The intramolecular sp^2 and sp^3 C–H bond activation of (*p*-cymene)ruthenium(II) N-heterocyclic carbene complexes†

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The intramolecular sp^2 and sp^3 C–H activated products, as well as the monometalated products, based on the "(*p*-cymene)Ru(NHC)" framework were synthesised by treatment of a series of NHCs (1-R-3-methylimidazol-2-ylidene [R = Ph (**1**), Bn (**2**), *t*-Bu (**3**), *i*-Pr (**4**), Mes (**5**), Cy (**6**)] and 1,3-bis(isopropyl)imidazol-2-ylidene (**7**)) with $[(p\text{-cymene})RuCl_2]_2$ under mild conditions. A new NHC precursor (1-*tert*-butyl-3-phenyl-4,5-dihydro-imidazol-2-ylidene) was also designed to compare the reactivity of sp^2 C–H and sp^3 C–H bonds upon cyclometalation, and only the sp^3 C–H activated product (**8**) was observed. The factors that possibly determine the selectivity of intramolecular sp^2 or sp^3 C–H activation are elucidated by a series of experiments. In the cases where activation of both sp^2 C–H and sp^3 C–H is possible, steric factors overrode the others to dominate the regioselectivity of activation. All complexes were characterised by ^{1}H NMR, ^{13}C NMR and HRMS spectra. The molecular structures of **1**, **3**, **5**, **6**, **7**, and **8** were confirmed by X-ray diffraction.

Introduction

Over the past decades, the activation of unreactive bonds by transition metal complexes has emerged as a new field of organometallic chemistry.[1–3] Recently, the major interest of this area has focused on the development of new procedures for catalytic activation processes.[2,4–7]

The extensive studies of N-heterocyclic carbenes (NHCs) and the corresponding organometallic derivatives have been carried out since the first convenient preparation method of NHC precursors was reported by Arduengo and co-workers in 1991.[8] Due to the great σ-electron-donating capability of NHC ligands, the corresponding complexes have been proven to be very effective in a variety of metal-catalysed organic reactions, such as olefin metathesis reactions,[9] Suzuki–Miyaura coupling,[10] Heck-type C–C coupling reactions[10,11] *etc.*[9,10,12–14] Recently, various interesting reactions with intramolecular aromatic and aliphatic C–H activation of NHC complexes have been published by several pioneers.[15–24] According to these discoveries, certain NHC-based ruthenium complexes could undergo intramolecular C–H activation processes and generate the stable cyclometalated species.[11–17] In last decade, normal carbene complexes with the backbone of $[(p\text{-cymene})Ru(NHC)X_2]$ have been widely studied.[18–30] Recently, Dixneuf and co-workers reported an unexpected cyclometalated (*p*-cymene)Ru(NHC) species which resulted from plausible intramolecular metal insertion to C–H bond on the vinyl moiety of imidazolylidene ligand.[31] These discoveries suggest great potential for development in this new area of organometallic chemistry. Furthermore, Ir(III) NHC complexes were also found to furnish intramolecular C–H activation products. Considering that the electronic configurations of Ir(III) complexes are close to those of Ru(II) complexes, intramolecular C–H activations of Ru(II)(NHC) complexes are expected.[32–38] Therefore, more details about the structures and reactivities of interesting cyclometalated Ru(II)(NHC) complexes are required.

On the basis of previous observations and our experiments, we now report the preparation and reactivity of a series of alkyl- and aryl-functionalised imidazolylidene complexes of Ru(II), including several interesting cyclometalated products. In all cases, the cyclometalation process takes place under mild conditions—room temperature and absence of any base. The ability of these complexes to activate the aliphatic or aromatic C–H bond is also generally studied.

Results and discussion

The sp^2 C–H Activation

According to the published method,[31] 1-phenyl-3-methylimidazolium iodide as the imidazolylidene precursor was deprotonated at 0 °C with *n*-BuLi, followed by addition of $[(p\text{-cymene})RuCl_2]_2$ at room temperature, and directly achieved the aromatic C–H activation (Scheme 1). The iodine atom attached to the Ru centre may originate from the imidazolium iodide through halogen exchange (complex **1**). This reaction procedure took place at room temperature with no presence of any base and was monitored by thin-layer chromatography (TLC), obtaining only the C–H activated species. Therefore, the intramolecular sp^2 C–H activation might be an extremely feasible process. This experimental result is consistent with what Dixneuf *et al.* had reported.[31]

However, complex **2** was obtained as a normally monometalated species under the same experimental conditions (Scheme 2).

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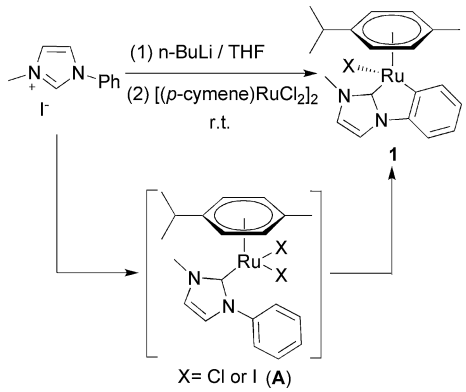
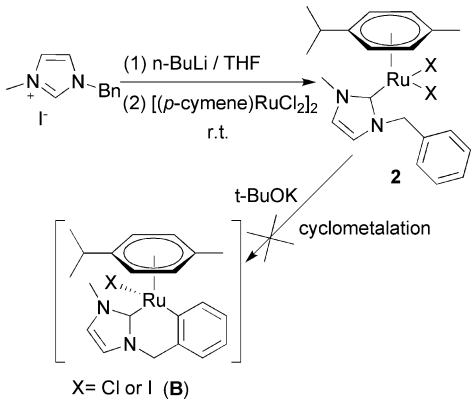
† Electronic supplementary information (ESI) available: ^{1}H NMR and ^{13}C NMR spectra of all compounds. CCDC reference numbers 675611 (for **3**), 675612 (for **5**), 675613 (for **6**), 705186 (for **1**), 705187(for **7**), and 705188 (for **8**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b818091a



Scheme 1 Synthesis of complex **1**.



Scheme 2 Synthesis of complex **2**.

Similar to the five-membered ruthenacycle in complex **1**, a six-membered ruthenacycle might have formed as a result of subsequent intramolecular sp^2 C–H activation of complex **2**. Actually, the larger ring size (six-membered or larger) may not be favoured by (*p*-cymene)Ru(II) species, which is contrary to the Ir(III) complexes where many cyclometalated six-membered ring examples have been reported to form under similar conditions.[33,37]

The ^{1}H NMR spectra of complexes **1** and **2** show conspicuous differences in signals of phenyl protons. Complex **1** has a signal of four protons at δ 8.04–6.92 ppm, while complex **2** has a signal of five protons at δ 7.34–7.24 ppm. The differences unambiguously reveal the orthometalation in complex **1**. Moreover, the $^{13}C\{^1H\}$ NMR spectra of complexes **1** and **2** show the signals of the carbene carbons at 160.9 and 171.5 ppm, respectively, while the metalated phenyl carbon of complex **1** appears at 124.0 ppm.

