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A simple synthesis of [$RuCl_2$(NHC)(*p*-cymene)] complexes and their use in olefin oxidation catalysis†‡

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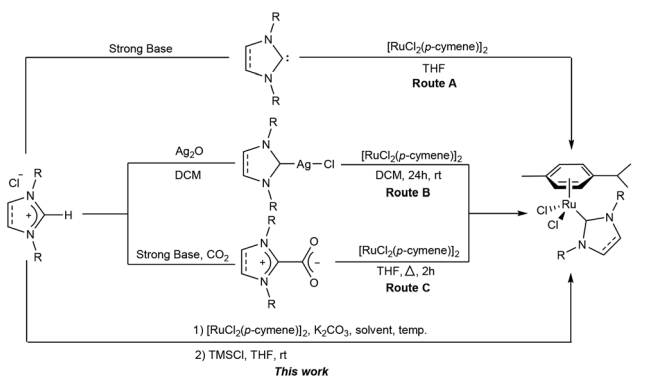
A simple and efficient synthetic route to [$RuCl_2$(NHC)(*p*-cymene)] and [$Ru(CO_3)$(NHC)(*p*-cymene)] complexes making use of a weak base, under aerobic conditions, is reported. This method enables access to a series of NHC-ruthenium compounds with moderate to good yields under mild conditions. The Ru pre-catalysts were successfully used in olefin oxidation catalysis at low catalyst loading and reach complete conversion in short times.

Introduction

N-Heterocyclic carbenes (NHCs) have become indispensable ligands for transition metals and homogeneous catalysis, since their first successful isolation by Arduengo *et al.* in 1991.[1] Due to their topological and electronic versatility, these complexes have been at the forefront of organometallic,[2] materials,[3] medicinal[4] and, more recently, polymerization chemistry,[5] and homogeneous[6] and heterogeneous catalysis.[7]

During the last decade, complexes of the [RuX_2(NHC)(*p*-cymene)] family have been of great interest.[8] This class of well-defined ruthenium(II) complexes has shown high catalytic activity in hydrogenation, alkene metathesis and amidation.[9] The most commonly used synthetic routes leading to [$RuCl_2$(NHC)(*p*-cymene)] complexes are depicted in Scheme 1. The free carbene pathway (Scheme 1, Route A) uses a strong base such as KO^{t}Bu, KHMDS or NaH in conjunction with the imidazolium salt to generate the free carbene *in situ*,[10] or alternatively the strong base can be used to generate the free isolated NHC that can be used subsequently in a ligand binding event.[11] However, the free carbene is sensitive to water, which requires handling under anhydrous conditions. The transmetalation route, from silver or copper complexes (Scheme 1, Route B), is a more user-friendly method as it alleviates the need for the free carbene generation. Some ruthenium-NHC complexes have been synthesised using this pathway from a silver–carbene intermediate and [$RuCl_2$(*p*-cymene)]$_2$.[12] However, the silver pathway is not only very sensitive to light and air but also produces silver waste which needs to be removed upon workup. For these reasons, the copper variation of the method is often superior to the silver alternative.[13] The third route uses an imidazolium carboxylate (Scheme 1, Route C) as source of free carbene that is generated upon thermal decarboxylation. This approach although lauded in the literature requires Route A to be used in the presence of CO_2 to trap the free carbene as the carboxylate.[14] Therefore, the development of more facile, cost-effective, sustainable[15] and more easily accessible procedure to these Ru-NHC complexes is of significant interest.

During the past few years, several metal-NHC complexes, (*i.e.* gold, copper, iridium, rhodium and palladium) have been successfully prepared by direct treatment of a metal precursor and an imidazolium salt by action of a weak base.[16] The weak base route greatly simplifies the procedure while avoiding the



Scheme 1 Synthetic routes to [$RuCl_2$(NHC)(*p*-cymene)] complexes.

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† Dedicated to the memory of Professor Paul Kamer.

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use of transition metal reagents. It is more eco-friendly and brings significant improvements to the state-of-the-art.

In 2012, axially chiral Au(I) complexes with an *N*-naphthyl framework were generated using NaOAc and [AuCl(DMS)] (DMS = dimethylsulfide).[17] Subsequently and concomitantly, Nolan[18] and Gimeno[19] described an efficient synthetic route leading to Au-NHC complexes using this weak base approach. Recently, we have successfully elaborated and developed straightforward and sustainable methods for the synthesis of well-defined Au, Cu, Pt and Pd-NHC complexes, using imidazol(idin)ium salts and the "weak base synthetic approach".[20] Plenio has followed up on the initial reports and extended the weak base method to reactions of $[MCl(cod)]_2$ (M = Rh, Ir) with different NHC·HX (X = Cl, I) and K_2CO_3, providing simple access to various [(NHC)MX(cod)] complexes.[21] Additionally, in our recent report on NHC complexes of main-group elements, the complexes were obtained using NEt_3 under mild conditions in excellent yields.[22]

