ARTICLE

Simple synthesis of [Ru(CO$_3$)(NHC)(*p*-cymene)] complexes and their use in transfer hydrogenation catalysis

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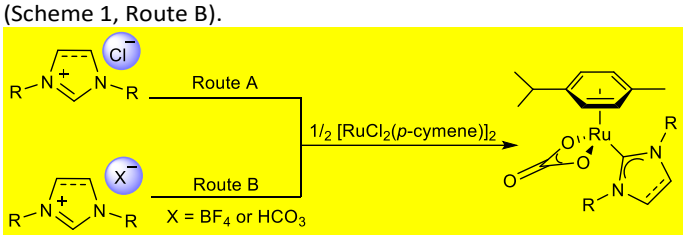
A novel, efficient and facile protocol for the synthesis of a series of [Ru(NHC)(CO$_3$)(*p*-cymene)] complexes is reported. This family of Ru-NHC complexes was obtained from imidazol(in)ium tetrafluoroborate or imidazolium hydrogen carbonate salts in moderate to excellent yields, employing sustainable weak base. The ruthenium complexes were successfully utilized in the transfer hydrogenation of ketones as highly active multifunctional catalysts.

Introduction

N-heterocyclic carbenes (NHCs) ligands form stable complexes with a variety of metals, many of which have now become widely used in catalysis.[1] The initial synthetic approach leading to numerous metal-NHC complexes, including a series of Ru-NHC compounds, made use of a strong base such as KO^{t}Bu, KHMDS or NaH in combination with the imidazolium salt to isolate[2] or to generate *in situ* the free carbene.[3] This reagent was then used in ligand substitution reactions. However, this pathway requires strictly anhydrous and inert conditions. Subsequently, the transmetalation route through the intermediary of copper[4] or light-sensitive silver[5], alleviates the need for free carbene generation, and has been widely employed as a more common and user-friendly method. The above synthetic routes, whether free carbene or transmetalation, involve multiple steps and are not atom economical.[4a,4c] In the past few years, the direct treatment of metal precursors and imidazolium salts in the presence of a weak base has become an emerging method and has been widely used, allowing a series of metal-NHC complexes to be successfully prepared.[6] The advantage of this method is that it does not only simplify the synthetic reaction, but also uses eco-friendly reagents instead of strong bases to prepare a wide range of NHC complexes under mild conditions. Recently, we have developed straightforward and sustainable methods for the synthesis of well-defined Au[7], Cu[6c, 8], Pt[9], Ru[10] and Pd-NHC[11] species, using imidazol(idin)ium salts and weak bases. In addition, other research groups have also developed similar methods for Au, Rh, Cu, etc.[12]

Although the use of K_2CO_3 in the synthesis of Ru-NHC complex has been described as early as 2006 by Dixneuf and co-workers, this method was limited to one example of Ru complex and was never further explored.[13] Our group also has recently demonstrated the efficiency of the weak base route to synthesis Ru complexes[10]. Both methods use NHC·HCl as starting material (Scheme 1, Route A). To the best of our knowledge, only a handful of reports using a weak base to synthesize [Ru(NHC)(CO$_3$)(*p*-cymene)] have been disclosed so far, and the directly and highly efficient synthesis method starting from imidazol(in)ium salts to prepare [Ru(NHC)(CO$_3$)(*p*-cymene)] complexes has seen only limited exemplification. Therefore, the development of this potentially versatile method is necessary, and can effectively promote the wide application of such compounds. We next turned our attention to the less studied tetrafluoroborate and hydrogen carbonate imidazolium salts which are easy to handle and non-hygroscopic,[14] as reagents in the transformation leading to well defined Ru-NHC complexes (Scheme 1, Route B).



Scheme 1. Synthetic route of [Ru(NHC)(CO$_3$)(*p*-cymene)] complexes.

The synthetic access to such complexes is key and their use in related complexes as pre-catalysts in transfer hydrogenation drew our attention as an area worthy of further exploration. Transfer hydrogenation (TH),[15] a reaction leading to the reduction of carbonyl compounds to their corresponding alcohols, important block in pharmaceuticals, agrochemicals and fine chemicals,[16] has been extensively studied. A number of investigation in this area have shown catalysts to display high catalytic activity utilizing 2-propanol (^{i}PrOH) as a hydrogen-donor reagent in organic synthesis.[17-20] In this process, low catalyst loading, green solvents and short reaction times have been the targets. Due to the high thermal stability and tunability