The structure of complex **1** was further confirmed by X-ray diffraction analysis. The ORTEP diagram of complex **1** is illustrated in Fig. 1, with the most representative bond distances and angles shown. It clearly shows that orthometalation on the phenyl substituent of the NHC ligand has been achieved, with formation of a five-membered ruthenacycle in coplanar conformation. The plane of the imidazole moiety shares the same plane with that of both ruthenacycle and Ph ring. The chelate bite angle [C(11)–Ru(1)–C(19)] is 76.3(4)°, similar to that for the previously reported cyclometalated complex [76.59(18)°].[31] The Ru–$C_{carbene}$ bond distance of 2.007(8) Å lies in the range of other (*p*-cymene)Ru(NHC) complexes.[16,25–30]. The Ru–C bond distance for the cyclometalated phenyl ring is 2.060(9) Å, which

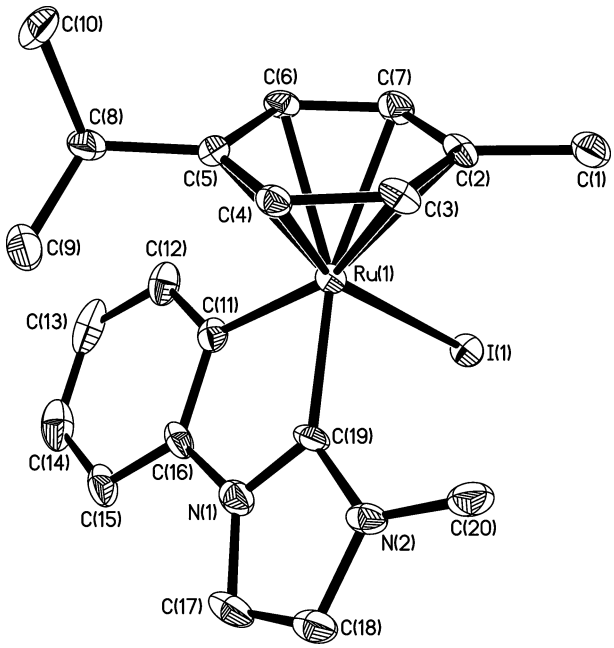
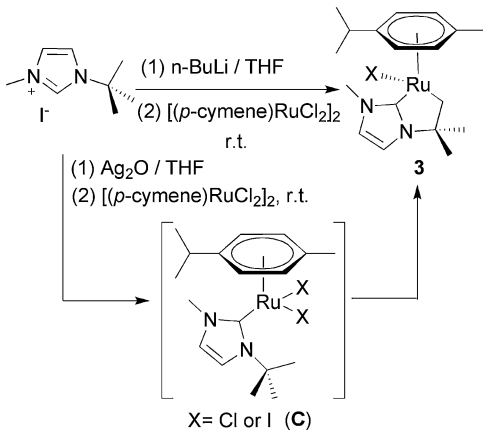


Fig. 1 ORTEP diagram of **1**. All the hydrogen atoms are omitted for clarity for clarity. Thermal ellipsoids are shown at the 30% level. Selected bond distances (Å) and angles (°): Ru(1)–C(11) 2.060(9), Ru(1)–C(19) 2.007(8), Ru(1)–I(1) 2.7217(12), Ru(1)–centroid (arene) 1.731, average of Ru–C in the arene ligand 2.234, C(11)–Ru(1)–C(19) 76.3(4), C(11)–Ru(1)–I(1) 87.8(2), C(19)–Ru(1)–I(1) 87.4(2), C(11)–Ru(1)–centroid (arene) 128.71, C(19)–Ru(1)–centroid (arene) 132.62, I(1)–Ru(1)–centroid (arene) 127.00.

is practically identical with the reported vinyl cyclometalated complex [2.071(5) Å].[31]

The sp^3 C–H Activation

By analogy to the Cp*Ir(III) analogues,[24] the sp^3 C–H activation of Ru(II)(NHC) complexes might be also achieved. Therefore, 1-*tert*-butyl-3-methylimidazolium iodide was synthesised and utilised as a NHC precursor. This imidazolium salt was allowed to react with *n*-BuLi at 0 °C in THF, then with [(*p*-cymene)$RuCl_2$]$_2$ at room temperature to provide complex **3**, and cyclometalation of the NHC ligand upon one of C–H bonds in *tert*-butyl group was observed (Scheme 3).



Scheme 3 Synthesis of complex **3**.

As with what has been already described for the preparation of complex **1**, the presence of the monometalated species (**C**) was not detected, although the reaction was carried out at room temperature—a considerably mild condition. Utilisation of the transmetalation reagent Ag_2O as an alternative in preparing the normally coordinated complex (**C**) merely obtained the cyclometalation product **3**, possibly suggesting the monometalated species [(*p*-cymene)Ru(NHC)X_2] is too reactive to exist. The ^{1}H NMR spectrum of **3** shows the signals of the non-equivalent geminal protons of the metalated CH_2 group at 3.14 and 3.06 ppm ($^2J_{H-H}$ = 9.35 Hz). The other two methyl groups of the *tert*-butyl group are diastereotopic and appear as two singlets at 1.42 and 1.11 ppm. The $^{13}C\{^1H\}$ NMR spectrum shows the signals of carbene carbon and metalated methylene carbon at 181.5 and 24.4 ppm, respectively. Single crystal X-ray diffraction analysis confirms that complex **3** is also a cyclometalated five-membered ruthenacycle species (Fig. 2).

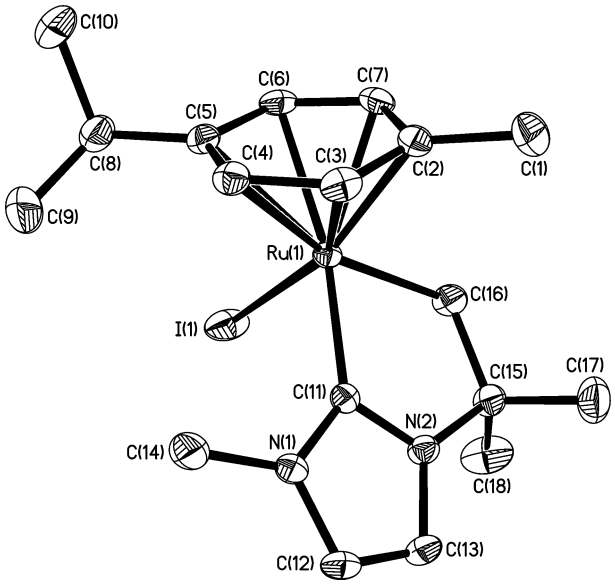


Fig. 2 ORTEP diagram of **3**. All the hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 30% level. Selected bond distances (Å) and angles (°): Ru(1)–C(11) 2.023(3), Ru(1)–C(16) 2.134(3), Ru(1)–I(1) 2.7423(4), Ru(1)–centroid (arene) 1.737, average of Ru–C in the arene ligand 2.237, C(11)–Ru(1)–C(16) 77.24(11), C(11)–Ru(1)–I(1) 86.92(8), C(16)–Ru(1)–I(1) 87.49(10), C(11)–Ru(1)–centroid (arene) 134.09, C(16)–Ru(1)–centroid (arene) 127.78, I(1)–Ru(1)–centroid (arene) 126.45.

