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Synthesis of [RuX(CO)(dppp)(NN)]Cl (X = H, Cl; NN = en, ampy) Complexes and Their Use as Catalysts for Transfer Hydrogenation

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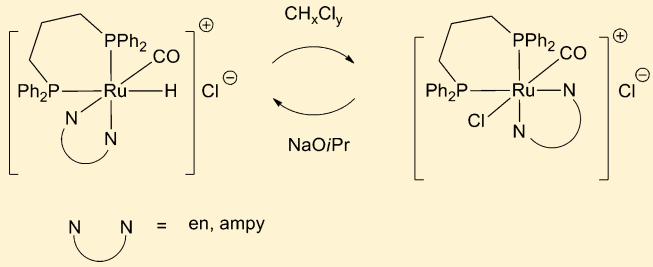
Supporting Information

ABSTRACT: The monocarbonyl hydride complexes [RuH(CO)(dppp)(NN)]Cl (dppp = $Ph_2P(CH_2)_3PPh_2$; NN = ethylenediamine (en), **1**; NN = 2-aminomethylpyridine (ampy), **3**) have been isolated in high yield by reaction of $RuHCl(CO)(PPh_3)(dppp)$ with en and ampy, respectively, in toluene at reflux. The chloride complexes [RuCl(CO)(dppp)(NN)]Cl (NN = en, **2**; NN = ampy, **4**) have been obtained quantitatively by dissolution of **1** in CH_2Cl_2 and **3** in $CHCl_3$, through substitution of the hydride with a chloride and isomerization. Treatment of **4** with NaO*i*Pr in 2-propanol at room temperature cleanly leads to the hydride complex **3**. Complexes **1**−**4** have been proven to be robust and productive catalysts for the transfer hydrogenation of alkyl aryl, diaryl, dialkyl, and cyclic ketones using 0.2−0.004 mol % of catalyst and in the presence of 2 mol % of NaO*i*Pr, affording TOF values up to 2.5×10^5 h^{-1}.



INTRODUCTION

The search for new, more efficient transition-metal catalysts is of crucial importance for the preparation of high-value-added organic compounds. Ligand design plays a key role for achieving catalysts with high productivity and selectivity for industrial applications. Among the transition metals, ruthenium has attracted a great deal of attention on account of its high performance and versatility for a large number of catalytic organic transformations.[1] The catalytic reduction of the carbonyl bond via hydrogenation (HY)[2] and transfer hydrogenation (TH)[3] is widely accepted in industry as a cost-effective and environmentally benign way for the production of a number of organic products.[4] The Noyori catalysts *trans*-$RuCl_2(PP)(1,2\text{-diamine})$[5] (PP = diphosphine) and (η^6-arene)-$RuCl(TsNCHPhCHPhNH_2)$[6] (Ts = $SO_2C_6H_4CH_3$), displaying the N−H function,[7] have paved the way for the development of new more efficient catalysts for the HY and TH of carbonyl compounds.[8] In the past decade, ruthenium monocarbonyl complexes have been intensively investigated on account of their high catalytic performance for several organic transformations, including HY of carboxylic and carbonic acid derivatives,[9] alcohol dehydrogenation,[10] and borrowing hydrogen reactions.[11] In addition to the catalysts developed by Robinson $[Ru(OCOCF_3)_2(CO)(PPh_3)_2]$[12] and later by Hulshof $[Ru(\mu\text{-}OCOC_2F_4OCO)(CO)(diphosphine)]_2$[13] relevant examples are those reported by Milstein,[14] Gusev,[15] and Saito (Takasago catalyst)[16] (Figure 1).

The presence of one CO ligand stabilizes the Ru(II) hydride complexes, leading to highly productive catalysts with a low tendency to decarbonylate substrates, a known pathway of catalyst deactivation.[16,17] For the Milstein complexes the high activity has been ascribed to the active role played by the pyridine ligand, which undergoes an aromatization/dearomatization process.[18] Incidentally, in 2004 we described monocarbonyl cyclometalated ruthenium complexes of type **A** (Figure 2), containing N−H bidentate nitrogen ligands which efficiently catalyze the TH of ketones.[19]

The derivative bearing 2-aminomethylpyridine (ampy) was found to be more active with respect to the ethylenediamine (en) complex, with TOF values up to 6.3×10^4 h^{-1}. The diphosphine ampy complexes *cis*-$RuCl_2(PP)(ampy)$[20] (**B**) are among the most active catalysts for the ketone TH (TOFs up to 5×10^5 h^{-1}) and for the HY of bulky substrates. These complexes also show activity in dehydrogenation and racemization of alcohols.[20c] On account of their easy deactivation, they are usually employed with a catalyst loading of 0.1 mol % or higher. Therefore, the development of new robust carbonyl Ru catalysts, containing *active ligands*, such as those with an N−H function or a pyridine ring, represents a crucial target for achieving clean catalytic organic transformations.