In an effort to illustrate the viability of this simple assembly route to ruthenium, an economical and efficient protocol using the mild and inexpensive K_2CO_3 as a base was investigated to prepare several $[Ru(CO_3)(NHC)(p\text{-cymene})]$ complexes. A limited number of examples of such complexes was reported by Dixneuf and Demerseman in 2006 and was stated to possibly act as synthons for catalytic species although without exemplification.[23]

Results and discussion

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

Initially, one might have expected that, as with the other metals investigated so far, the weak base route using K_2CO_3 might lead directly to $[RuCl_2(NHC)(p\text{-cymene})]$ complexes. However, the reaction of $[RuCl_2(p\text{-cymene})]_2$ **1** and IPr·HCl **2a** (IPr = *N,N′*-bis[2,6-(diisopropyl)phenyl]imidazol-2-ylidene) using 3 equivalents of K_2CO_3 led to the formation of the carbonate complex $[Ru(CO_3)(IPr)(p\text{-cymene})]$ **3a** as indicated by ^{13}C NMR in which the carbon peak of the carbonate ligand appears at 166.16 ppm, as previously reported for $[Ru(CO_3)(IMes)(p\text{-cymene})]$ (IMes = *N,N′*-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene) by Dixneuf and Demerseman.[23] However, the limited reports on such $[Ru(CO_3)(NHC)(p\text{-cymene}]$ complexes have encouraged us to delve deeper into the generality of the approach and into the catalytic activity of these complexes.[24]

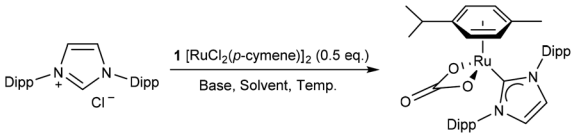
Our initial conditions were further optimised. When adding 5 equivalents of K_2CO_3, the yield of compound **3a** increased to 72%, and led to complete conversion after 17 hours at 60 °C in technical-grade acetone (green acetone). Several solvents were examined, including toluene (PhMe), DCM and EtOAc. Compared with the greener acetone, these solvents have a negative effect on the formation of the product (Table 1).

In order to test the versatility of this simple route, we examined other saturated and unsaturated imidazolium salts such as IMes·HCl **2b**, ICy·HCl (*N,N′*-bis(cyclohexyl)imidazol-2-ylidene) **2c**, IMe·HCl (*N,N′*-dimethyl-imidazol-2-ylidene) **2d** and SIMes·HCl (*N,N′*-bis(2,4,6-trimethylphenyl)-imidazolidin-2-ylidene) **2e** (Table 2).

Gratifyingly, this weak base method proved to be highly effective for the synthesis of $[Ru(CO_3)(IMes)(p\text{-cymene})]$ **3b** (Table 2, entry 2). The product was obtained in 83% yield after 3 hours at 60 °C in acetone. Compared with the strategy reported by the Demerseman group, this method involves a greener solvent to produce the desired complex in a shorter reaction time and provides higher yields.[23] To our surprise, when alkyl-substituted (**2c** and **2d**) or saturated NHC (**2e**) were used, no reactivity was observed at 60 °C in acetone, even after 24 hours of reaction time.

Considering that toluene was also a viable solvent for the synthesis of **3a**, the effect of this solvent on the other targeted NHCs was further studied (ESI, Table S2‡). Thus, complexes **3c** (110 °C, 3 h) and **3d** (80 °C, 26 h) could be obtained in

Table 1 Selected entries for the optimization of reaction conditions leading to **3**[a]

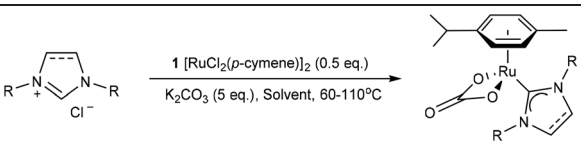


2a **3a**

Entry	K_2CO_3 (eq.)	Solvent	*T* (°C)	Time (h)	Yield[b] (%)
1	3	Acetone	60	17	64
2	**5**	**Acetone**	**60**	**17**	**72**
3	7	Acetone	60	12	58
4	5	EtOAc	60	24	54
5	5	DCM	40	24	0
6	5	PhMe	60	22	62
7	5	PhMe	80	3	51
8	5	PhMe	110	3	0

[a] Reaction conditions: **1** (0.12 mmol, 0.5 eq.), **2a** (0.24 mmol, 1 eq.), K_2CO_3, solvent (1.0 mL) in a 4 mL vial. [b] Isolated yields.