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† Footnotes relating to the title and/or authors should appear here.
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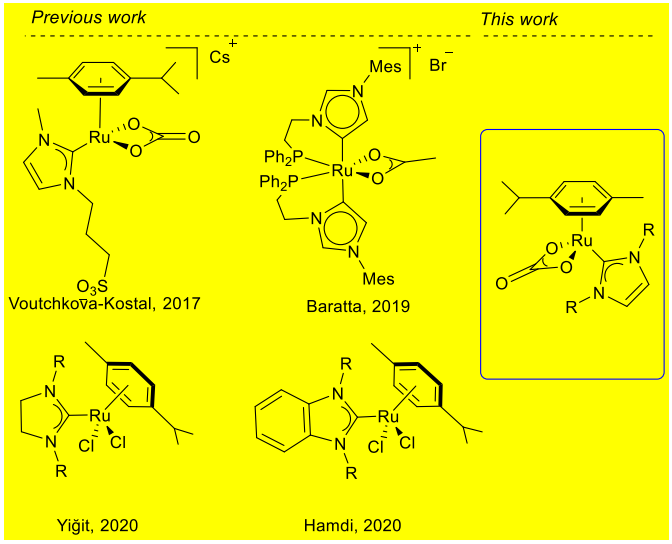
of their steric properties, N-heterocyclic carbenes have emerged as versatile tools in modern synthetic chemistry.[21] For the transfer hydrogenation reaction, Ru(II)-NHC complexes, as most attractive catalysts, have been developed bearing different ligand types.[22] Recently, a series of normal and abnormal-NHC Ru(II) complexes have appeared as active promoters in transfer hydrogenation (Scheme 2). The Voutchkova-Kostal group have presented TH reaction using sulfonate-functionalized ruthenium N-heterocyclic carbene catalysts which resulted in modest yield at 130 °C.[23] Subsequently, Baratta and co-workers have recently reported a highly efficient abnormal NHC ruthenium catalyst, displaying outstanding catalytic activity in the Oppenauer-type oxidation of alcohols and in the reverse TH of ketones under mild reaction conditions and at low catalyst loading.[24] The Hamdi and Yiğit groups have synthesized a series of [Ru(NHC)Cl_2(*p*-cymene)] complexes and used them as catalysts for the TH of aromatic ketones. However, the reaction required equivalent amount of base or long reaction times to obtain high yields.[25]



Scheme 2. Ru-catalyzed transfer hydrogenation catalysts.

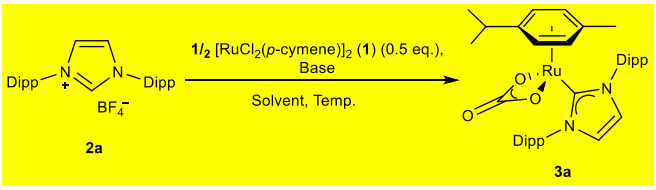
Therefore, we explored a potentially quite versatile and efficient route to access a series of [Ru(NHC)(CO_3)(*p*-cymene)] compounds by using NHCs tetrafluoroborate and hydrogen carbonate salt as synthons and tested the efficiency of the resulting well-defined complexes in the TH reaction.

Results and discussion

Synthesis of [Ru(NHC)(CO_3)(*p*-cymene)]

The study was initiated by investigating the reaction of IPr·HBF_4 with [$RuCl_2$(*p*-cymene)]$_2$ based on the conditions we previously reported.[10] Gratifyingly, the targeted [Ru(IPr)(CO_3)(*p*-cymene)] complex **3a** was obtained in a moderate yield after 29 hours when the reaction was carried out in acetone at 60°C (Table 1, entry 1). Subsequently, we optimized the reaction parameters, including solvent, base and temperature, in order to provide the most practical and efficient method to these complexes. As shown in Table 1, by replacing acetone by ethanol, ethyl acetate or toluene, no product was observed (Table 1, entries 2-4). However, THF proved to be an effective solvent, producing an 80% yield after 7h (Table 1, entry 5). Moreover, two solvents that are more sustainable than THF were tested separately. Cyclopentyl methyl ether (CPME), as a more eco-friendly solvent,[26] resulted in a 68% yield at the boiling point (106°C). Additionally, environmentally friendly 2-methyltetrahydrofuran (2-MeTHF)[27] gave a similar yield as THF (Table 1, entries 6-7). Therefore, considering the principles of green chemistry, we favoured to use 2-MeTHF as reaction solvent in following reactions. Decreasing the reaction temperature resulted in a relatively low yield, even with a longer time, and a large amount of starting material was observed to remain after the reaction (Table 1, entries 8-10). When lowering the amount of K_2CO_3, longer reaction times were required and lead to moderate yield (Table 1, entry 11). In exploring various inorganic bases, $NaHCO_3$ or Cs_2CO_3 proved insufficiently effective as a carbonate source and only traces or 67% of the product could be observed (Table 1, entries 12-13).

Table 1 Optimization of the reaction conditions for **3a**.[a]



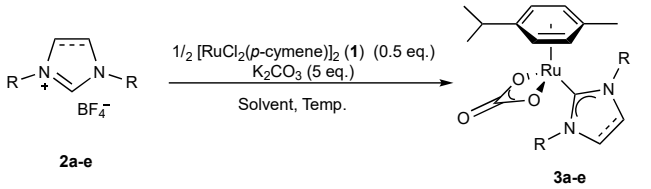
Entry	Base	Temp. (°C)	Solvent	Time(h)	Yield (%)[b]
1	K_2CO_3	60	acetone	29	50
2	K_2CO_3	80	EtOH	12	-
3	K_2CO_3	80	EtOAc	12	-
4	K_2CO_3	80	PhMe	12	-
5	K_2CO_3	70	THF	7	80
6	K_2CO_3	106	CPME	4	68
7	***K_2CO_3***	***80***	***2-MeTHF***	***7***	***77***
8	K_2CO_3	80	CPME	10	50
9	K_2CO_3	70	2-MeTHF	12	70
10	K_2CO_3	60	2-MeTHF	12	29
11[c]	K_2CO_3	80	2-MeTHF	24	62
12	$NaHCO_3$	80	2-MeTHF	7	trace
13	Cs_2CO_3	80	2-MeTHF	7	67

[a] Reaction conditions: **1** (0.12 mmol, 0.5eq.), **2** (0.24 mmol, 1 eq.), K_2CO_3 (1.18 mmol, 5 eq.), solvent (1.0 mL). [b] Isolated yields. [c] 3 eq. of K_2CO_3.

