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Cyclometalated Dicarbonyl Ruthenium Catalysts for Transfer Hydrogenation and Hydrogenation of Carbonyl Compounds

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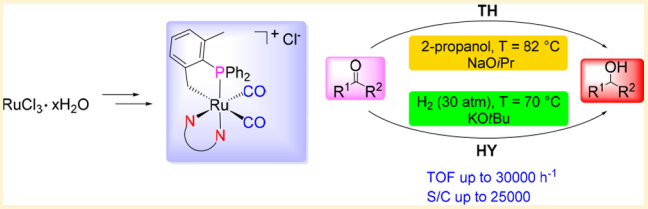
Supporting Information

ABSTRACT: The dicarbonyl complex $RuCl_2(L)_2(CO)_2$ (**1**) was easily prepared by reaction of ruthenium chloride hydrate with formic acid and L (L = $(2,6\text{-}Me_2C_6H_3)PPh_2$) in ethanol at reflux, via the $[RuCl_2(CO)_2]_n$ intermediate. Alternatively, **1** was obtained from $[RuCl_2(CO)_3]_2$ and L by CO elimination. Reaction of **1** with NEt_3 in toluene at reflux afforded the cyclometalated derivative $RuCl\{(2\text{-}CH_2\text{-}6\text{-}MeC_6H_3)PPh_2\}(L)(CO)_2$ (**2**). A simple one-pot synthesis of **2** was achieved by treatment of $RuCl_3$ hydrate with formic acid, L, and NEt_3. The cyclometalated dicarbonyl complexes $[Ru\{(2\text{-}CH_2\text{-}6\text{-}MeC_6H_3)PPh_2\}(NN)(CO)_2]Cl$ (NN = ethylenediamine, **3**; 2-(aminomethyl)pyridine, **4**; (*R*,*R*)-1,2-diphenylethane-1,2-diamine, **5**) were isolated by reaction of **2** with the corresponding dinitrogen ligand in methanol at reflux. Complexes **1**−**4** catalyze the transfer hydrogenation (TH) of acetophenone in 2-propanol at reflux (S/C = 1000 and TOF up to 30 000 h^{-1}) with alkali base (1−5 mol %), whereas **5** leads to (*S*)-1-phenylethanol with 68% *ee*. The derivatives **1**−**5** catalyze the hydrogenation (HY) of several ketones (H_2, 30 bar) at 70 °C in MeOH and EtOH with KO*t*Bu (2 mol %) (S/C and TOF up to 25 000 and 14 000 h^{-1}). Addition of NN ligands to **1** and **2** in situ increases both the TH and HY activity, with ampy displaying the better performance. Heating of the cationic complex **3** in solid state and in solution leads to decarbonylation, affording the neutral monocarbonyl compound $RuCl\{(2\text{-}CH_2\text{-}6\text{-}MeC_6H_3)PPh_2\}(en)(CO)$ (**6**) which was found active in the ketone HY.



INTRODUCTION

The catalytic hydrogenation (HY)[1] and transfer hydrogenation (TH)[2] of carbonyl compounds are cost-effective and environmentally benign ways widely accepted in the industry for the production of alcohols.[3] Several ruthenium complexes have been described as efficient catalysts for HY or TH, whereas only few systems display high activity for both reactions.[4] High selectivity and productivity, which are crucial issues for industrial applications, can be achieved through an appropriate ligand design. Several strategies have been developed and involve the use of polydentate P, N or cyclometalated ligands,[5,6] with suitable electronic/steric properties, featuring amine N-H[7] or redox[8] functions (bifunctional catalysis). Despite the large number of ruthenium complexes employed in organic transformations,[9] very few examples of efficient *cyclometalated PC* catalysts have been described.[10] The use of phosphines, which easily undergo cyclometalation, would lead to a straightforward access to complexes displaying a robust and basic RuPC fragment for catalytic applications, a simpler approach to that involving pincer PCP ligands.[5] Thus, we have reported that $(2,6\text{-}Me_2C_6H_3)PPh_2$ easily gives activation of one *o*-methyl group, affording cyclometalated species with several transition metals.[11]

In the past decade, ruthenium *monocarbonyl* complexes have attracted a great deal of attention because of their ability to catalyze a number of organic transformations, including TH and HY of carbonyl compounds,[12] HY of carboxylic and carbonic acid derivatives,[13] alcohol dehydrogenation,[14] and borrowing hydrogen reactions.[15] Relevant examples are $Ru(TFA)_2(PPh_3)_2(CO)$, RuH(PNN)(CO), RuHCl(PNN)(CO), and RuHCl(PNP)(CO) complexes developed by Dobson,[16] Milstein,[17] Gusev,[18] and Saito,[19] respectively (Figure 1).

The presence of one CO ligand at the metal affords catalysts displaying low tendency to decarbonylate carbonyl substrates (i.e., aldehydes), which is a pathway of catalyst deactivation.[20] In the course of our studies, we reported that the monocarbonyl ruthenium complexes $RuCl\{(2\text{-}CH_2\text{-}6\text{-}MeC_6H_3)PPh_2\}(NN)(CO)$[10b] (**A**) and $[RuH\{Ph_2P(CH_2)_3PPh_2\}(NN)(CO)]Cl$[21] (**B**) (NN = en, ampy[22]) are highly active catalysts for the ketone TH (Figure 1).[23] More recently, we have demonstrated that $Ru(OAc)_2(DiPPF)(CO)$ (**C**)[22,24] is an efficient catalyst for N-alkylation of amines with alcohols via a borrowing hydrogen reaction.

As regards *dicarbonyl* ruthenium catalysts, the major concern has been focused on cyclopentadienyl Ru complexes, such as the Shvo catalyst $(\eta^5\text{-}C_5H_4O)_2HRu_2H(CO)_4$[25] and $(\eta^5\text{-}C_5R_5)$-

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Organometallics XXXX, XXX, XXX–XXX

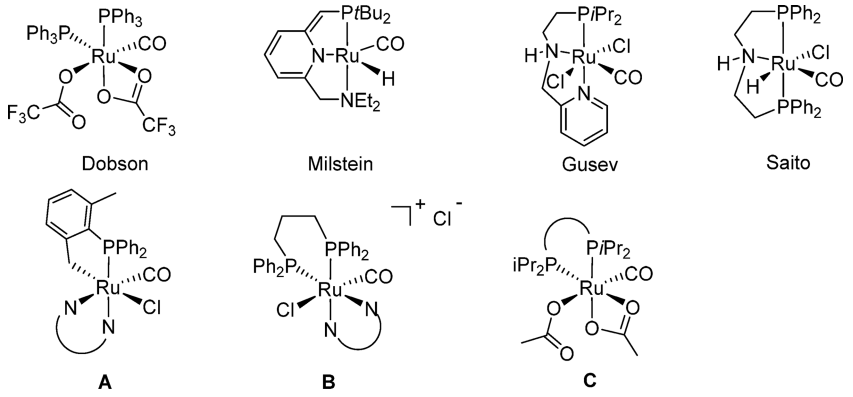


Figure 1. Monocarbonyl ruthenium catalysts.

$RuCl(CO)_2$[26] described by Bäckvall, which display catalytic activity in the dynamic kinetic resolution of alcohols, ammines, as well as in HY and DHY reactions (Figure 2).[27]

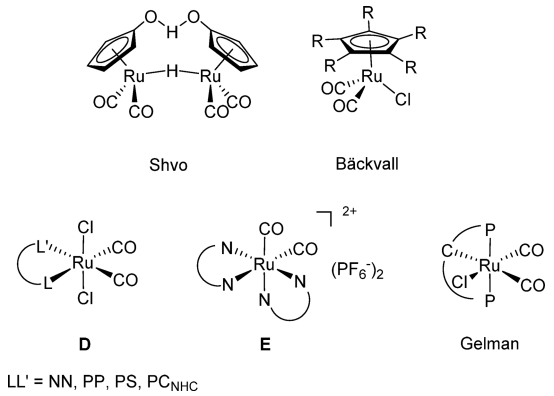


Figure 2. Dicarbonyl ruthenium catalysts.