Table 2 Synthesis of $[Ru(CO_3)(NHC)(p\text{-cymene}]$ complexes *via* the weak base route[a]



2a-e **3a-e**

Entry	NHC	Solvent	*T* (°C)	Time(h)	Yield[b] (%)
1	IPr	Acetone	60	17	72
2	IMes	Acetone	60	3	83
3	ICy	PhMe	110	3	63
4	IMe	PhMe	80	26	67
5	SIMes	PhMe/acetone	60	3	42

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

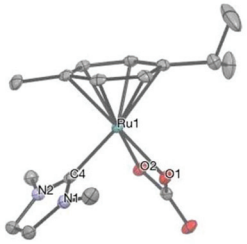


Fig. 1 Crystal structure of complex **3d**. H atoms are omitted for clarity, ellipsoid reported at 50% probability. Selected bond distances (Å) and angles (deg): Ru1–C4, 2.065, Ru1–O1, 2.091, Ru1–O2, 2.114; O1–Ru1–C4, 84.38, O2–Ru1–C4, 85.68, O1–Ru1–O2, 62.41. CCDC: 2045650.‡

toluene. After recrystallization, the pure complexes were obtained in moderate yields. The structure of compound **3d** was confirmed by X-ray diffraction studies on single crystals grown by vapor diffusion of pentane into a saturated DCM solution containing **3d** (Fig. 1). It is obvious that the reaction towards [Ru(CO_3)(IMe)(*p*-cymene)] **3d** takes a longer time at 80 °C. However, increasing the reaction temperature led to significant decomposition. This result illustrates that for the weak base route, both the polarity of the solvent and the reaction temperature are important factors for selective product formation.

Analogous SIMes-Ru compound **3e** was found to be more challenging. Through screening of various reaction conditions, (ESI, Table S2‡) we isolated the target product **3e** using a mixture of toluene and acetone (v : v = 1 : 1)as reaction solvent at 60 °C after 3 h. In this manner, the product was obtained in a modest 42% yield.

With the success of the user-friendly protocol, the reaction of **1** with IMes·HCl **2b** was performed on a gram-scale. In the manner illustrated in Scheme 2, 1.5 g of **3b** was obtained, representing an 82% isolated yield. The use of acetone as a green solvent (reagent grade) in the synthesis performed here, is noteworthy.

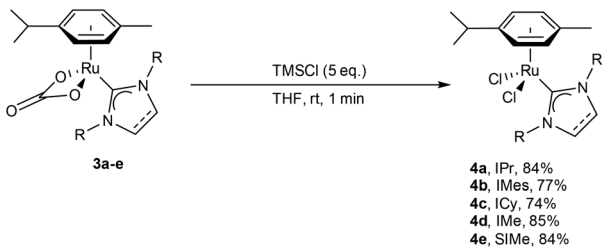
Transformation of [Ru(NHC)(CO_3)(*p*-cymene)] into [Ru(NHC)Cl_2(*p*-cymene)]

With these complexes in hand, the reaction to convert the carbonate-Ru complexes into their corresponding [$RuCl_2$(NHC)(*p*-cymene)] derivatives was next explored. The synthesis of **4a** was rapidly obtained by the treatment of **3a** with 5 equiv. of TMSCl in THF at room temperature leading to an 84% isolated yield. A longer reaction time proved deleterious, leading to some decomposition of the targeted product. The use of HCl in Et_2O could be used as an alternative to form [$RuCl_2$(NHC)(*p*-cymene)] complexes, although this led to lower yields than the TMSCl variant. This experimental result also indicates that the small amount of HCl produced during the hydrolysis of TMSCl can still be fully utilized. [**Caution**: TMSCl is prone to hydrolysis, releasing HCl when exposed to a wet atmosphere. Handling it under dry conditions is recommended] Using this protocol, the congeners **4b–4e** were obtained in high isolated yields (Scheme 3).

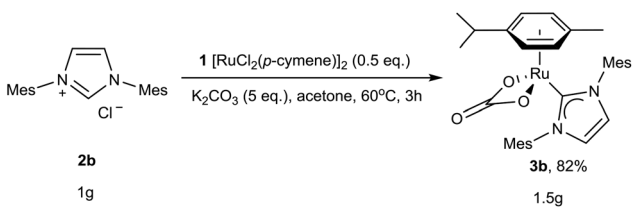
The synthesis of **4b** in a one-pot method using IMes·HCl **2b** as the starting reagent was also attempted, thereby eliminating the need for the isolation of **3a**. Gratifyingly, not only can the target product **4b** be obtained smoothly but the isolated yield is excellent. It is noteworthy that although excessive K_2CO_3 and TMSCl were used in this process, it still represents a significant cost lowering than using the silver oxide method. This one-pot procedure further simplifies the process and improves the efficiency of the reaction. It provides a convenient and efficient route for the preparation of [$RuCl_2$(NHC)(*p*-cymene)] complexes (Scheme 4).

Catalytic studies

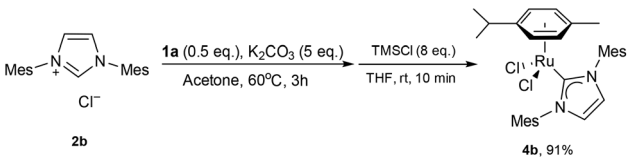
Finally, as illustrated in Scheme 5, we explored the catalytic activity of these Ru complexes in olefin oxidation catalysis. In this context, a few examples of methylstyrene oxidation have been recently reported using a ruthenium-(*p*-cymene) complex as catalyst,[25] and these conditions proved a good starting point to gauge the efficacy of our well-defined ruthenium(II) species. Satisfyingly, complexes **3** and **4** proved very effective as catalysts in olefin oxidation reactions. Indeed, in the presence of 1 mol% of [Ru(CO_3)(IPr)(*p*-cymene)] **3a**, α-methylstyrene **5** can be completely oxidized to acetophenone **6** in 20 minutes at 35 °C in the presence of $NaIO_4$ as co-oxidant. When reducing the catalyst loading or lowering the temperature, more time was required to achieve complete conversion, but complete



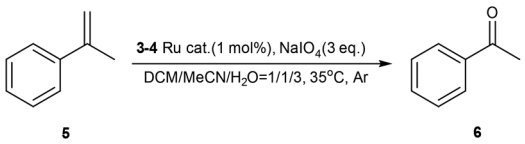
Scheme 3 Synthesis of the [$RuCl_2$(NHC)(*p*-cymene)] complexes.