We then examined the versatility of our optimized conditions as a function of the NHCs (Table 2). Our protocol proved successful for most of the tested ligands, either unsaturated and saturated, such as IMes (N,N'-(2,4,6-trimethylphenyl)imidazol-2-ylidene) **2b**, SIMes (N,N'-bis(2,4,6-trimethylphenyl)-imidazolidin-2-ylidene) **2c**, ICy (N,N'-bis(cyclohexyl)imidazol-2-ylidene) **2d** and IMe (N,N'-dimethyl-

imidazol-2-ylidene) **2e**. From the obtained results, we can see that a series of Ru complexes **3a**-**3c** can be easily obtained in moderate to excellent yields with NHC·HBF_4 as the precursors in 2-MeTHF. Among them, **2b** can be efficiently transformed into the corresponding **3b** in only 3 hours at 70°C. In addition, compound **3d** can also be successfully synthesized in 72% yield by using CPME as solvent. Although ICy·HCl can also be used as a material to obtain the target product **3d**,[10] ICy·HCl salt is highly hygroscopic, resulting in partial hydrolysis. Therefore, ICy·HBF_4 **2d** as a material is an effective reaction partner in the above method. [14b-c] Unfortunately, the smaller N-alkyl substituted NHC complex **3e** was obtained only in moderate yield in THF after recrystallization. This may be associated with the previously calculated higher bond dissociation energy of the NHC-H bond.[7b]

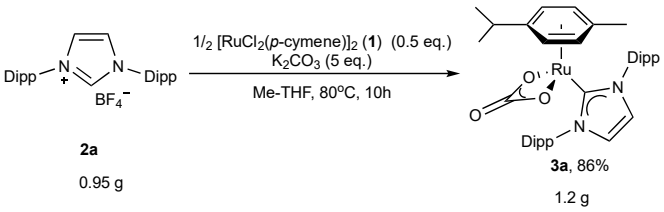
Table 2 Synthesis of [Ru(CO_3)(NHC)(*p*-cymene] complexes *via* the weak base route.[a]



Entry		NHC	Solvent	Temp. (°C)	Time(h)	Yield (%)[b]
1	**3a**	IPr	2-MeTHF	80	7	78
2	**3b**	IMes	2-MeTHF	70	3	94
3	**3c**	SIMes	2-MeTHF	80	3	62
4	**3d**	ICy	CPME	106	20	72
5	**3e**	IMe	THF	70	7	53

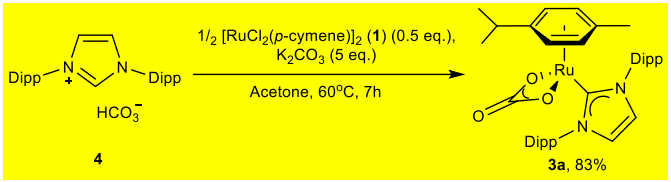
[a] Reaction conditions: **1** (0.12 mmol, 0.5eq.), **2** (0.24 mmol, 1 eq.), K_2CO_3 (1.18 mmol, 5 eq.), solvent (1.0 mL). [b] Isolated yields.

With the success of this simple and efficient protocol, the reaction of **1** with IPr·HBF_4 **2a** was performed on a >1 gram-scale (Scheme 3) to simply illustrate scalability.



Scheme 3. Larger scale synthesis of **3a**.

We next also explored imidazolium salt bearing hydrogen carbonate as a counterion (Scheme 4). To our delight, the well-defined [Ru(IPr)(CO_3)(*p*-cymene)] complex can also be obtained under mild conditions by using acetone as "green" solvent at 60°C, resulting in 83% yield after 7h. As the result shows, [NHC(H)][HCO_3] salts can also be deployed as reagents in this simple transformation.



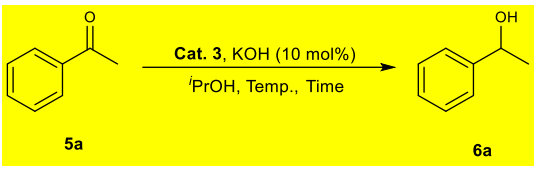
Scheme 4. Synthesis of [Ru(IPr)(CO_3)(*p*-cymene)] complex from IPr·HCO_3.

Catalytic studies

With the above ruthenium complexes (**3a**-**e**) in hand, the TH was tested under various conditions. The use of [Ru(NHC)(CO_3)(*p*-cymene)] complexes as catalysts in this transformation has yet to be explored or reported.

