Bu solution (1 mL, 0.1 mmol, 0.1 M) in ethanol were added. Further addition of ethanol led to a 2 M ketone solution. The vessels were purged with N_2 and H_2 (three times each), then the system was charged with H_2 (30 bar) and heated to 70 °C for the required time (3 or 16 h). The S/C molar ratio was 2000/1, whereas the base concentration was 2 mol%. A similar method was applied for the reactions with other S/C (in the range 500-10000) using the appropriate amount of catalysts, base, ligands (ligand/catalyst ratio = 2) and solvent. The reaction vessels were then cooled to room temperature vented and purged three times with N_2. A drop of the reaction mixture was then diluted with 1 mL of methanol and analyzed by GC.

†Electronic supplementary information (ESI) available: NMR spectra of the isolated complexes and further data of aldehyde and ketone TH and HY catalyzed by the ruthenium derivatives. For ESI and other electronic format, see DOI: 10.1039/x0xx00000x.

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Conflicts of interest

The authors declare no competing financial interests.

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52. ampy = 2-(aminomethyl)pyridine; en = 1,2-ethylendiamine; (*R*,*R*)- or (*S*,*S*)-DPEN = (1*R*,2*R*)- or (1*S*,2*S*)-1,2-diphenylethylenediamine; (±)-iPr-ampy = (rac)-2-methyl-1-(pyridin-2-yl)propan-1-amine; dppb = 1,4-bis(diphenylphosphino)butane; dppp = 1,3-bis(diphenylphosphino)propane; 1,1'-bis(diphenylphosphino)ferrocene; dippf = 1,1'-bis(disopropylphosphino)ferrocene; (R,S_p)-Josiphos = (*R*)-1-[(S_p)-2-(diphenylphosphino)ferrocenylethyl]diphenylphosphine; (*R*)-BINAP = (*R*)-(+)-2,2'-bis(diphenylphosphino)-1,1'-binaphthalene; (*R*,*R*)-Skewphos = (2*R*,4*R*)-bis(diphenylphosphino)pentane.
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Preparation of Monocarbonyl Ruthenium Complexes Bearing Bidentate Nitrogen and Phosphine Ligands and their Catalytic Activity in the Carbonyl Compound Reduction

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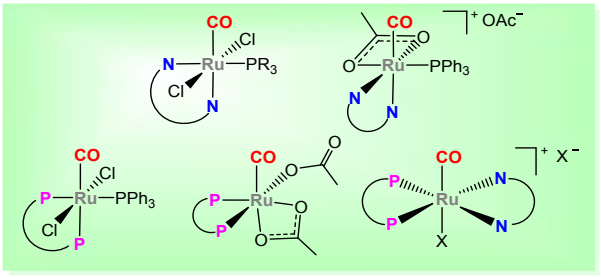
A series of novel monocarbonyl ruthenium catalysts containing bidentate dinitrogen or/and diphosphine ligands are easily obtained through a general and straightforward approach.



X = OAc, Cl; R = Cy, *i*Pr