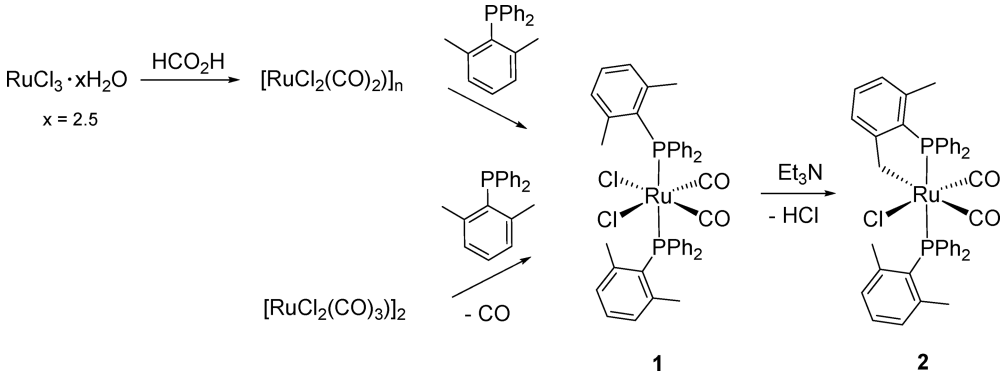
The derivatives of general formula **D** and **E**, namely, $RuCl_2(bpy)(CO)_2$ and $[Ru(bpy)_2(CO)_2][PF_6]_2$ (bpy = 2,2′-bipyridine), were found active in the water gas shift reaction (WGSR)[28] and in the electro- and photochemical CO_2 reduction.[29] The complexes $RuCl_2(LL')(CO)_2$ (LL′ = PP, PS, PC_{NHC})[30] (Figure 2) catalyze the TH of ketones in basic 2-propanol (TOF < 10^3 h^{-1}), whereas $RuCl(PCP)(CO)_2$, described by Gelman,[31] promotes alcohol dehydrogenative reactions. In addition, the ruthenium carbonyl $Ru_3(CO)_{12}$ in combination with polydentate N and P ligands has been proven to catalyze the ketone TH.[32] Both TH and HY reactions entail the formation of catalytically active Ru-H species in basic media, which are usually generated by reaction of a Ru-X (X = Cl, carboxylate) precursor with an alkali alkoxide (via β-H-elimination) or with dihydrogen. It is worth pointing out that, when a ruthenium carbonyl precursor is employed, the Ru-H species can also be formed by decarboxylation of hydroxocarbonyl complexes, via the Hieber base reaction.[33]

We report herein the straightforward preparation of *cyclometalated dicarbonyl* ruthenium complexes $[Ru\{(2\text{-}CH_2\text{-}6\text{-}MeC_6H_3)PPh_2\}(NN)(CO)_2]Cl$ (NN = bidentate ligand) obtained by reaction of ruthenium(II) carbonyl precursors, or directly from ruthenium chloride hydrate, with $(2,6\text{-}Me_2\text{-}C_6H_3)PPh_2$ and a bidentate NN ligand. These cationic dicarbonyl complexes display high catalytic activity in both TH and HY of ketones with S/C up to 25 000 and involve CO dissociation.

RESULTS AND DISCUSSION

Synthesis of Cyclometalated Dicarbonyl Ruthenium Complexes. Treatment of ruthenium(III) chloride hydrate with formic acid afforded the intermediate $[RuCl_2(CO)_2]_n$, following a slightly modified procedure with respect to that reported in the literature.[34] By carrying out the reaction in a sealed tube at 110 °C, complete conversion was achieved within 1 h. This reaction which occurs with evolution of CO_2 and CO, as inferred by IR analysis, is faster in a closed reactor, whereas it requires several hours to be completed in air. Reaction of $[RuCl_2(CO)_2]_n$ with L (L = $(2,6\text{-}Me_2C_6H_3)PPh_2$) in ethanol at 80 °C (2 h) led to the thermally stable derivative

Scheme 1. Synthesis of Complexes 1 and 2



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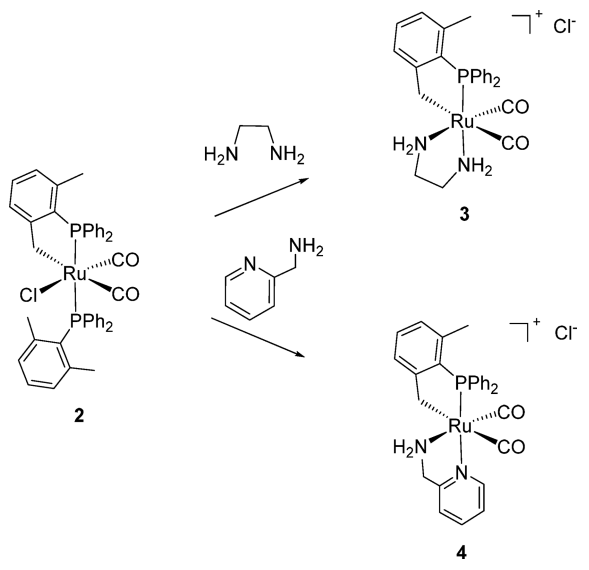
Organometallics XXXX, XXX, XXX−XXX

$RuCl_2(L)_2(CO)_2$ (**1**) which was isolated in 68% yield (method A; see the Experimental Section) (Scheme 1).

Alternatively, **1** (84% yield) was prepared by reaction of the tricarbonyl precursor $[RuCl_2(CO)_3]_2$ with L in ethanol at 80 °C overnight (method B). The four *ortho*-methyl groups of **1** appear as a singlet at δ 2.10 in the ^{1}H NMR spectrum in CD_2Cl_2 at RT and as a triplet at δ 25.9 (^3J(C,P) = 2.3 Hz) in the $^{13}C\{^1H\}$ NMR spectrum. The two CO carbons appear at δ 194.0 in tetrachloroethane-d_2 at 80 °C. The presence of two strong and sharp IR ν_{CO} absorption bands at 2039 and 2001 cm^{-1} is in agreement with a *cis*-coordination of the two carbonyl ligands.[35] Reaction of **1** with the weak base NEt_3 (5 equiv) in toluene at reflux overnight afforded the cyclometalated complex $RuCl\{(2\text{-}CH_2\text{-}6\text{-}MeC_6H_3)PPh_2\}(L)(CO)_2$ (**2**) in 65% yield (method A). In addition, compound **2** (63% and 57% yields) can also be obtained directly through a one-pot synthesis from $RuCl_3{\cdot}xH_2O/HCO_2H$ (method B), or from $[RuCl_2(CO)_2]_n$ (method C), followed by reaction with L in ethanol and in the presence of NEt_3. These procedures allow a more straightforward preparation of **2** with respect to that previously reported, which entails the isolation of the 14-electron complex $RuCl_2(L)_2$[36] and reaction with H_2CO and CO.[11b] The $^{31}P\{^1H\}$ NMR spectrum of **2** in $CDCl_3$ shows two doublets at δ 54.2 and 26.2 with a ^2J(P,P) = 293 Hz, consistent with two *trans* phosphines. The broad doublet at high field is for L, while the cyclometalated phosphine displays a narrow doublet at low field. The cyclometalated methylene protons of **2** appear in the ^{1}H NMR spectrum as two doublets of doublets at δ 3.07 (^2J(H,H) = 14.8 Hz, ^3J(H,P) = 5.5 Hz) and 2.89 (^2J(H,H) = 14.8 Hz, ^3J(H,P) = 6.3 Hz). The $^{13}C\{^1H\}$ NMR spectroscopic data for complex **2** shows a triplet at δ 32.2 (^2J(C,P) = 4.9 Hz), for the $RuCH_2$ group, and two signals at δ 198.3 (t, ^2J(C,P) = 12.6 Hz) and 194.2 (dd, ^2J(C,P) = 8.7 and 7.9 Hz) for the CO ligands. The IR spectrum reveals two CO stretching bands at 2020 and 1957 cm^{-1}, in agreement with the presence of two *cis* CO groups.

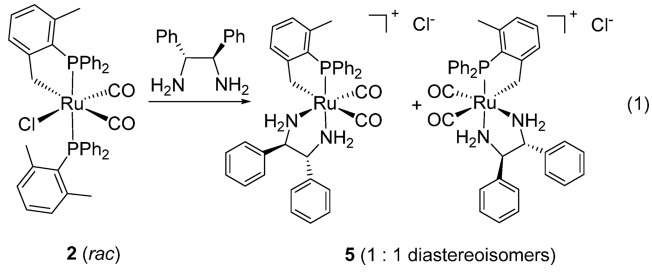
Treatment of **2** with ethylenediamine in methanol affords the cationic complex $[Ru\{(2\text{-}CH_2\text{-}6\text{-}MeC_6H_3)PPh_2\}(en)(CO)_2]Cl$ (**3**) in 88% yield, by displacement of the bulky phosphine and the chloride ligands (Scheme 2).

