RSC Advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Journal Name

ARTICLE

Ruthenium hydroxycyclopentadienyl *N*-heterocyclic carbene complexes as transfer hydrogenation catalysts

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Cristiana Cesari,[a] Andrea Cingolani,[a] Chiara Parise,[a] Stefano Zacchini,[a] Valerio Zanotti,[a] Maria Cristina Cassani[a] and Rita Mazzoni [a,*]

A series of novel cationic hydroxycyclopentadienyl and methoxycyclopentadienyl *N*-heterocyclic carbene ruthenium(II) complexes have been synthesized from the corresponding neutral ruthenium(0) complexes containing both the non-innocent cyclopentadienone ligand and variously functionalized *N*-heterocyclic carbenes (NHCs). In particular an NHC derivative containing a pyridine group in the side chain has been designed and developed in order to evaluate the influence of a basic, potentially cooperative substituent in the catalytic activity of these complexes. All the prepared complexes were employed as selective catalysts for transfer hydrogenation reactions employing refluxing ^{i}PrOH as hydrogen source and several ketones and aldehydes as substrates. We found that while the presence of oxidizing additives such as CAN and benzoquinone is mandatory to activate the neutral ruthenium(0) complexes, no activation is needed for the cationic Ru(II) catalysts. The catalytic activity of the latter is also influenced by the coordinating ability of the counterion, and indeed the cationic complexes having a pyridine-functionalized NHC ligand and $CF_3SO_3^-$ as counterion, present the best conversion (> 99%) thus demonstrating the fundamental role played by the basic pyridine in the catalytic activity. With regard to the hydrogenation reaction mechanism, the release of the CO ligand was demonstrated to be the key step and the presence of hydride species has been detected at the end of the reaction.

Introduction

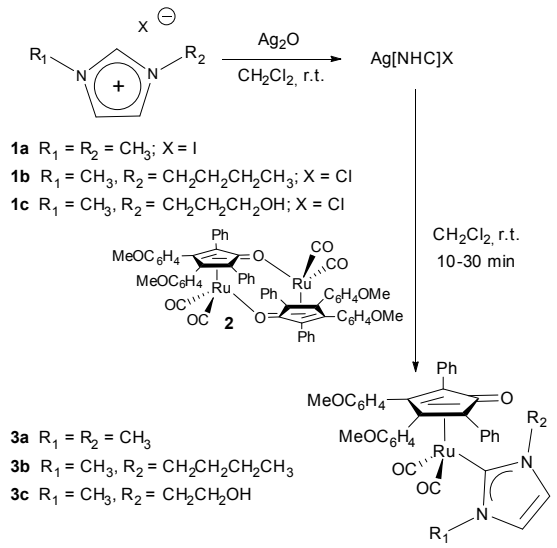
N-Heterocyclic carbenes (NHCs) are among the most popular ancillary ligands due to a combination of unique features, such as the tunability of electronic and steric properties that influence the metal center. Moreover the synthesis of NHC ligand precursors and of the corresponding complexes is rather simple and very versatile[1] allowing the rational design of transition metal catalysts and the improvement of catalytic activity.[2] Several catalytic reactions such as ruthenium-catalyzed olefin metathesis,[3] palladium-catalyzed cross-coupling reaction,[4] iridium-catalyzed reductions and oxidations,[5] and gold-catalyzed activation of π-bonds[6] benefited from the introduction of NHC ligands. Apart from olefin metathesis, Ru-NHC complexes have shown catalytic activity in various redox transformations,[7] including: transfer hydrogenation,[8] hydrogenation of olefins[9] and esters,[10] asymmetric hydrogenation,[11] amide synthesis from alcohols and nitriles,[12] dehydrogenation of esters and imines from alcohols,[13] racemization of chiral alcohols,[14] oxidation of alcohols[15] and water oxidation.[16] Regarding the Ru-NHC complexes, most of the literature features Ru(II) complexes, while low-valent Ru(0)-NHC systems are restricted to a few examples based on either $[Ru_3(CO)_{12}]$ or $[Ru(CO)_2(PPh_3)_3]$ as precursors.[17]