Scheme 2 Larger scale synthesis of **3b**.



Scheme 4 One-pot synthesis of **4b**.



Scheme 5 Olefin oxidation with complexes **3** and **4**.

conversion was indeed reached. In addition, **3b–e** and **4a–4e** proved to be active catalysts in this reaction reaching full conversion within 5 to 35 minutes under the same conditions. As expected, no product is generated without a Ru complex (ESI, Table S3‡).

The catalyst comparison tables and reaction profiling curves show that α-methylstyrene oxidation can be completely achieved after 5 minutes using complexes bearing the smaller IMe ligand. In addition, compound **4d** showed the fastest initial rate in the first 5 minutes and the trend of the conversion over time indicated that **4d** had the best catalytic profile in the olefin oxidation examined (ESI, Fig. S1‡). We are presently extending the scope of this oxidation reaction and these results will be reported shortly.

Experimental

General information

All manipulations were carried out under air atmosphere in vials. Solvents and reagents were used as received without any further purification or distillation. ^{1}H NMR and ^{13}C NMR (all carbon NMR spectra are proton decoupled apt spectra) 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. Elemental analyses were performed at Université de Namur, rue de Bruxelles, 55 B-5000 Namur, Belgium.

Typical procedure for [Ru(CO$_3$)(NHC)(*p*-cymene)] complexes

[Ru(CO$_3$)(IPr)(*p*-cymene)] (3a). In a 4 mL vial, 72.0 mg of $[RuCl_2(p\text{-cymene})]_2$ (0.12 mmol, 0.5 eq.) and 100 mg of IPr·HCl (0.24 mmol, 1 eq.) were stirred in 1 mL of acetone at 60 °C for 20 min. 163 mg of K_2CO_3 (1.18 mmol, 5 eq.) was added to the above mixture and stirred overnight at 60 °C. After this time, the mixture was allowed to cool to room temperature, filtered through a microfilter, the precipitate was washed with 6 mL acetone (2 mL × 3), and concentrated under reduced pressure. The crude product was obtained after trituration/precipitation and then recrystallized with 1 ml of CH_2Cl_2 and 10 ml of pentane. The product was collected by filtration and washed with pentane (2 mL × 3) and dried in vacuum, leading to 120.5 mg (72%) of the desired [Ru(CO$_3$)(IPr)(*p*-cymene)] complex **3a** as a pale yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 (dd, J = 8.3, 7.1 Hz, 2H, Dipp sp^2-C*H*), 7.33 (d, J = 7.4 Hz, 4H, Dipp sp^2-C*H*), 7.06 (s, 2H, NC*H*), 5.11 (d, J = 6.1 Hz, 2H, cym sp^2-C*H*), 4.79 (d, J = 5.9 Hz, 2H, cym sp^2-C*H*), 2.91 (dt, J = 13.4, 6.7 Hz, 4H, Dipp ^{i}Pr C*H*), 1.57 (d, J = 6.7 Hz, 13H, cym ^{i}Pr C*H*, Dipp ^{i}Pr CH_3), 1.16 (s, 3H, cym *p*-CH_3), 1.08 (d, J = 6.8 Hz, 12H, Dipp ^{i}Pr CH_3), 0.76 (d, J = 6.9 Hz, 6H, ^{i}Pr CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.1 (Ru=*C*), 166.1 (*C*O$_3$), 147.4 (Dipp, *C*CH$_3$), 136.6 (Dipp, *C*N), 130.1 (Dipp, *C*H), 125.6 (Dipp, *C*H), 123.8 (N*C*H=), 99.4 (*p*-cymene, *C*^{i}Pr), 94.9 (*p*-cymene, *C*CH$_3$), 84.5 (C$_6$H$_4$, *C*H), 31.7 (*p*-cymene, *C*HC$_2$H$_6$), 29.3 (Dipp, *C*H$_3$), 27.5 (Dipp, *C*HC$_2$H$_6$), 22.8 (*p*-cymene, CH*C*$_2$H$_6$), 16.8 (*C*H$_3$C$_6$H$_4$). Elemental analysis calcd (%) for $C_{38}H_{50}N_2O_3Ru{\cdot}0.4CH_2Cl_2$ (717.8698): C, 64.24; H, 7.15; N, 3.90; found: C 64.49; H 6.99; N 3.50. HRMS (ESI) m/z [M + H]$^+$: calcd for $C_{38}H_{51}N_2O_3Ru$: 685.2938, found: 685.3125.