Initially, the TH reaction was tested using acetophenone, KOH as the base, and a 1 mol% loading of [Ru(IPr)(CO_3)(*p*-cymene)] (**3a**) in ^{i}PrOH at 100°C (Table 3, entry 1). Monitoring the reaction by ^{1}H NMR allowed the observation of the clean formation of the desired product, without any by-product. Based on the initial experiment, we investigated the effect of different bases (ESI,† Table S1, entries 1-4). Although NaOH and KO^{t}Bu could promote the reaction with high yields, KOH proved to be the best choice. Substituting the strong base by the weaker K_2CO_3 or K_3PO_4, resulted in reduced yield. When the amount of base is reduced to 10%, 93% of the target product can be obtained (ESI,† Table S1, entry 5). Greater decreases in the base amount leads to lower hydrogenation conversion. Although the time was extended to 36 hours when using 5% of KOH, the yield did not increase significantly. (ESI,† Table S1, entries 6-8).

Table 3 Optimization of the reaction conditions for transfer hydrogenation reaction. [a]



Entry	Ru-NHC	Time (h)	T (°C)	Yield (%)[b]
1[c]	**3a**	16	100	99
2	**3a**	4	80	83
3	**3b**	4	80	79
4	**3c**	4	80	85
5	**3d**	4	80	94
6	**3e**	4	80	99
7	**3f**	4	80	58
8	**3g**	4	80	60
9	**3e**	4	60	86
10	**3e**	4	40	trace
11	**3e**	4	rt	-
12	***3e***	*2*	*80*	*99*
13	**3e**	40mins	80	81

[a] Reaction conditions: **5a** (0.5 mmol, 1 eq.), **3** (1 mol%), KOH (10 mol%), ^{i}PrOH(1.5 mL). [b] NMR yields using 1,3,5-trimethoxybenzene as internal standard. [c] 20 mol% of KOH. (**3f** = [Ru(IPr)Cl_2(*p*-cymene)], **3g** = [Ru(IMes)Cl_2(*p*-cymene)])

Furthermore, different Ru-NHC complexes were examined for comparison (Table 3, entries 2-8). It is worth noting that nearly full conversion was observed with [Ru(IMe)(CO_3)(*p*-cymene)] after only 4h, and a 99% NMR yield was obtained (Table 3, entry 6). Whereas [Ru(IPr)(CO_3)(*p*-cymene)] showed a lower catalytic performance after 4h. Under identical conditions an 83% yield of the product was obtained with **3a** (Table 3, entry 2). Further exploration indicated that the steric parameter of the NHC moiety of Ru complexes is an important factor in determining the catalytic efficiency. The yield decreased as the steric hindrance around the Ru complexes increased. It is clear that the smallest NHC has the highest catalytic activity, the best one being catalyst **3e** followed by complexes **3a**-**3c** (Table 3, entries 5 and 6 vs 2, 3 and 4). By comparison, we found that [Ru(NHC)(CO_3)(*p*-cymene)] complexes **3a**-**3e** outperformed the two [Ru(NHC)Cl_2(*p*-cymene)] counterparts **3f** and **3g** (Table 3, entries 2-3 vs 7-8) and the ruthenium sulfonate-functionalized NHC complex[23]. A control experiment without any metal complex showed the reaction to generate a mere 25% yield of product in this control reaction (ESI,† Table S1, entry 9). Subsequently, other factors such as temperature, solvents and catalyst loading were examined. The yield decreases as the temperature is lowered, with no hydrogenation product being observed at room temperature (Table 3, entries 9-11). ^{i}PrOH is the best choice for this reaction by comparison with other solvents under the same conditions (ESI,† Table S1, entries 10-12). Monitoring the progress of the reaction shows that the transformation is much faster than 4 hours (Table 3, entries 12-13). Figure 1 shows reaction profiles as a function of time and identity of the pre-catalyst. As depicted below, [Ru(IMe)(CO_3)(*p*-cymene)] shows the best initiation rate in the first 40 minutes. The conversion over time trend clearly indicates that **3e** possesses the best catalytic profile among catalysts tested. Finally, upon using 0.5 mol% or less of the pre-catalyst significantly depressed conversions are observed. (ESI,† Table S1, entries 13-14).