Another class of versatile ligands is represented by cyclopentadienones which behave as non-innocent ligands exploiting the cyclopentadienone/hydroxycyclopentadienyl reversible transformation. The most famous example of its cooperativity with ruthenium in bifunctional catalysis is the Shvo catalyst, a well-known system employed in a plethora of catalytic applications.[18] In principle by combining NHC and cyclopentadienone ligands on ruthenium complexes the properties of both ligand should be exploited allowing the design of novel catalysts finely tuning steric and electronic properties, solubility and the insertion of substituents suitable for heterogenization. Furthermore by choosing a proper substituent, NHC ligand itself could cooperate with the metal as a non-innocent species.[19]

With this aim in mind, a straightforward approach towards Ru(0)-NHC complexes has been recently communicated by our group,[20] based on a dimeric Ru(0) cyclopentadienone dicarbonyl dimer (**2**). Cleavage of **2** in the presence of a silver carbene precursor provided access to a new class of ruthenium complexes in quantitative yields (some examples in Scheme 1).

[a] *Dipartimento di Chimica Industriale "Toso Montanari", viale Risorgimento 4, 40136 Bologna, Italy.*
* E-mail: rita.mazzoni@unibo.it

Electronic Supplementary Information (ESI) available: NMR spectra of novel complexes; selected ESI-MS; crystal data and experimental details; catalytic time-conversion profiles. X-Ray diffraction CCDC: 1421543-1421546. See DOI: 10.1039/x0xx00000x



Scheme 1. Synthesis of cyclopentadienone imidazolylidene ruthenium(0) complexes **3a-c**.

In this paper we first describe an extention of this synthetic methodology to a complex containing a pyridine-funtionalized NHC ligand (**3d**: R_1 = butyl; R_2 = 2-pyridine) then the main body of this work concerns the transformation of the cyclopentadienone imidazolylidene ruthenium(0) complexes (**3a-d**) into their corresponding cationic hydroxyl- and methoxy-cyclopentadienyl ruthenium(II) derivatives [**4a-d[X]** (X = Cl, BF_4, NO_3, CF_3SO_3) and **5a,d[CF_3SO_3]**], and the use of both Ru(0) and Ru(II) complexes as catalysts for transfer hydrogenation of ketones and aldehydes in refluxing isopropanol. Comparison between monodentate and pyridine-functionalized NHC ligands, has provided some insights into the reaction mechanism.

Results and discussion

Synthesis of imidazolylidene Ru complexes

The novel complex **3d** (R_1 = butyl; R_2 = 2-pyridine) was prepared in one pot following the same procedure described in Scheme 1 and fully characterized by spectroscopic methods and elemental analysis. In particular, the ^{13}C NMR spectrum shows the downfield shifted resonance of the carbene (δ = 173.20 ppm), whereas in the IR spectrum the CO stretching bands are consistent with those of similar complexes (vCO = 2008 cm^{-1}, 1949 cm^{-1} (**3d**) vs vCO = 2004 cm^{-1}, 1945 cm^{-1} (**3a**)). Further evidences were produced by ESI-MS and X-Ray diffraction analyses.

The molecular structure of **3d** has been determined by single crystal X-ray crystallography as its **3d·0.5CH_2Cl_2** solvate (Figure 1).

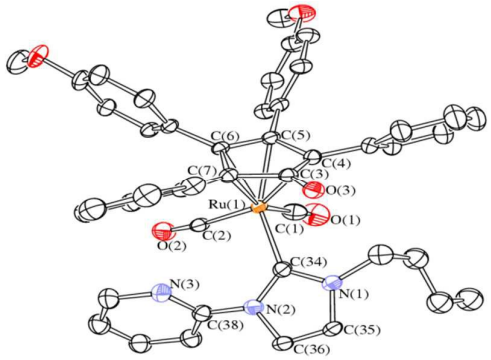
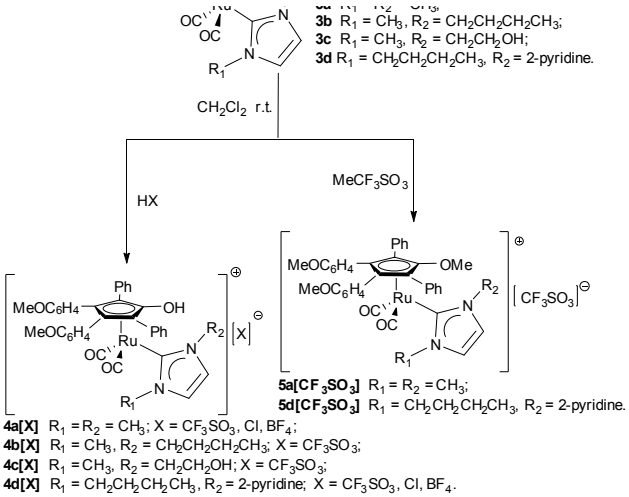