This structure can be regarded as a distorted three-legged piano stool, with a planar five-membered imidazolylidene–methylene chelating ligand. The plane of imidazole moiety shares the same plane with that of ruthenacycle. The Ru–$C_{carbene}$ bond distance of 2.023(3) Å, which is practically the same as in complex **1** [2.007(8) Å], and still lies in the range of Ru–$C_{carbene}$ lengths observed from other (*p*-cymene)Ru(NHC) complexes.[16,25–30] The distance of Ru–CH_2 [2.134(3) Å] is longer than those for complex **1** [2.060(9) Å] and the vinyl cyclometalated complex [2.071(5) Å],[31] possibly due to the different hybridisation of the carbon atoms. The bite angle of the chelate ligand [C(11)–Ru(1)–C(16)] is 77.24(11)°, similar to that for complex **1** [76.3(4)°].

Three other substituted imidazolium iodides were also used as NHC precursors to react with [(*p*-cymene)$RuCl_2]_2$ under the same reaction conditions mentioned. Unfortunately, no C–H activated cyclometalated product was observed either under room temperature or under solvent reflux. Only normally coordinated products [(*p*-cymene)Ru(L)I_2] [L = 1-isopropyl-3-methylimidazol-2-ylidene (**4**), 1-(2,4,6-trimethylphenyl)-3-methylimidazol-2-ylidene (**5**) (Fig. 3), and 1-cyclohexyl-3-methylimidazol-2-ylidene (**6**) (Fig. 4)] were obtained for these ligands (Scheme 4).

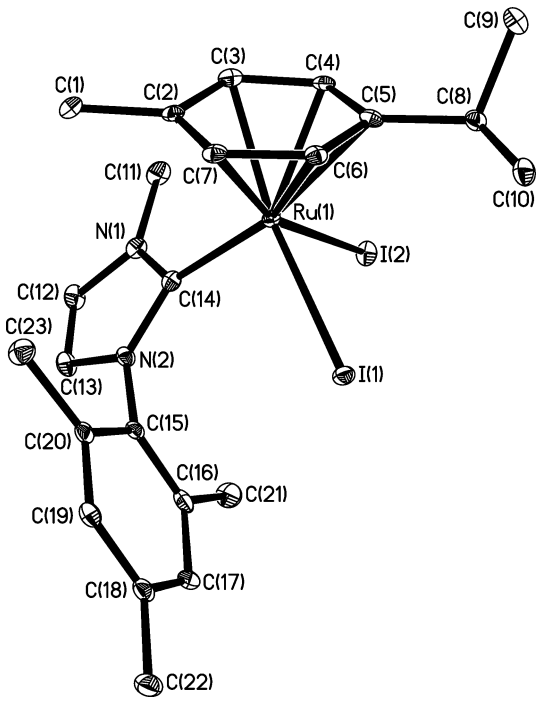
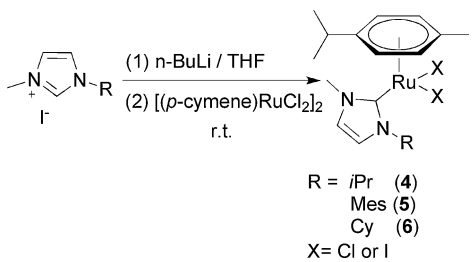


Fig. 3 ORTEP diagram of **5**. All the hydrogen atoms and solvent are omitted for clarity. Thermal ellipsoids are shown at the 30% level. Selected bond distances (Å) and angles (°): Ru(1)–C(14) 2.103(3), Ru(1)–I(1) 2.7492(6), Ru(1)–I(2) 2.7381(5), Ru(1)–centroid (arene) 1.720, average of Ru–C in the arene ligand 2.227, C(14)–Ru(1)–I(1) 95.83(8), C(14)–Ru(1)–I(2) 85.68(8), I(1)–Ru(1)–I(2) 86.748(12), C(16)–Ru(1)–centroid (arene) 130.27, I(1)–Ru(1)–centroid (arene) 121.08, I(2)–Ru(1)–centroid (arene) 125.03.



Scheme 4 Synthesis of complexes **4**–**6**.

In particular, we also attempted to utilise 1,3-bis(isopropyl)-imidazol-2-ylidene for the cyclometalation process. However, the normally coordinated complex **7** (Fig. 5) instead of the cyclometalated product was observed (Scheme 5).

In the molecular structure of complex **5** (Fig. 3), the mesityl plane is nearly perpendicular to the NHC plane (dihedral

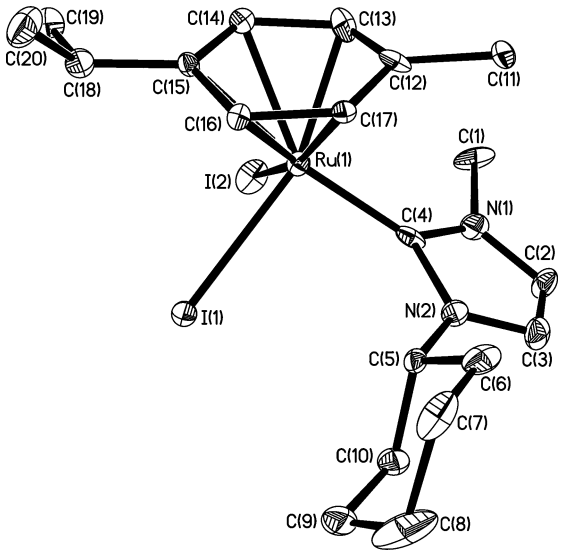


Fig. 4 ORTEP diagram of **6** shows only one molecule of the two in the asymmetric unit. All the hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 10% level. Selected bond distances (Å) and angles (°): Ru(1)–C(4) 2.03(4), Ru(1)–I(1) 2.782(4), Ru(1)–I(2) 2.784(4), Ru(1)–centroid (arene) 1.712, average of Ru–C in the arene ligand 2.23, C(4)–Ru(1)–I(1) 94.9(9), C(4)–Ru(1)–I(2) 92.5(9), I(1)–Ru(1)–I(2) 83.71(13), C(4)–Ru(1)–centroid (arene) 124.70, I(1)–Ru(1)–centroid (arene) 122.73, I(2)–Ru(1)–centroid (arene) 127.25.