Scheme 2. Synthesis of Complexes 3 and 4



The ^{1}H NMR spectrum of **3** in CD_3OD shows four different resonances for the NCH_2CH_2N moiety at δ 4.30, 4.04, 3.07, and 2.83. The NH_2 groups appear as broad signals at δ 5.30 and in the 2.75−2.25 range, as demonstrated by H/D exchange of the amino protons performed by addition of basic D_2O (NaOD), whereas the $RuCH_2$ protons give two doublets at δ 2.99 and 2.57 with ^2J(H,H) = 15.0 Hz. In the $^{13}C\{^1H\}$ NMR spectrum of **3**, the two doublets at δ 201.3 (^2J(C,P) = 13.5 Hz) and 191.9 (^2J(C,P) = 6.5 Hz) are for the CO ligands, while the singlet at δ 46.7 and the doublet at δ 45.4 (^3J(C,P) = 3.9 Hz) are for the en methylene carbons. Finally, the doublet at δ 31.9 (^2J(C,P) = 4.1 Hz) is attributable to the $RuCH_2$ group. In the IR spectrum of **3**, the CO stretching bands appear at 2028 and 1959 cm^{-1}, close to those of the precursor **2**. Similarly, the cationic complex $[Ru\{(2\text{-}CH_2\text{-}6\text{-}MeC_6H_3)PPh_2\}(ampy)(CO)_2]Cl$ (**4**) (43% yield) has been synthesized by reaction of **2** with ampy in methanol at reflux. The $^{31}P\{^1H\}$ NMR spectrum of **4** in CD_3OD displays a singlet at δ 64.4, a value very close to that of **3** (δ 64.6). In the ^{1}H NMR spectrum of **4** ($CDCl_3$), the methylene protons of the ampy ligand appear as two doublets of triplets at δ 5.58 (^2J(H,H) = 11.0 Hz, ^3J(H,H) = 5.7 Hz) and 3.07 (^2J(H,H) = 11.0 Hz, ^3J(H,H) = 5.2 Hz), while the NH_2 amino group signal is at δ 4.37. The $^{13}C\{^1H\}$ NMR spectrum of **4** in CD_3OD shows a doublet at δ 52.2 (^3J(C,P) = 3.4 Hz) for the methylene carbon of the ampy ligand, whereas the cyclometalated CH_2 moiety gives a doublet at δ 33.9 (^2J(C,P) = 3.9 Hz). The carbonyl groups exhibts two doublets at δ 201.3 (^2J(C,P) = 14.6 Hz) and 191.5 (^2J(C,P) = 6.5 Hz), the latter being attributed to the CO *trans* the cyclometalated methylene group. The low field signal at δ 201.3 has the same value reported for the CO *trans* to the amino moiety in **3**, suggesting a *trans* arrangemet of the NH_2 and CO groups in **4**. The *cis* CO ligands display two strong stretching bands in the IR spectrum at 2032 and 1966 cm^{-1}.

Reaction of **2**, as racemate, with (*R*,*R*)-dpen[22] in methanol at reflux afforded the complex **5** (68% yield) as a mixture of two diastereoisomers in a 1:1 ratio (eq 1). The $^{31}P\{^1H\}$ NMR spectrum of **5** in $CDCl_3$ shows two singlets at δ 64.2 and 63.9, which are values close to that of the en derivative **3** (δ 64.6). In the ^{1}H NMR spectrum, the two couple of doublets at δ 3.29, 2.64 (^2J(H,H) = 14.0 Hz) and at δ 3.04, 2.58 (^2J(H,H) = 14.1 Hz) have been attributed to the two cyclometalated CH_2 moieties, whereas the singlets at δ 1.73 and 1.68 are for the *o*-methyl groups. The IR CO stretching absorptions are at 2032 and 1965 cm^{-1}, which are values very close to those of analogous derivative **3**. The formation of two diastereoisomers of **5** in a 1:1 ratio suggests that the substitution of the phosphine and Cl with (*R*,*R*)-dpen in the racemate **2** occurs with no interconversion of the $Ru(CP)(CO)_2$ fragment in methanol at reflux.



Reduction of Ketones via TH and HY Catalyzed by Carbonyl Ruthenium Complexes. The catalytic activity of the complexes **1**−**5** have been investigated in the TH with 2-

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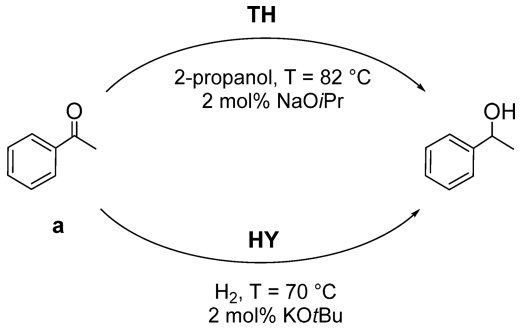
Organometallics XXXX, XXX, XXX−XXX

propanol and HY with dihydrogen of acetophenone **a** in the presence of an alkali base. The complexes **3**−**4** have proven to efficiently hydrogenate **a** with a S/C = 500−25 000 (Scheme 3).

Scheme 3. Reduction of Acetophenone via TH and HY Catalyzed by Ruthenium Complexes 1−5



Complexes **1** and **2** (S/C = 1000) with NaO*i*Pr (2 mol %) display poor activity in the TH of **a** (0.1 M) in 2-propanol at reflux, affording 39% and 48% conversion into 1-phenylethanol in 7 and 8 h, respectively (Table 1, entries 1−2).

Addition of the bidentate ligand en (2 equiv) to the dicarbonyl **2** in situ increases dramatically the activity of complex (TOF = 1200 h^{-1}, entry 3, Table 1), indicating an accelerating N-H effect upon coordination at the Ru center. An even higher rate has been observed by addition of ampy to **2** (2 equiv), achieving a TOF = 30 000 h^{-1} (entry 4). The isolated cationic dicarbonyl **3** containing the en ligand shows, in the presence of NaO*i*Pr (2 mol %), much the same activity (TOF = 1500 h^{-1}) observed for the in situ generated **2**/en system (entry 5). By changing the base concentration (1 to 5 mol %), a higher rate was attained at 1 mol % NaO*i*Pr (TOF = 2500 h^{-1}; see Table S1 (Supporting Information)), whereas no TH was observed without base. Employment of KOH or KO*t*Bu (1 to 5 mol %) as base leads to complete conversion of MeCOPh with TOF values in the range 1500−3000 h^{-1} (entries 7, 8 and Table S1 (Supporting Information)), indicating not a strong influence of the nature of the alkali metal for **3** (see Table S1 (Supporting Information)). Addition of water (2% in volume) to **3** with NaO*i*Pr, however, has a strong detrimental effect (13% conversion in 1 h, entry 6). The isolated ampy derivative **4** displays the highest activity (TOF = 17 000−30 000 h^{-1}), affording quantitative reduction in 5 min, with moderate influence of the nature of the base (NaO*i*Pr, KOH, and KO*t*Bu) and its concentration (1−5 mol %, entries 9, 11, 12 and Table S1 (Supporting Information)). In the presence of water (2% in volume), complex **4** leads to 81% conversion in 20 min, with a lower rate (TOF = 3000 h^{-1}, entry 10), in line with the results obtained with **3**, indicating that water hinders the TH, possibly by formation of Ru hydroxo species. Complex **5**, containing the chiral diamine ligand (*R*,*R*)-dpen, affords the quantitative TH of **a** to (*S*)-1-phenylethanol with 68% *ee* at 82 °C in 40 min (S/C of 500) (entry 13, Table 1). By carrying out the reaction at lower temperature (60 °C), incomplete conversion has been observed (15% in 8 h) with no substantial increase of *ee*. Notably *60−80% ee* has been reported for the hydrogenation of **a** with Ru-achiral phosphine with (*R*,*R*)-dpen complexes[37] and for the HY of 1-acetylnaphthalene with diastereoisomeric mixtures of Ru-biphenyl phosphine with (*S*,*S*)-dpen derivatives.[38] Thus, for **5** the enantiosectivity is mainly controlled by the chiral dpen, with a small contribution of the other ligands, taken into account that, during catalysis, a CO dissociation occurs (vide infra). In refluxing 2-propanol with KOH and in the absence of ruthenium catalyst, almost no conversion of **a** (< 2%) into alcohol has been observed in 1 h, in agreement with the data reported by Le Page, who showed quantitative reduction of **a** in 1 day with a concentrated NaOH solution (34 mol %).[39]

Complexes **1**−**6** have been studied in the HY of **a** at 30 bar of H_2 pressure in ethanol and methanol in the presence of KO*t*Bu with S/C in the range 2000−25 000. The HY was carried out both in a catalyst screening system (8 vessels Endeavor Biotage system), which allows parallel reactions to be performed, and in a stainless steel autoclave following the single process. Compound **1** (S/C = 2000) with KO*t*Bu (2 mol %) displays poor activity in the HY of **a** in ethanol (8% of conv. in 16 h) at 70 °C (Table 2, entry 1). Addition of diamine ligands to **1** (S/C = 10 000) increases significantly the activity, affording 96% conversion after 16 h (entry 2) in the presence of en (2 equiv). A similar behavior has been observed using the cyclometalated complex **2** (S/C = 2000), affording 11% of 1-

Table 1. Catalytic TH of Acetophenone (0.1 M) with 1−5 (S/C = 1000) in 2-Propanol at 82 °C in the Presence of an Alkali Base (2 mol %)

entry	complex	ligand and additives	base	time (min)	conv.[a] (%)	TOF[b] (h^{-1})
1	**1**		NaO*i*Pr	420	39	
2	**2**		NaO*i*Pr	480	48	
3	**2**	en	NaO*i*Pr	60	65	1200
4	**2**	ampy	NaO*i*Pr	40	99	30 000
5	**3**		NaO*i*Pr	60	92	1500
6	**3**[c]	H_2O	NaOiPr	60	13	
7	**3**		KOH	60	95	1500
8	**3**		KO*t*Bu	60	93	2300
9	**4**		NaO*i*Pr	5	91	18 000
10	**4**[c]	H_2O	NaO*i*Pr	20	81	3000
11	**4**		KOH	5	91	17 000
12	**4**		KO*t*Bu	5	92	30 000
13	**5**[d]		NaO*i*Pr	40	99 (68% *ee S*)	1500

[a]The conversion was determined by GC analysis. [b]Turnover frequency (moles of ketone converted to alcohol per mole of catalyst per hour) at 50% conversion. [c]Reaction carried out in the presence of 200 μL (2% in volume) of H_2O. [d]Reduction performed with S/C = 500.