[Ru(CO$_3$)(IMes)(*p*-cymene)] (3b). In a 4 mL vial, 72 mg of $[RuCl_2(p\text{-cymene})]_2$ (0.12 mmol, 0.5 eq.) and 80.2 mg of IMes·HCl (0.2.4 mmol, 1 eq.) were stirred in 1 mL of acetone at 60 °C for 20 min 162.6 mg of K_2CO_3 (1.18 mmol, 5 eq.) was added to the above mixture and stirred at 60 °C for another 3 h. The mixture was allowed to cool to room temperature after this time, filtered through a frit and washed with 6 mL acetone (2 mL × 3). The solvent was removed under vacuum and the residue triturated with 6 mL of pentane. The resulting solid was collected by filtration and dried under vacuum to afford 119.2 mg (83%) of the desired [Ru(CO$_3$)(IMes)(*p*-cymene)] complex **3b** as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.99 (d, J = 1.6 Hz, 6H, Mes sp^2-C*H*, NC*H*), 5.13 (d, J = 6.2 Hz, 2H, cym sp^2-C*H*), 4.77 (d, J = 6.1 Hz, 2H, cym sp^2-C*H*), 2.34 (s, 6H, Mes *p*-CH_3), 2.21 (s, 12H, Mes *o*-CH_3), 1.71 (dt, J = 13.7, 6.9 Hz, 1H, cym ^{i}Pr C*H*), 1.33 (s, 3H, cym *p*-CH_3), 0.82 (d, J = 6.9 Hz, 6H, ^{i}Pr CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 180.9 (Ru=*C*), 166.4 (*C*O$_3$), 138.9 (Mes, *C* CH$_3$), 136.7 (Mes, *C*N), 128.9 (Mes, *C*H), 124.6 (N*C*H=), 99.7 (*p*-cymene, *C*^{i}Pr), 95.1 (*p*-cymene, *C*CH$_3$), 85.1 (C$_6$H$_4$, *C*H), 83.6 (C$_6$H$_4$, *C*H), 32.0 (*p*-cymene, *C*HC$_2$H$_6$), 23.5 (Mes, *C*H$_3$), 21.1 (*p*-cymene, CH*C*$_2$H$_6$), 18.7 (Mes, *C*H$_3$), 16.9 (*C*H$_3$C$_6$H$_4$). Data are in agreement with reported information.[23]

[Ru(CO$_3$)(ICy)(*p*-cymene)] (3c). In a 4 mL vial, 72.0 mg of $[RuCl_2(p\text{-cymene})]_2$ (0.12 mmol, 0.5 eq.) and 54.9 mg of ICy·HCl (0.24 mmol, 1 eq.) were stirred in 1 mL of PhMe at 110 °C during 20 min 162.6 mg of K_2CO_3 (1.18 mmol, 5 eq.) were added to the above mixed system and stirred at 110 °C for another 3 h. The mixture was allowed to cool to room temperature, filtered through a microfilter and the precipitate washed with 6 mL CH_2Cl_2 (2 mL × 3). Then the solution was concentrated under reduced pressure and pentane (5 mL) was added. The product was collected by filtration and washed with pentane (2 mL × 3), leading to 82 mg (63%) of the desired [Ru(CO$_3$)(ICy)(*p*-cymene)] complex **3c** as a dark green solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.98 (s, 2H, NC*H*), 5.40 (d, J = 6.0 Hz, 2H, cym sp^2-C*H*), 5.12 (d, J = 6.0 Hz, 2H, cym sp^2-C*H*), 4.33 (tt, J = 12.4, 3.7 Hz, 2H, Cy NC*H*(CH$_2$)), 2.69 (hept, J = 6.9 Hz, 1H, ^{i}Pr C*H*), 2.20–2.07 (m, 5H, Cy CH$_2$, cym *p*-CH_3), 1.96 (m, 6H,

Cy), 1.84–1.65 (m, 6H, Cy), 1.45 (m, 2H, Cy), 1.36 (d, J = 6.9 Hz, 6H, ^{i}Pr CH_3), 1.32–1.14 (m, 4H, Cy). ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.4 (Ru=C), 166.5 (CO_3), 118.4 (NCH=), 105.1 (p-cymene, C^{i}Pr), 94.5 (p-cymene, CCH$_3$), 83.0 (C_6H_4, CH), 82.0 (C_6H_4, CH), 59.8 (Cy, CN), 35.3 (Cy, CHCH$_2$), 34.9, 32.3 (p-cymene, CHC$_2$H$_6$), 26.1, 25.7, 25.4, 23.3 (p-cymene, CHC_2H$_6$), 19.4 (CH$_3$C$_6$H$_4$). Elemental analysis calcd (%) for $C_{26}H_{38}N_2O_3Ru{\cdot}0.6CH_2Cl_2$ (578.6272): C, 55.21; H, 6.67; N, 4.84; found: C, 55.06; H, 6.58; N, 4.55. HRMS (ESI) m/z [M + H]$^+$: calcd for $C_{26}H_{39}N_2O_3Ru$: 529.1999, found: 529.2224.