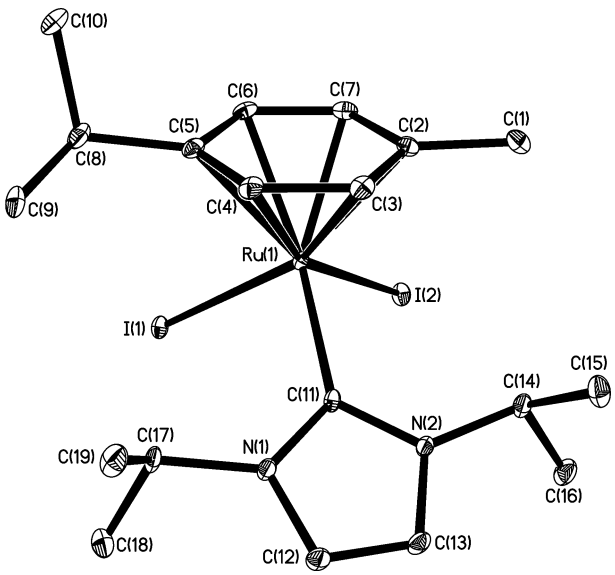
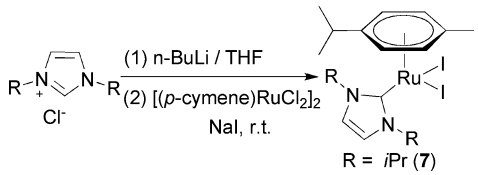


Fig. 5 ORTEP diagram of **7**. All the hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 30% level. Selected bond distances (Å) and angles (°): Ru(1)–C(11) 2.101(2), Ru(1)–I(1) 2.7521(6), Ru(1)–I(2) 2.7431(6), Ru(1)–centroid (arene) 1.711, average of Ru–C in the arene ligand 2.219, C(11)–Ru(1)–I(1) 93.77(7), C(11)–Ru(1)–I(2) 93.61(6), I(1)–Ru(1)–I(2) 83.660(17), C(11)–Ru(1)–centroid (arene) 126.30, I(1)–Ru(1)–centroid (arene) 125.11, I(2)–Ru(1)–centroid (arene) 123.00.

angle = 84.4°). The methyl groups of the mesityl substituent are away from the ruthenium atom, accounting for the absence of C–H activation. As the only consequence of cyclometalation which failed to occur, the mesityl-substituted NHC might have formed the disfavoured six-membered ring.



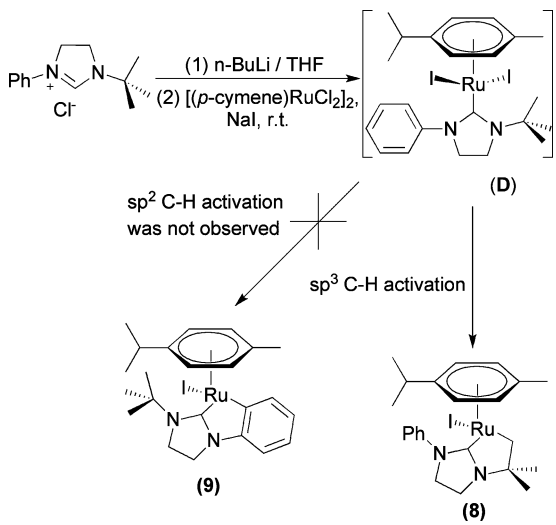
Scheme 5 Synthesis of complex **7**.

According to the observation of *t*-Bu substituted NHC ligand, we assume that, besides the ruthenacycle size, the steric repulsion between the NHC substituents and the metal centre might influence or even dominate the feasibility of cyclometalation.

Competition of sp^2 *vs.* sp^3 C–H Activation

In order to determine the relative activity between sp^2 and sp^3 C–H activation, a straightforward synthesis of 1-*tert*-butyl-3-phenyl-imidazol-2-ylidene or its analogues is thus required. Two candidates for synthetic methodology are available according to the literature published by the groups of Furstner[39] and Grubbs.[40] The synthesis of 1-phenyl-3-*tert*-butyl-4,5-dihydro-imidazolium chloride was finally chosen because of the efficiency of Grubbs' protocol.

According to the phenomena observed in the previous sections of this work, both activation processes (sp^2/sp^3 C–H bond) are possible in the current issue. The aromatic and aliphatic C–H activations and formations of complexes **8** and **9** were both originally expected. However, the reaction of 1-phenyl-3-*tert*-butyl-4,5-dihydro-imidazol-2-ylidene with $[(p\text{-cymene})RuCl_2]_2$ selectively proceeded to the cyclometalated species **8**, without any detectable formation of complex **9** (Scheme 6).



Scheme 6 Synthesis of complex **8**.

As predicted, the monometalated species **D** was not detected. The ^1H NMR spectrum of **8** shows the signal of the two protons in the metalated CH_2 at 3.20 ppm as a singlet, which is different from that of complex **3** in which the metalated CH_2 protons are non-equivalent and split. The methyl protons of the *tert*-butyl group appear at 1.34 and 1.10 ppm. The signals of the CH in *p*-cymene groups are diastereotopic because of asymmetry after the cyclometalation. The $^{13}C\{^1H\}$ NMR spectrum of **8** confirms

cyclometalation, with significant signals shown at 162.3 (carbene carbon) and 24.2 ppm (metalated CH_2). The molecular structure of **8** was further confirmed by X-ray diffraction analysis (Fig. 6).

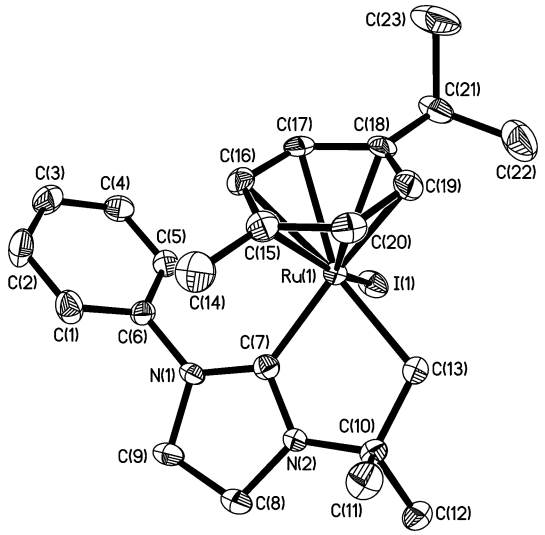


Fig. 6 ORTEP diagram of **8**. All the hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 60% level. Selected bond distances (Å) and angles (°): Ru(1)–C(7) 2.010(2), Ru(1)–C(13) 2.128(2), Ru(1)–I(1) 2.7408(9), Ru(1)- centroid (arene) 1.725, average of Ru–C in the arene ligand 2.232, C(7)–Ru(1)–C(13) 77.54(9), C(7)–Ru(1)–I(1) 87.42(7), C(13)–Ru(1)–I(1) 86.48(7), C(7)–Ru(1)–centroid (arene) 132.85, C(13)–Ru(1)–centroid (arene) 128.96, I(1)–Ru(1)–centroid (arene) 126.68.

This structure can also be regarded as a distorted three-legged piano stool, with a five-membered dihydroimidazolylidene–methylene chelating ligand. The plane of imidazole moiety shares the same plane with that of ruthenacycle. The Ru–$C_{carbene}$ bond distance is 2.010(2) Å, the Ru–CH_2 distance is 2.128(2) Å, and the bite angle of the chelate ligand [C(7)–Ru(1)–C(13)] is 77.54(9)°.

