Preparation of monocarbonyl ruthenium complexes bearing bidentate nitrogen and phosphine ligands and their catalytic activity in carbonyl compound reduction

June 11, 2019

Dalton Transaction

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

Steven Giboulot,[#,£] Clara Comuzzi,[#] Alessandro Del Zotto,[#] Rosario Figliolia,[#] Giovanna Lippe,[#] Denise Lovison,[#] Paolo Strazzolini,[#] Sabina Susmel,[#] Ennio Zangrando,[$] Daniele Zuccaccia,[#] Salvatore Baldino, [#,┘] Maurizio Ballico,[#,*] Walter Baratta[#,*]

[#]*Dipartimento DI4A - Università di Udine, Via Cotonificio 108, I-33100 Udine, Italy*

[£]*Johnson Matthey, 28 Cambridge Science Park, Milton Road Cambridge, CB4 0FP, United Kingdom*

[$]*Department of Chemical and Pharmaceutical Sciences, University of Trieste, Via Licio Giorgieri, 1, 34127 Trieste, Italy*

[┘]*Dipartimento di Chimica, Università di Torino, Via Pietro Giuria, 7, I-10125 Torino, Italy*

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 while the other is not coordinated. The diphosphine complexes $[RuCl_2(CO)(PP)(PPh_3)]$ (PP = dppb **6**, dppf **7**, (*R*)-BINAP **8**, (*S*,*R*)-Josiphos **9** and (*R*,*R*)-Skewphos **10**) were obtained starting from $[RuCl_2(CO)(dmf)(PPh_3)_2]$ and the PP ligand in $CHCl_3$ or toluene at reflux. Treatment of $[Ru(OAc)_2(CO)(PPh_3)_2]$ with PP in CH_2Cl_2 or toluene afford 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 from 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 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}.

Introduction

Ruthenium complexes have widely been investigated in the last decades on account of their high catalytic activity for a large number of organic transformations. In addition to C-C coupling reactions, the reduction of the C=O bond via hydrogenation (HY)[1-4] and transfer hydrogenation (TH)[5-11] reactions promoted by ruthenium catalysts are extensively accepted in the industry as efficient and environmentally benign way for the preparation of alcohols,[12] only few examples have been demonstrated active in both HY or TH reactions.[13-16] The search of the appropriate set of ligands remains crucial for achieving high selectivity and productivity, which are prerequisites for industrial 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,[17-21] esters and amides[22-26] dehydrogenation of alcohols,[27-36] borrowing hydrogen reactions,[37-41] some relevant examples are shown in Figure 1.

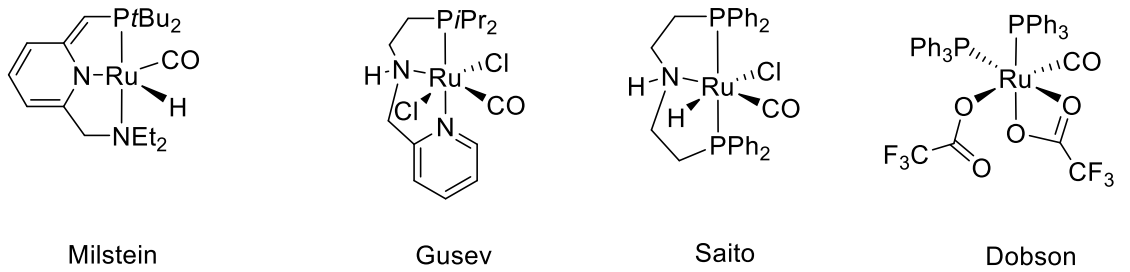


Figure 1. Monocarbonyl ruthenium catalysts

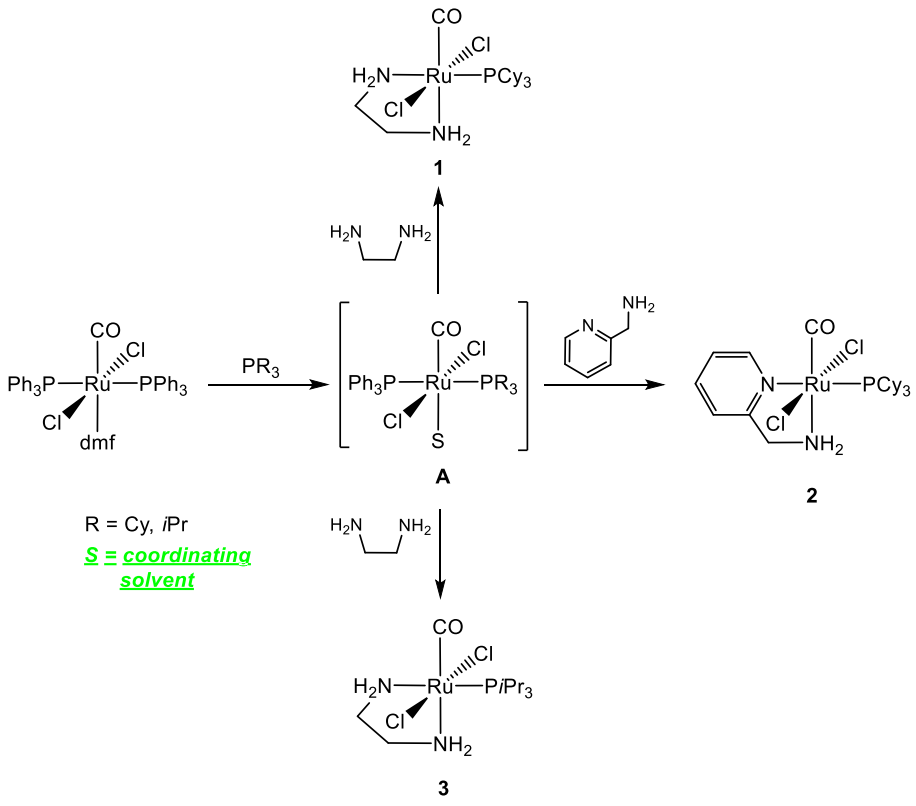
It is worth noting that a number of dicarbonyl ruthenium complexes employed in catalysis, have proven to dissociate one CO, resulting in the formation of catalytically active monocarbonyl complexes.[42-46] The presence of a CO ligand on ruthenium may prevent side reactions, such as decarbonylation of the substrates (i.e. aldehydes), which is regarded as a pathway of catalyst deactivation.[47-49] As regard the preparation of monocarbonyl complexes, $RuHCl(CO)(XPh_3)_3]$ (X = P, As) and $[RuH_2(CO)(PPh_3)_3]$ have been widely employed as suitable precursors via displacement of PPh_3 and chloride 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,[50] a reaction which failed when we used related diphosphines, namely dppb, dppf, limiting the scope of this reaction.[51]

In our ongoing interest in the synthesis of carbonyl ruthenium complexes for homogeneous catalysis[52, 53] 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 $[RuCl_2(CO)(dmf)(PPh_3)_2]$ and $[Ru(OAc)_2(CO)(PPh_3)_2]$ precursors. The monocarbonyl phosphine ruthenium complexes in the presence of primary amine ligands (i.e. en, ampy[54]) display catalytic activity in the reduction of ketones and aldehydes, including furfural derivatives and *trans*-cinnamaldehyde, at S/C up to 10000.

Results and Discussion

Synthesis of monocarbonyl ruthenium chloride and acetate complexes with NN ligands. Complexes of 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 diacetate $[Ru(OAc)(CO)(PPh_3)(NN)]OAc$ are prepared from $[Ru(OAc)_2(CO)(PPh_3)_2]$ and a dinitrogen ligand. Thus, 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).

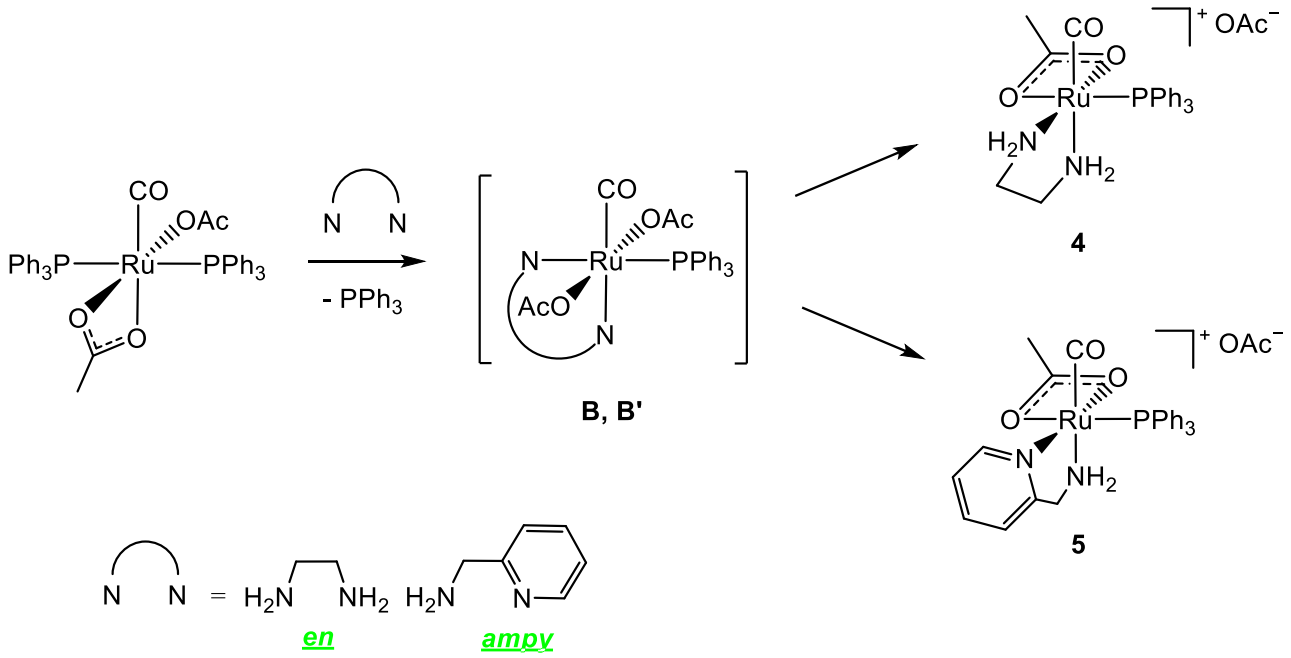


Scheme 1. Synthesis of *trans*-[$RuCl_2(CO)(PR_3)(NN)$] (**1**-**3**)

The ^1H NMR spectrum of **1** in CD_2Cl_2 displays two multiplets at δ 3.10 and 2.93 for the methylene groups of the en[50] ligand, while the NH_2 moieties appears at δ 3.70 and 3.27 ppm. The $^{13}C\{^1H\}$ NMR doublet at δ 206.0 (^2J(C,P) = 16.8 Hz) is for the CO carbon, whereas the doublets at δ 43.5 and 42.3 are for the CH_2 groups of en. 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.[17, 55] 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 with a ^2J(P,P) = 330 Hz, consistent with the formation of the intermediate *trans*-[$RuCl_2(CO)(S)(PCy_3)(PPh_3)$] (S = dmf) (**A**) by substitution of one PPh_3 with PCy_3 (Scheme 1).