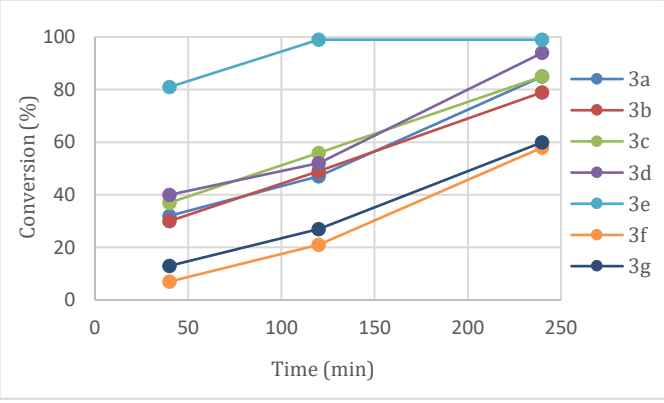
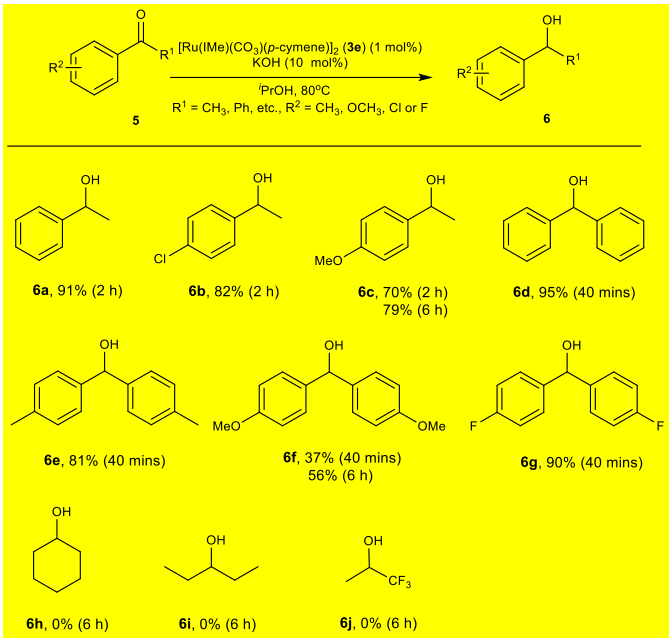


Figure 1. Reaction time for the different synthesized pre-catalysts.

These excellent results prompted us to screen a small range of ketones for this Ru-catalysed TH (Scheme 5). We tested substrates bearing various substituents, almost all of them can be converted in good yields. By comparison, the catalysts are more active for benzophenone compounds than for otherwise substituted acetophenones. Substrates bearing strong electron-donating groups reduce the efficiency of the reaction and require a longer time to reach full conversion. This may be ascribed to the electronic effects of the ketone structure. Unfortunately, the use of cyclohexanone, 3-pentanone and even the 1,1,1-trifluoroacetone did not lead to the corresponding alcohols, even after 6 hours of reaction under standard conditions. Indeed, halides functionalised acetophenones appear to be slightly more active, when *para*-methoxy functionalised congeners require consequently longer reaction times to be converted.



Scheme 5. Ketone substrate scope.

Experimental

General information

Unless otherwise specified, all manipulations were carried out under air in scintillation vials. Solvents and reagents were used as received without any further purification or distillation. ^{1}H NMR and ^{13}C NMR (DEPT-135) were recorded in $CDCl_3$ at room temperature on Bruker spectrometer (300 MHz or 400 MHz). Chemical shifts (ppm) are referenced to the residual solvent peak. Coupling constants (J) are given in hertz. Abbreviations used in the designation of the signals: s = singlet, br s = broad singlet, d = doublet, br d = broad doublet, dd = doublet of doublets, ddd = doublet of doublets of doublets, m = multiplet, td = triplet of doublets, tt = triplet of triplets, q = quadruplet, qt = quadruplet of triplets, hept = heptet. NMR yields are calculated using 1,3,5-trimethoxybenzene as internal standard.

Typical procedure for [Ru(CO_3)(NHC)(*p*-cymene)] complexes

[Ru(CO_3)(IPr)(*p*-cymene)] (3a)

Procedure A: In a 4 mL scintillation vial, 72.0 mg of [$RuCl_2$(*p*-cymene)]$_2$ (0.12 mmol, 0.5 eq.), IPr·HBF_4 (0.24 mmol, 1 eq., 112.0 mg) and K_2CO_3 (1.2 mmol, 5 eq., 162.5 mg) were magnetically stirred in 1 mL of 2-MeTHF at 80 °C for 7 hours. The mixture was allowed to cool to room temperature, was then filtered through a microfilter with 6 mL of acetone (3 x 2 mL), and concentrated under reduced pressure. The crude product was recrystallized with 1 ml of CH_2Cl_2 and 10 ml of anti-solvent (pentane). The product was collected by filtration and washed with pentane (3 x 2 mL), leading to the desired [Ru(CO_3)(IPr)(*p*-cymene)] complex in 78% yield.

Procedure B: In a 4 mL vial, 100 mg of [IPr(H)][HCO_3] (0.22 mmol, 1 eq.), 67.36 mg of [$RuCl_2$(*p*-cymene)]$_2$ (0.11 mmol, 0.5 eq.) and K_2CO_3 (1.1 mmol, 5 eq., 152.0 mg) were stirred in 1 mL of acetone at 60 °C for 7 hours. The mixture was allowed to cool to room temperature, filtered through a microfilter with 6 mL of acetone (3 x 2 mL), and concentrated under reduced pressure. The crude product was recrystallized with 1 ml of CH_2Cl_2 and 10 ml of pentane. The product was collected by filtration and washed with pentane (3 x 2 mL), leading to the desired [Ru(CO_3)(IPr)(*p*-cymene)] complex in 83%yield.