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Organometallics XXXX, XXX, XXX−XXX

Table 2. Catalytic HY of Acetophenone (2 M) with Complexes 1−6 under 30 bar of H_2 Pressure, 2 mol % of KO*t*Bu at 70 °C

entry	complex	ligand	solvent	S/C	time (h)	conv.[a] (%)	TOF[b] (h^{-1})
1	**1**		EtOH	2000	16	8	
2	**1**	en	EtOH	10 000	16	96	
3	**2**		EtOH	2000	16	11	
4	**2**	en	EtOH	2000	16	99	
5	**2**	en	EtOH	10 000	16	80	
6	**2**	ampy	EtOH	2000	16	99	
7	**2**	ampy	EtOH	10 000	16	99	
8	**3**		EtOH	2000	16	99	
9	**3**[c]		EtOH	2000	16	98	600
10	**3**[d]		EtOH	10 000	23	85	1100
11	**3**		MeOH	10 000	16	99	
12	**3**[d]		MeOH	10 000	3	95	4500
13	**3**[d]		MeOH	25 000	22	97	3300
14	**4**		EtOH	10 000	16	98	
15	**4**		MeOH	10 000	16	99	
16	**4**[d]		MeOH	10 000	22	99	14 000
17	**4**[d]		MeOH	25000	22	97	4000
18	**5**[c]		EtOH	2000	16	99 (36% *ee S*)	300
19	**6**[c,e]		EtOH	2000	16	98	

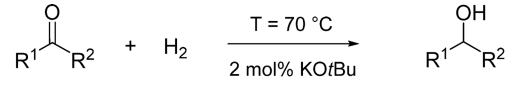
[a]The HY was carried out in an 8 vessels Endeavor Biotage system, and the conversion was determined by GC analysis. [b]Turnover frequency (moles of ketone converted to alcohol per mole of catalyst per hour) at 50% conversion. [c]At 40 °C. [d]Reaction performed in stainless steel autoclave (see the Experimental Section). [e]5 bar H_2 pressure.

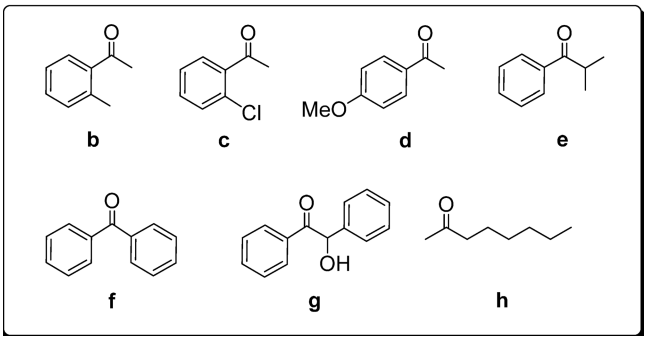
phenylethanol in 16 h, whereas, in the presence of en or ampy (2 equiv), quantitative formation of alcohol is attained (entries 3, 4, and 6). At lower catalyst loading (S/C = 10 000), addition of ampy gave higher conversion with respect to the en ligand (99% vs 80% in 16 h; entries 7 and 5). The isolated en derivative **3** led to 99% and 57% conversion of **a** at S/C 2000 and 10 000, respectively (entry 8 and Table S2 (Supporting Information)). Quantitative reduction of **a** (98%) was also attained at 40 °C in ethanol with a relatively low rate (S/**3** = 2000, TOF = 600 h^{-1}; entry 9). Employment of **3** in methanol with KO*t*Bu or KOH leads to the quantitative reduction of **a**, indicating that the reaction occurs via HY and not TH, on account of the higher redox potential of methanol compared to ethanol (entries 11−13 and Table S2 (Supporting Information)).[40] By performing the HY in a stainless steel autoclave in ethanol, 85% conversion was attained in 23 h (TOF = 1100 h^{-1}) with S/**3** = 10 000 (entry 10). Employment of methanol at S/**3** = 10 000 and 25 000, 95% and 97% conversion was achieved in 3 and 22 h (TOF = 4500 and 3300 h^{-1}; entries 12 and 13), respectively. In line with the results obtained in TH, the cationic ampy complex **4** displays a higher rate compared to **3** in HY. Thus, complete conversion of **a** is obtained, in ethanol and methanol at S/C 2000−25 000 (entries 14−17 and Table S2 (Supporting Information)) within 16−22 h (TOF up to 14 000 h^{-1}; entry 16).

A similar catalytic activity was observed for the in situ generated catalysts **2**/NN ligand (NN = en, ampy) and the isolated complexes **3** and **4**, respectively. The chiral derivative **5** catalyzes the HY of **a** but with poor enantioselectivity (36%) of (*S*)-1-phenylethanol (Table 2, entry 18). Finally, the monocarbonyl derivative [RuCl{(2-CH_2-6-MeC_6H_3)PPh_2}-(en)(CO)] (**6**)[10b] (vide infra) has been found active also in the HY in EtOH with quantitative reduction of **a** in 16 h at 40 and 70 °C (S/C = 2000; entry 19 and Table S2 (Supporting Information)).

Complexes **3** and **4** have proven to catalyze the HY of diaryl, dialkyl, and bulky ketones. The HY was performed at 70 °C under 30 bar of H_2 with the substrate (2 M) dissolved in ethanol and in the presence of KO*t*Bu (2 mol %) (Scheme 4).

Scheme 4. HY of Ketones Catalyzed by Ruthenium Complexes 3−5





As with **a**, 2′-methylacetophenone **b** and 2′-chloroacetophenone **c** are quantitatively hydrogenated to the corresponding alcohols in 16 h using complexes **3** and **4** at S/C = 10 000 (Table 3, entries 1−4).

4′-Methoxyacetophenone **d** is fully hydrogenated by **3** and **4** with an S/C = 500 in 3 h (entries 5 and 6). By contrast, 4′-nitroacetophenone is not reduced by **3** and **4** (about 2% conv. at S/C = 10 000 in 16 h). The bulky substrate isobutyrophenone **e** is partially hydrogenated with **2**/en and with **3** (Ru/S = 1000) in 3 h (33% and 35% conv.; Table S3 (Supporting Information) and entry 7), whereas, with complex **4**, quantitative reduction is attained (99%; entry 8). Benzophenone **f** is converted to benzhydrol (99%) in 3 h with **3** and **4** (S/C = 500; entries 9 and 10). As regards the benzoin substrate **g**, complexes **3** and **4** display poor catalytic activity, affording 9% and 6% conv. respectively, after 16 h with

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Organometallics XXXX, XXX, XXX−XXX

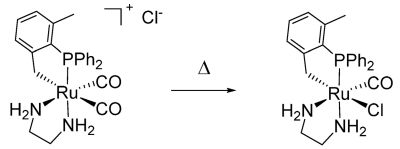
Table 3. Catalytic HY of Ketones (2 M) with Complexes 3−5 under 30 bar of H_2 Pressure, 2 mol % of KO*t*Bu at 70 °C in Ethanol

entry	complex	substrate	S/C	time (h)	conv.[a] (%)
1	**3**	**b**	10 000	16	99
2	**4**	**b**	10 000	16	98
3	**3**	**c**	10 000	16	97
4	**4**	**c**	10 000	16	99
5	**3**	**d**	500	3	98
6	**4**	**d**	500	3	99
7	**3**	**e**	1000	3	35
8	**4**	**e**	1000	3	99
9	**3**	**f**	500	3	99
10	**4**	**f**	500	3	99
11	**3**	**g**	10 000	16	9
12	**3**	**h**	1000	3	99
13	**4**	**h**	1000	3	99
14	**5**	**c**	10 000	16	98 (35% *ee S*)
15	**5**	**d**	500	16	99 (23% *ee S*)

[a]The reaction was carried out in an 8 vessels Endeavor Biotage system, and the conversion was determined by GC analysis.