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[50] (84% yield), while *trans*-[$RuCl_2(CO)(PiPr_3)$(en)] (**3**) has been obtained from the ruthenium precursor with 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, a value very close to that of **1** (δ 55.6). 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 with ^3J(H,H) = 6.0 Hz, respectively. The $^{13}C\{^1H\}$ NMR signal of the carbonyl group is a doublet at δ 207.6 (d, ^2J(C,P) = 17.8 Hz), while in the IR spectrum the CO stretching band is at 1941 cm^{-1}, values close to those of **1**. Complex **3** shows spectroscopic data related to those of **1** and **2** with a IR CO stretching absorbance at 1921 cm^{-1}.

Treatment of the acetate precursor [$Ru(OAc)_2(CO)(PPh_3)_2$] with en in methanol 70 °C for 2 h, affords the cationic [$Ru(OAc)(CO)(PPh_3)$(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

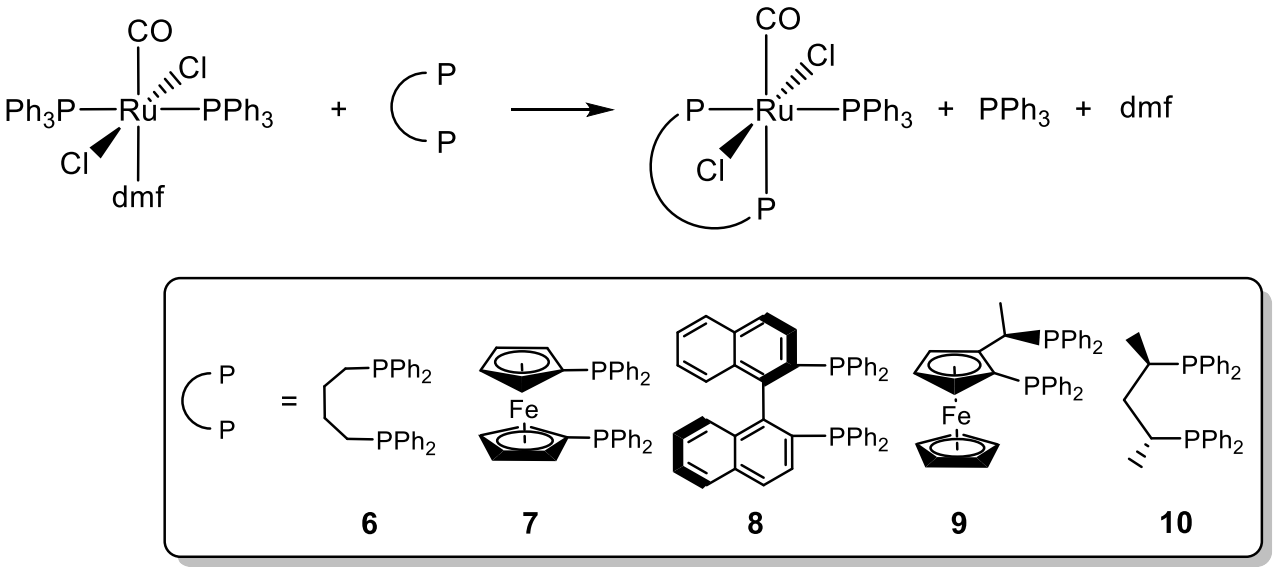
The $^{31}P\{^1H\}$ NMR spectrum of **4** in CD_2Cl_2 shows a singlet at δ 47.3. The en NH protons give four broad signals at δ 6.97, 5.22, 3.13 and 2.66 in the ^1H NMR spectrum, consistent with the presence of an N-H···O hydrogen bond interaction, whereas the acetate methyl groups afford two singlets at δ 1.98 and 1.58. In the $^{13}C\{^1H\}$ NMR spectrum the CO appears as a doublets at δ 204.9 (^2J(C,P) = 18.4 Hz), whereas the *C*H_2N appear as doublets at δ 46.7 and 43.9. The two acetate give two signals at δ 181.4 and 179.3 for the CO and at δ 25.2 and 24.3 for the CH_3 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) in about 2/3 molar ratio. The ^1H NMR spectrum of **B** shows triplets at δ 4.95 and 3.90 for the NH_2CH_2 moiety, respectively, and a singlet at δ 1.62 for the acetate ligand (see SI, Figures S13, S14). By refluxing this mixture in methanol for 12 h affords complete conversion to **4**, indicating that upon trans to cis isomerization the thermodynamically most stable complex displays a bidentate acetate with the second acetate as 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, while the ampy NH protons give two signals at δ 8.87 and 1.27 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 (^2J(C,P) = 17.9 Hz), whereas the two acetate groups give two resonances at δ 182.0 and 177.7 for the CO and δ 25.0 and 24.2 for the CH_3 moieties,

similarly 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 for $CH_3CO_2^-$, confirming that one acetate of **5** is not coordinated to ruthenium (Fig. S18 (SI)).

As for **4** the intermediate species *trans*-[$Ru(OAc)_2(CO)(PPh_3)$(ampy)] (**B'**) was observed in dichloromethane (δ_P 53.8) which converts quantitatively in refluxing methanol to **5** (see SI, Figures S19, 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 bidentate NN ligands affording the derivatives *trans*-[$RuX_2(CO)(PPh_3)$(NN)] (X = Cl OAc). While the chloride derivatives are stable in solution, the acetate compounds easily undergo ~~easy~~ isomerization in ~~solution~~ alcohol media, with formation of the cationic [Ru(OAc)$(CO)(PPh_3)$(NN)]OAc species ~~complexes~~ in which one acetate acts as bidentate ligand while the other is present as counterion.

Synthesis of monocarbonyl ruthenium chloride and acetate complexes with PP ligands. The monocarbonyl diphosphine derivatives [$RuX_2(CO)(PP)(PPh_3)_n$] (X = Cl, n= 1 and X = OAc n = 0) are easily obtained by reaction of the precursors [$RuCl_2(CO)(dmf)(PPh_3)_2$] and [$Ru(OAc)_2(CO)(PPh_3)_2$] 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).

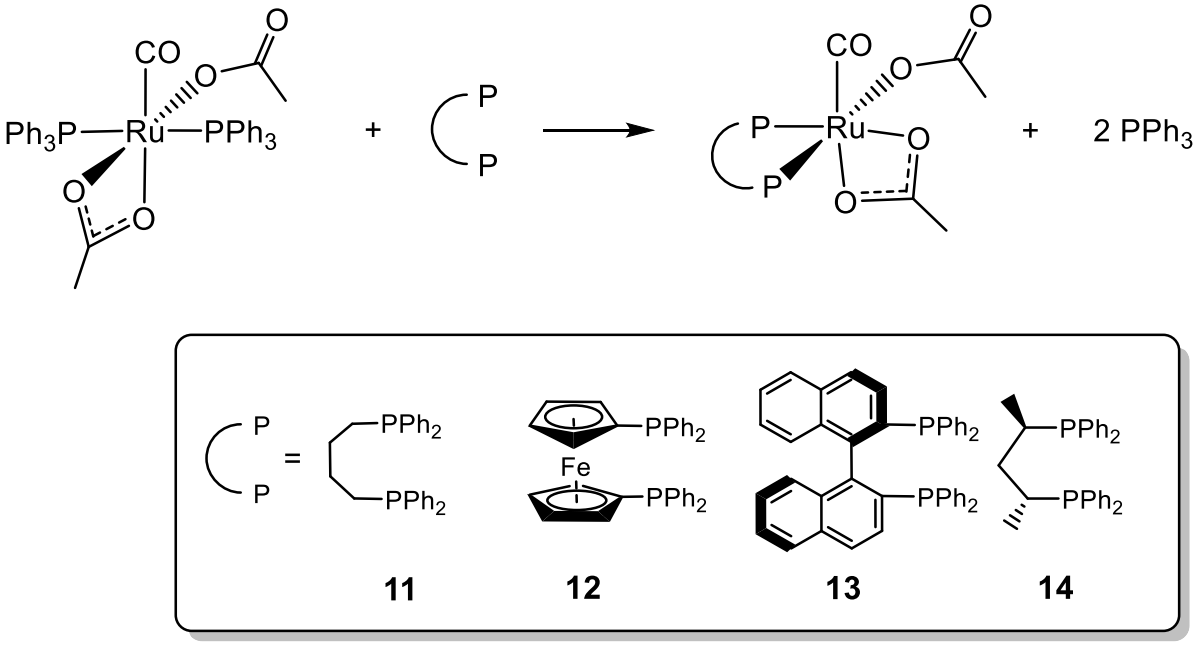


Scheme 3. Synthesis of *trans*-[$RuCl_2(CO)(PP)(PPh_3)$] (**6-10**)

The $^{31}P\{^1H\}$ 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 (^2J(P,P) = 25.8 Hz) for one P atom of dppb and a broad multiplet in the

range of δ 16.4-14.8 for PPh_3 and one P atom of the dppb ligand.[56] The NMR spectra of **6** show broad signals for the dppb methylene protons (δ_H 3.3-1.5) and a resonance at δ_C 200.1 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[50, 57] 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 in a 1:2 ratio, with a carbonyl signal at δ_C 199.7 while the a IR ν_{CO} band is at 1979 cm^{-1}. Similarly to **9**, treatment of $[RuCl_2(CO)(dmf)(PPh_3)_2]$ with one equivalent of the chiral (*R*)-BINAP[50] 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 $^{31}P\{^1H\}$ NMR spectrum of **8** in $[D_8]$toluene displays an ABX pattern at 293 K, with a pseudo-triplet at δ 31.2 and two doublet of doublets at δ 25.8 and 21.3. The upfield signals present a large coupling constant ($^2J(P,P)$ = 348.7 Hz) for a PPh_3 and a (*R*)-BINAP P atom in trans configuration. The CO ligands gives a doublet of triplets at δ_C 199.9 with a $^2J(C,P)_{trans}$ of 83.6 Hz and a $^2J(C,P)_{cis}$ of 15.8 Hz, in agreement with a planar arrangement of the three P and a CO ligands. Finally the monocarbonyl derivatives *trans*-$[RuCl_2(CO)((S,R)\text{-Josiphos})(PPh_3)]$ (**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 (Scheme 3). While the Josiphos[50] derivative **9** was obtained as a single stereoisomer, the Skewphos[50] complex **10** consists of a mixture of two different stereoisomers, as inferred from ^1H and $^{31}P\{^1H\}$ NMR measurements. Notably, a $[RuCl_2(CO)(PP)(P)]$ arrangement has been reported for a dinuclear ruthenium complex with a bridged dppb, prepared through a solid state carbonylation of $[RuCl_2(dppb)]_2(dppb)$[58] or from $[RuCl_2(CO)_2]_n$ with dppb in CH_3OH at reflux.[59]

Treatment of the acetate $[Ru(OAc)_2(CO)(PPh_3)_2]$ 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 two PPh_3 (Scheme 4).