Gram-scale yield 86%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.42 (m, 2H, Dipp sp^2-C*H*), 7.33 (d, *J* = 7.7 Hz, 4H, Dipp sp^2-C*H*), 7.06 (s, 2H, NC*H*), 5.11 (d, *J* = 6.0 Hz, 2H, cym sp^2-C*H*), 4.79 (d, *J* = 5.9 Hz, 2H, cym sp^2-C*H*), 2.90 (hept, *J* = 6.6 Hz, 4H, Dipp ^{i}Pr C*H*), 1.64 – 1.52 (m, 13H, cym ^{i}Pr C*H*, Dipp ^{i}Pr CH_3), 1.16 (s, 3H, cym *p*-CH_3), 1.07 (d, *J* = 6.8 Hz, 12H, Dipp ^{i}Pr CH_3), 0.75 (d, *J* = 6.9 Hz, 6H, ^{i}Pr CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.02 (Ru=*C*), 166.18 (*C*O_3), 147.41 (Dipp, *C*CH_3), 136.66 (Dipp, *C*N), 130.13 (Dipp, *C*H), 125.70 (Dipp, *C*H), 123.84 (N*C*H=), 99.47 (*p*-cymene, *C*^{i}Pr), 94.92(*p*-cymene, *C*CH_3), 84.53 (C_6H_4, *C*H), 83.42, 31.76 (*p*-cymene, *C*HC_2H_6), 29.34 (Dipp, *C*H_3), 27.52 (Dipp, *C*HC_2H_6), 22.87 (*p*-cymene, CH*C*$_2H_6$), 16.88 (*C*$H_3C_6H_4$). Data are in agreement with reported information.[10]

[Ru(CO_3)(IMes)(*p*-cymene)] (3b)

In a 4 mL vial, 72.0 mg of [$RuCl_2$(*p*-cymene)]$_2$ (0.12 mmol, 0.5 eq.), IMes·HBF_4 (0.24 mmol, 1 eq., 92.2 mg) and K_2CO_3 (1.2 mmol, 5 eq., 162.5 mg) were stirred in 1 mL of 2-MeTHF at 70 °C for 3 hours. The mixture was filtered through a microfilter with 6 mL of acetone (3 x 2 mL), and concentrated under reduced pressure. The crude product was recrystallized with 1 ml of CH_2Cl_2 and 10 ml of pentane. The product was collected by filtration and washed with pentane (3 x 2 mL), then dried under vacuum and leads to the desired [Ru(CO_3)(IMes)(*p*-cymene)] complex.

Yield 94%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 (d, *J* = 1.9 Hz, 6H, Mes sp^2-C*H*, NC*H*), 5.14 (d, *J* = 6.2 Hz, 2H, cym sp^2-C*H*), 4.81 (d, *J* = 6.1 Hz, 2H, cym sp^2-C*H*), 2.34 (s, 6H, Mes *p*-CH_3), 2.20 (s, 12H, Mes *o*-CH_3), 1.75 – 1.62 (hept, 1H, cym ^{i}Pr C*H*), 1.35 (s, 3H, cym *p*-CH_3), 0.82 (d, *J* = 6.9 Hz, 6H, ^{i}Pr CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.57 (Ru=*C*), 166.39 (*C*O_3), 139.05 (Mes, *C*CH_3), 136.65 (Mes, *C*N), 128.97 (Mes, *C*H), 124.71 (N*C*H=), 99.89 (*p*-cymene, *C*^{i}Pr), 95.03 (*p*-cymene, *C*CH_3), 84.99 (C_6H_4, *C*H), 83.78 (C_6H_4, *C*H), 32.00 (*p*-cymene, *C*HC_2H_6), 23.47 (Mes, *C*H_3), 21.12 (*p*-cymene, CH*C*$_2H_6$), 18.70 (Mes, *C*H_3), 16.92 (*C*$H_3C_6H_4$). Data are in agreement with reported information.[13]

[Ru(CO_3)(SIMes)(*p*-cymene)] (3c)

In a 4 mL vial, 72.0 mg of [$RuCl_2$(*p*-cymene)]$_2$ (0.12 mmol, 0.5 eq.), SIMes·HBF_4 (0.24 mmol, 1 eq., 92.7 mg) and K_2CO_3 (1.2 mmol, 5 eq., 162.5 mg) were stirred in 1 mL of 2-MeTHF at 80 °C for 3 hours. The mixture was allowed to cool down to room temperature, filtered through a microfilter with 6 mL of acetone (3 x 2 mL), and concentrated under reduced pressure. The crude product was recrystallized with 1 ml of CH_2Cl_2 and 10 ml of pentane. The product was collected by filtration and washed with pentane (3 x 2 mL), leading to the desired [Ru(CO_3)(SIMes)(*p*-cymene)] complex.