Figure 1. ORTEP drawing of **3d**. Displacement ellipsoids are at the 30% probability level. H-atoms have been omitted for clarity. Selected bond lengths (Å): Ru(1)-C(1) 1.845(16), Ru(1)-C(2) 1.883(12), Ru(1)-C(3) 2.511(11), Ru(1)-C(4) 2.279(11), Ru(1)-C(5) 2.199(11), Ru(1)-C(6) 2.212(10), Ru(1)-C(7) 2.280(11), Ru(1)-C(34) 2.139(12), C(3)-O(3) 1.246(13).

Its structure is similar to those previously reported for the analogous complexes **3a–c**.[20] In particular, the Ru(1)-C(3) distance [2.511(11) Å] is significantly longer than Ru(1)-C(4-7) [2.199(11)-2.280(11) Å, average 2.242(2) Å] and C(3)-O(3) [1.246(13) Å] is essentially a double bond.[21] The Ru(1)-C(34) contact [2.117(3) Å] is in the typical range for the interaction between Ru(0) and a N-heterocyclic carbene.[22]

The reaction of **3a-d** with strong acids or a methylating agent such as $MeCF_3SO_3$, leads to the quantitative formation of the hydroxycyclopentadienyl and methoxycyclopentadienyl cationic complexes **4a-d[X]** (X = Cl, BF_4, NO_3, CF_3SO_3) and **5a,d[CF_3SO_3]** (Scheme 2), in which Ru(0) is formally oxidized to Ru(II).



Scheme 2. Synthesis of hydroxycyclopentadienyl imidazolylidene ruthenium complexes **4a-d[X]** and methoxycyclopentadienyl imidazolylidene ruthenium complexes **5a,d[CF_3SO_3]**.

Infrared spectroscopy provides a convenient technique for monitoring the progress of the protonation as, in agreement with the reduced back-donation from the metal center to the

carbonyl ligands, ν-C≡O stretch vibrations undergo a significative high-energy shift upon formation of the cationic complex [*e.g.* ν_{CO} = 2008 cm^{-1}, 1949 cm^{-1} (**3d**), and 2041 cm^{-1}, 1991 cm^{-1} (**4d[CF_3SO_3]**)]. The change in the coordination from η^4 (cyclopentadienone ligand) to η^5 (hydroxycyclopentadienyl ligand) is further evidenced by ^{13}C-NMR shift of the resonance due to the endocyclic carbon involved in the ketone-alcohol transformation [δ 168.22 ppm (C=O, Cp, in **3d**) vs δ 142.00 ppm (C-OH, Cp, in **4d[CF_3SO_3]**)]. Ru-carbene signals are also shifted to higher fields; from δ 173.20 ppm (**3d**) to δ 166.07 ppm (**4d[CF_3SO_3]**) (see experimental section for more details).

With regard to the methylated complexes **5a[CF_3SO_3]** and **5d[CF_3SO_3]** IR spectra show a shift of 40 cm^{-1} from the neutral to the cationic species (*e.g.* ν_{CO} = 2004 cm^{-1}, 1945 cm^{-1} (**3a**), and 2045 cm^{-1}, 1995 cm^{-1} (**5a[CF_3SO_3]**) and both IR and NMR data are similar to those obtained for the hydroxycyclopentadienyl complexes **4a[CF_3SO_3]** and **4d[CF_3SO_3]** with the methyl group arising at δ 3.19 (^{1}H NMR) and δ 61.93 (^{13}C NMR) ppm.