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

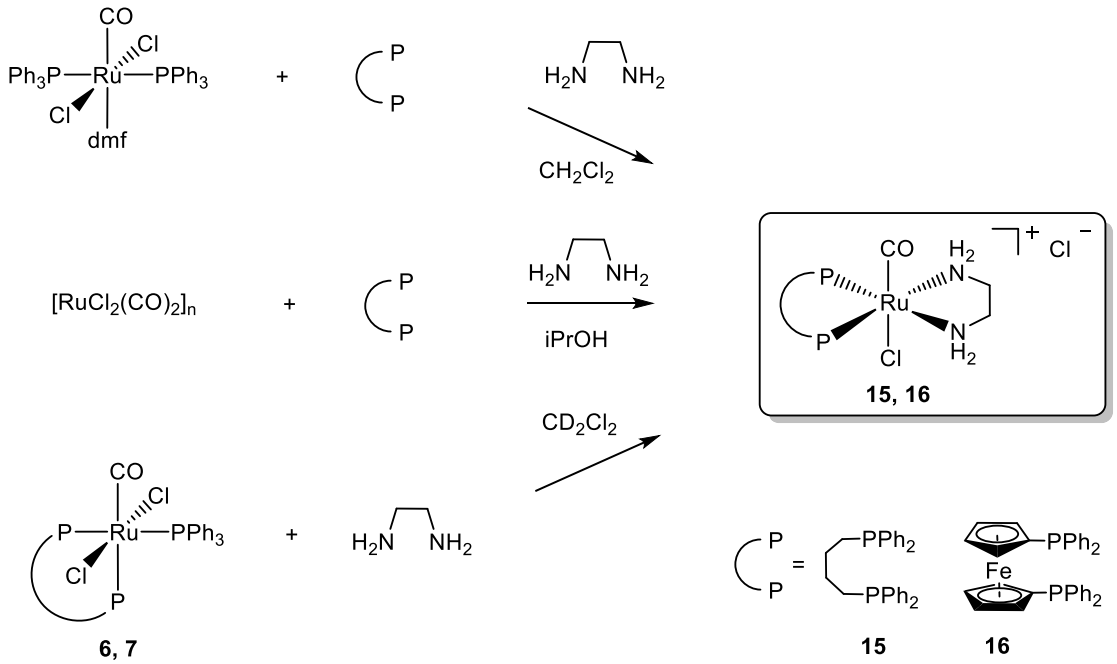
The $^{31}P\{^1H\}$ NMR spectrum of **11** in CD_2Cl_2 at RT displays a broad signal at δ 46.8, while upon cooling two doublets at δ 48.0 and 46.2 with $^2J(P,P)$ = 26.4 Hz and two broad signals in the range δ 45.2-34.0 appear at 193 K, indicating the presence of two species in about 3:1 ratio (see SI). 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, respectively, whereas at low temperature the spectra reveal the presence of two species, in agreement with the $^{31}P\{^1H\}$ NMR data, with a IR CO stretching band at 1954 cm^{-1}. The fluxional behavior of **11** is likely due to the rapid intramolecular exchange of the monodentate and bidentate acetate groups, a well-known behavior also observed for the analogous trifluoroacetate $[Ru(CF_3CO_2)_2(CO)(PPh_3)_2]$.[35, 36, 60] It is likely that the presence of various species is due to different coordination modes of the acetate groups and the different 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 has been 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, 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 with $^2J(P,P)$ of 30.4 Hz. In the ^1H NMR spectrum the broad signals at δ 1.56 is for the two acetate, while at low temperature three isomers containing two non-equivalent acetate (δ 1.73-1.33) are observed, in agreement with the $^{31}P\{^1H\}$ measurements (see SI). The IR ν_{CO} of **12** is 1974 cm^{-1} shifted at higher wavenumber, compared to **11** and $[Ru(OAc)_2(CO)(dippf)]$[50] (1939 cm^{-1}), on account of the low basicity of the dppf phosphine.[61-66] 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 behavior of these complexes, whereas at low temperature several isomers appear in the NMR spectra (see SI).

Thus, while the monocarbonyl ruthenium diphosphine complexes with chloride ligands contain an addition PPh_3, the corresponding acetate derivative do not present PPh_3 on account of the ability of the acetate 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 from reactions of the precursors $[RuX_2(CO)(dmf)_n(PPh_3)_2]$ (X = Cl, n = 1; X = OAc, n = 0), $[RuCl_2(CO)_2]_n$ and the above reported derivatives $[RuX_2(CO)(PP)(PPh_3)_n]$] (X = Cl, n = 1; X = OAc, n = 0) with diphosphine or / and dinitrogen ligand. 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).

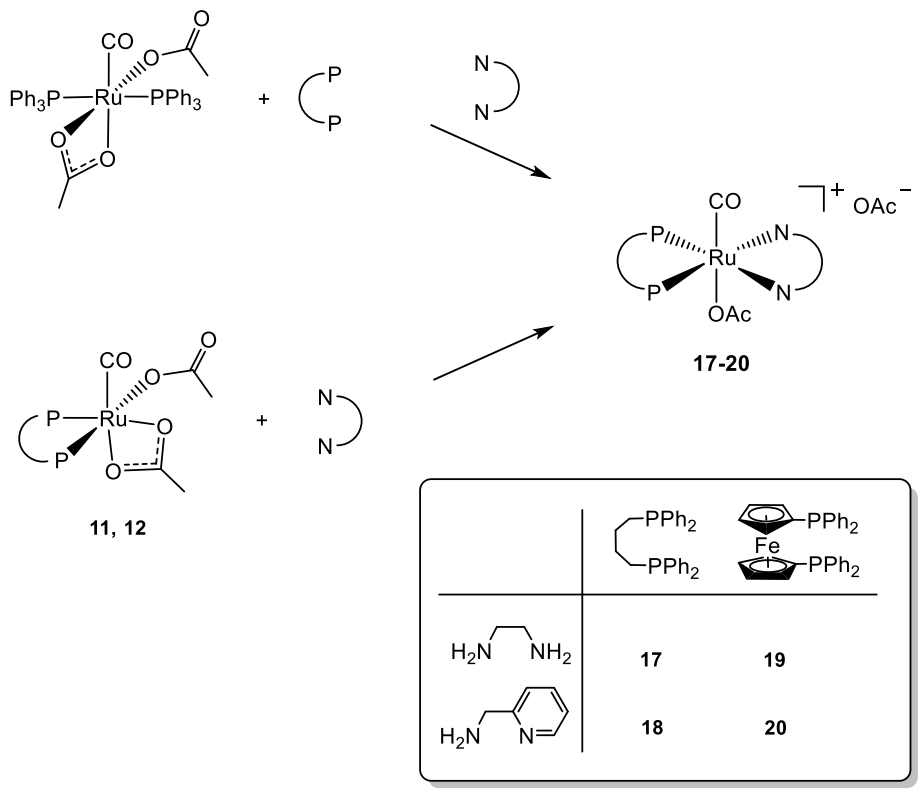


Scheme 5. Synthesis of the cationic [RuCl(CO)(PP)(en)]Cl complexes **15** and **16**

Alternatively, **15** can be prepared in a more advantageous way (98% 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,

whereas the $^{13}C\{^{1}H\}$ NMR measurements gives a triplet at δ 199.5 (^{2}J(C,P) = 13.6 Hz) for the CO and a singlet at δ 45.9 for the en ligand. The IR CO stretching absorbance of **15** is at 1969 cm^{-1}.[51] 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 and IR ν_{CO} at 1960 cm^{-1}. In addition, complexes **15** and **16** are also formed quantitatively 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).

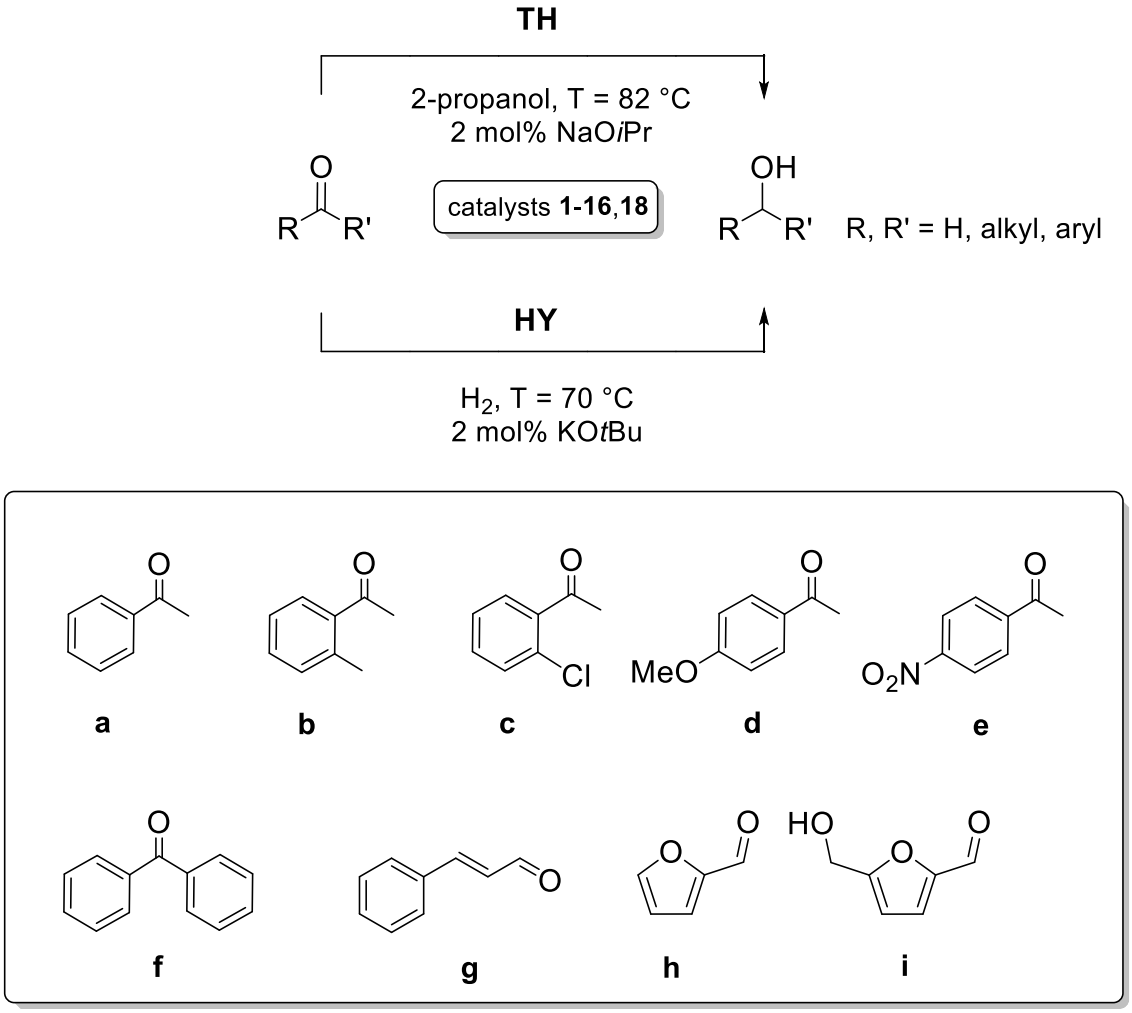


Scheme 6. Synthesis of the acetate complexes [Ru(OAc)(CO)(PP)(NN)]OAc complexes

Likewise the analogous chlorine complex **15**, the acetate derivative **17** displays in the $^{31}P\{^{1}H\}$ NMR spectrum (CD_3OD) one singlet at δ 37.1, while the $^{13}C\{^{1}H\}$ NMR CO gives a triplet at δ 203.8 (^{2}J(C,P) = 14.8 Hz). The doublet at δ 46.6 (^{3}J(C,P) = 11.0 Hz) and the singlet at δ 44.9 are ascribed to the en *C*H_2 moieties, whereas the two acetate ligands display the signals at δ 182.8 and 182.5 for the carbonyls and at δ 25.7 and 24.1 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, suggests an