S/C = 10 000, possibly due to the chelate effect exerted by the 1,2-diol product resulting in catalyst poisoning (entry 11 and Table S3 (Supporting Information)). Finally, the dialkyl 2-octanone **h** is completely reduced by **3** and **4** in 3 h (S/C = 1000; entries 12 and 13). Use of complex **5** with the substrates **c** and **d** led to complete reduction to alcohol in ethanol but with poor enantioselectivity (23−35% of (*S*)) (Table 3, entries 14 and 15). The different value of *ee* observed in the HY of **a** with **5** with respect to TH at high temperature (68% *ee*) is likely due to the alcohol media, as also observed with Ru ampy complexes.[4c]

The TH and HY reactions promoted by ruthenium complexes usually occur in basic media through the formation of catalytically active mono- or dihydride Ru species,[41] starting from Ru-X (e.g., X = Cl, carboxylate) precursors via X substitution. In the TH with 2-propanol, the Ru-H species is generated from a Ru-O*i*Pr complex through a β-hydrogen elimination and extrusion of acetone (inner sphere mechanism). When a NH_2 functionality is present at the Ru-X center, the Ru-hydride is formed from a 16-electron Ru-amide[42] or a Ru-amine/alkoxide[43] species by elimination of HX (outer sphere mechanism), involving hydrogen bonding and proton transfer reactions with the alcohol media.[7,43,44] In the HY, the Ru-H species are formed in basic alcohol via dihydrogen splitting from a labile Ru-X species (X = Cl, carboxylate, alkoxide). In the presence of a NH_2 function, the Ru-H is formed from a 16-electron Ru-amide[42] or Ru-amine/alkoxide species, as also proposed recently by Dub and Gordon.[45] It is worth noting that the cyclometalated dicarbonyl complexes **3** and **4**, which catalyze both the TH and HY reactions, are bifunctional catalysts that do not display a Ru-X coordinated anionic ligand X (i.e., Cl, carboxylate) and, therefore, the formation of the Ru-hydride species requires some considerations. As possible routes for the Ru-H formation, we can envisage: (a) a nucleophilic attack of OH^- (due to the presence of water in the basic alcohol media) on Ru-CO, with formation of a hydroxocarbonyl species, followed by decarboxylation (Hieber base reaction);[46,47] (b) thermal dissociation of one CO ligand. Addition of water in the TH reduction of **a** with **3** and **4** has proven to lead to a drastic decrease of the reaction rates, suggesting that it is unlikely that the Ru-H may originate via a OH^- nucleophilic attack at the CO.[33,48] Conversely, control experiments on **3** reveal a thermal dissociation of one CO ligand in solid state and in solution. Thus, heating **3** under reduced pressure (10^{-2} mmHg) at 85 °C for 36 h leads to quantitative formation of the neutral monocarbonyl derivative RuCl{(2-CH_2-6-MeC_6H_3)PPh_2}(CO)(en) (**6**),[11b] by elimination of one CO (eq 2).



3 **6** (2)

VT $^{31}P\{^1H\}$ NMR measurements of **3** in solution (tetrachloroethane-d_2) show that, by heating, the intensity of the singlet at δ 62.5 for **3** decreases, while the signal at δ 69.5 for **6** increases progressively (see the Supporting Information). Thus, at 40 and 90 °C, the **6**/**3** ratio was 1/4 and 1/2 after 40 min, respectively, whereas, at 100 °C overnight, **3** led to **6** and other uncharacterized species. The ^1H NMR spectra confirm these results, with the appearance of two doublets at δ 2.98 and 2.01 (^2J(H,H) = 14.6 Hz) for the $RuCH_2$ group and a singlet at δ 1.74 for the methyl group of **6**. The comparison of the $^{13}C\{^1H\}$ NMR data of the CO ligand in the complexes **1**−**4** and **6** indicates that, for **3**, the absorbance at δ 191.9, slightly shifted at low field compared to free CO (δ 184.2),[49] is for the CO *trans* to the CH_2 group, consistent with a *trans* influence[50] exerted by the cyclometalated group. It is worth pointing out that **3** was obtained by reaction of **2** with en in methanol at reflux without decarbonylation. Therefore, the nature of the solvent plays a crucial role in the decarbonylation, which is favored for the chloride derivative **3** in apolar solvents (e.g., via an ion pair)[51] with respect to polar ones. Thermal CO dissociation in $RuCl_2(PP)(CO)_2$ (PP = *t*$Bu_2PCH_2CH_2P$*t*Bu_2, $Cy_2P(CH_2)_4PCy_2$) complexes, bearing bulky alkyl diphosphines, has been reported by Whittlesey[52] and Fogg.[53] Displacement of one CO ligand in the dicarbonyl ruthenium complex (η^5-Ph_5C_5)$Ru(CO)_2Cl$ has been described by Bäckvall as the rate-limiting reaction step in the racemization of *sec*-alcohols[26] and by Gelman in dehydrogenation of alcohols.[31]

Complex **6** in the presence of KO*t*Bu was proven to hydrogenate the substrate **a** (98−99% conv.) in ethanol under 30 bar of H_2 at 70 °C and at 40 °C under 5 bar of H_2 (16 h), similarly to **3** (Table 2 (entries 19 and 9), and Table S2 (Supporting Information)). In the TH of **a** in 2-propanol at reflux, a higher rate was observed for **6** (NaOH as base), compared to **3** (KOH or NaO*i*Pr) with TOF values of 2800[10b] and 1500 h^{-1} (Table 1, entry 7), respectively. Therefore, it is likely that, during catalysis, the dicarbonyl derivatives **3** and **4** undergo thermal CO dissociation in the presence of a large excess of alkoxides, leading to the formation of monocarbonyl derivatives RuX(PC)(NN)(CO) (NN = en, ampy) (X = H, OR). Attempts to isolate the Ru-H species by treatment of **3** and **4** with NaO*i*Pr in 2-propanol failed, resulting in the formation of dark solutions containing several uncharacterized species, as inferred from NMR measurements. The high performance of the dicarbonyl catalyst **4** relies on the presence of the ampy ligand in combination with a robust cyclometalated phosphine, which retards deactivation and facilitates the decarbonylation, on account of the strong *trans* influence of the alkyl group. Thus, according to our studies on related

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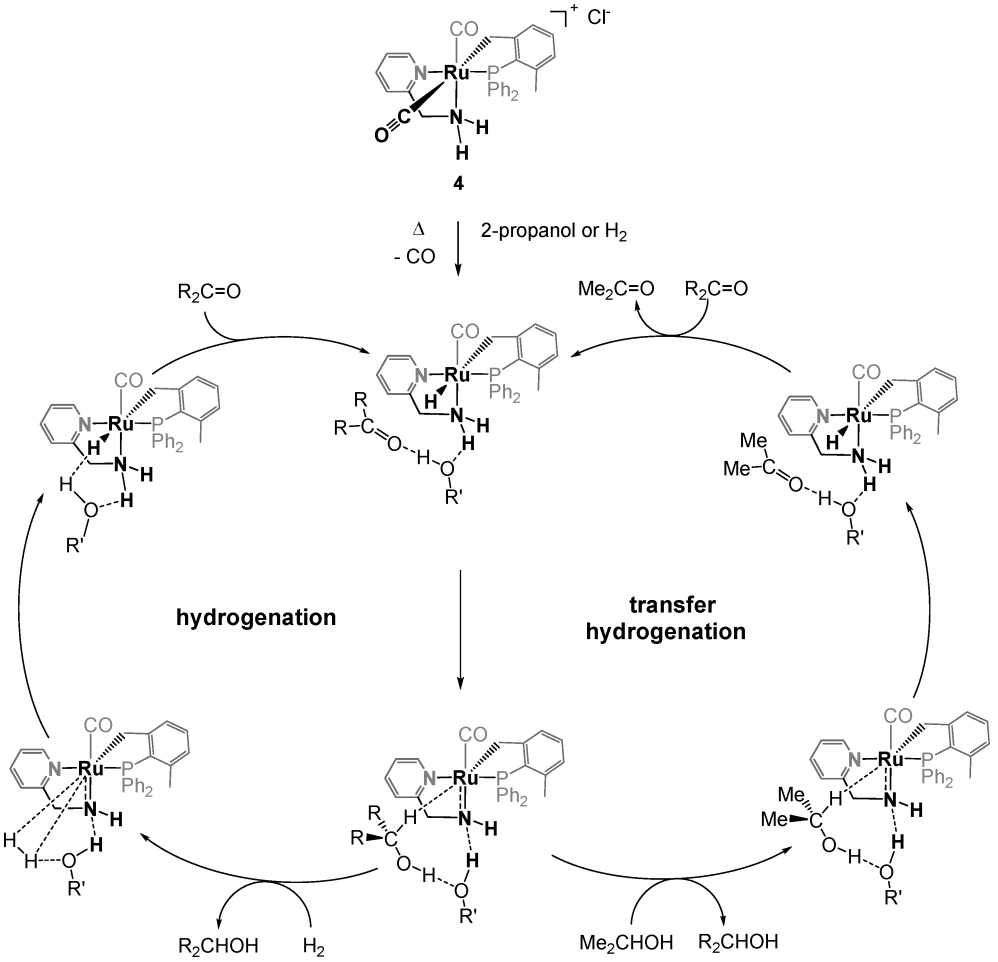
Organometallics XXXX, XXX, XXX−XXX

Scheme 5. Possible Mechanism for TH and HY Reduction of Ketones Involving Complex 4



pincer Ru complexes,[43] a possible mechanism for the TH and HY of ketones promoted by the cationic complex **4** is depicted in Scheme 5.