We describe herein the preparation and characterization of monocarbonyl ruthenium complexes of formula [RuX(CO)(PP)(NN)]Cl (X = H, Cl; dppp = $Ph_2P(CH_2)_3PPh_2$; NN = en, ampy), containing H and Cl and the N−H function, which in the presence of a base show high catalytic activity for the TH of ketones.

RESULTS AND DISCUSSION

Synthesis of the Complexes [RuX(CO)(dppp)(NN)]Cl (X = H, Cl; NN = ampy, en). The monocarbonyl ruthenium

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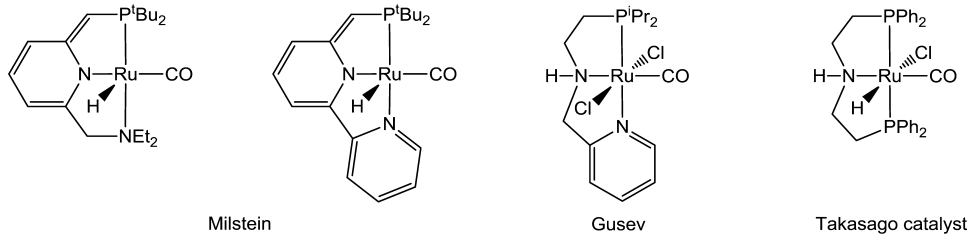


Figure 1.

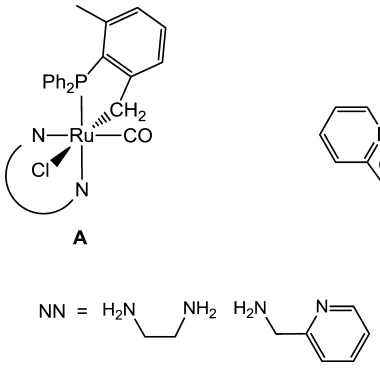


Figure 2.

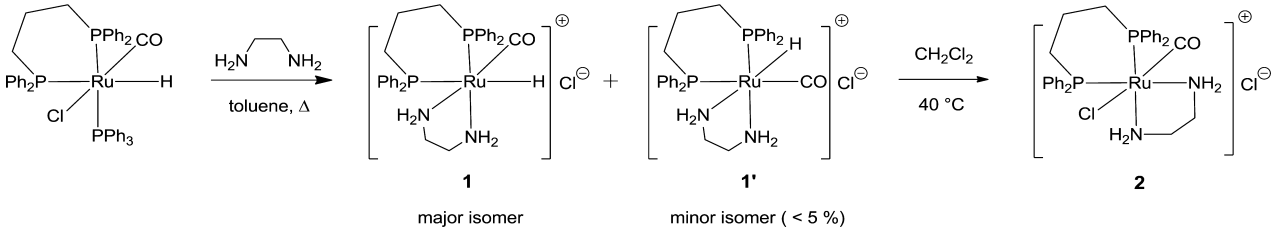
complex RuHCl(CO)(PPh_3)(dppp) has been prepared by reaction of the RuHCl(CO)(PPh_3)$_3$[21] precursor with the diphosphine dppp, according to the procedure reported in the literature.[22] The reaction of RuHCl(CO)(PPh_3)(dppp) with ethylenediamine (1.1 equiv) in toluene at reflux (4 h) affords the cationic complex [RuH(CO)(dppp)(en)]Cl (**1**) in the presence of a small amount of the isomer **1**′ (<5%), as inferred from NMR measurements (Scheme 1).

The $^{31}P\{^1H\}$ NMR spectrum of **1** in CD_2Cl_2 shows two doublets at δ 44.2 and 14.9 with a relatively small $^2J(P,P)$ value of 21.2 Hz, consistent with the presence of two nonequivalent cis phosphorus atoms bound to a Ru−H moiety.[23] The hydride ligand gives rise in the ^1H NMR spectrum to a doublet of doublets at δ −5.86 with $^2J(H,P)$ = 113 and 18.9 Hz, indicating that the phosphorus atoms are trans and cis with respect to the hydride. The IR carbonyl stretching of **1** is at ν 1948 cm^{-1}, while the absorbance at 1854 cm^{-1} is for Ru−H. The minor isomer **1**′ displays in the $^{31}P\{^1H\}$ NMR spectrum two doublets at δ 45.5 and 22.6 with $^2J(P,P)$ = 38.4 Hz, whereas the hydride signal is at δ −13.18 with $^2J(H,P)$ = 25.2 and 20.0 Hz, consistent with the presence of a hydride with two cis nonequivalent phosphorus atoms. Complex **1** cleanly reacts with chlorinated solvents, such as $CHCl_3$ and CH_2Cl_2, leading to the chloride complex [RuCl(CO)(dppp)(en)]Cl (**2**) (Scheme 1).[24] With CH_2Cl_2 quantitative conversion of **1** into **2** was achieved at 40 °C after 15 h. It is worth noting that the hydride **1** is significantly more reactive than **1**′, on account of the presence of the phosphine ligand, which exerts a stronger trans influence to the hydride with respect to the amine.[25] The $^{31}P\{^1H\}$ NMR spectrum of **2** shows one singlet at δ 30.8, whereas the $^{13}C\{^1H\}$ NMR signals of the CO and ethylenediamine ligands appear as a triplet at δ 199.7, with $^2J(C,P)$ = 15.6 Hz, and a singlet at δ 46.8, respectively. These results indicate that the substitution of the hydride with the chloride in **1** occurs with a concomitant isomerization, affording complex **2** with the CO ligand trans to Cl.