[Ru(CO$_3$)(IMe)(p-cymene)] (3d). In a 4 mL vial, 72.0 mg of [RuCl$_2$(p-cymene)]$_2$ (0.12 mmol, 0.5 eq.) and 31.4 mg of IMe·HCl (0.24 mmol, 1 eq.) were stirred in 1 mL of PhMe at 80 °C for 20 min 162.6 mg of K_2CO_3 (1.18 mmol, 5 eq.) were added to the above suspension and it was stirred at 80 °C overnight. The mixture was allowed to cool to room temperature, filtered through a microfilter, the filter was washed with 6 mL CH_2Cl_2 (2 mL × 3), then the filtrate was concentrated under reduced pressure and 6 mL of pentane was added. The precipitate was collected by filtration on a frit and dried under vacuum, leading to 66 mg (67%) of the desired [RuCl$_2$(p-cymene)(IMe)] complex **3d** as an orange solid. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 6.96 (s, 2H, NCH), 5.45 (d, J = 6.0 Hz, 2H, cym sp^2-CH), 5.17 (d, J = 6.0 Hz, 2H, cym sp^2-CH), 3.72 (s, 6H, NCH_3), 2.72 (hept, J = 6.9 Hz, 1H, ^{i}Pr CH), 2.07 (s, 3H, cym p-CH_3), 1.27 (d, J = 6.9 Hz, 6H, ^{i}Pr CH_3). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 178.5 (Ru=C), 166.8 (CO_3), 123.2 (NCH=), 106.9 (p-cymene, C^{i}Pr), 96.3 (p-cymene, CCH$_3$), 83.0 (C_6H_4, CH), 81.3 (C_6H_4, CH), 38.1 (CH$_3$N), 32.5 (p-cymene, CHC$_2$H$_6$), 23.0 (p-cymene, CHC_2H$_6$), 19.2 (CH$_3$C$_6$H$_4$). HRMS (ESI) m/z [M + H]$^+$: calcd for $C_{16}H_{23}N_2O_3Ru$: 393.0946, found: 393.1002.

[Ru(CO$_3$)(SIMes)(p-cymene)] (3e). In a 4 mL vial, 72.0 mg of [RuCl$_2$(p-cymene)]$_2$ (0.12 mmol, 0.5 eq.) and 80.7 mg of SIMes·HCl (0.24 mmol, 1 eq.) were stirred in 1 mL of PhMe/acetone (v/v = 1 : 1) at 60 °C for 20 min 162.6 mg of K_2CO_3 (1.18 mmol, 5 eq.) were added to the above mixture which was stirred at 60 °C for another 3 h. The mixture was allowed to cool to room temperature, filtered through a microfilter, washed with 6 mL CH_2Cl_2 (2 mL × 3), then the solute was concentrated to 0.5 mL under reduced pressure and pentane (5 mL) was added. The precipitate was collected by filtration and washed with pentane (2 mL × 3), leading to 61 mg (42%) of the desired [Ru(CO$_3$)(SIMes)(p-cymene)] complex **3e** as a brown solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.95 (s, 4H, Mes sp^2-CH), 5.13 (d, J = 6.2 Hz, 2H, cym sp^2-CH), 4.74 (d, J = 6.1 Hz, 2H, cym sp^2-CH), 3.92 (s, 4H, NCH_2), 2.45 (s, 12H, Mes o-CH_3), 2.30 (s, 6H, Mes p-CH_3), 1.62 (hept, J = 6.9 Hz, 1H, ^{i}Pr CH), 1.23 (s, 3H, cym p-CH_3), 0.77 (d, J = 6.9 Hz, 6H, ^{i}Pr CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 211.55 (Ru=C), 166.61 (CO_3), 138.14 (Mes, CCH$_3$), 136.96 (Mes, CN), 129.33 (Mes, CH), 99.91 (p-cymene, C^{i}Pr), 95.41 (p-cymene, CCH$_3$), 85.45 (C_6H_4, CH), 84.21 (C_6H_4, CH), 51.81, 31.79 (p-cymene, CHC$_2$H$_6$), 23.46 (Mes, CH$_3$), 21.05 (p-cymene, CHC_2H_6), 19.12 (Mes, CH$_3$), 16.70 (CH$_3$C$_6$H$_4$). Elemental analysis calcd (%) for $C_{32}H_{40}N_2O_3Ru{\cdot}0.8CH_2Cl_2$ (669.6946): C, 58.82; H, 6.15; N, 4.18; found: C, 58.72; H, 6.07; N, 3.72.

Typical procedure for [RuCl$_2$(NHC)(p-cymene)] catalysts

Procedure A: In a 4 mL vial, 0.1 mmol of [Ru(CO$_3$)(NHC)(p-cymene)] and 5 equivalents of TMSCl (0.5 mmol, 63.6 μL) were stirred in 1 mL of THF at room temperature for 1 min. The volatiles were removed under reduced pressure and the residue was triturated with 6 mL of pentane. The crude product was then recrystallized with DCM/Pentane, leading to the desired [RuCl$_2$(NHC)(p-cymene)] complexes as a red-brown solid.