The thermal displacement of CO in the presence of 2-propanol or H_2 in basic alcohol media leads to the monohydride Ru complex which affords the reduction of the carbonyl substrate through a hydrogen bonding network promoted by the NH_2 function. The catalytically active Ru-hydride is regenerated by 2-propanol (reverse process) in TH or by H_2 splitting in HY.

CONCLUDING REMARKS

In conclusion, we have reported a straightforward synthesis of cyclometalated dicarbonyl ruthenium complexes of formula $[Ru\{(2\text{-}CH_2\text{-}6\text{-}MeC_6H_3)PPh_2\}(NN)(CO)_2]Cl$ (NN = en, ampy, (*R*,*R*)-dpen) obtained from $RuCl_3$ hydrate (via $[RuCl_2(CO)_2]_n$) and from $[RuCl_2(CO)_3]_2$ with $(2,6\text{-}Me_2C_6H_3)PPh_2$ and a bidentate NN ligand. These derivatives display catalytic activity in both TH and HY of ketones, the ampy complex being more active with respect to the en one. The reduction of acetophenone via TH with 2-propanol (S/C = 1000) and HY (30 bar of H_2, S/C = 10 000) afforded TOFs up to 30 000 and 14 000 h^{-1}, respectively, in the presence of 1−5 mol % of alkali base. In addition, complete HY has also been observed with S/C = 25 000 in methanol. Thermal CO dissociation of $[Ru\{(2\text{-}CH_2\text{-}6\text{-}MeC_6H_3)PPh_2\}(en)(CO)_2]Cl$ leads to the corresponding monocarbonyl complex which is active in the ketone HY and TH reactions. Studies are ongoing to extend this protocol to other cyclometalated carbonyl ruthenium complexes for catalytic organic transformations.

EXPERIMENTAL SECTION

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 $RuCl_3{\cdot}xH_2O$ (x = 2.5) and $[RuCl_2(CO)_3]_2$ were from Alfa/Aesar, whereas all other chemicals were purchased from Aldrich and Strem and used without further purification. NMR measurements were recorded on a Bruker AC 200 spectrometer. Chemical shifts, in ppm, are relative to TMS for ^1H and $^{13}C\{^1H\}$, 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 $RuCl_2\{(2,6\text{-}Me_2C_6H_3)PPh_2\}_2(CO)_2$ (1). *Method A.* The compound $RuCl_3{\cdot}xH_2O$ (200 mg, 0.792 mmol) was suspended in HCO_2H (6.7 mL, 0.178 mol) and heated to 110 °C in a pressure Schlenk tube. After 1 h, the resulting yellow solution was cooled to room temperature and carefully vented. The solvent was removed under reduced pressure, affording $[RuCl_2(CO)_2]_n$ which was dissolved in ethanol (7 mL) and treated with $(2,6\text{-}Me_2C_6H_3)PPh_2$ (849.5 mg, 2.93 mmol). The solution was heated to 80 °C for 2 h,

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Organometallics XXXX, XXX, XXX−XXX

obtaining a light yellow precipitate. After filtration, the solid was washed with diethyl ether (4 × 3 mL) and dried under reduced pressure. Yield: 435.5 mg (68%). Anal. Calcd (%) for $C_{42}H_{38}Cl_2O_2P_2Ru$: C 62.38, H 4.74; found: C 62.50, H, 4.86. IR (Nujol): 2039 (s), 2001 (s) cm^{-1} ($\nu_{C\equiv O}$). ^1H NMR (200.1 MHz, CD_2Cl_2, 20 °C): δ 8.52−7.03 (m, 26H; aromatic protons), 2.10 (s, 12 H; CH_3). ^1H NMR (200.1 MHz, tetrachloroethane-d_2, 50 °C): δ 8.54−7.06 (m, 26H; aromatic protons), 2.13 (s, 12 H; CH_3). $^{13}C\{^1H\}$ NMR (50.3 MHz, CD_2Cl_2, 20 °C): δ 143.1 (t, ^2J(C,P) = 2.9 Hz; CCH_3), 132.1−128.5 (m; aromatic carbon atoms), 25.9 (t, ^3J(C,P) = 2.3 Hz; CH_3). $^{13}C\{^1H\}$ NMR (50.3 MHz, tetrachloroethane-d_2, 80 °C): δ 194.0 (m; CO), 143.5 (t, ^2J(C,P) = 4.7 Hz; CCH_3), 135.4−128.5 (m; aromatic carbon atoms), 26.1 (t, ^3J(C,P) = 2.3 Hz; CH_3). $^{31}P\{^1H\}$ NMR (81.0 MHz, tetrachloroethane-d_2, 20 °C): δ 10.3 (s). $^{31}P\{^1H\}$ NMR (81.0 MHz, tetrachloroethane-d_2, 50 °C): δ 10.4 (s).

Method B. The complex $[RuCl_2(CO)_3]_2$ (50 mg, 0.098 mmol) was suspended in ethanol (5 mL), (2,6-$Me_2C_6H_3$)PPh_2 (126 mg, 0.434 mmol) was added, and the mixture was heated at 80 °C overnight. The solvent was evaporated under reduced pressure and, after addition of chloroform (2 mL), the suspension was stirred at room temperature for 2 h. The volume was reduced to about 1 mL, diethyl ether (5 mL) was added, and the light yellow precipitate was filtrated, washed with diethyl ether (2 × 3 mL), *n*-pentane (3 mL), and dried under reduced pressure. Yield: 133 mg (84%).

Synthesis of RuCl{(2-CH_2-6-MeC_6H_3)PPh_2}{(2,6-$Me_2C_6H_3$)-PPh_2}$(CO)_2$ (2). *Method A.* Complex **1** (100 mg, 0.124 mmol) was suspended in toluene (5 mL), Et_3N (87 μL, 0.624 mmol) was added, and the mixture was refluxed overnight, obtaining a yellow solution. The solvent was evaporated under reduced pressure, and the residue was dissolved in dichloromethane (5 mL). The solution was stirred at room temperature for 2 h and concentrated to about 0.5 mL. Addition of methanol (2 mL) afforded a light yellow precipitate, which was filtrated, washed with diethyl ether (2 × 5 mL), *n*-pentane (2 × 5 mL), and dried under reduced pressure. Yield: 62.2 mg (65%). Anal. Calcd (%) for $C_{42}H_{37}ClO_2P_2Ru$: C 65.33, H 4.83; found: C 65.40, H, 4.88. IR (Nujol): 2020 (s), 1957 (s) cm^{-1} ($\nu_{C\equiv O}$). ^1H NMR (200.1 MHz, $CDCl_3$, 20 °C): δ 8.11−7.77 (m, 6H; aromatic protons), 7.64 (m, 2H; aromatic protons), 7.55−7.13 (m, 15H; aromatic protons), 7.05 (dd, ^3J(H,H) = 7.3 Hz, ^4J(H,H) = 3.0 Hz, 2H; aromatic protons), 6.93 (d, ^3J(H,H) = 4.4 Hz, 1H; aromatic proton), 3.07 (dd, ^2J(H,H) = 14.8 Hz, ^3J(H,P) = 5.5 Hz, 1H; $RuCH_2$), 2.89 (dd, ^2J(H,H) = 14.8 Hz, ^3J(H,P) = 6.3 Hz, 1H; $RuCH_2$), 1.98 (s, 6H; CH_3), 1.72 (s, 3H; CH_3). $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$, 20 °C): δ 198.3 (t, ^2J(C,P) = 12.6 Hz; CO), 194.2 (dd, ^2J(C,P) = 8.7 Hz, ^2J(C,P) = 7.9 Hz; CO), 163.2 (dd, ^2J(C,P) = 35.8 Hz, ^3J(C,P) = 6.3 Hz; CCH_2Ru), 142.8 (s, CCH_3), 142.6 (s; CCH_3), 138.2−124.9 (m; aromatic carbon atoms), 32.2 (t, ^2J(C,P) = 4.9 Hz; $RuCH_2$), 25.6 (d, ^3J(C,P) = 4.9 Hz; CH_3), 22.3 (d, ^3J(C,P) = 3.3 Hz; CH_3). $^{31}P\{^1H\}$ NMR (81.0 MHz, $CDCl_3$, 20 °C): δ 54.2 (d, ^2J(P,P) = 293 Hz), 26.3 (d, ^2J(P,P) = 293 Hz).