NH···O hydrogen bond interaction with one acetate,[62] and the other at δ 1.24, as inferred from ^{15}N-^{1}H HSQC 2D NMR analysis (see SI), while the infrared stretching band at 1939 is for CO ligand. On the other hand, **17** is also formed from **11**, bearing dppb, and ~~ethylenediamine~~ en in CD_2Cl_2 at RT. Reaction of **11** with ampy in toluene at RT (30 min.) leads to the cationic complex [Ru(OAc)(CO)(dppb)(ampy)]OAc (**18**), isolated in 87% yield (Scheme 6). ^{31}P{^{1}H} NMR spectrum of **18** in [D_8]toluene displays two doublets at δ 46.4 and 34.0 with a ^{2}J(P,P) = 28.8 Hz, whereas the diastereotopic methylene protons of the ampy give two signals at δ 4.22 and 3.21 with ^{2}J(H,H) = 12.4 Hz and ^{3}J(H,H) = 10.2 and 10.7 Hz, in the ^{1}H NMR spectrum. The ^{15}N-^{1}H HSQC 2D NMR analysis reveals that the NH_2 signals are at δ 6.21 and 1.67, 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 with ^{2}J(C,P) = 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 in CD_2Cl_2, whereas the ^{13}C{^{1}H} NMR CO signal appears as triplet at δ 203.2 (^{2}J(C,P) = 15.1 Hz). The acetate carbonyl resonances appear as a singlet at δ 181.4 for the free acetate, and the doublet of doublets at δ 176.6 (^{3}J(C,P) = 12.1 Hz, ^{3}J(C,P) = 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 ligands. Finally, 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 for the diastereotopic CH_2N protons, whereas the NH_2 resonances are at δ 6.07, and 2.33. The ^{31}P{^{1}H} NMR spectrum of **20** displays two doublets at δ 51.2 and 40.5 with a ^{2}J(P,P) = 29.1 Hz, whereas the ^{13}C{^{1}H} NMR CO signal is a triplet at δ 210.3 (^{2}J(C,P) = 16.4 Hz), while IR CO stretching band at 1959 cm^{-1}.

Reduction of aldehydes and ketones via TH and HY catalyzed by monocarbonyl ruthenium complexes. The catalytic activity of the monocarbonyl ruthenium complexes have 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 dinitrogen ligands to the ruthenium phosphine derivatives has proven to accelerate the catalytic reactions.



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

Complexes **1**, **2** and **3** (S/C = 1000), bearing the en and ampy ligands in combination with a strongly coordinating alkyl monophosphines PCy_3 and 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 1, entries 1-3).

Table 1. **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**	-	30	63		25 (*R*)
19	**14**	ampy	30	95	10000	25 (*R*)
20	**14**	(±)-*i*Pr-ampy[c]	5	90	15000	39 (*R*)
21	**15**	-	90	90	-	-
22	**16**	-	90	88	-	-
23	**18**	-	90	91	-	-

[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.

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) in 90 min. (entries 4-5). The diphosphine dppb and dppf complexes **6** and **7** of the type $[RuCl_2(CO)(PP)(PPh_3)]$ show poor activity (10 % in 120 min and 98% in 48 h), while ~~by~~ the addition of ampy and displacement of PPh_3 (vide infra), leads to an increase of activity, as observed for the dppf derivative **7** with ampy (90 % conv.; entries 6-8). Employment of the chiral (*R*)-BINAP complex **8** in the presence of (*R*,*R*)-DPEN,[50] affords high conversion (97%) with TOF of 8400 h^{-1}, respectively, but ~~with~~ poor *ee* (entries 9). The rate of the TH of **a** with the (*S*,*R*)-Josiphos derivative **9** is low and increases by addition of (*R*,*R*)-DPEN, (*S*)-1-phenylethanol is

obtained in 59% *ee* (entries 10-11). Complex **10** bearing the (*R*,*R*)-Skewphos in combination (±)-*i*Pr-ampy[50] affords the (*R*) alcohol with 67% *ee* (TOF= 5800 h^{-1}) (entry 12). The acetate complexes [$Ru(OAc)_2(CO)(PP)$] increase their activity by addition of diamine and ampy ligands in *in situ*. The dppb **11** and dppf **12** derivatives are poorly active and addition of ampy lead to 93 and 72 % conversion in 2 h with TOF 7400 and 6900 h^{-1}, showing a faster rate with respect to their corresponding chloride **6**, **7** complexes which require displacement of a PPh_3 by the nitrogen 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*)-DPEN a considerable increase of the rate is observed, with 90-97% conversions 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 much of the same performances obtained through the *in situ* reactions from **6**, **7**, **11** and the nitrogen ligands (entries 21-23).

The monocarbonyl derivatives have been investigated in the TH of ketones and aldehydes. Thus, the ampy **5** (S/C = 1000) catalyzes the quantitative reduction of benzophenone **f** to benzhydrol in 0.5 h (Table 2; entry 1). Interestingly, the en PCy_3 **1** complex affords the TH of *trans*-cinnamaldehyde **g**, furfural **h** and 5-(hydroxymethyl)furfural (5-HMF) **Ł 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 side reactions, which may lead to catalyst deactivation.[67, 68]

A higher activity has been observed with the ampy dppb **18** for **g** and **h** with 98 and 99% conversion in 12 and 1 h (entries 5-6).

Table 2. **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 conversions has been determined by GC analysis. [b]Using K_2CO_3 5 mol% as base.

These catalytic results indicate that the chloride and the acetate monocarbonyl phosphine complexes display low activity in TH reactions and their performances increase by addition of primary amine ligands, which facilitate the formation of Ru–H species.[69, 70]

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 (δ -5.58) *trans* to a phosphorus atom ($^2J(H,P)_{trans}$ = 115.6 Hz and $^2J(H,P)_{cis}$ = 19.8 Hz), in agreement with the results observed for [RuCl(CO)(dppp)(ampy)]Cl complex[51] (see SI). In addition, the formation of *trans* H-Ru-P species may account of the low enantioselectivity observed for the BINAP **8** and **13** compounds, with respect to the Noyori *trans*-[$RuCl_2$(BINAP)(NN)] system.[71, 72]

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 3; entries 1-4).

Table 3. **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 conversions 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'-Me-acetophenone **b**, 2'-Cl-acetophenone **c** and 4'-MeO-acetophenone **d** are quantitatively reduced to the corresponding alcohols with **2**, whereas 4'-NO_2-acetophenone **e** leads to poor conversion (10 %) (Table 4; entries 1-4).

Table 4. **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 conversions has been determined by GC analysis.

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 4; entries 5-8).

Conclusions

In summary, we have described a general approach for the straightforward preparation of a series of monocarbonyl ruthenium complexes, containing bidentate dinitrogen or / and diphosphine ligands with chloride and acetate, starting from the precursors $[RuCl_2(CO)(PPh_3)_2(dmf)]$ and $[Ru(OAc)_2(CO)(PPh_3)_2]$. Several ruthenium 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), Ru(CO)(PP)(NN) motifs show good to high catalytic activity in the transfer hydrogenation and hydrogenation of carbonyl compounds including 5-HMF and trans-cinnamaldehyde. These results will be helpful for the designing of novel monocarbonyl complexes based on ruthenium containing chelate ligands. Studies are in progress to extend this protocol for the preparation of new ruthenium monocarbonyl derivatives with pincer ligands and to expand the use of ruthenium carbonyl complexes in catalytic C-H activation reactions.

Experimental Section

General Procedures and Materials: All reactions were carried out under an argon atmosphere using standard Schlenk techniques. The solvents were carefully dried by standard methods and distilled under argon before use, unless stated otherwise. The ruthenium compounds

$[RuCl_2(CO)(dmf)(PPh_3)_2]$,[73] $[RuCl_2(CO)_2]_n$,[74] and $[Ru(OAc)_2(CO)(PPh_3)_2]$[75] were prepared according to the 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, in 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 elemental analyzer, whereas the GC analyses were performed with a Varian CP-3380 gas chromatograph equipped with a MEGADEX-ETTBDMS-β chiral column of 25 m length, column pressure 5 psi, hydrogen as 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 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: 149.1 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, $[D_2]$dichloromethane, 20 °C): δ = 3.70 (pseudo-t, J(H,H) = 5.0 Hz, 2H; NH_2), 3.27 (m, 2H; NH_2), 3.10 (dd, ^2J(H,H) = 11.3 Hz, ^3J(H,H) = 5.5 Hz, 2H; CH_2N), 2.93 (dd, ^2J(H,H) = 9.6 Hz, ^3J(H,H) = 5.5 Hz, 2H; CH_2N), 2.20 (dd, ^3J(H,H) = 23.4 Hz, ^3J(H,H) = 12.3 Hz, 3H; PCH), 2.14-1.08 ppm (m, 30H; CH_2 (Cy)). $^{13}C\{^1H\}$, NMR (50.3 MHz, $[D_2]$dichloromethane, 20 °C): δ = 206.0 (d, ^2J(C,P) = 16.8 Hz; CO), 43.5 (d, ^3J(C,P) = 2.8 Hz; *C*H_2N), 42.3 (d, ^3J(C,P) = 1.5 Hz; *C*H_2N), 35.3 (d, ^1J(C,P) = 21.0 Hz; P*C*H), 29.7 (d, ^3J(C,P) = 1.3 Hz; PCHCH$_2$*C*H$_2$), 28.2 (d, ^2J(C,P) = 10.0 Hz; PCH*C*H$_2$), 27.0 ppm (d, ^4J(C,P) = 1.0 Hz; CH_2). $^{31}P\{^1H\}$ NMR (81.0 MHz, $[D_2]$dichloromethane, 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: 153.3 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,