Similarly to the synthesis of **1**, treatment of RuHCl(CO)-(PPh_3)(dppp) with ampy in toluene at reflux (12 h) leads to the cationic complex [RuH(CO)(dppp)(ampy)]Cl (**3**), which was isolated in 84% yield (Scheme 2).

The $^{31}P\{^1H\}$ NMR spectrum of **3** shows two doublets at δ 42.6 and 12.8 with $^2J(P,P)$ = 22.7 Hz, whereas in the ^1H NMR spectrum the resonance of the ruthenium hydride appears as a doublet of doublets at δ −5.23 with $^2J(H,P)$ = 113 and 19.2 Hz, which are values similar to those of **1**. The bidentate ampy ligand shows one N−H proton at δ 3.87 and the ortho pyridine proton at δ 8.38, shifted to low field with respect to that of the free ligand. The CO and Ru−H infrared absorbances are at ν 1944 and 1853 cm^{-1}, respectively, very close to those of **1**, suggesting that the CO ligand is trans to the NH_2 function. Similarly to **1**, dissolution of **3** in chlorinated solvents leads to the corresponding chloride complex [RuCl(CO)(dppp)-(ampy)]Cl (**4**) by hydride substitution and isomerization (Scheme 2). Complex **4** is quantitatively obtained from **3** and $CHCl_3$ at room temperature overnight, while the reaction of **3** with CH_2Cl_2 at reflux requires 3 days for complete conversion into **4**. The $^{31}P\{^1H\}$ NMR spectrum of **4** shows two doublets at δ 35.4 and 22.7 with $^2J(P,P)$ = 38.2 Hz, which is a value higher than that of the hydride **3**.[23] The ^{13}C NMR signal of CO is a doublet of doublets at δ 203.6 with $^2J(C,P)$ = 15.5 and 14.2 Hz, consistent with a *fac* Ru(PP)(CO) arrangement. In the ^1H NMR spectrum (CD_2Cl_2) one N−H proton resonates at δ 4.13, whereas the second N−H is shifted significantly to low field at δ 8.16, as established by a $^1H-^1H$ COSY experiment,[24] suggesting an NH···Cl hydrogen bond. The IR CO stretching absorbance is at 1974 cm^{-1}, similar to that of **2** (ν 1975 cm^{-1}), in agreement with a CO trans to the chloride. In the solid state,

Scheme 1



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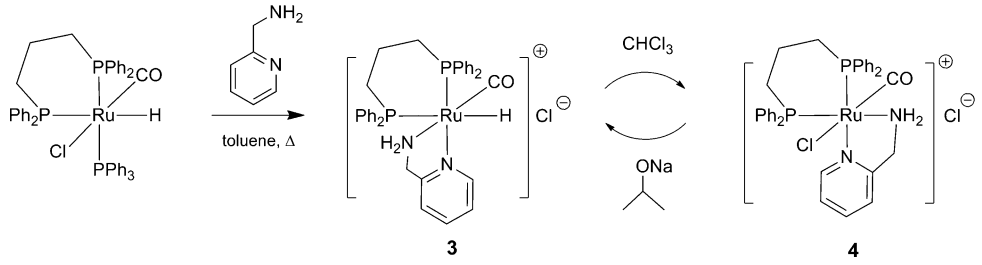
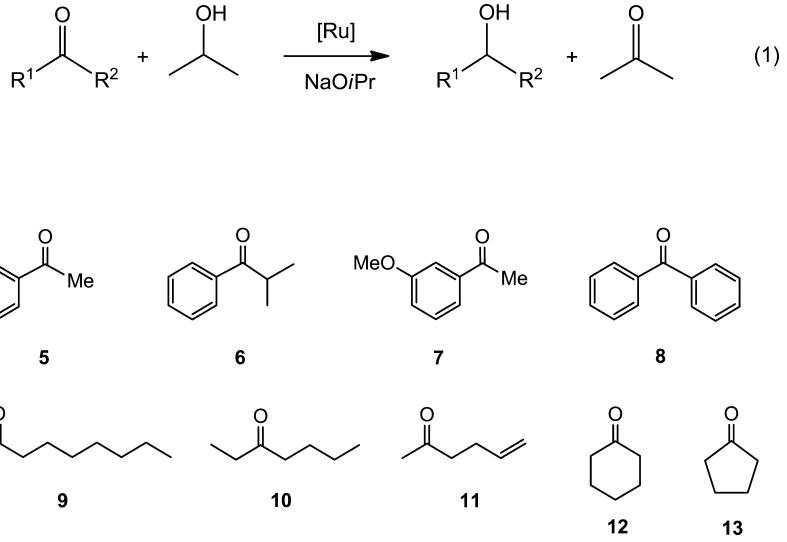
Scheme 2