Method B. The compound $RuCl_3{\cdot}xH_2O$ (208.2 mg, 0.825 mmol) was suspended in HCO_2H (7 mL, 0.186 mol) and heated to 110 °C in a pressure Schlenk tube. After 1 h, the resulting yellow solution was cooled to room temperature and carefully vented. The solvent was removed under reduced pressure, affording $[RuCl_2(CO)_2]_n$, which was dissolved in distilled ethanol (6 mL). The solution was reacted with (2,6-$Me_2C_6H_3$)PPh_2 (881.9 mg, 3.04 mmol), Et_3N (680 μL, 4.88 mmol), and stirred at 80 °C overnight. The volume was reduced by about half, affording a precipitate, which was filtrated and washed with ethanol (3 × 3 mL), diethyl ether (2 × 3 mL), *n*-pentane (2 mL), and dried under reduced pressure. Yield: 398 mg (63%).

Method C. $[RuCl_2(CO)_2]_n$ (502.2 mg, 2.20 mmol of Ru), obtained as described in the method B for the synthesis of **2**, and (2,6-$Me_2C_6H_3$)PPh_2 (1.78 g, 6.13 mmol) were dissolved in ethanol (10 mL). Et_3N (1.4 mL, 10.0 mmol) was added, and the solution was refluxed overnight. A yellow solid precipitated overnight, the solvent was eliminated under reduced pressure, obtaining a residue, which was dissolved in chloroform, and the solution was stirred at room temperature for 2 h. The solution was concentrated to about 0.5 mL, and addition of diethyl ether (5 mL) afforded a light yellow precipitate, which was filtrated, washed with diethyl ether (2 × 4 mL), *n*-pentane (4 mL), and dried under reduced pressure. Yield: 967 mg (57%).

Synthesis of [Ru{(2-CH_2-6-MeC_6H_3)PPh_2}(en)$(CO)_2$]Cl (3). Complex **2** (252.2 mg, 0.47 mmol) and $CaCO_3$ (22.8 mg, 0.23 mmol) were suspended in methanol (5 mL). Ethylenediamine (63 μL, 0.94 mmol) was added, and the mixture was refluxed overnight. The suspension was filtrated, and the solvent was eliminated under reduced pressure. Diethyl ether (4 mL) was added to the residue, and the suspension was stirred for 1 h. The precipitate was filtrated, washed with diethyl ether (2 × 3 mL), *n*-pentane (4 mL), and dried under reduced pressure. Yield: 224.2 mg (88%). Anal. Calcd (%) for $C_{24}H_{26}ClN_2O_2PRu$: C 53.19, H 4.84, N 5.17; found: C 53.32, H 4.79, N 5.02. IR (Nujol): 2028 (s), 1959 (s) cm^{-1} ($\nu_{C\equiv O}$). ^1H NMR (200.1 MHz, CD_3OD, 20 °C): δ 7.61−7.26 (m, 12H; aromatic protons), 7.04 (ddd, ^3J(H,H) = 7.2 Hz, ^4J(H,H) = 3.8 Hz, ^4J(H,H) = 0.9 Hz, 1H, aromatic proton), 5.30 (m, 1H; NH_2), 4.30 (m, 1H; NCH_2), 4.04 (m, 1H; NCH_2), 3.07 (m, 1H; NCH_2), 2.99 (d, ^2J(H,H) = 15.0 Hz, 1H; $RuCH_2$), 2.83 (m, 1H; NCH_2), 2.75−2.49 (br m, 2H; NH_2), 2.57 (d, ^2J(H,H) = 14.7 Hz, 1H; $RuCH_2$), 2.41 (m, 1H; NH_2), 1.69 (s, 3H; CH_3). $^{13}C\{^1H\}$ NMR (50.3 MHz, CD_3OD, 20 °C): δ 201.3 (d, ^2J(C,P) = 13.5 Hz; CO), 191.9 (d, ^2J(C,P) = 6.5 Hz; CO), 163.3 (d, ^2J(C,P) = 33.1 Hz; CCH_2Ru), 143.0 (d, ^2J(C,P) = 1.7 Hz; CCH_3), 136.3−113.8 (m; aromatic carbon atoms), 46.7 (s; NCH_2), 45.4 (d, ^3J(C,P) = 3.9 Hz; NCH_2), 31.9 (d, ^2J(C,P) = 4.1 Hz; $RuCH_2$), 22.3 (d, ^3J(C,P) = 3.9 Hz; CH_3). $^{31}P\{^1H\}$ NMR (81.0 MHz, CD_3OD, 20 °C): δ 64.6 (s).

Synthesis of [Ru{(2-CH_2-6-MeC_6H_3)PPh_2}(ampy)$(CO)_2$]Cl (4). Complex **2** (250.5 mg, 0.42 mmol) and $CaCO_3$ (21.3 mg, 0.21 mmol) were suspended in methanol (5 mL). 2-(Aminomethyl)pyridine (87 μL, 0.84 mmol) was added, and the mixture was refluxed overnight. After filtration, the solvent was eliminated under reduced pressure. Diethyl ether (4 mL) was added to the residue, obtaining a mixture that was stirred for 1 h at room temperature. The resulting suspension was filtrated, and the precipitate was washed with diethyl ether (2 × 3 mL), *n*-pentane (4 mL), and dried under reduced pressure. Yield: 107.9 mg (43%). Anal. Calcd (%) for $C_{28}H_{26}ClN_2O_2PRu$: C 57.00, H 4.44, N 4.75; found: C 57.12, H 4.34, N 4.63. IR (Nujol): 2032 (s), 1966 (s) cm^{-1} ($\nu_{C\equiv O}$). ^1H NMR (200.1 MHz, $CDCl_3$, 20 °C): δ 8.61 (dd, ^3J(H,H) = 7.6 Hz, ^4J(H,H) = 1.9 Hz, 1H; ortho-C*H* of C_5H_4N), 7.79 (td, ^3J(H,H) = 7.7 Hz, ^4J(H,H) = 1.5 Hz, 1H; para-C*H* of C_5H_4N), 7.73−7.21 (m, 14H; aromatic protons), 7.00 (dd, ^3J(H,H) = 8.8 Hz, ^3J(H,H) = 3.6 Hz, 1H; meta-C*H* of C_5H_4N), 5.58 (dt, ^2J(H,H) = 11.0 Hz, ^3J(H,H) = 5.7 Hz, 1H; NCH_2), 4.37 (td, ^3J(H,H) = 5.7, ^3J(H,H) = 2.2 Hz, 2H; NH_2), 3.08 (dt, ^2J(H,H) = 11.0 Hz, ^3J(H,H) = 5.2 Hz, 1H; NCH_2), 2.86 (d, ^2J(H,H) = 15.0 Hz, 1H; $RuCH_2$), 2.71 (d, ^2J(H,H) = 15.0 Hz, 1H; $RuCH_2$), 1.71 (s, 3H; CH_3). ^1H NMR (200.1 MHz, CD_3OD, 20 °C): δ 8.74 (d, ^3J(H,H) = 5.5 Hz, 1H; ortho-C*H* of C_5H_4N), 7.96 (ddd, ^3J(H,H) = 7.7 Hz, ^3J(H,H) = 7.5 Hz, ^4J(H,H) = 1.6 Hz, 1H; para-C*H* of C_5H_4N), 7.71−7.28 (m, 14H; aromatic protons), 7.08 (ddd, ^3J(H,H) = 8.0 Hz, ^3J(H,H) = 4.2 Hz, ^4J(H,H) = 1.1 Hz, 1H; meta-C*H* of C_5H_4N), 4.34−4.07 (m, 1H; NCH_2), 4.21 (ddd, ^3J(H,H) = 7.3 Hz, ^3J(H,H) = 4.7 Hz, ^4J(H,H) = 1.3 Hz, 2H; NH_2), 3.97 (m, 1H; NCH_2), 2.94 (d, ^2J(H,H) = 15.4 Hz, 1H; $RuCH_2$), 2.14 (d, ^2J(H,H) = 15.4 Hz, 1H; $RuCH_2$), 1.70 (s, 3H; CH_3). $^{13}C\{^1H\}$ NMR (50.3 MHz, CD_3OD, 20 °C): δ 201.3 (d, ^2J(C,P) = 14.6 Hz; CO), 191.5 (d, ^2J(C,P) = 6.5 Hz; CO), 162.8 (s; $NCCH_2$), 162.7 (d, ^2J(C,P) = 32.1 Hz; CCH_2Ru), 153.7 (s; ortho-CH of C_5H_4N), 143.1 (d, ^2J(C,P) = 2.2 Hz; CCH_3), 140.3 (s; para-CH of C_5H_4N), 135.1−112.8 (m; aromatic carbon atoms), 52.2 (d, ^3J(C,P) = 3.4 Hz; NCH_2), 33.9 (d, ^2J(C,P) = 3.9 Hz; $RuCH_2$), 22.3 (d, ^3J(C,P) = 3.9 Hz; CH_3). $^{31}P\{^1H\}$ NMR (81.0 MHz, CD_3OD, 20 °C): δ 64.4 (s).