[D_2]dichloromethane, 20 °C): δ = 9.11 (d, ^3J(H,H) = 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(H,H) = 6.0 Hz, 2H; CH_2), 4.19 (t, ^3J(H,H) = 6.0 Hz, 2H; NH_2), 2.34 (qt, ^3J(H,H) = 12.1 Hz, ^4J(H,H) = 2,5 Hz, 3H; PCH), 2.18-1.09 ppm (m, 30H; CH_2 (Cy)). $^{13}C\{^1H\}$ NMR (50.3 MHz, [D_2]dichloromethane, 20 °C): δ = 207.6 (d, ^2J(C,P) = 17.8 Hz; CO), 160.1 (s; N*C*CH_2), 152.6 (d, ^2J(C,P) = 1.2 Hz; ortho-*C*H of C_5H_4N), 137.6 (s; para-*C*H of C_5H_4N), 124.5 (d, ^4J(C,P) = 2.3 Hz; meta-*C*H of C_5H_4N), 121.7 (d, ^4J(C,P) = 1.8 Hz; meta-*C*H of C_5H_4N), 50.6 (d, ^3J(C,P) = 2.2 Hz; *C*H_2N), 34.5 (d, ^1J(C,P) = 21.1 Hz; P*C*H), 29.6 (d, ^3J(C,P) = 1.3 Hz; PCHCH_2*C*H_2), 28.1 (d, ^2J(C,P) = 10.0 Hz; PCH*C*H_2), 27.0 ppm (s, CH_2). $^{31}P\{^1H\}$ NMR (81.0 MHz, [D_2]dichloromethane, 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, [D_2]dichloromethane, 20 °C): δ = 3.62 (m, 2H; NH_2), 3.31 (m, 2H; NH_2), 3.09 (dd, ^3J(H,H) = 11.3 Hz, ^3J(H,H) = 5.7 Hz, 2H; CH_2N), 2.94 (dd, ^3J(H,H) = 5.4 Hz, ^3J(H,H) = 2.1 Hz, 2H; CH_2N), 2.52 (m, 3H; PC*H*$(CH_3)_2$), 1.33 ppm (dd, ^3J(H,P) = 13.1 Hz, ^3J(H,H) = 7.3 Hz, 18H; CH(C*H*$_3)_2$). $^{13}C\{^1H\}$ NMR (50.3 MHz, [D_2]dichloromethane, 20 °C): δ = 205.8 (d, ^2J(C,P) = 17.0 Hz; CO), 43.5 (d, ^3J(C,P) = 2.9 Hz; CH_2N), 42.2 (d, ^3J(C,P) = 1.5 Hz; CH_2N), 25.1 (d, ^1J(C,P) = 22.3 Hz; P*C*H$(CH_3)_2$), 19.6 ppm (d, ^2J(C,P) = 0.7 Hz; CH(C*H*$_3)_2$). $^{31}P\{^1H\}$ NMR (81.0 MHz, [D_2]dichloromethane, 20 °C): δ = 55.9 ppm (s). IR (Nujol): $\tilde{\nu}$ = 1921 (s) (C≡O) cm^{-1}.

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

[$Ru(OAc)_2$(CO)(PPh_3)$_2$] (200 mg, 0.26 mmoli) 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 added of 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: 108.4 mg (73.2%). 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. ^1H NMR (200.1 MHz, [D_2]dichloromethane, 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). $^{13}C\{^1H\}$ NMR (50.3 MHz, [D_2]dichloromethane, 20 °C): δ = 204.9 (d, ^2J(C,P) = 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(C,P) = 3.1 Hz; NCH_2), 44.3 (d, ^3J(C,P) = 2.3 Hz; NCH_2), 25.2 (s; CH_3CO), 24.3 ppm (s; CH_3CO). $^{31}P\{^1H\}$ NMR (81.0 MHz, [D_2]dichloromethane, 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. ^1H NMR (200.1 MHz, [D_2]dichloromethane, 20 °C): δ = 8.87 (m, 1H; NH_2), 8.54 (m, 1H; ortho-C*H* of C_5H_4N), 7.81 (td, ^3J(H,H) = 7.6 Hz, ^3J(H,H) = 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(H,H) = 7.7 Hz, 1H; meta-C*H* of C_5H_4N), 4.09 (dd, ^2J(H,H) = 16.0 Hz, ^3J(H,H) = 5.0 Hz, 1H; NCH_2), 3.87 (ddd, ^2J(H,H) = 16.0 Hz, ^3J(H,H) = 10.0 Hz, ^3J(H,H) = 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). $^{13}C\{^1H\}$ NMR (50.3 MHz, [D_2]dichloromethane, 20 °C): δ = 205.7 (d, ^2J(C,P) = 17.9 Hz; CO), 182.0 (s; CH_3CO), 177.7 (s; CH_3CO), 161.2 (d, ^3J(C,P) = 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(C,P) = 2.3 Hz; NCH_2), 25.0 (s; CH_3CO), 24.2 ppm (s; CH_3CO). $^{31}P\{^1H\}$ NMR (81.0 MHz, [D_2]dichloromethane, 20 °C): δ = 49.8 ppm (s). IR (Nujol): $\tilde{\nu}$ = 1923 (s) (C≡O), 1579 (C=O) cm^{-1}.

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

[$RuCl_2$(CO)(dmf)(PPh_3)$_2$] (103.7 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: 86.7 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. ^1H NMR (200.1 MHz, [D_2]dichloromethane, 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). $^{13}C\{^1H\}$ NMR (50.3

MHz, [D_2]dichloromethane, 20 °C): δ = 200.1 (dt, ^2J(C,P) = 11.9 Hz, ^2J(C,P) = 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). $^{31}P\{^1H\}$ NMR (81.0 MHz, [D_2]dichloromethane, 20 °C): δ = 27.5 (t, ^2J(P,P) = 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)$_2$] (199.3 mg, 0.25 mmol) suspended in toluene (5 mL), was reacted with dppf (138.6 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: 99.1 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. ^1H NMR (200.1 MHz, [D_2]dichloromethane, 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). $^{13}C\{^1H\}$ NMR (100.6 MHz, [D_2]dichloromethane, 20 °C): δ = 199.7 (br t, ^2J(C,P) = 16.0 Hz; CO), 135.2-125.0 (m; aromatic carbon atoms), 78.6 (d, ^1J(C,P) = 56.0 Hz; *ipso*-C_5H_4), 77.2 (d, ^1J(C,P) = 60.6 Hz; *ipso*-C_5H_4), 76.6 (d, ^2J(C,P) = 9.3 Hz; *C*H of C_5H_4), 75.7 (d, ^2J(C,P) = 9.8 Hz; *C*H of C_5H_4), 75.6 (d, ^2J(C,P) = 11.0 Hz; *C*H of C_5H_4), 74.8 (d, ^3J(C,P) = 7.2 Hz; *C*H of C_5H_4), 74.2 (d, ^3J(C,P) = 7.0 Hz; *C*H of C_5H_4), 72.6 (d, ^3J(C,P) = 6.0 Hz; *C*H of C_5H_4), 72.1 ppm (d, ^3J(C,P) = 6.4 Hz; *C*H of C_5H_4). $^{31}P\{^1H\}$ NMR (81.0 MHz, [D_2]dichloromethane, 20 °C): δ = 53.8 (m; 1P), 46.4 (m; 2P). IR (Nujol): $\tilde{\nu}$ = 1979 (s) (C≡O) cm^{-1}.

Synthesis of *trans*-[$RuCl_2$(CO)((*S*,*R*)-Josiphos)(PPh_3)] (8)

Complex **8** was prepared following the procedure used for **7**, with (*S*,*R*)-Josiphos (145.6 mg, 0.25 mmol, 1 equiv.) in place of dppf. Yield: 227.2 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. ^1H NMR (200.1 MHz, [D_8]toluene, 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*$_3$). $^{13}C\{^1H\}$ NMR (100.6 MHz, [D_8]toluene, 20 °C): δ = 197.1 (m; CO), 142.8-124.2 (m; aromatic carbon atoms), 94.9 (dd, ^1J(C,P) = 18.7 Hz, ^3J(C,P) = 4.1 Hz; *ipso*-

C_5H_3), 77.1 (dd, ^1J(C,P) = 40.4 Hz, ^3J(C,P) = 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(C,P) = 21.3 Hz; P*C*HCH$_3$), 13.8 ppm (d, ^2J(C,P) = 5.7 Hz; PCH*C*H$_3$). ^{31}P{^{1}H} NMR (81.0 MHz, [D$_8$]toluene, 20 °C): δ = 47.7 (pseudo-t, ^2J(P,P) = 23.0 Hz; 1P), 14.3 (dd, ^2J(P,P) = 357.2 Hz, ^2J(P,P) = 23.0 Hz; 1P), 12.0 ppm (dd, ^2J(P,P) = 357.2 Hz, ^2J(P,P) = 22.7 Hz; 1P); IR (Nujol): $\tilde{\nu}$ = 1979 (s) (C≡O) cm^{-1};

Synthesis of *trans*-[RuCl$_2$(CO)((*R*)-BINAP)(PPh$_3$)] (9)

Complex **9** was prepared following the procedure used for **7**, with (*R*)-BINAP (155.7 mg, 0.25 mmol, 1 equiv.) in place of dppf. Yield: 238.7 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, [D$_8$]toluene, 20 °C): δ = 8.73 (t, ^3J(H,H) = 8.6 Hz, 1H; aromatic proton), 8.14 (t, ^3J(H,H) = 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(H,H) = 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(H,H) = 6.0 Hz, 1H; aromatic proton). ^{13}C{^{1}H} NMR (100.6 MHz, [D$_8$]toluene, 20 °C): δ = 199.9 (dt, ^2J(C,P) = 83.6 Hz, ^2J(C,P) = 15.8 Hz; CO), 138.3-124.2 ppm (m; aromatic carbon atoms). ^{31}P{^{1}H} NMR (162.0 MHz, [D$_8$]toluene, 20 °C): δ = 31.2 (pseudo-t, ^2J(P,P) = 24.3 Hz, 1P; Ar*P*Ph$_2$), 25.8 (dd, ^2J(P,P) = 348.7 Hz, ^2J(P,P) = 25.2 Hz, 1P; *P*Ph$_3$), 21.3 ppm (dd, ^2J(P,P) = 348.6 Hz, ^2J(P,P) = 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*,*R*)-Skewphos)(PPh$_3$)] (10)

Complex **10** was prepared following the procedure used for **7**, with (*R*,*R*)-Skewphos (110.1 mg, 0.25 mmol, 1 equiv.) in place of dppf. Yield: 146.7 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, [D$_2$]dichloromethane, 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(H,P) = 13.7 Hz, ^3J(H,H) = 7.2 Hz; CHC*H*$_3$), 1.05 (dd, ^3J(H,P) = 11.7 Hz, ^3J(H,H) = 6.6 Hz; CHC*H*$_3$), 0.68 (dd, ^3J(H,P) = 11.5 Hz, ^3J(H,H) = 6.4 Hz; CHC*H*$_3$), 0.55 ppm (dd, ^3J(H,P) = 12.3 Hz, ^3J(H,H) = 7.2 Hz; CHC*H*$_3$). ^{31}P{^{1}H} NMR (81.0 MHz, [D$_2$]dichloromethane, 20 °C): δ = 28.6 (d, ^2J(P,P) = 29.3 Hz, 1P), 24.4 (d, ^2J(P,P)