Scheme 3



complexes **1**–**4** are not air sensitive, whereas in solution the chloride complexes **2** and **4** are significantly less sensitive than the hydride species **1** and **3**. Attempts to prepare the analogous bipyridine Ru carbonyl derivative by treatment of RuHCl(CO)(PPh_3)(dppp) with 2,2′-bipyridine in toluene at reflux (24 h) failed, leading to the recovery of the starting materials.

Since hydride complexes are the key species involved in the catalytic hydrogenation reactions, we studied the reactivity of the chloride complex **4** with a base in alcohol media, i.e. under the conditions in which the catalysis takes place. Treatment of **4** with NaO*i*Pr (2 equiv) in 2-propanol at room temperature (1 h) affords the hydride **3** as the only product, as inferred from NMR measurements (Scheme 2). This reaction is likely to occur through chloride substitution and formation of the Ru alkoxide, which leads to the hydride **3** via *β*-elimination and isomerization of the complex, in line with the reaction of *trans,cis*-RuHCl(PPh_3)$_2$(ampy) with NaO*i*Pr which gave *cis,cis*-Ru(H)$_2$(PPh_3)$_2$(ampy) as an intermediate species.[20a] The clean and reversible conversion of **4** into **3** is ascribed to the presence of the CO ligand, which stabilizes the Ru hydride. Attempts to observe deprotonation of the NH_2 function in basic media by NMR spectroscopy failed. Dissolution of the hydride **3** in methanol-d_4 leads to two $^{31}P\{^1H\}$ NMR doublets at δ 47.4 and 13.7 with ^2J(P,P) = 20.3 Hz. Addition of KO*t*Bu (5 equiv) at room temperature does not significantly affect the resonance at δ 47.4, whereas the second peak at δ 13.6 appears as a pseudoquartet with ^2J(P,P) = ^2J(P,D) ≈ 20 Hz,[26] suggesting the formation of the corresponding deuteride complex [RuD(CO)(dppp)(ampy)]Cl, in agreement with the disappearance of the Ru–H signal at δ −4.85 (^2J(H,P) = 118 and 19.5 Hz). Finally, in CD_2Cl_2 the reaction of **3** with KO*t*Bu results in the formation of the chloride **4** in the presence of uncharacterized diphosphine complexes.[27]

Catalytic Transfer Hydrogenation. The ruthenium complexes **1**–**4** have been studied in the TH of ketones in 2-propanol and under basic conditions (Scheme 3). The hydride diamine derivative **1** (0.1 mol %) catalyzes the reduction of acetophenone **5** to 1-phenylethanol (94% after 40 min) under reflux conditions and in the presence of NaO*i*Pr (2 mol %) with a TOF of 2.5 × 10^3 h^{-1} (Table 1). Using the chloride **2**, quantitative reduction was attained in 40 min with a lower rate (TOF = 1.5 × 10^3 h^{-1}).

An increase of speed was achieved with the ampy hydride **3** (0.2 mol %), which led to the quantitative formation of 1-phenylethanol in 20 min with a TOF value of 1.0 × 10^4 h^{-1}.

Table 1. Catalytic TH of Acetophenone 5 with Complexes 1–4 in the Presence of NaO*i*Pr (2 mol %)

catalyst	amt of Ru (mol %)	time (min)	conversion (%)	TOF (h^{-1})[a]
1	0.1	40	94	2.5 × 10^3
2	0.1	80	98	1.5 × 10^3
3	0.2	20	98	1.0 × 10^4
3	0.1	30	98	1.2 × 10^4
3	0.01	80	96	1.1 × 10^4
3	0.004	210	60	3.6 × 10^3
4	0.1	40	99	4.0 × 10^3

[a]The conversion and TOF (moles of acetophenone converted into alcohol per mole of catalyst per hour at 50% conversion) were determined by GC analysis. Conditions: T = 82 °C, substrate 0.1 M in 2-propanol.