Yield 62%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95 (s, 4H, Mes sp^2-C*H*), 5.13 (d, *J* = 6.2 Hz, 2H, cym sp^2-C*H*), 4.75 (d, *J* = 6.1 Hz, 2H, cym sp^2-C*H*), 3.92 (s, 4H, NCH_2), 2.45 (s, 12H, Mes *o*-CH_3), 2.30 (s, 6H, Mes *p*-CH_3), 1.67 – 1.52 (hept, 1H, ^{i}Pr C*H*), 1.24 (s, 3H, cym *p*-CH_3), 0.77 (d, *J* = 6.9 Hz, 6H, ^{i}Pr CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.45 (Ru=*C*), 166.60 (*C*O_3), 138.15 (Mes, *C*CH_3), 136.93 (Mes, *C*N), 129.81, 129.32 (Mes, *C*H), 99.91 (*p*-cymene, *C*^{i}Pr), 95.36 (*p*-cymene, *C*CH_3), 85.41 (C_6H_4, *C*H), 84.23 (C_6H_4, *C*H), 51.81, 31.77 (*p*-cymene, *C*HC_2H_6), 23.43 (Mes, *C*H_3), 21.04 (*p*-cymene, CHC_2H_6), 19.10 (Mes, *C*H_3), 16.70 (*C*$H_3C_6H_4$). Elemental analysis calcd (%) for $C_{32}H_{40}N_2O_3Ru$: C, 63.87; H, 6.70; N, 4.66; found: C, 63.51; H, 6.32; N, 4.08. Data are in agreement with reported information.[10]

[Ru(CO_3)(ICy)(*p*-cymene)] (3d)

In a 4 mL vial, 72.0 mg of [$RuCl_2$(*p*-cymene)]$_2$ (0.12 mmol, 0.5 eq.), ICy·HBF_4 (0.24 mmol, 1 eq., 75.3 mg) and K_2CO_3 (1.2 mmol, 5 eq., 162.5 mg) were stirred in 1 mL of CPME at 106 °C for 20 hours. The mixture was allowed to cool down to room temperature, filtered through a microfilter with 6 mL of CH_2Cl_2 (3 x 2 mL), and concentrated under reduced pressure. The crude product was recrystallized with 1 ml of CH_2Cl_2 and 10 ml of anti-solvent (pentane). The product was collected by filtration and washed with pentane (3 x 2 mL), leading to the desired [Ru(CO_3)(ICy)(*p*-cymene)] complex.

Yield 72%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97 (s, 2H, NC*H*), 5.40 (d, *J* = 6.0 Hz, 2H**,** cym sp^2-C*H*), 5.11 (d, *J* = 6.0 Hz, 2H, cym sp^2-C*H*), 4.32 (tt, *J* = 12.3, 3.7 Hz, 2H, Cy NC*H*(CH_2)), 2.77 – 2.58 (m, 1H, ^{i}Pr C*H*), 2.19 – 2.11 (m, 5H, Cy CH_2, cym *p*-CH_3), 2.01 – 1.90 (m, 4H, Cy), 1.82 – 1.64 (m, 6H, Cy), 1.51 – 1.32 (m, 10H, ^{i}Pr CH_3, Cy), 1.22 (dddd, *J* = 24.2, 16.4, 9.5, 3.4 Hz, 4H, Cy). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.36 (Ru=*C*), 166.56 (*C*O_3), 118.46 (N*C*H=), 105.11 (*p*-cymene, *C*^{i}Pr), 94.54 (*p*-cymene, *C*CH_3), 83.03 (C_6H_4, *C*H), 82.08 (C_6H_4, *C*H), 59.83 (Cy, *C*N), 53.56, 35.09 (Cy, CH*C*H_2), 32.33 (*p*-cymene, *C*HC_2H_6), 25.74, 23.34 (*p*-cymene, CH*C*$_2H_6$), 19.44 (*C*$H_3C_6H_4$). Data are in agreement with reported information.[10]

[Ru(CO_3)(IMe)(*p*-cymene)] (3e)

In a 4 mL vial, 72.0 mg of [$RuCl_2$(*p*-cymene)]$_2$ (0.12 mmol, 0.5 eq.), IMe·HBF_4 (0.24 mmol, 1 eq., 43.2 mg) and K_2CO_3 (1.2 mmol, 5 eq., 162.5 mg) were stirred in 1 mL of THF at 70 °C for 7 hours. The mixture was allowed to cool down to room temperature, filtered through a microfilter with 6 mL of CH_2Cl_2 (3 x 2 mL), and concentrated under reduced pressure. The crude product was recrystallized with 1 ml of CH_2Cl_2 and 10 ml of anti-solvent

(hexane). The product was collected by filtration and washed with hexane (3 x 2 mL), leading to the desired [Ru(CO_3)(ICy)(*p*-cymene)] complex.

Yield 53%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.91 (s, 2H, NC*H*), 5.45 (d, *J* = 6.0 Hz, 2H, cym sp^2-C*H*), 5.16 (d, *J* = 6.0 Hz, 2H, cym sp^2-C*H*), 3.75 (s, 6H, NCH_3), 2.76 (dt, *J* = 13.8, 6.9 Hz, 1H, ^{i}Pr C*H*), 2.08 (s, 3H, cym *p*-CH_3), 1.28 (d, *J* = 6.9 Hz, 6H, ^{i}Pr CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.86 (Ru=*C*), 166.68 (*C*O_3), 122.83 (NC*H*=), 107.15 (*p*-cymene, *C*^{i}Pr), 96.01 (*p*-cymene, *C*CH_3), 82.54 (C_6H_4, *C*H), 81.08 (C_6H_4, *C*H), 37.90 (*C*H_3N), 32.04 (*p*-cymene, *C*HC_2H_6), 22.87 (*p*-cymene, CH*C*$_2H_6$), 19.12 (*C*$H_3C_6H_4$). [10]

Typical procedure for catalytic transfer hydrogenation.