= 29.3 Hz, 2P), 22.6 (dd, ^{2}J(P,P) = 29.1 Hz, ^{2}J(P,P) = 20.9 Hz, 3P), 17.2 ppm (d, ^{2}J(P,P) = 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$_3$)$_2$] (300.3 mg, 0.39 mmol) was suspended in CH_2Cl_2 (5 mL) and reacted with dppb (166.3 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: 231.2 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, [D$_2$]dichloromethane, 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, [D$_2$]dichloromethane, - 80 °C): δ = 8.05-7.74 (m, 3H; aromatic protons), 7.72-7.20 (m, 15H; aromatic protons), 7.03 (t, ^{3}J(H,H) = 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, [D$_2$]dichloromethane, 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, [D$_2$]dichloromethane, - 80 °C): δ = 204.5 (dd, ^{2}J(C,P) = 21.6 Hz, ^{2}J(C,P) = 15.8 Hz; CO), 202.6 (t, ^{2}J(C,P) = 17.0 Hz; CO), 189.1 (s; CH_3*C*O), 182.4 (t, ^{3}J(C,P) = 38.5 Hz; CH_3*C*O), 175.3 (d, ^{3}J(C,P) = 2.6 Hz; CH_3*C*O), 137.3-122.7 (m; aromatic carbon atoms), 29.9 (d, ^{1}J(C,P) = 35.3 Hz; P*C*H_2), 27.7 (d, ^{1}J(C,P) = 32.7 Hz; P*C*H_2), 25.2 (br s; *C*H_2), 24.4 (s; *C*H_3CO), 21.9 (d, ^{4}J(C,P) = 4.3 Hz; *C*H_3CO), 20.5 ppm (br s; *C*H_2). ^{31}P{^{1}H} NMR (81.0 MHz, [D$_2$]dichloromethane, 20 °C): δ = 46.8 ppm (br s). ^{31}P{^{1}H} NMR (81.0 MHz, [D$_2$]dichloromethane, - 60 °C): δ = 48.2 (d, ^{2}J(P,P) = 27.0 Hz, major isomer), 46.1 (d, ^{2}J(P,P) = 27.0 Hz, major isomer), 43.3 ppm (br s, minor isomer). ^{31}P{^{1}H} NMR (81.0 MHz, [D$_2$]dichloromethane, - 80 °C): δ = 48.0 (d, ^{2}J(P,P) = 26.4 Hz, major isomer), 46.2 (d, ^{2}J(P,P) = 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$_3$)$_2$] (200.5 mg, 0.26 mmol) suspended in toluene (5 mL), was added of dppf (144.1 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: 139.6 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. ^{1}H NMR (200.1 MHz, [D$_2$]dichloromethane, 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). ^{1}H NMR (200.1 MHz, [D$_2$]dichloromethane, - 70 °C): δ = 7.94 (t, ^3J(H,H) = 9.0 Hz; aromatic protons), 7.74 (t, ^3J(H,H) = 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{^{1}H} NMR (50.3 MHz, [D$_2$]dichloromethane, 20 °C): δ = 134.6-.2 (m; aromatic carbon atoms), 75.6 (dd, ^2J(C,P) = 37.0 Hz, ^4J(C,P) = 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{^{1}H} NMR (50.3 MHz, [D$_2$]dichloromethane, - 70 °C): δ = 203.3 (t, ^2J(C,P) = 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(C,P) = 5.4 Hz; C_5H_4), 75.4 (d, J(C,P) = 7.3 Hz; C_5H_4), 75.0 (d, J(C,P) = 7.4 Hz; C_5H_4), 74.4 (d, J(C,P) = 8.9 Hz; C_5H_4 major isomer), 72.7 (d, J(C,P) = 6.1 Hz; C_5H_4 major isomer), 71.8 (d, J(C,P) = 5.4 Hz; C_5H_4), 71.1 (d, J(C,P) = 5.4 Hz; C_5H_4), 25.4 (s; *C*H_3CO major isomer), 24.5 (d, ^4J(C,P) = 4.8 Hz; *C*H_3CO), 23.8 ppm (s; *C*H_3CO major isomer). ^{31}P{^{1}H} NMR (81.0 MHz, [D$_2$]dichloromethane, 20 °C): δ = 50.7 ppm (br s). ^{31}P{^{1}H} NMR (81.0 MHz, [D$_2$]dichloromethane, - 70 °C): δ = 53.1 (d, ^2J(P,P) = 26.8 Hz), 52.0 (d, ^2J(P,P) = 27.5 Hz), 50.4 (d, ^2J(P,P) = 27.5 Hz), 49.8 (d, ^2J(P,P) = 30.4 Hz; major isomer), 45.4 (d, ^2J(P,P) = 30.4 Hz; major isomer), 43.5 ppm (d, ^2J(P,P) = 26.8 Hz). IR (Nujol): $\tilde{\nu}$ = 1974 (s) (C≡O), 1613 (s), 1569 (s) (C=O) cm^{-1}.

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: 210.3 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,

[D_2]dichloromethane, 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(H,H) = 8.4 Hz, 2H; aromatic protons), 6.79 (d, ^3J(H,H) = 6.6 Hz, 2H; aromatic protons), 6.69 (d, ^3J(H,H) = 8.4 Hz, 2H; aromatic protons), 6.60 (d, ^3J(H,H) = 6.5 Hz, 2H; aromatic protons), 1.29 ppm (br s, 6H; CH_3CO). ^{1}H NMR (200.1 MHz, [D_2]dichloromethane, - 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, [D_2]dichloromethane, - 60 °C): δ = 205.0 (t, ^2J(C,P) = 27.2 Hz; CO), 189.1 (d, ^3J(C,P) = 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(C,P) = 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(C,P) = 7.3 Hz; CH_3CO), 22.3 (d, ^4J(C,P) =7.4 Hz; CH_3CO major isomer), 21.1 ppm (s; CH_3CO). ^{31}P{^{1}H} NMR (81.0 MHz, [D_2]dichloromethane, 20 °C): δ = 50.5 (d, ^2J(P,P) = 25.3 Hz), 43.4 ppm (br s). ^{31}P{^{1}H} NMR (81.0 MHz, [D_2]dichloromethane, - 60 °C): δ = 49.6 (d, ^2J(P,P) = 27.6 Hz; major isomer), 40.1 ppm (d, ^2J(P,P) = 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 (114.5 mg, 0.26 mmol, 1 equiv.) in place of dppf. Yield: 126.9 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, [D_2]dichloromethane, 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(H,H) = 15.6 Hz, ^3J(H,P) = 7.5 Hz, 3H; CHC*H*$_3$), 0.89 ppm (dd, ^3J(H,H) = 12.5 Hz, ^3J(H,P) = 7.0 Hz, 3H; CHC*H*$_3$). ^{1}H NMR (200.1 MHz, [D_2]dichloromethane, - 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(H,H) = 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(H,H) = 15.2 Hz, ^3J(H,P) = 6.6 Hz; CHC*H*$_3$), 0.75 ppm (dd, ^3J(H,H) = 12.2 Hz, ^3J(H,P) = 6.4 Hz; CHC*H*$_3$). ^{13}C{^{1}H} NMR (50.3 MHz, [D_2]dichloromethane, - 60 °C): δ = 203.4 (m; CO), 201.80 (t, ^2J(C,P) = 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; CH*C*H$_2$), 35.5 (br s; CH*C*H$_2$), 35.0 (br

s; CH*C*H$_2$ major isomer), 34.5 (br s; CH*C*H$_2$), 31.0 (d, ^1J(C,P) = 31.6 Hz; P*C*H), 30.0 (d, ^1J(C,P) = 35.0 Hz; P*C*H major isomer), 25.2 (s; *C*H$_3$CO major isomer), 24.9 (d, ^4J(C,P) = 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(C,P) = 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{^{1}H} NMR (81.0 MHz, [D$_2$]dichloromethane, 20 °C): δ = 55.0 (br s), 50.6 ppm (br s). ^{31}P{^{1}H} NMR (81.0 MHz, [D$_2$]dichloromethane, - 60 °C): δ = 59.5 (d, ^2J(P,P) = 35.1 Hz), 58.6 (d, ^2J(P,P) = 33.8 Hz), 56.7 (d, ^2J(P,P) = 34.2 Hz), 54.3 (d, ^2J(P,P) = 38.8 Hz; major isomer), 52.3 (d, ^2J(P,P) = 38.7 Hz), 51.6 (d, ^2J(P,P) = 36.5 Hz), 48.8 (d, ^2J(P,P) = 38.8 Hz; major isomer), 48.1 (d, ^2J(P,P) = 34.6 Hz), 48.0 (d, ^2J(P,P) = 36.5 Hz), 47.0 (d, ^2J(P,P) = 28.2 Hz), 46.1 ppm (d, ^2J(P,P) = 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$_2$Cl$_2$ (5 mL) and reacted with dppb (123.7 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: 149.3 mg (87%). Elemental analysis calcd (%) for C$_{31}$H$_{36}$Cl$_2$N$_2$OP$_2$Ru (686.56): C 54.23, H 5.29, N 4.08; found: C 54.18, H 5.22, N 4.10. ^{1}H 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$_2$N), 2.35-1.65 ppm (m, 8H; CH$_2$ and CH$_2$N). ^{13}C{^{1}H} NMR (50.3 MHz, CD$_2$Cl$_2$, 20 °C): δ = 199.5 (t, ^2J(C,P) = 13.6 Hz; CO), 136.9-128.6 (aromatic carbon atoms), 45.9 (s; *C*H$_2$N), 25.5 (t, ^1J(C,P) = 14.8 Hz; P*C*H$_2$), 22.1 ppm (s; PCH$_2$*C*H$_2$). ^{31}P{^{1}H}0 NMR (81.0 MHz, CD$_2$Cl$_2$, 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: 148.0 mg (98%).