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Interestingly, a similar rate was observed at lower catalyst loading. With 0.1 mol % of **3**, the substrate **5** was reduced to the corresponding alcohol in 30 min (TOF = 1.2×10^4 h^{-1}), whereas with 0.01% of **3**, 96% conversion was achieved in 80 min (TOF = 1.1×10^4 h^{-1}), indicating that **3** is a productive catalyst. Conversely, at 0.004 mol % of **3** only 60% of the alcohol was observed in 3.5 h. It is worth noting that, by performing the TH of **5** with **3** (0.1 mol %) in air, 72% conversion was achieved in 30 min (TOF = 2×10^3 h^{-1}), whereas quantitative formation of 1-phenylethanol is attained in 3 h.

Finally, the chloride ampy complex **4** (0.1 mol %) catalyzes the TH of **5** with complete conversion in 40 min and TOF = 4.0×10^3 h^{-1}. The most active system, **3**, has been proven to efficiently catalyze the TH of alkyl aryl, diaryl, dialkyl, and cyclic ketones. Using 0.2 mol % of **3**, the bulky ketone *i*PrCOPh (**6**) was quantitatively reduced to the corresponding alcohol (98%) in 24 min with a TOF of 7.5×10^3 h^{-1}, a value slightly lower in comparison to that of acetophenone (Table 2).

Table 2. Catalytic TH of the Ketones 5−13 with Complex 3 in the Presence of NaO*i*Pr (2 mol %)

ketone	amt of catalyst (mol %)	time (min)	conversion (%)	TOF (h^{-1})[a]
5	0.2	20	98	1.0×10^4
6	0.2	24	98	7.5×10^3
7	0.1	20	98	4.6×10^3
8	0.2	150	99	8.8×10^3
9	0.1	10	97	1.5×10^4
10	0.1	30	93	4.2×10^3
11	0.1	300	99	3.3×10^2
12	0.1	10	99	7.5×10^3
13	0.1	3	99	n.d.[b]
13	0.01	4	99	2.5×10^5
13	0.004	90	94	7.5×10^4

[a]The conversion and TOF (moles of ketone converted into alcohol per mole of catalyst per hour at 50% conversion) were determined by GC analysis. Conditions: T = 82 °C, substrate 0.1 M in 2-propanol. [b]On account of the high reaction rate, the TOF value could not be determined.

With 0.1 mol % of **3**, 3-methoxyacetophenone **7** is converted to alcohol in 20 min (98%). The diaryl ketone **8** is efficiently reduced to benzhydrol (99%, 2.5 h) with a relatively high TOF (8.8×10^3 h^{-1}). The aliphatic ketones 2-nonanone (**9**) and 3-heptanone (**10**) have efficiently been reduced in 10 and 30 min, the substrate **9** displaying the highest rate (TOF = 1.5×10^4 h^{-1}). The unsaturated aliphatic ketone hex-5-en-2-one **11** undergoes chemoselective reduction at the C═O bond (99% conversion) after 5 h, with no hydrogenation or isomerization of the C═C bond (TOF = 3.3×10^2 h^{-1}). It is worth noting that cyclohexanone **12** and cyclopentanone **13** give complete conversion to the corresponding alcohols in 10 and 3 min (0.1 mol % of **3**), respectively, the substrate **13** being significantly more quickly reduced than **12**. As a matter of fact, **13** leads to cyclopentanol with 0.01 and also 0.004 mol % of **3** in 4 and 90 min, respectively, achieving surprisingly high TOF values (2.5×10^5 and 7.5×10^4 h^{-1}) (Table 2). Conversely, at a lower loading of **3** (0.002 mol %) incomplete conversion has been observed (45% in 4 h), suggesting a deactivation of the catalyst.

The influence of the base on the catalytic activity of the ruthenium hydride **3** has also been investigated. It is worth noting that, without transition-metal complexes, acetophenone is quantitatively reduced in 1 day in 2-propanol at reflux in the presence of NaOH (34 mol %), as described by James.[28] Complex **3** (0.1 mol %) in the absence of base is not active in the TH of **5** in 2-propanol at reflux (Table 3).

Table 3. Influence of NaO*i*Pr on TH of Acetophenone 5 with 3

amt of **3** (mol %)	amt of NaO*i*Pr (equiv)	time (h)	conversion (%)	TOF (h^{-1})[a]
0.1	0	1	0	
0.1	1	2.5	70	1.9×10^2
0.1	2	4	95	1.0×10^3
0.1	5	1	94	2.5×10^3
0.1	20	0.5	98	1.2×10^4
0.01	200	1.5	96	1.1×10^4

[a]The conversion and TOF (moles of acetophenone converted into alcohol per mole of catalyst per hour at 50% conversion) were determined by GC analysis. Conditions: T = 82 °C, substrate 0.1 M in 2-propanol.