A 4 mL vial equipped with a septum cap and a stirring bar was charged with ketone (0.5 mmol, 1 eq.), [Ru(IMe)(CO_3)(*p*-cymene)] (2 mg, 1 mol%), KOH (2.8 mg, 10 mol%), and ^{i}PrOH (1.5 mL). The reaction mixture was stirred at 80 °C under Ar. The progress of the reaction was monitored by TLC or NMR. After reaction was judged completed, the solvent was removed under vacuum. Purification by column chromatography on silica gel with PE/EA (v/v = 10/1~8/1) as eluting solvent to give the desired products **6**.

α-Methylbenzenemethanol (**6a**)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 – 7.32 (m, 4H, C_{Ar}*H*), 7.31 – 7.26 (m, 1H, C_{Ar}*H*), 4.91 (qd, *J* = 6.4, 3.6 Hz, 1H, C*H*CH_3), 1.78 (d, *J* = 3.6 Hz, 1H, O*H*), 1.51 (d, *J* = 6.5 Hz, 3H, CHCH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.95, 128.66, 127.64, 125.53, 70.60, 25.31. Data are in agreement with reported information.[20a]

4-Methoxy-*α*-methylbenzyl alcohol (**6b**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.4 Hz, 2H, C_{Ar}*H*), 6.87 (d, *J* = 8.8 Hz, 2H, C_{Ar}*H*), 4.84 (q, *J* = 6.4 Hz, 1H, C*H*CH_3), 3.79 (s, 3H, OCH_3), 2.01 (s, 1H, O*H*), 1.47 (d, *J* = 6.4 Hz, 3H, CHCH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.06, 138.16, 126.76, 113.93, 70.03, 55.38, 25.12. Data are in agreement with reported information.[20a]

4-Chlorobenzenemethanol (**6c**)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 (s, 4H, C_{Ar}*H*), 4.88 (qd, *J* = 6.4, 3.1 Hz, 1H, C*H*CH_3), 1.87 (d, *J* = 3.1 Hz, 1H, O*H*), 1.47 (d, *J* = 6.5 Hz, 3H, CHCH_3).^{13}C NMR (75 MHz, $CDCl_3$) δ 144.39, 133.22, 128.74, 126.93, 69.89, 25.41. Data are in agreement with reported information.[20a]

Diphenylmethanol (**6d**)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 – 7.31 (m, 8H, C_{Ar}*H*), 7.30 – 7.24 (m, 2H, C_{Ar}*H*), 5.85 (d, *J* = 3.5 Hz, 1H, C*H*OH), 2.22 (d, *J* = 3.6 Hz, 1H, O*H*). ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.95, 128.65, 127.73, 126.69, 76.43. Data are in agreement with reported information.[20a]

4,4'-Dimethoxylbenzhydrol (**6e**)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.5 Hz, 4H, C_{Ar}*H*), 6.86 (d, *J* = 8.8 Hz, 4H, C_{Ar}*H*), 5.76 (d, *J* = 3.3 Hz, 1H, C*H*OH), 3.79 (s, 6H, OCH_3), 2.22 (d, *J* = 3.5 Hz, 1H, O*H*).^{13}C NMR (75 MHz, $CDCl_3$) δ 159.10, 136.52, 127.88, 113.96, 75.51, 55.41. Data are in agreement with reported information.[20a]

4,4'-Dimethylbenzhydrol (**6f**)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 – 7.21 (m, 4H, C_{Ar}*H*), 7.15 (d, *J* = 7.9 Hz, 4H, C_{Ar}*H*), 5.79 (d, *J* = 3.5 Hz, 1H, C*H*OH), 2.34 (s, 6H, CH_3), 2.18 (d, *J* = 3.6 Hz, 1H, O*H*).^{13}C NMR (75 MHz, $CDCl_3$) δ 141.26, 137.26, 129.26, 126.57, 76.06, 21.23. Data are in agreement with reported information.[28]

4,4'-Difluorobenzhydrol (**6g**)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 4H, C_{Ar}*H*), 7.07 – 6.97 (m, 4H, C_{Ar}*H*), 5.80 (d, *J* = 3.3 Hz, 1H, C*H*OH), 2.31 (d, *J* = 3.5 Hz, 1H, O*H*).^{13}C NMR (75 MHz, $CDCl_3$) δ 163.99, 160.73, 128.30 (d, *J* = 8.1 Hz), 115.52 (d, *J* = 21.5 Hz), 75.06. Data are in agreement with reported information.[28]

Conclusion

A versatile and efficient protocol granting access to a series of well-defined [Ru(NHC)(CO_3)(*p*-cymene)] complexes using the weak base approach has been described from azolium salts bearing different counter anions. The strategy can be applied to a variety of ligands leading from good to excellent yields. The catalytic performance of the complexes has been established in TH reactions. The complexes exhibited high catalytic activity at low loading in a short time. This study paves the way for further developments and applications of such complexes now that a simple, versatile and more sustainable synthetic route to them has been established.

Conflicts of interest

There are no conflicts to declare.

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