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: 179.2 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, [D$_2$]dichloromethane, 20 °C): δ = 7.80-7.35 (m, 20H; aromatic protons), 5.59 (br s, 2H; NH_2), 5.05 (m, 2H; 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, 2H; C_5H_4), 2.51 (m, 2H; CH_2N), 2.14-1.85 ppm (m, 2H; CH_2N). ^{13}C{^{1}H} NMR (50.3 MHz, [D$_2$]dichloromethane, 20 °C): δ = 199.9 (t, ^2J(C,P) = 14.4 Hz; CO), 135.9-128.4 (m; aromatic carbon atoms), 89.7 (d, ^1J(C,P) = 55.1 Hz; *ipso*-C_5H_4), 89.0 (d, ^1J(C,P) = 52.4 Hz; *ipso*-C_5H_4), 77.9 (t, J(C,P) = 4.9 Hz; C_5H_4), 75.8 (t, J(C,P) = 3.1 Hz; C_5H_4), 73.6 (t, J(C,P) = 3.3 Hz; C_5H_4), 71.4 (t, J(C,P) = 3.0 Hz; C_5H_4), 45.8 ppm (s; CH_2N). ^{31}P{^{1}H} NMR (81.0 MHz, [D$_2$]dichloromethane, 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$_3$)$_2$] (200.5 mg, 0.26 mmol) was suspended in CH_2Cl_2 (2 mL) and reacted with dppb (122.0 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: 185.0 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, [D$_4$]methanol, 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, [D$_4$]methanol, 20 °C): δ = 203.9 (t, ^2J(C,P) = 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(C,P) = 11.0 Hz; CH_2N), 44.9 (br s; CH_2N), 33.1 (br s; CH_2), 30.0 (d, ^1J(C,P) = 21.5 Hz; PCH_2), 29.8 (d, ^1J(C,P) = 28.9 Hz; PCH_2), 25.6 (s; CH_3CO), 24.1 (s; CH_3CO), 23.5 ppm (br s; CH_2). ^{31}P{^{1}H} NMR (81.0 MHz, [D$_4$]methanol, 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** (124.0 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: 125.1 mg (87%). Elemental analysis calcd (%) for $C_{39}H_{42}N_2O_5P_2Ru$ (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, [D$_8$]toluene, 20 °C): δ = 8.15 (m, 1H; ortho-C*H* of C_5H_4N), 7.62-6.81 (m, 22H; aromatic protons), 6.61 (d, ^3J(H,H) = 7.7 Hz, 1H; meta-C*H* of C_5H_4N), 6.21 (pseudo-t, *J*(H,H) = 8.8 Hz, 1H; NH_2), 4.22 (dd, ^2J(H,H) = 12.4 Hz, ^3J(H,H) = 10.2 Hz, 1H; CH_2N), 3.21 (dd, ^2J(H,H) = 12.4 Hz, ^3J(H,H) = 10.7 Hz, 1H; CH_2N), 3.02 (m, 1H; PCH_2), 2.56 (m, 1H; PCH_2), 2.04 (s, 3H; CH_3CO), 1.94 (s, 3H; CH_3CO), 1.67 (m, 2H; PCH_2 + NH_2), 1.49-1.14 ppm (m, 5H; PCH_2CH_2). ^{13}C{^{1}H} NMR (50.3 MHz, [D$_8$]toluene, 20 °C): δ = 203.2 (t, ^2J(C,P) = 12.7 Hz; CO), 187.6 (s; CH_3CO), 177.0 (s; CH_3CO), 159.8 (d, ^3J(C,P) = 3.8 Hz; N*C*CH_2), 149.1 (d, ^3J(C,P) = 22.9 Hz; ortho-*C*H of C_5H_4N), 135.7-120.8 (m; aromatic carbon atoms), 50.4 (s; *C*H_2N), 30.2 (d, ^1J(C,P) = 33.5 Hz; P*C*H_2), 29.8 (d, ^1J(C,P) = 36.1 Hz; P*C*H_2), 26.1 (d, ^2J(C,P) = 2.7 Hz; *C*H_2), 25.8 (s; *C*H_3CO), 24.6 ppm (d, ^4J(C,P) = 4.8 Hz; *C*H_3CO). ^{31}P{^{1}H} NMR (81.0 MHz, [D$_8$]toluene, 20 °C): δ = 46.4 (d, ^2J(P,P) = 28.8 Hz), 34.0 ppm (d, ^2J(P,P) = 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** (127.6 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: 120.6 mg (88%). Elemental analysis calcd (%) for $C_{41}H_{42}FeN_2O_5P_2Ru$ (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, [D$_2$]dichloromethane, 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_5H_4), 4.42 (br s, 5H; C_5H_4), 4.16 (br s, 2H; C_5H_4), 2.87 (br s, 4H; CH_2N), 2.62 (br s, 2H; NH_2), 1.79 (br s, 6H; CH_3CO), 1.27 ppm (br s. 1H; NH_2). ^{13}C{^{1}H} NMR (50.3 MHz, [D$_2$]dichloromethane, 20 °C): δ = 203.2 (t, ^2J(C,P) = 15.1 Hz; *C*O), 181.4 (s; CH_3CO), 176.6 (dd, ^3J(C,P) = 12.1 Hz, ^3J(C,P) = 5.6 Hz; CH_3CO), 135.5-128.5 (m; aromatic carbon atoms), 79.6 (dd, ^1J(C,P) = 65.8 Hz, ^3J(C,P) = 9.6 Hz; ipso-C_5H_4), 75.7 (dt, *J*(C,P) = 18.9 Hz, *J*(C,P) = 4.3 Hz; C_5H_4), 73.0 (dt, *J*(C,P) = 14.6 Hz,

J(C,P) = 2.9 Hz; *C*$_5$H$_4$), 45.7 (s; *C*H$_2$N), 26.1 ppm (s; *C*H$_3$CO). ^{31}P{^{1}H} NMR (81.0 MHz, [D$_2$]dichloromethane, 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** (120.3 mg, 0.150 mmol) in place of **11**. Yield: 118.7 mg (87%). Elemental analysis calcd (%) for C$_{45}$H$_{42}$FeN$_2$O$_5$P$_2$Ru (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, [D$_8$]toluene, 20 °C): δ = 8.68 (d, ^{3}*J*(H,H) = 4.9 Hz, 1H; ortho-C*H* of C$_5$H$_4$N), 8.00 (dd, ^{3}*J*(H,H) = 7.9 Hz, ^{4}*J*(H,H) = 1.5 Hz, 1H; para-C*H* of C$_5$H$_4$N), 7.46-6.79 (m, 21H; aromatic protons), 6.61 (d, ^{3}*J*(H,H) = 7.8 Hz, 1H; meta-C*H* of C$_5$H$_4$N), 6.07 (pseudo-t, *J*(H,H) = 9.2 Hz, 1H; NH$_2$), 4.84 (m, 1H; CH$_2$N), 4.77 (s, 1H; C$_5$H$_4$), 4.22 (s, 1H; C$_5$H$_4$), 3.91 (s, 1H; C$_5$H$_4$), 3.72 (br s, 4H; C$_5$H$_4$), 3.42 (s, 1H; C$_5$H$_4$), 2.55 (t, ^{3}*J*(H,H) = 13.5 Hz, 1H; CH$_2$N), 2.33 (m, 1H; NH$_2$), 1.85 (s, 3H; CH$_3$CO), 1.67 ppm (s, 3H; CH$_3$CO). ^{13}C{^{1}H} NMR (50.3 MHz, [D$_8$]toluene, 20 °C): δ = 210.3 (t, ^{2}*J*(C,P) = 16.4 Hz; CO), 178.4 (s; CH$_3$*C*O), 177.0 (d, ^{3}*J*(C,P) = 2.7 Hz; CH$_3$*C*O), 160.1 (d, ^{2}*J*(C,P) = 3.7 Hz; N*C*CH$_2$), 149.1 (s; ortho-*C*H of C$_5$H$_4$N), 137.1-121.2 (m; aromatic carbon atoms), 81.5 (d, ^{1}*J*(C,P) = 51.0 Hz; ipso-*C*$_5$H$_4$), 81.4 (d, ^{1}*J*(C,P) = 49.3 Hz; ipso-*C*$_5$H$_4$), 77.0 (d, *J*(C,P) = 4.0 Hz; C$_5$H$_4$), 76.5 (d, *J*(C,P) = 7.3 Hz; C$_5$H$_4$), 75.3 (d, *J*(C,P) = 7.3 Hz; C$_5$H$_4$), 75.0 (d, *J*(C,P) = 5.2 Hz; C$_5$H$_4$), 74.8 (s; C$_5$H$_4$), 71.3 (d, *J*(C,P) = 5.2 Hz; C$_5$H$_4$), 70.3 (d, *J*(C,P) = 5.7 Hz; C$_5$H$_4$), 50.4 (s; *C*H$_2$N), 26.1 (s; *C*H$_3$CO), 24.6 ppm (d, ^{4}*J*(C,P) = 4.9 Hz; *C*H$_3$CO). ^{31}P{^{1}H} NMR (81.0 MHz, [D$_8$]toluene, 20 °C): δ = 51.2 (d, ^{2}*J*(P,P) = 29.1 Hz), 40.5 ppm (d, ^{2}*J*(P,P) = 29.1 Hz). IR (Nujol): $\tilde{\nu}$ = 1959 (s) (C≡O), 1609 (s), 1586 (s) (C=O) cm^{-1}.

Procedure for the TH of 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).

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 or16 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.

Supporting Information. NMR spectra of the isolated complexes and further data about the aldehyde and ketone TH and HY reductions catalyzed by these derivatives. This material is available free of charge via the Internet at http://pubs.acs.org

Corresponding Authors. E-mails: maurizio.ballico@uniud.it, walter.baratta@uniud.it

ORCID

Walter Baratta: 0000-0002-2648-1848

Notes

The authors declare no competing financial interests.

Acknowledgments. This work was supported by the Fellowship Program "Talents for an International House (TALENTS UP)" (7th R&D FP: PEOPLE - Marie Curie Actions - COFUND) and AREA Consortium of Trieste for a fellowship for S. G. and by the Ministero dell'Università e della Ricerca (MIUR), PRIN 2015 program n° 20154X9ATP_005. We thank Mr. Francesco Cesaro for carrying out transfer hydrogenation tests, Mr. Pierluigi Polese for the elemental analyses and Dr. Paolo Martinuzzi for NMR assistance. Dr. Antonio Zanotti-Gerosa Johnson Matthey (Cambridge) is also acknowledged for helpful discussions on hydrogenation reactions.

References

1. X. Xie, B. Lu, W. Li and Z. Zhang, *Coord. Chem. Rev.*, 2018, **355**, 39-53.
2. M. Yoshimura, S. Tanaka and M. Kitamura, *Tetrahedron Lett.*, 2014, **55**, 3635-3640.
3. G. Shang, W. Li and X. Zhang, in *Catalytic Asymmetric Synthesis*, ed. I. Ojima, John Wiley & Sons, Inc., Hoboken, 3rd edn., 2010, vol. 1, ch. 7, pp. 343-436.
4. *The Handbook of Homogeneous Hydrogenation, Vol. 1-3*, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, 2007.
5. D. Wang and D. Astruc, *Chem. Rev.*, 2015, **115**, 6621-6686.
6. F. Foubelo, C. Nájera and M. Yus, *Tetrahedron: Asymmetry*, 2015, **26**, 769-790.
7. J.-i. Ito and H. Nishiyama, *Tetrahedron Lett.*, 2014, **55**, 3133-3146.
8. R. H. Morris, *Chem. Soc. Rev.*, 2009, **38**, 2282-2291.
9. W. Chao, W. Xiaofeng and X. Jianliang, *Chem. Asian J.*, 2008, **3**, 1750-1770.
10. W. Baratta and P. Rigo, *Eur. J. Inorg. Chem.*, 2008, 4041-4053.
11. J. S. M. Samec, J.-E. Bäckvall, P. G. Andersson and P. Brandt, *Chem. Soc. Rev.*, 2006, **35**, 237-248.
12. J. Magano and J. R. Dunetz, *Org. Process Res. Dev.*, 2012, **16**, 1156-1184.
13. T. Ohkuma, N. Utsumi, K. Tsutsumi, K. Murata, C. Sandoval and R. Noyori, *J. Am. Chem. Soc.*, 2006, **128**, 8724-8725.
14. T. Ohkuma, C. A. Sandoval, R. Srinivasan, Q. Lin, Y. Wei, K. Muñiz and R. Noyori, *J. Am. Chem. Soc.*, 2005, **127**, 8288-8289.
15. W. Baratta, E. Herdtweck, K. Siega, M. Toniutti and P. Rigo, *Organometallics*, 2005, **24**, 1660-1669.
16. S. Hashiguchi, A. Fujii, K. J. Haack, K. Matsumura, T. Ikariya and R. Noyori, *Angew. Chem. Int. Ed. Engl.*, 1997, **36**, 288-290.
17. D. A. Cavarzan, F. D. Fagundes, O. Fuganti, C. W. P. da Silva, C. B. Pinheiro, D. F. Back, A. Barison, A. L. Bogado and M. P. de Araujo, *Polyhedron*, 2013, **62**, 75-82.
18. R. N. Prabhu and R. Ramesh, *J. Organomet. Chem.*, 2012, **718**, 43-51.
19. J.-i. Ito, T. Teshima and H. Nishiyama, *Chem. Commun.*, 2012, **48**, 1105-1107.
20. B. J. Sarmah and D. K. Dutta, *J. Organomet. Chem.*, 2010, **695**, 781-785.
21. J. Zhang, G. Leitus, Y. Ben-David and D. Milstein, *Angew. Chem. Int. Ed.*, 2006, **45**, 1113-1115.
22. D. Spasyuk and D. G. Gusev, *Organometallics*, 2012, **31**, 5239-5242.
23. W. Kuriyama, T. Matsumoto, O. Ogata, Y. Ino, K. Aoki, S. Tanaka, K. Ishida, T. Kobayashi, N. Sayo and T. Saito, *Org. Process Res. Dev.*, 2012, **16**, 166-171.
24. P. A. Dub and T. Ikariya, *ACS Catal.*, 2012, **2**, 1718-1741.
25. E. Fogler, E. Balaraman, Y. Ben-David, G. Leitus, L. J. W. Shimon and D. Milstein, *Organometallics*, 2011, **30**, 3826-3833.
26. E. Balaraman, C. Gunanathan, J. Zhang, L. J. W. Shimon and D. Milstein, *Nat. Chem.*, 2011, **3**, 609-614.