Conclusions

We have demonstrated that (*p*-cymene)Ru(NHC) complexes can undergo facile intramolecular sp^2 and sp^3 C–H activation with certain NHC precursors. In the cases of the formation of cyclometalated complexes **2** and **4**, C–H activation is so favoured that we could not even trap the noncyclometalated intermediate species (**A** and **C** in Schemes 1 and 3). The same result was also obtained for the reaction of transmetalation (Scheme 3). Only the sp^3 C–H activation was observed in the case of *N*-phenyl-*N*′-*tert*-butyl-4,5-dihydro-imidazol-2-ylidene, although the favoured five-membered ruthenacycle can be formed either *via* sp^3 or sp^2 C–H activation process. Herein, we believe that steric repulsion should be the dominant factor for C–H activation.[33] The presence of the *tert*-butyl group in complex **C** (Scheme 3) and **D** (Scheme 6) provides the structures in which one of the methyl groups is closely oriented toward the Ru centre. This steric bulk between methyl group and Ru may trigger the cyclometalation, which seems to be the only way to release the hindrance around the metal centre. The case of 1,3-bis(isopropyl)imidazol-2-ylidene (complex **7**) strongly supports this point of view. Under similar experimental conditions, only monometalated species was obtained without any trace of cyclometalated product. Since 1,3-bis(isopropyl)imidazol-2-ylidene is less bulky than 1-*tert*-butyl-3-methylimidazol-2-ylidene, it is considered that the experimental consequence might result from the steric factor and support the former discussion. In all processes discussed in this paper, six-membered ruthenacycles from the cyclometalation did not form at all, indicating that five-membered ruthenacycle is more stable for (*p*-cymene)Ru(II)-centred organometallic complexes.

Experimental section

General

Solvents were dried over sodium diphenyl ketyl (THF, hydrocarbons), or calcium hydride (dichloromethane) and distilled under argon prior to use. The reactions were carried out under argon, using Schlenck vacuum line techniques. $[(Me)(Ph)ImH]^+I^-$, $[(Me)(t\text{-}Bu)ImH]^+I^-$, $[(Me)(Mes)ImH]^+I^-$, $[(Me)(iPr)ImH]^+I^-$ and $[(Me)(Cy)ImH]^+I^-$ were prepared by treating the corresponding N-substituted imidazoles with methyl iodide.[41] $[(Me)(Bn)ImH]^+I^-$ was prepared by treating *N*-methylimidazole with benzyl iodide. $[(iPr)_2ImH]^+Cl^-$ was prepared by a previous literature method.[42] NMR spectra were recorded on a Bruker AV300 or VARIAN AS-400 at room temperature with TMS as internal standard. Elemental analyses were performed on a Perkin-Elmer 240C analyzer. HR ESI mass spectra were performed on a Varian 7.0 T FTICR-Mass Spectrometer. Crystal structure and X-ray data collection data are given in Table 1.

Synthesis of 1-*tert*-butyl-3-phenyl-4,5-dihydro-imidazolium chloride

This synthesis is a modification from the published protocol by Waltman and Grubbs.[40]

The *tert*-butylamine (100 mmol, 7.32 g) and triethylamine (100 mmol, 10.2 g) were dissolved in dry THF (150 mL) and cooled to 0 °C, ethyl chlorooxoactetate (100 mmol, 15.3 g) was added slowly. The mixture was allowed to warm to room temperature and stirred overnight. After filtration, the solvent was removed under reduced pressure to give *N*-*tert*-butyloxanilic acid ethyl ester as a yellowish liquid. Then aniline (100 mmol, 9.31 g), toluene (50 mL), triethylamine (200 mmol, 20.24 g) were added. The mixture was heated under reflux overnight, the product precipitated while being cooled to room temperature. Ethyl acetate was added until the solid redissolved. The solution was washed with 2 M HCl solution (2 × 100 mL). The aqueous layer was then extracted with ethyl acetate, and the combined organic layers were washed with brine (100 mL), and dried over $MgSO_4$. The solvents were then removed under reduced pressure, leaving a yellowish solid. This product was directly used for reduction with $LiAlH_4$ (400 mmol, 15.18 g) in THF (100 mL) under reflux overnight. A saturated aqueous solution of NaOH was then added very carefully to the mixture. After filtration the solid was washed several times with ethyl acetate. The organic layers were combined and dried with $MgSO_4$. Removal of the solvents in vacuum gave an orange oil, to which was added 10 mL of concentrated HCl with vigorously stirring. Then 150 mL of triethylorthoformate and several drops of HCO_2H were added. The mixture was heated under 120 °C for 12 h. After it was cooled to room temperature, the solvent was removed in vacuum and the resulting residue was washed with

Table 1 Crystal data and summary of X-ray data collection for complexes **1**, **3**, **5**, **6**, **7** and **8**[a]

	1	**3**	**5**·CH_2Cl_2	**6**	**7**	**8**
Formula	$C_{20}H_{23}IN_2Ru$	$C_{18}H_{27}IN_2Ru$	$C_{24}H_{32}Cl_2I_2N_2Ru$	$C_{20}H_{30}I_2N_2Ru$	$C_{19}H_{30}I_2N_2Ru$	$C_{23}H_{31}IN_2Ru$
Fw	519.37	499.39	774.29	653.33	641.32	563.47
T/K	113(2)	294(2)	113(2)	294(2)	113(2)	113(2)
λ/Å	0.71070	0.71073	0.71070	0.71073	0.71073	0.71073
Cryst. Syst.	Orthorhombic	Monoclinic	Triclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	$Pna2_1$	$P2_1/c$	$P\bar{1}$	$Pna2_1$	$P2_1/n$	$P2/c$
a/Å	7.729(3)	13.331(2)	8.8274(17)	18.958(6)	8.7376(17)	14.538(3)
b/Å	14.184(6)	8.5497(15)	11.8707(18)	24.186(8)	14.070(3)	9.827(2)
c/Å	17.532(8)	17.376(3)	14.782(3)	10.345(4)	17.591(4)	15.987(3)
α/°	90	90	67.695(8)	90	90	90
β/°	90	102.401(3)	83.695(10)	90	99.91(3)	101.10(3)
γ/°	90	90	70.037(7)	90	90	90
V/Å^3	1922.0(15)	1934.2(6)	1346.6(4)	4743(3)	2130.4(7)	2241.2(8)
Z	4	4	2	8	4	4
D_c/g cm^{-3}	1.795	1.715	1.910	1.830	2.000	1.670
μ/mm^{-1}	2.425	2.406	3.088	3.270	3.638	2.087
$F(000)$	1016	984	748	2512	1232	1120
Cryst. size/mm	0.04 × 0.03 × 0.02	0.30 × 0.24 × 0.20	0.18 × 0.16 × 0.16	0.22 × 0.20 × 0.16	0.08 × 0.06 × 0.04	0.14 × 0.12 × 0.08
θ range/°	1.85–27.86	1.56–26.40	1.96–25.01	1.36–25.02	1.86–27.88	2.45–27.48
No. of reflns collected	22 777	10 851	12 738	18 648	15 091	25 938
No. of indep. reflns/R_{int}	4572/0.1006	3944/0.0295	4754/0.0354	8095/0.1413	5063/0.0320	5133/0.0494
No. of params	223	206	287	460	224	249
Goodness-of-fit on F^2	1.150	1.024	1.044	1.036[b]	1.020	1.031
R_1, wR_2 ($I > 2\sigma(I)$)	0.0570, 0.1242	0.0264, 0.0599	0.0233, 0.0551	0.0948, 0.1629	0.0192, 0.0445	0.0263, 0.0571
R_1, wR_2 (all data)	0.0633, 0.1277	0.0365, 0.0643	0.0277, 0.0568	0.2499, 0.2366	0.0236, 0.0455	0.0316, 0.0586
Flack parameter	0.34(4)	n/a	n/a	–0.02(8)	n/a	n/a