Procedure B (one pot, **4b** as an example): In a 4 mL vial, 72.0 mg of [RuCl$_2$(p-cymene)]$_2$ (0.12 mmol, 0.5 eq.) and 80.2 mg of IMes·HCl (0.24 mmol, 1 eq.) and 162.6 mg of K_2CO_3 (1.18 mmol, 5 eq.) were added to 1 mL acetone and stirred at 60 °C for 3 h. The mixture was allowed to cool to room temperature and the volatiles were removed under reduced pressure. Then 8 equivalents of TMSCl (1.88 mmol, 239.4 μL) and 1 mL of THF were added. The reaction mixture was stirred at room temperature for 10 min. THF was removed under reduced pressure, the residue was washed with 6 mL of pentane then recrystallized with DCM/pentane, leading to the desired [RuCl$_2$(IMes)(p-cymene)] complexes as a red-brown solid in 91% yield.

[RuCl$_2$(IPr)(p-cymene)] (4a). Procedure A: Yield = 84% (58 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49–7.39 (m, 2H, Dipp sp^2-CH), 7.26 (t, J = 3.9 Hz, 4H, Dipp sp^2-CH), 6.94 (s, 2H, NCH), 5.01 (d, J = 6.0 Hz, 2H, cym sp^2-CH), 4.72 (d, J = 5.9 Hz, 2H, cym sp^2-CH), 3.15 (hept, J = 6.7 Hz, 4H, Dipp ^{i}Pr CH), 2.44 (hept, J = 6.8 Hz, 1H, ^{i}Pr CH), 1.86 (s, 3H, cym p-CH_3), 1.42 (d, J = 6.7 Hz, 12H, Dipp ^{i}Pr CH_3), 1.11 (d, J = 6.9 Hz, 6H, ^{i}Pr CH_3), 1.07 (d, J = 6.8 Hz, 12H, Dipp ^{i}Pr CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.40 (Ru=C), 146.21 (Dipp, CCH$_3$), 145.21, 139.55, 132.26, 129.73, 126.62, 124.85, 123.64, 86.30 (C_6H_4, CH), 84.46 (C_6H_4, CH), 30.21 (p-cymene, CHC$_2$H$_6$), 28.74, 26.33, 23.25, 18.77. Data are in agreement with reported data.[11c]

[RuCl$_2$(IMes)(p-cymene)] (4b). Procedure A: Yield = 77% (41 mg); Procedure B: Yield = 90%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95 (s, 4H, Mes sp^2-CH), 6.90 (s, 2H, NCH), 5.03 (d, J = 6.1 Hz, 2H, cym sp^2-CH), 4.64 (d, J = 5.8 Hz, 2H, cym sp^2-CH), 2.52 (hept, J = 6.9 Hz, 1H, ^{i}Pr CH), 2.35 (s, 6H, Mes p-CH_3), 2.24 (s, 12H, Mes o-CH_3), 1.79 (s, 3H, cym p-CH_3), 1.08 (d, J = 7.0 Hz, 6H, ^{i}Pr CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.95 (Ru=C), 138.78 (Mes, C CH$_3$), 136.25 (Mes, CN), 129.06 (Mes, CH), 128.78, 126.36, 125.27, 95.89 (CCH$_3$, p-cymene), 86.91 (C_6H_4, CH), 85.81 (C_6H_4, CH), 30.30 (p-cymene, CHC$_2$H$_6$), 24.19 (Mes, CH$_3$), 22.60 (p-cymene, CHC_2H$_6$), 21.21 (Mes, CH$_3$), 19.15 (CH$_3$C$_6$H$_4$). Elemental analysis calcd (%) for $C_{31}H_{38}Cl_2N_2Ru$ (610.6290): C, 60.98; H, 6.27; N, 4.59; found: C, 60.55; H, 6.07; N, 3.97. Data are in agreement with reported data.[10c]

[RuCl$_2$(ICy)(p-cymene)] (4c). Procedure A: Yield = 74% (40 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.05 (s, 2H, NCH), 5.47 (d, J = 6.0 Hz, 2H, cym sp^2-CH), 5.14 (d, J = 6.0 Hz, 2H, cym sp^2-CH), 4.85 (ddd, J = 11.6, 7.5, 3.4 Hz, 2H, Cy NCH(CH$_2$)), 2.86 (hept, J = 6.9 Hz, 1H, ^{i}Pr CH), 2.37 (d, J = 10.3 Hz, 2H, Cy), 2.14 (s, 3H, cym p-CH_3), 1.95–1.84 (m, 4H, Cy), 1.79–1.65 (m, 6H, ^{i}Pr CH_3), 1.49 (d, J = 13.3 Hz, 2H, Cy), 1.39 (t, J = 8.4 Hz, 10H, Cy), 1.25–1.15 (m, 2H, Cy). ^{13}C NMR (75 MHz, $CDCl_3$) δ