27. S. Muthaiah and S. H. Hong, *Adv. Synth. Catal.*, 2012, **354**, 3045-3053.
28. T. C. Johnson, D. J. Morris and M. Wills, *Chem. Soc. Rev.*, 2010, **39**, 81-88.
29. G. E. Dobereiner and R. H. Crabtree, *Chem. Rev.*, 2010, **110**, 681-703.
30. E. Balaraman, B. Gnanaprakasam, L. J. W. Shimon and D. Milstein, *J. Am. Chem. Soc.*, 2010, **132**, 16756-16758.
31. J. Zhang, M. Gandelman, L. J. W. Shimon and D. Milstein, *Dalton Trans.*, 2007, 107-113.
32. C. Gunanathan, Y. Ben-David and D. Milstein, *Science*, 2007, **317**, 790-792.
33. J. van Buijtenen, J. Meuldijk, J. A. J. M. Vekemans, L. A. Hulshof, H. Kooijman and A. L. Spek, *Organometallics*, 2006, **25**, 873-881.
34. J. Zhang, G. Leitus, Y. Ben-David and D. Milstein, *J. Am. Chem. Soc.*, 2005, **127**, 10840-10841.
35. C. J. Creswell, A. Dobson, D. S. Moore and S. D. Robinson, *Inorg. Chem.*, 1979, **18**, 2055-2059.
36. A. Dobson and S. D. Robinson, *Inorg. Chem.*, 1977, **16**, 137-142.
37. A. J. A. Watson, B. N. Atkinson, A. C. Maxwell and J. M. J. Williams, *Adv. Synth. Catal.*, 2013, **355**, 734-740.
38. J. R. Zbieg, E. L. McInturff and M. J. Krische, *Org. Lett.*, 2010, **12**, 2514-2516.
39. A. Denichoux, T. Fukuyama, T. Doi, J. Horiguchi and I. Ryu, *Org. Lett.*, 2010, **12**, 1-3.
40. T. D. Nixon, M. K. Whittlesey and J. M. J. Williams, *Dalton Trans.*, 2009, 753-762.
41. S. Burling, B. M. Paine, D. Nama, V. S. Brown, M. F. Mahon, T. J. Prior, P. S. Pregosin, M. K. Whittlesey and J. M. J. Williams, *J. Am. Chem. Soc.*, 2007, **129**, 1987-1995.
42. M. C. Warner and J.-E. Bäckvall, *Acc. Chem. Res.*, 2013, **46**, 2545-2555.
43. B. Stewart, J. Nyhlen, B. Martin-Matute, J.-E. Backvall and T. Privalov, *Dalton Trans.*, 2013, **42**, 927-934.
44. M. C. Warner, O. Verho and J.-E. Bäckvall, *J. Am. Chem. Soc.*, 2011, **133**, 2820-2823.
45. J. Nyhlén, T. Privalov and J.-E. Bäckvall, *Chem. Eur. J.*, 2009, **15**, 5220-5229.
46. Y. Ahn, S.-B. Ko, M.-J. Kim and J. Park, *Coord. Chem. Rev.*, 2008, **252**, 647-658.
47. L. A. Saudan, C. M. Saudan, C. Debieux and P. Wyss, *Angew. Chem. Int. Ed.*, 2007, **46**, 7473-7476.
48. J. R. Miecznikowski and R. H. Crabtree, *Organometallics*, 2004, **23**, 629-631.
49. C. M. Beck, S. E. Rathmill, Y. J. Park, J. Chen, R. H. Crabtree, L. M. Liable-Sands and A. L. Rheingold, *Organometallics*, 1999, **18**, 5311-5317.
50. 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; (*S*,*R*)-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.
51. S. Zhang, S. Baldino and W. Baratta, *Organometallics*, 2013, **32**, 5299-5304.
52. S. Giboulot, S. Baldino, M. Ballico, R. Figliolia, A. Pöthig, S. Zhang, D. Zuccaccia and W. Baratta, *Organometallics*, 2019, **38**, 1127-1142.
53. S. Giboulot, S. Baldino, M. Ballico, H. G. Nedden, D. Zuccaccia and W. Baratta, *Organometallics*, 2018, **37**, 2136-2146.
54. G. Chelucci, S. Baldino and W. Baratta, *Coord. Chem. Rev.*, 2015, **300**, 29-85.
55. M. M. Rahman, H. Y. Liu, A. Prock and W. P. Giering, *Organometallics*, 1987, **6**, 650-658.
56. C. W. Jung, P. E. Garrou, P. R. Hoffman and K. G. Caulton, *Inorg. Chem.*, 1984, **23**, 726-729.
57. E. Putignano, G. Bossi, P. Rigo and W. Baratta, *Organometallics*, 2012, **31**, 1133-1142.

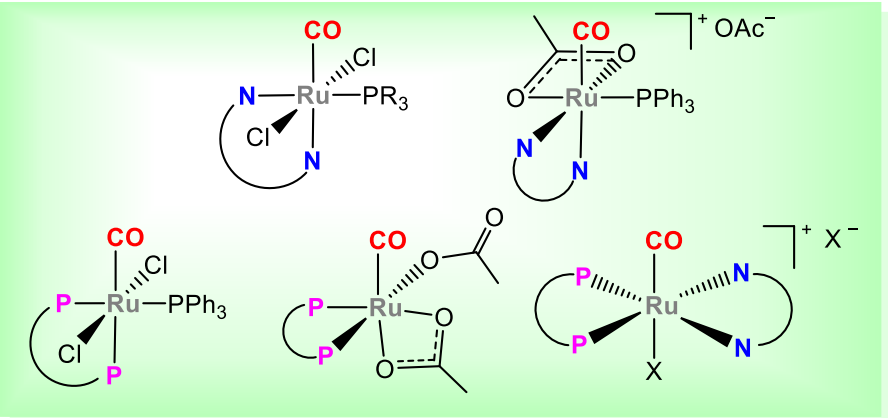
58. M. I. Frazão Barbosa, E. M. A. Valle, S. L. Queiroz, J. Ellena, E. E. Castellano, V. R. S. Malta, J. R. de Sousa, O. Piro, M. P. de Araujo and A. A. Batista, *Polyhedron*, 2010, **29**, 2297-2303.
59. A. Mukherjee, P. Paul and S. Bhattacharya, *J. Organomet. Chem.*, 2017, **834**, 47-57.
60. D. A. Hey, P. J. Fischer, W. Baratta and F. E. Kühn, *Dalton Trans.*, 2019, **48**, 4625-4635.
61. R. Figliolia, S. Baldino, H. G. Nedden, A. Zanotti-Gerosa and W. Baratta, *Chem. Eur. J.*, 2017, **23**, 14416-14419.
62. J. Berstler, A. Lopez, D. Ménard, W. G. Dougherty, W. S. Kassel, A. Hansen, A. Daryaei, P. Ashitey, M. J. Shaw, N. Fey and C. Nataro, *J. Organomet. Chem.*, 2012, **712**, 37-45.
63. N. Fey, J. N. Harvey, G. C. Lloyd-Jones, P. Murray, A. G. Orpen, R. Osborne and M. Purdie, *Organometallics*, 2008, **27**, 1372-1383.
64. M. A. Beckett, D. S. Brassington, S. J. Coles, T. Gelbrich, M. E. Light and M. B. Hursthouse, *J. Organomet. Chem.*, 2003, **688**, 174-180.
65. R. J. Angelici, *Acc. Chem. Res.*, 1995, **28**, 51-60.
66. T. S. A. Hor and L.-T. Phang, *J. Organomet. Chem.*, 1989, **373**, 319-324.
67. S. Baldino, S. Facchetti, A. Zanotti-Gerosa, H. G. Nedden and W. Baratta, *ChemCatChem*, 2016, **8**, 2279-2288.
68. S. Baldino, S. Facchetti, H. G. Nedden, A. Zanotti-Gerosa and W. Baratta, *ChemCatChem*, 2016, **8**, 3195-3198.
69. W. Baratta, S. Baldino, M. J. Calhorda, P. J. Costa, G. Esposito, E. Herdtweck, S. Magnolia, C. Mealli, A. Messaoudi, S. A. Mason and L. F. Veiros, *Chem. Eur. J.*, 2014, **20**, 13603-13617.
70. W. Baratta, M. Ballico, A. Del Zotto, E. Herdtweck, S. Magnolia, R. Peloso, K. Siega, M. Toniutti, E. Zangrando and P. Rigo, *Organometallics*, 2009, **28**, 4421-4430.
71. P. A. Dub, N. J. Henson, R. L. Martin and J. C. Gordon, *J. Am. Chem. Soc.*, 2014, **136**, 3505-3521.
72. C. A. Sandoval, T. Ohkuma, K. Muñiz and R. Noyori, *J. Am. Chem. Soc.*, 2003, **125**, 13490-13503.
73. B. R. James, L. D. Markham, B. C. Hui and G. L. Rempel, *J. Chem. Soc., Dalton Trans.*, 1973, 2247-2252.
74. P. A. Anderson, G. B. Deacon, K. H. Haarmann, F. R. Keene, T. J. Meyer, D. A. Reitsma, B. W. Skelton, G. F. Strouse, N. C. Thomas, J. A. Treadway and A. H. White, *Inorg. Chem.*, 1995, **34**, 6145-6157.
75. A. Spencer and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1974, 786-792.

Table of content

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

Steven Giboulot,[#,£] Clara Comuzzi,[#] Alessandro Del Zotto,[#] Rosario Figliolia,[#] Giovanna Lippe,[#] Denise Lovison,[#] Paolo Strazzolini,[#] Sabina Susmel,[#] Ennio Zangrando, Daniele Zuccaccia,[#] Salvatore Baldino, [#,⊥] Maurizio Ballico,[#,*] Walter Baratta[#,*]

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