[a] Single crystals of complexes **1**, **3**, **5**, **6**, **7** and **8** suitable for X-ray diffraction were obtained from hexane–CH_2Cl_2 or hexane–THF solution. Data collection was performed on a BRUKER SMART 1000 (for **3** and **6**) or a Rigaku Saturn 70 (for **1**, **5**, **7** and **8**) equipped with a rotating anode system, using graphite-monochromated Mo-Kα radiation (ω-2θ scans, λ = 0.71073 or 0.71070 Å). Semiempirical absorption corrections were applied for all complexes. The structures were solved by direct methods and refined by full-matrix least-squares. All calculations were using the SHELXTL-97 program system. [b] Due to poor quality of the single crystal of **6**, some atoms' thermal parameters (C23, C37, N4, C18, C14, C15, C17, C33, C16) were restrained to be isotropic.

THF. Subsequent suction filtration afforded the desired 1-*tert*-butyl-3-phenyl-4,5-dihydroimidazolium chloride as white powder. Total yield is 23%. Mp: 210–212 °C. ^{1}H NMR (400 MHz, 293 K, d^6-DMSO): δ = 9.42 (s, 1H, NC*H*N), 7.64 (d, J = 7.95 Hz, 2H, Ph-C*H*), 7.45 (t, J = 7.36 Hz, J = 7.18 Hz, 2H, Ph-C*H*), 7.27 (t, J = 7.36 Hz, J = 7.18 Hz, 1H, Ph-C*H*), 4.38 (t, J = 9.79 Hz, J = 10.99 Hz, 2H, NCH_2), 4.18 (t, J = 10.99 Hz, J = 9.79 Hz, 2H, NCH_2), 1.47 (s, 9H, C(CH_3)$_3$). ^{13}C{^{1}H} NMR (100 MHz, 293 K, d^6-DMSO): δ = 136.6 (NCHN), 129.3 (Ph), 125.7 (Ph), 117.7 (Ph), 57.4 (NCH_2), 47.6 (NCH_2), 45.4 (N(*C*(CH$_3$)$_3$), 27.4 (N(C(*C*H$_3$)$_3$). Anal. Calcd. for $C_{13}H_{19}ClN_2$: C, 65.40, H, 8.02, N, 11.73. Found: C, 65.42, H, 8.03, N, 11.76%.

Synthesis of complex 1

A mixture of [(Me)(Ph)ImH]$^+$I$^-$ (286 mg, 1 mmol) and *n*-BuLi (1 mmol) was stirred in THF (30 mL) for 5 h under 0 °C. Powdered [(*p*-cymene)RuCl$_2$]$_2$ (306 mg, 0.5 mmol) was then added and the mixture was stirred at room temperature over night. After removal of solvents in vacuum, the residue was extracted with CH_2Cl_2 and filtered through Celite. CH_2Cl_2 was afterwards removed in vacuum and a red solid was obtained. After recrystallisation from hexane–THF complex **1** was obtained (198 mg, 38%) as orange red crystals.

Mp: 208–210 °C. ^{1}H NMR (400 MHz, 293 K, CDCl$_3$): δ = 8.04 (m, 1H, Ph-C*H*), 7.34(d, J = 1.56 Hz, 1H, NC*H*), 7.08 (m, 1H, Ph-C*H*), 6.97 (d, J = 1.56 Hz, 1H, NC*H*), 6.92 (m, 2H, Ph-C*H*), 5.50 (d, J = 5.97 Hz, 1H, *p*-cymene-C*H*), 5.46 (m, 2H, *p*-cymene-C*H*), 5.38 (d, J = 5.97 Hz, 1H, *p*-cymene-C*H*), 4.05 (s, 3H, N(CH_3)), 2.34 (m, 1H, *p*-cymene-C*H*(CH$_3$)$_2$), 2.30 (s, 3H, *p*-cymene-CH_3), 0.92 (d, J = 6.89 Hz, 3H, *p*-cymene-CH(CH_3)$_2$) 0.80 (d, J = 6.89 Hz, 3H, *p*-cymene-CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (100 MHz, 293 K, CDCl$_3$): δ = 160.9 (C–Ru carbene), 142.7 (Ph), 124.0 (Ph), 121.8 (Ph), 114.1 (N*C*H), 110.8 (N*C*H), 91.3 (*p*-cymene-*C*), 89.2 (*p*-cymene-*C*), 88.0 (*p*-cymene-*C*), 84.5 (*p*-cymene-*C*), 38.2 (NCH_3), 31.4 (*p*-cymene-*C*H(CH$_3$)$_2$), 23.0 (*p*-cymene-*C*H$_3$), 21.7 (*p*-cymene-CH(*C*H$_3$)$_2$), 20.8 (*p*-cymene-CH(*C*H$_3$)$_2$). HRMS (ESI, *m*/*z*): calcd for $C_{20}H_{23}N_2Ru^+$ (M – X) 393.0903, found 393.0906.

Synthesis of complex 2

Using a procedure similar to that as described for **1**, reaction of [(Me)(Bn)ImH]$^+$I$^-$ (1 mmol) with *n*-BuLi (1 mmol) and [(*p*-cymene)RuCl$_2$]$_2$ (0.5 mmol) gave complex **2** in 40% yield as black red crystals. Mp: 165–167 °C. ^{1}H NMR (400 MHz, 293 K, CDCl$_3$): δ = 7.34 (m, 4H, Ph-C*H*), 7.24 (m, 1H, Ph-C*H*), 7.04 (s, 1H, NC*H*), 6.85 (s, 1H, NC*H*), 5.87 (m, 1H *p*-cymene-C*H*), 5.65 (m, 2H *p*-cymene-C*H*), 5.54 (m, 1H *p*-cymene-C*H*), 5.27 (m, 1H, Bn-CH_2), 4.84 (m, 1H, Bn-CH_2), 4.14 (s, 3H, N(CH_3)), 3.26 (m, 1H, *p*-cymene-C*H*(CH$_3$)$_2$), 1.98 (s, 3H, *p*-cymene-CH_3), 1.25 (m, 6H, *p*-cymene-CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (100 MHz, 293 K, CDCl$_3$): δ = 171.5 (C–Ru carbene), 137.2 (Ph), 128.8 (Ph), 128.0 (Ph), 127.7 (Ph), 123.9 (Ph), 123.2 (Ph), 109.9 (N*C*H), 99.0 (*p*-cymene-*C*), 58.7 (PhCH_2), 45.1 (NCH_3), 45.1 (*p*-cymene-*C*H(CH$_3$)$_2$), 31.6 (*p*-cymene-*C*H$_3$), 19.1 (*p*-cymene-CH(*C*H$_3$)$_2$).

HRMS (ESI, m/z): calcd for $C_{21}H_{26}N_2IRu^+$ (M – X) 535.0183, found 534.9977.