With 1 equiv of NaO*i*Pr the catalyst **3** shows a moderate activity, affording 1-phenylethanol (70% conversion) in 2.5 h (TOF = 190 h^{-1}). When the amount of base is increased, namely NaO*i*Pr/**3** = 2, 5 and 20, a faster reduction occurs with TOF values of 1000, 2500, and 12000 h^{-1}, respectively. Employment of a lower amount of **3** (0.01 mol %) with 200 equiv of NaO*i*Pr gives complete conversion of MeCOPh in 1.5 h with TOF = 1.1×10^4 h^{-1} (Table 3). A high rate in TH is achieved when **3** (0.01 mol %) is activated by reaction of NaO*i*Pr (20 equiv) in 2-propanol at reflux (5 min). Subsequent addition of the substrate **5** leads to 86% of the alcohol in 6 min. Conversely, when the complex **3** is added to a basic 2-propanol solution of ketone at reflux, a lower conversion (64%) is achieved in 10 min. This indicates that the hydride **3** requires a base to form the catalytically active species, which does not deactivate at high temperature. It is likely that under catalytic conditions in the presence of an excess of base, the cationic carbonyl complex **3** is deprotonated by NaO*i*Pr, affording the neutral Ru−H amide complex RuH(CO)(dppp)(2-PyCH$_2$NH). It is worth noting that in basic alcohol media the Noyori catalyst (η^6-arene)RuCl(TsNCHPhCHPhNH$_2$)[6] and the pincer complexes RuCl(CNN)(diphosphine)[29] lead to neutral Ru−H amine species. Conversely, the *trans*-RuCl$_2$(PP)-(1,2-diamine) system leads to Ru−H amine and Ru−H amide species.[5b]

Preliminary results show that the complexes [RuX(CO)-(dppp)(NN)]Cl catalyze the acceptorless dehydrogenation and racemization of alcohols.[20c,30] With 0.4 mol % of **3**, 1-tetralol was converted into 1-tetralone (50%, 12 h) in *tert*-butyl alcohol and toluene (1/1 in volume) at 130 °C (bath temperature) in the presence of KOtBu (0.8 mol %), whereas 60% conversion was achieved with **2** and KO*t*Bu (4 mol %). Complex **3** (1 mol %) was found to racemize (*R*)-1-phenylethanol quantitatively in the presence of KO*t*Bu (2 mol %) at 70 °C (1 h), while at 0.5 mol % of **3** the reaction requires 2.5 h.

These results indicate that the Ru carbonyl complexes **1**−**4** efficiently catalyze the TH of ketones, affording complete conversion with 0.2−0.004 mol % loading of catalyst. The ampy derivatives **3** and **4** display a higher rate with respect to the ethylenediamine complexes **1** and **2**. In addition, the hydride complexes **1** and **3** show higher rates in comparison to the

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corresponding chloride species **2** and **4**. This is in agreement with our previous studies on the catalytic TH with ruthenium phosphine complexes with ampy vs ethylenediamine ligands[19a] and their conversion to the catalytically active hydride species. Despite the extensive studies on the TH and HY catalysts $RuCl_2(PP)(NN)$ bearing N−H nitrogen ligands, the related monocarbonyl ruthenium(II) complexes with the "Ru(CO)(PP)(NN)"[31] moiety have been reported only with diimine ligands, and they show poor activity in the HY of acetophenone.[31b] A comparison of the properties of [RuH(CO)(dppp)(ampy)]Cl with those of $RuCl_2$(dppp)(ampy)[20a] suggests that the presence of the CO ligand leads to less active but thermally more stable and less air sensitive catalytically active hydride species, allowing a lower ruthenium loading.

■ CONCLUDING REMARKS

In summary, we have reported the synthesis of the monocarbonyl ruthenium complexes [RuX(CO)(dppp)(NN)]Cl (X = Cl, H; dppp = $PPh_2P(CH_2)_3PPh_2$; NN = en, ampy), containing a diphosphine and N−H nitrogen ligands. The hydride complexes cleanly convert into the chloride derivatives in chlorinated solvents, whereas the reverse formation of the hydride from the chloride is observed for the ampy complex using NaO*i*Pr. These complexes show catalytic activity in the transfer hydrogenation of ketones, affording TOF values up to 2.5×10^5 h^{-1} at 0.01 mol % of Ru loading. The hydride derivatives show higher reactivity in comparison to the chloride species, while the ampy complexes are more active in comparison to the ethylenediamine complexes. It is worth pointing out that the hydride complex [RuH(CO)(dppp)(ampy)]Cl shows catalytic activity only in the presence of NaO*i*Pr and the rate increases on addition of the base. The presence of CO stabilizes the hydride complexes and leads to less air sensitive systems which undergo slower deactivation in catalysis. The straightforward preparation of these hydride carbonyl ruthenium complexes holds promise for their use in other catalytic organic transformations, and studies are underway to extend this protocol to asymmetric catalysis.