171.51 (Ru=*C*), 119.46 (NCH=), 105.31 (*p*-cymene, *C*^{i}Pr), 97.49 (*p*-cymene, *C*CH$_3$), 85.46 (C_6H_4, *C*H), 83.77 (C_6H_4, *C*H), 59.44 (Cy, *C*N), 35.99, 35.48, 31.36 (*p*-cymene, *C*HCH$_3$), 26.18, 25.58, 23.26 (*p*-cymene, CH*C*$_2$H$_6$), 18.97 (*C*H$_3$C$_6$H$_4$). Data are in agreement with reported data.[11a]

[RuCl$_2$(IMe)(*p*-cymene)] (4d). Procedure A: Yield = 85% (34 mg). ^{1}H NMR (300 MHz, CDCl$_3$) δ 6.97 (s, 2H, NC*H*), 5.40 (d, J = 5.9 Hz, 2H, cym sp^2-C*H*), 5.13 (d, J = 5.9 Hz, 2H, cym sp^2-C*H*), 4.00 (s, 6H, NC*H*$_3$), 2.94 (hept, J = 7.0 Hz, 1H, ^{i}Pr C*H*), 2.07 (s, 3H, cym *p*-C*H*$_3$), 1.25 (d, J = 6.9 Hz, 6H, ^{i}Pr C*H*$_3$). ^{13}C NMR (101 MHz, CDCl$_3$) δ 173.57 (Ru=*C*), 123.89 (NCH=), 109.02 (*C*^{i}Pr, *p*-cymene), 99.43 (*C*CH$_3$, *p*-cymene), 84.90 (C_6H_4, *C*H), 82.94 (C_6H_4, *C*H), 39.70 (*C*H$_3$N), 30.93 (*p*-cymene, *C*HC$_2$H$_6$), 22.62 (*p*-cymene, CH*C*$_2$H$_6$), 18.78 (*p*-cymene, *C*H$_3$C$_6$H$_4$). Data are in agreement with reported data.[11b]

[RuCl$_2$(SIMes)(*p*-cymene)] (4e). Procedure A: Yield = 84% (51 mg). ^{1}H NMR (300 MHz, CDCl$_3$) δ 6.91 (s, 4H, Mes sp^2-C*H*), 5.03 (d, J = 6.0 Hz, 2H, cym sp^2-C*H*), 4.64 (d, J = 5.9 Hz, 2H, cym sp^2-C*H*), 3.86 (s, 4H, NC*H*$_2$), 2.47 (s, 12H, Mes *o*-C*H*$_3$), 2.44–2.35 (m, 1H, ^{i}Pr C*H*), 2.30 (s, 6H, Mes *p*-C*H*$_3$), 1.75 (s, 3H, cym *p*-C*H*$_3$), 1.07 (d, J = 6.9 Hz, 6H, ^{i}Pr C*H*$_3$). ^{13}C NMR (101 MHz, CDCl$_3$) δ 202.12 (Ru=*C*), 139.26, 137.83, 136.73, 129.18, 126.35, 102.90 (*p*-cymene, *C*^{i}Pr), 96.34 (*p*-cymene, *C*CH$_3$), 87.24 (C_6H_4, *C*H), 86.41 (C_6H_4, *C*H), 52.80, 30.49 (*p*-cymene, *C*HC$_2$H$_6$), 24.18, 22.72, 21.12, 19.46, 18.10. Data are in agreement with reported data.[9d]

Typical procedure for catalytic olefin oxidation

In a 10 mL Schlenk tube, α-methylstyrene **5** (0.2 mmol, 26 μL) and $NaIO_4$ (0.6 mmol, 128.3 mg) were added to a deoxygenated mixture of $CH_3CN/CH_2Cl_2/H_2O$ (v/v/v = 1 : 1 : 3; 1.5 mL) and the reaction mixture was stirred under Ar at 35 °C until $NaIO_4$ was completely dissolved. Catalyst **3** or **4** (0.002 mmol) was added and Ar was bubbled into the reaction mixture. The process of the reaction was followed by ^{1}H NMR spectroscopy or TLC. The product was extracted with CH_2Cl_2 and washed with H_2O. The organic layer was separated and dried over anhydrous $MgSO_4$, the solvent was evaporated under vacuum. The crude product was obtained as a grey oil. Purification by column chromatography on silica gel with EtOAc–hexane (1 : 10) afforded the desired product **6**. ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.00–7.93 (m, 2H), 7.61–7.52 (m, 1H), 7.47 (m, 2H), 2.61 (s, 3H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 198.3 (*C*=O), 137.3 (Ph, *C*CO), 133.2 (Ph, *C*H), 128.7 (Ph, *C*H), 128.4 (Ph, *C*H), 26.7 (CO*C*H$_3$). Data are in agreement with reported data.[26]

Conclusions

In summary, a new method for the synthesis of a series of well-defined ruthenium-(*p*-cymene) complexes using the weak base approach is reported. This general synthetic method has shown that several Ru-NHC complexes were accessible in moderate to good yields. Their performance as catalysts in olefin oxidation reactions was tested and these all proved efficient, achieving complete conversions in short reaction times. Current research in our laboratories focuses on further applications of the weak base route to access catalytically relevant systems.

Conflicts of interest

There are no conflicts to declare.

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