Synthesis of complex 3

Using a procedure similar to that as described for **1**, reaction of [(Me)(*t*-Bu)ImH)]$^+$I$^-$ (1 mmol) with *n*-BuLi (1 mmol) and [(*p*-cymene)$RuCl_2]_2$ (0.5 mmol) gave complex **3** in 30% as orange red crystals. Mp: 142–144 °C. ^{1}H NMR (400 MHz, 293 K, $CDCl_3$): δ = 6.87 (s, 1H, NC*H*), 6.65 (s, 1H, NC*H*), 5.36 (m, 2H, *p*-cymene-C*H*), 5.22 (d, J = 5.72 Hz, 1H, *p*-cymene-C*H*), 4.79 (d, J = 5.72 Hz, 1H, *p*-cymene-C*H*), 3.92 (s, 3H, N(CH_3)), 3.14 (d, J = 9.35 Hz, 1H, C(CH_3)$_2$(CH_2Ru)), 3.06 (d, J = 9.35 Hz, 1H, C(CH_3)$_2$(CH_2Ru)), 2.66 (m, 1H, *p*-cymene-C*H*(CH_3)$_2$), 1.95 (s, 3H, *p*-cymene-CH_3), 1.42 (s, 3H, C(CH_3)$_2$(CH_2Ru)), 1.12 (d, J = 7.20 Hz, 3H, *p*-cymene-CH(CH_3)$_2$), 1.11 (s, 3H, C(CH_3)$_2$(CH_2Ru)), 1.05 (d, J = 7.20 Hz, 3H, *p*-cymene-CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (100 MHz, 293 K, $CDCl_3$): δ = 181.5 (C–Ru carbene), 122.6 (N*C*H), 121.8 (N*C*H), 115.8 (*p*-cymene-*C*), 104.6 (*p*-cymene-*C*), 86.7 (*p*-cymene-*C*), 81.7(*p*-cymene-*C*), 64.7 (*C*(CH_3)$_2$(CH_2Ru)), 32.1 (N*C*H_3), 31.1 (*p*-cymene-*C*H(CH_3)$_2$), 30.7 (*p*-cymene-*C*H_3), 28.3 (C(*C*H_3)$_2$(CH_2Ru)), 24.4 (C(CH_3)$_2$(*C*H_2Ru)), 21.4 (*p*-cymene-CH(*C*H_3)$_2$). HRMS (ESI, m/z): calcd for $C_{18}H_{27}N_2Ru^+$ (M – X) 373.1216, found 373.1216.

Synthesis of complex 4

Using a procedure similar to that as described for **1**, reaction of [(Me)(*i*Pr)ImH]$^+$I$^-$ (1 mmol) with n-BuLi (1 mmol) and [(*p*-cymene)$RuCl_2]_2$ (0.5 mmol) gave complex **4** in 44% yield as black red crystals. Mp: 176 °C (dec). ^{1}H NMR (400 MHz, 293 K, $CDCl_3$): δ = 7.07 (s, 2H, NC*H*), 5.69 (m, 2H, *p*-cymene-C*H*), 5.45 (m,1H, NC*H*(CH_3)$_2$), 5.23 (m, 1H, *p*-cymene-C*H*), 5.00 (m, 1H, *p*-cymene-C*H*), 4.08 (s, 3H, NCH_3), 3.27 (m, 1H, *p*-cymene-C*H*(CH_3)$_2$), 1.90 (s, 3H, *p*-cymene-CH_3), 1.43 (d, J = 6.41 Hz, 6H, NCH(CH_3)), 1.26 (m, 6H, *p*-cymene-CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (100 MHz, 293 K, $CDCl_3$): δ = 168.7 (C–Ru carbene), 124.4 (N*C*H), 119.0 (N*C*H), 108.8 (*p*-cymene-*C*), 99.6 (*p*-cymene-*C*), 87.9 (*p*-cymene-*C*), 86.7 (*p*-cymene-*C*), 81.2 (*p*-cymene-*C*), 80.7 (*p*-cymene-*C*), 54.8 (N*C*H(CH_3)$_2$), 44.9 (N*C*H_3), 44.9 (*p*-cymene-*C*H(CH_3)$_2$), 31.5 (*p*-cymene-*C*H_3), 25.0 (NCH(*C*H_3)), 19.0 (*p*-cymene-CH(*C*H_3)$_2$). HRMS (ESI, m/z): calcd for $C_{17}H_{26}N_2IRu^+$ (M – X) 487.0182, found 487.0189.

Synthesis of complex 5

Using a procedure similar to that as described for **1**, reaction of [(Me)(Mes)ImH]$^+$I$^-$ (1 mmol) with *n*-BuLi (1 mmol) and [(*p*-cymene)$RuCl_2]_2$ (0.5 mmol) gave complex **5** in 35% yield as black red crystals. Mp: 189–191 °C. ^{1}H NMR (400 MHz, 293 K, $CDCl_3$): δ = 7.23(s, 1H, NC*H*), 6.86 (s, 2H, Mes-C*H*), 6.77 (s,1H, NC*H*), 5.71 (d, J = 5.74 Hz, 2H, *p*-cymene-C*H*), 5.10 (d, J = 5.74 Hz, 2H, *p*-cymene-C*H*), 4.19 (s, 3H, N(CH_3)), 3.27(m, 1H, *p*-cymene-C*H*(CH_3)$_2$), 2.32 (s, 3H, *p*-cymene-CH_3), 2.05 (s, 3H, Mes-CH_3), 2.00 (s, 6H, Mes-CH_3), 1.24 (s, 3H, *p*-cymene-CH(CH_3)$_2$), 1.23 (s, 3H, *p*-cymene-CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (100 MHz, 293 K, $CDCl_3$): δ = 169.3 (C–Ru carbene), 139.1 (Mes-Ph), 136.6 (Mes-Ph), 129.4 (Mes-Ph), 128.8 (Mes-Ph), 125.8 (Mes-Ph), 125.5 (Mes-Ph), 125.3 (N*C*H), 123.8 (N*C*H), 107.3 (*p*-cymene-*C*), 100.2 (*p*-cymene-*C*), 89.6 (*p*-cymene-*C*), 88.8 (*p*-cymene-*C*), 83.3 (*p*-cymene-*C*), 82.2 (*p*-cymene-*C*), 45.6 (N*C*H_3), 45.2 (*p*-cymene-*C*H(CH_3)$_2$), 31.8 (Mes-*C*H_3), 31.2 (*p*-cymene-*C*H_3), 23.4 (*p*-cymene-CH(*C*H_3)$_2$). HRMS (ESI, m/z): calcd for $C_{23}H_{30}N_2IRu^+$ (M – X) 563.0497, found 563.0490.