■ EXPERIMENTAL SECTION

All manipulations were carried out under an inert argon atmosphere, using standard Schlenk-line conditions and dried, freshly distilled solvents. The complexes $RuHCl(CO)(PPh_3)_3$[21] and $RuHCl(CO)(PPh_3)$(dppp)[22] were prepared according to literature procedures. All other chemicals were purchased from Aldrich and used without further purification. Unless otherwise stated, the ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded at 298 K at 200, 60, and 80 MHz, respectively; chemical shifts, in ppm, are relative to TMS or H_3PO_4 (85% in D_2O) as external standards. Infrared measurements were obtained using an FT-IR spectrometer. The elemental analyses were carried out with an elemental analyzer, whereas the GC analyses were performed with a gas chromatograph equipped with a MEGADEX-ETTBDMS-β chiral column.

Preparation of [RuH(CO)(dppp)(en)]Cl (1). Ethylenediamine (en; 13 mg, 0.22 mmol) was added to a suspension of $RuHCl(CO)(PPh_3)$(dppp) (168 mg, 0.20 mmol) in 2 mL of toluene under argon. The suspension was refluxed for 4 h, and the precipitate was filtered and dried under reduced pressure, affording a pale yellow solid (isomer **1′** < 5%) (110 mg, 86% yield). Anal. Calcd for $C_{30}H_{35}ClN_2OP_2Ru$: C, 56.47; H, 5.53; N, 4.39. Found: C, 56.50; H, 5.47; N, 4.28. ^1H NMR (CD_2Cl_2): δ 7.92−7.23 (m, 21H, aromatic and NH), 4.27 (m, 1H), 3.92 (m, 1H), 3.80 (m, 1H), 3.34 (m, 1H), 3.02 (m, 1H), 2.72 (m, 3H), 2.51 (m, 2H), 2.28 (m, 3H), −5.86 (dd, ^2J(H,P) = 113 Hz, ^2J(H,P) = 18.9 Hz, 1H, RuH of **1**), −13.18 (dd, ^2J(H,P) = 25.2 Hz, ^2J(H,P) = 20.0 Hz, RuH of **1′**). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 45.5 (d, ^2J(P,P) = 38.4 Hz, **1′**), 44.2 (d, ^2J(P,P) = 21.2 Hz, **1**), 22.6 (d, ^2J(P,P) = 38.4 Hz, **1′**), 14.9 (d, ^2J(P,P) = 21.2 Hz, **1**). IR (Nujol): ν 1948 (CO), 1854 cm^{-1} (br, Ru−H).

Preparation of [RuCl(CO)(dppp)(en)]Cl (2). Compound **1** (100 mg, 1.6 mmol) was dissolved in CH_2Cl_2 (0.5 mL), and the solution was stirred at 40 °C for 15 h. Addition of diethyl ether (10 mL) afforded a pale yellow precipitate, which was filtered and dried under reduced pressure (100 mg, 95% yield). Anal. Calcd for $C_{30}H_{34}Cl_2N_2OP_2Ru$: C, 53.58; H, 5.10; N, 4.17. Found: C, 53.40; H, 5.05; N, 3.98. ^1H NMR (CD_2Cl_2): δ 7.72−7.25 (m, 20H, aromatic hydrogens), 5.48 (br, 2H, NH_2), 3.44 (br, 2H, NH_2), 2.77 (br, 2H, PCH_2), 2.67 (br, 4H, NCH_2), 2.51 (br, 4H, PCH_2 and PCH_2CH_2). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 199.7 (t, ^2J(C,P) = 15.6 Hz, CO), 161.0−128.0 (aromatic carbons), 46.8 (s, NCH_2), 25.5 (t, ^1J(C,P) = 26.1 Hz, PCH_2), 18.4 (s, PCH_2CH_2). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 30.8 (s). IR (Nujol): ν 1975 cm^{-1} (CO).