Synthesis of [Ru{(2-CH_2-6-MeC_6H_3)PPh_2}{(*R*,*R*)-dpen}$(CO)_2$]Cl (5). Complex **2** (82.5 mg, 0.107 mmol) and $CaCO_3$ (5.4 mg, 0.05 mmol) were suspended in methanol (5 mL). (1*R*,2*R*)-1,2-Diphenylethane-1,2-diamine (45.3 mg, 0.21 mmol) was added, and the mixture was refluxed overnight. After filtration, the solvent was eliminated

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Organometallics XXXX, XXX, XXX−XXX

under reduced pressure and diethyl ether (4 mL) was added to the residue, affording a mixture, which was stirred for 1 h. The resulting suspension was filtrated, and the precipitate was washed with diethyl ether (2 × 3 mL), *n*-pentane (4 mL), and dried under reduced pressure. The product was obtained as a mixture of two diastereoisomers in a 1:1 ratio. Yield: 50.1 mg (68%). Anal. Calcd (%) for $C_{36}H_{34}ClN_2O_2PRu$: C 62.29, H 4.94, N 4.04; found: C 62.32, H 4.98, N 4.01. IR (Nujol): 2032 (s), 1965 (s) cm^{-1} ($\nu_{C\equiv O}$). ^1H NMR (200.1 MHz, $CDCl_3$, 20 °C): δ 8.35−6.80 (m, 23H; aromatic protons), 6.25 (dd, $^2J(H,H)$ = 25.0 Hz, $^3J(H,H)$ = 11.7 Hz; NH_2), 5.57 (m; NH_2), 4.77 (m, 2H; NH_2), 4.25−3.55 (m, 2H; NCH), 3.29 (d, $^2J(H,H)$ = 14.0 Hz; $RuCH_2$), 3.04 (d, $^2J(H,H)$ = 14.1 Hz; $RuCH_2$), 2.64 (d, $^2J(H,H)$ = 14.0 Hz; $RuCH_2$), 2.58 (d, $^2J(H,H)$ = 14.1 Hz; $RuCH_2$), 1.73 (s; CH_3), 1.68 (s; CH_3). $^{31}P\{^1H\}$ NMR (81.0 MHz, $CDCl_3$, 20 °C): δ 64.2 (s), 63.9 (s).

Synthesis of RuCl{(2-CH_2-6-MeC_6H_3)PPh_2}(en)(CO) (6). Complex **3** (50 mg, 0.092 mmol) was heated at 85 °C under reduced pressure (10^{-2} mbar) for 36 h, affording a dark-yellow clean product. Yield: 46.5 mg (98%). Anal. Calcd (%) for $C_{23}H_{26}ClN_2OPRu$: C 53.75, H 5.10, N 5.45; found: C 53.68, H 5.24, N 5.41. IR (Nujol): 1906 (s) cm^{-1} ($\nu_{C\equiv O}$). ^1H NMR (200.1 MHz, tetrachloroethane-d_2, 50 °C): δ 7.80−6.80 (m, 13H; aromatic protons), 3.38 (m, 1H; NCH_2), 3.11 (m, 1H; NCH_2), 2.98 (d, $^2J(H,H)$ = 14.6 Hz, 1H; $RuCH_2$), 2.77 (m, 2H; NCH_2 and NH_2), 2.55−2.10 (m, 2H; NCH_2 and NH_2), 2.01 (d, $^2J(H,H)$ = 14.6 Hz, 1H; $RuCH_2$), 1.74 (s, 3H; CH_3), 1.70−1.56 (m, 1H; NH_2), 1.43 (m, 1H; NH_2). $^{31}P\{^1H\}$ NMR (81.0 MHz, tetrachloroethane-d_2, 50 °C): δ 68.7 (s).

Procedure for the TH of Acetophenone with 1−5. The ruthenium catalyst solution used for TH was prepared by dissolving the ruthenium complex (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 acetophenone (120 μL, 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 (0.2 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 % with respect to acetophenone (0.1 M). The same procedure was followed for TH with the other bases (KO*t*Bu and KOH) at different concentration (1−5 mol %), using the appropriate amount of 2-propanol.

Procedure for the TH of Acetophenone with in Situ Prepared Catalysts from 2. Complex **2** (15.4 mg, 0.02 mmol) was dissolved in 5 mL of 2-propanol, and en or ampy (0.1 mmol) was solubilized in 25 mL of 2-propanol. The solutions of **2** (250 μL, 1.0 μmol) and the ligand (500 μL, 2.0 μmol) were added subsequently to acetophenone (120 μL, 1.0 mmol) in 2-propanol (8.93 mL). The mixture was stirred under reflux for 10 min, and a 0.1 M solution of NaO*i*Pr (200 μL, 20 μmol) in 2-propanol was added (final volume 10 mL). The reaction was sampled by removing an aliquot of the reaction mixture (0.2 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 S/C molar ratio was 1000/1, whereas the NaO*i*Pr concentration was 2 mol %, with respect to acetophenone (0.1 M).

Procedure for the HY of Ketones with Catalysts 1−6. The HY reactions were performed in an 8 vessels Endeavor Biotage apparatus. The vessels were charged with the catalysts **1**−**6** (0.5 μmol), loaded with 5 bar of N_2, and slowly vented (five times). The liquid ketones **a**−**e** and **h** (5 mmol) and the KO*t*Bu or KOH solution (1 mL, 0.1 mmol, 0.1 M) in methanol or ethanol were added. In the case of the solid ketones **f**−**g** (5 mmol), they were loaded together with the ruthenium catalyst. Further addition of the solvent (methanol or ethanol) leads 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 (3−16 h). The S/C molar ratio was 10 000/1, whereas the base concentration was 2 mol %. A similar method was applied for the reactions with other S/C (in the range 500−10 000), using the appropriate amount of catalysts and solvent, and for the reactions conducted at 40 °C. 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.

Procedure for the HY of Ketones with in Situ Prepared Catalysts from 1 and 2. The vessels of the system were charged with the catalysts **1** or **2** (0.5 μmol), closed, loaded with 5 bar of N_2, and slowly vented five times. The ketone **a** or **e** (5 mmol), en or ampy in ethanol (50 μL, 1 μmol, 0.02 M), and KO*t*Bu in ethanol (1 mL, 0.1 mmol, 0.1 M) were added to the catalyst with about 1 mL of ethanol (2 M of ketone). 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 (3−16 h). The S/C molar ratio was 10 000/1, whereas the base concentration was 2 mol %. A similar method was applied for the reactions conducted with S/C in the range 1000−10 000, using the appropriate amount of catalysts, 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.

Procedure for the HY of Acetophenone in a Stainless Steel Autoclave. The autoclave was charged with the catalyst **3** or **4** (2.06 μmol), closed, and purged three times with N_2. Acetophenone (2.4 mL, 20.6 mmol), the solvent (4 mL of ethanol or methanol), and a solution of KO*t*Bu (4 mL, 0.1 M in the same solvent) were subsequently added. The system was purged with N_2 (two times) and with H_2 (three times). The autoclave was pressurized to 30 bar with H_2 and heated to 70 °C for the required time (3−23 h). The final concentration of acetophenone was 2 M, the S/C ratio was 10 000, whereas the base concentration was 2 mol %. This procedure was applied for the reactions with S/C = 25 000, using the appropriate amount of catalysts and solvent. Samples of 0.2 mL were then taken at regular intervals (2, 5, 10, 20, 30 min, and longer reaction times), added to 5 mL of methanol, and analyzed by GC. TOF values were calculated at 50% conversion.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00267.

NMR data of the isolated complexes and catalytic results of the TH and HY reactions (PDF)

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Notes

The authors declare no competing financial interest.

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Organometallics XXXX, XXX, XXX−XXX

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