Synthesis of complex 6

Using a procedure similar to that as described for **1**, reaction of [(Me)(Cy)ImH]$^+$I$^-$ (1 mmol) with n-BuLi (1 mmol) and [(*p*-cymene)$RuCl_2]_2$ (0.5 mmol) gave complex **6** in 37% yield as black red crystals. Mp: 201–203 °C. ^{1}H NMR (400 MHz, 293 K, $CDCl_3$): δ = 7.07 (d, J = 1.95 Hz, 1H, NC*H*), 7.04 (d, J = 1.95 Hz, 1H, NC*H*), 5.70 (d, J = 30.3 Hz, 2H, *p*-cymene-C*H*), 5.24 (m,1H, NC*H*-Cy), 4.96 (d, J = 30.3 Hz, 2H, *p*-cymene-C*H*), 4.10 (s, 3H, N(CH_3)), 3.30 (m, 1H, C*H*(CH_3)$_2$), 1.91 (s, 3H, *p*-cymene-CH_3), 1.78–1.75 (m, 4H, Cy-CH_2), 1.58 (m, 2H, Cy-CH_2), 1.30–1.27 (m, 10H, Cy-CH_2+*p*-cymene-CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (100 MHz, 293 K, $CDCl_3$): δ = 169.1 (C–Ru carbene), 124.1 (N*C*H), 119.7 (N*C*H), 109.7 (*p*-cymene-*C*), 108.9 (*p*-cymene-*C*), 99.6 (*p*-cymene-*C*), 88.2 (*p*-cymene-*C*), 87.0 (*p*-cymene-*C*), 81.0 (*p*-cymene-*C*), 62.1 (N*C*H_3), 44.9 (N*C*H-Cy), 31.5 (*p*-cymene-*C*H(CH_3)$_2$), 25.2 (*C*H_2-Cy), 19.0 (*p*-cymene-CH(*C*H_3)$_2$). HRMS (ESI, m/z): calcd for $C_{20}H_{30}N_2IRu^+$ (M – X) 527.0496, found 527.0494.

Synthesis of complex 7

A mixture of [(*i*Pr)$_2$ImH]$^+$Cl$^-$ (189 mg, 1 mmol) and n-BuLi (1 mmol) was stirred in THF (30 mL) for 5 h under 0 °C. Powdered [(*p*-cymene)$RuCl_2]_2$ (306 mg, 0.5 mmol) and excess NaI (300 mg, 2 mmol) was then added and the mixture was stirred at room temperature overnight. After removal of solvents in vacuum, the residue was extracted with CH_2Cl_2 and filtered through Celite. CH_2Cl_2 was removed in vacuum and red solid was obtained. After recrystallisation from hexane–CH_2Cl_2 complex **7** (192 mg, 30%) was obtained as black red crystals. Mp: 189–191 °C. ^{1}H NMR (300 MHz, 293 K, $CDCl_3$): δ = 7.19 (s, 1H, NC*H*), 7.06 (s, 1H, NC*H*), 5.70 (d, J = 5.82 Hz, 2H, *p*-cymene-C*H*), 5.52 (m, 2H, (CH_3)$_2$C*H*N), 5.06 (d, J = 5.82 Hz, 2H, *p*-cymene-C*H*), 3.29 (m, 1H, *p*-cymene-C*H*(CH_3)$_2$), 1.92 (s, 3H, *p*-cymene-CH_3), 1.39 (d, J = 5.01 Hz, 12H, (CH_3)$_2$CHN), 1.26 (d, J = 6.92 Hz, 6H, *p*-cymene-CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (75 MHz, 293 K, $CDCl_3$): δ = 167.4 (C–Ru carbene), 119.5 (N*C*H), 108.0 (*p*-cymene-*C*), 99.8 (*p*-cymene-*C*), 87.5 (*p*-cymene-*C*), 81.1 (*p*-cymene-*C*), 54.7 (N*C*H(CH_3)$_2$), 31.5 (*p*-cymene-*C*H(CH_3)$_2$), 25.5 (*p*-cymene-*C*H_3), 24.9 (NCH(*C*H_3)$_2$), 23.2 (NCH(*C*H_3)$_2$), 22.7 (*p*-cymene-CH(*C*H_3)$_2$), 19.6 (*p*-cymene-CH(*C*H_3)$_2$). HRMS (ESI, m/z): calcd for $C_{19}H_{34}O_2N_2NaRu^+$ (M – 2I + 2H_2O + Na^+) 447.1560, found 447.1570.

Synthesis of complex 8

Using a procedure similar to that as described for **7**, reaction of [(Ph)(*t*-Bu)dihydroImH]$^+$Cl$^-$ (1 mmol) with *n*-BuLi (1 mmol), [(*p*-cymene)$RuCl_2]_2$ (0.5 mmol) and excess NaI (300 mg, 2 mmol) gave **8** in 32% yield as orange red crystals. Mp: 160–161 °C. ^{1}H NMR (300 MHz, 293 K, $CDCl_3$): δ = 7.97 (d, J = 7.49 Hz, 1H, Ph-C*H*), 7.42 (t, J = 7.41 Hz, J = 8.06 Hz, 2H, Ph-C*H*), 7.29 (d, J = 7.29 Hz, 1H, Ph-C*H*), 4.87 (d, J = 5.93 Hz, 1H, *p*-cymene-C*H*), 4.71 (d, J = 5.63 Hz, 1H, *p*-cymene-C*H*), 5.55

(d, J = 5.93 Hz, 1H, *p*-cymene-C*H*), 4.24 (m, 1H, NCH_2), 3.89 (m, 1H, NCH_2), 3.57 (m, 1H, NCH_2), 3.46 (m, 1H, NCH_2), 3.20 (s, 2H, C(CH$_3$)$_2$(CH_2Ru)), 2.57 (m, 1H, *p*-cymene-C*H*(CH$_3$)$_2$), 1.94 (s, 3H, *p*-cymene-CH_3), 1.34 (s, 3H, C(CH_3)$_2$(CH$_2$Ru)), 1.10 (s, 3H, C(CH_3)$_2$(CH$_2$Ru)), 1.06 (d, J = 6.90 Hz, 3H, *p*-cymene-CH(CH_3)$_2$) 1.00 (d, J = 6.90 Hz, 3H, *p*-cymene-CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (75 MHz, 293 K, $CDCl_3$): δ = 162.3 (C–Ru carbene), 128.5 (Ph), 126.98 (Ph), 125.97 (Ph), 103.6 (*p*-cymene-*C*), 97.2 (*p*-cymene-*C*), 90.1 (*p*-cymene-*C*), 88.5 (*p*-cymene-*C*), 86.7 (*p*-cymene-*C*), 84.2 (*p*-cymene-*C*), 62.7 (N*C*H$_2$), 52.2 (N*C*H$_2$), 43.6 (*C*(CH$_3$)$_2$(CH$_2$Ru)), 30.7 (*p*-cymene-*C*H(CH$_3$)$_2$), 29.9 (*p*-cymene-*C*H$_3$), 27.6 (C(CH$_3$)$_2$(CH$_2$Ru)), 26.3 (C(*C*H$_3$)$_2$-(CH$_2$Ru)), 24.2 (C(*C*H$_3$)$_2$(*C*H$_2$Ru)), 21.2 (*p*-cymene-CH(*C*H$_3$)$_2$), 20.0 (*p*-cymene-CH(*C*H$_3$)$_2$). HRMS (ESI, m/z): calcd for $C_{23}H_{31}N_2Ru^+$ (M – I) 437.1530, found 473.1537.

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