Preparation of [RuH(CO)(dppp)(ampy)]Cl (3). 2-Aminomethylpyridine (ampy; 24 mg, 0.22 mmol) was added to a suspension of $RuHCl(CO)(PPh_3)$(dppp) (168 mg, 0.20 mmol) in 2 mL of toluene under argon. The suspension was refluxed for 12 h, and the solvent was evaporated. The residue was triturated with Et_2O (5 mL), affording a pale red product which was filtered and dried under reduced pressure (115 mg, 84% yield). Anal. Calcd for $C_{34}H_{35}ClN_2OP_2Ru$: C, 59.52; H, 5.14; N, 4.08. Found: C, 59.34; H, 4.98; N, 3.96. ^1H NMR (CD_2Cl_2): δ 8.38 (d, ^3J(H,H) = 6 Hz, 1 ortho H, Py), 7.98−6.85 (m, 24H, aromatic and NH), 4.10 (m, 1H, PCH_2), 3.99 (m, 1H, NCH_2), 3.87 (m, 1H, PCH_2), 3.87 (m, 1H, NH_2), 3.67 (m, 1H, NCH_2), 2.56 (m, 1H, PCH_2), 2.46 (m, 1H, PCH_2), 2.36 (m, 1H, PCH_2CH_2), 1.96 (m, 1H, PCH_2CH_2), −5.23 (dd, 1H, ^2J(H,P) = 113 Hz, ^2J(H,P) = 19.2 Hz, RuH). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 42.6 (d, ^2J(P,P) = 22.7 Hz), 12.8 (d, ^2J(P,P) = 22.7 Hz). IR (Nujol): ν 1944 (CO), 1853 cm^{-1} (br, Ru−H).

Preparation of [RuCl(CO)(dppp)(ampy)]Cl (4). Compound **3** (100 mg, 0.15 mmol) was dissolved in $CHCl_3$ (0.5 mL), and the solution was stirred at room temperature overnight. Addition of diethyl ether (10 mL) afforded a pink red precipitate, which was filtered and dried under reduced pressure (99 mg, 94% yield). Anal. Calcd for $C_{34}H_{34}Cl_2N_2OP_2Ru$: C, 56.67; H, 4.76; N, 3.89. Found: C, 56.50; H, 4.68; N, 3.83. ^1H NMR ($CDCl_3$): δ 8.61−6.77 (m, 24H, aromatic hydrogens), 8.19 (m, 1H, NH_2), 4.68 (m, 1H, PCH_2), 4.15 (m, 1H, NCH_2), 4.04 (m, 1H, NH_2), 3.94 (m, 1H, PCH_2), 3.44 (m, 1H, NCH_2), 2.81 (m, 1H, PCH_2), 2.58 (m, 1H, PCH_2), 2.15 (m, 1H, PCH_2CH_2), 1.72 (m, 1H, PCH_2CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 203.6 (dd, ^2J(C,P) = 15.5 Hz, ^2J(C,P) = 14.2 Hz, CO), 161.1−130.0 (aromatic carbons), 54.4 (d, ^3J(C,P) = 5.4 Hz, NCH_2), 27.8 (dd, ^1J(C,P) = 26.1 Hz, ^3J(C,P) = 3.1 Hz, PCH_2), 24.6 (dd, ^1J(C,P) = 26.1 Hz, ^3J(C,P) = 3.1 Hz, PCH_2), 18.1 (s, PCH_2CH_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 35.4 (d, ^2J(P,P) = 38.2 Hz), 22.7 (d, ^2J(P,P) = 38.2 Hz). IR (Nujol): ν 1974 cm^{-1} (CO).

NMR Evidence of the Formation of 3 from 4. Complex **4** (72 mg, 0.1 mmol) was suspended in 3 mL of 2-propanol, and 2 mL of a solution of NaO*i*Pr (0.1 M, 0.2 mmol) in 2-propanol were added. The mixture was stirred at room temperature for 1 h, and the volatiles were evaporated, affording a pale red product. The ^1H and $^{31}P\{^1H\}$ NMR analysis in CD_2Cl_2 showed the quantitative formation of **3**.

Typical Procedure for the Catalytic Transfer Hydrogenation of Ketones. Complex **3** (1.2 μmol) was dissolved in 3 mL of 2-propanol. The catalyst solution (250 μL, 0.1 μmol) was added to the ketone (1 mmol) in 2-propanol (total volume 9.8 mL), and the mixture was refluxed (90 °C bath temperature) under argon for 5 min. After the addition of 200 μL of NaO*i*Pr (0.1 M; 0.02 mmol) in 2-propanol the reduction of the substrate started immediately. The reaction was sampled by removing an aliquot of the reaction mixture, quenching the mixture with diethyl ether (1/1 in volume), and rapidly filtering over a short silica pad. The conversion was determined by GC analysis (Ru 0.01 mol %, substrate 0.1 M, NaO*i*Pr 2 mol %).

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■ ASSOCIATED CONTENT

Supporting Information

Figures giving NMR spectra of **1**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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