Moreover, structural evidences were obtained by X-ray diffraction analysis of single crystals of the cationic complexes **[4a]$^+$** and **[4c]$^+$** as their **[4a][CF_3SO_3]·0.5toluene** and **[4c][CF_3SO_3]·$CHCl_3$** solvate salts (Figure 2). X-ray crystallography confirms that protonation has occurred on the O-atom of the cyclopentadienone ligand. As a consequence, the C(3)-O(3) interaction [1.335(6) and 1.339(9) Å for **[4a]$^+$** and **[4c]$^+$**, respectively] is considerably elongated compared to the parent neutral complexes [e.g., 1.246(13) Å for **3d**] and displays the character of a C(sp_2)-O single bond. In addition the Ru(1)-C(3) distance [2.323(5) and 2.319(7) Å for **[4a]$^+$** and **[4c]$^+$**, respectively] is shortened in respect to the parent complexes [e.g., 2.511(11) Å for **3d**] and comparable to the other Ru(1)-C(4-7) distances [2.227(5)- 2.290(5) Å, average 2.253(10) Å for **[4a]$^+$**; 2.271(8)- 2.221(7) Å, average 2.248(12) Å for **[4c]$^+$**]. Thus, the protonated ligand of **[4a]$^+$** and **[4c]$^+$** is better described as a η^5-cyclopentadienyl ligand, as previously reported for analogous complexes.[18d, 23] The O(3)-H(3) group of **[4a]$^+$** is involved in an inter-molecular H-bond with the $[CF_3SO_3]^-$ anion [O(3)-H(3) 0.885(10) Å, H(3)···O(301) 1.80(3) Å, O(3)···O(301) 2.626(5) Å, <O(3)H(3)O(301) 155(5)°]. Conversely, the O(3)-H(3) group of **[4c]$^+$** forms an intra-molecular H-bond with the O(6) atom of the side chain of the NHC ligand [O(3)-H(3) 0.84 Å, H(3)···O(6) 1.83 Å, O(3)···O(6) 2.646(7) Å, <O(3)H(3)O(6) 163.7°]. In addition, there is in **[4c]$^+$** also an inter-molecular H-bond between the O(6)-H(6) group of the complex and the $[CF_3SO_3]^-$ [O(6)-H(6) 0.84 Å, H(6)···O(301)#1 1.91 Å, O(6)···O(301)#1 2.739(9) Å, <O(6)H(6)O(301)#1 167.7°; symmetry transformations used to generate equivalent atoms: #1 x+1,y,z #2 -x+1,-y+1,-z+1]. The carbene interaction Ru(1)-C(34) [2.101(5) and 2.109(7) Å for **[4a]$^+$** and **[4c]$^+$**, respectively] is almost unchanged compared to the parent neutral complexes [e.g., 2.117(3) Å for **3d**].

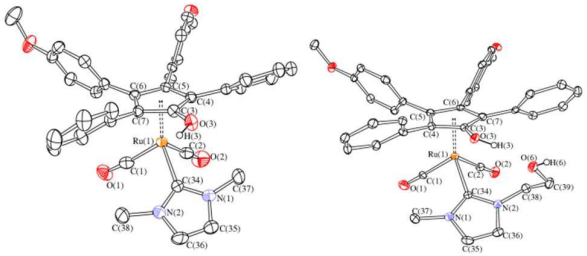
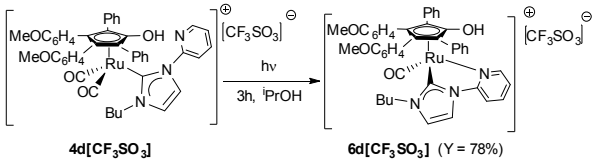


Figure 2. Left: ORTEP drawing of **[4a]$^+$**. Displacement ellipsoids are at the 30% probability level. H-atoms have been omitted for clarity, except H(3). Selected bond lengths (Å): Ru(1)-C(1) 1.882(7), Ru(1)-C(2) 1.881(7), Ru(1)-C(3) 2.323(5), Ru(1)-C(4) 2.290(5), Ru(1)-C(5) 2.238(5), Ru(1)-C(6) 2.227(5), Ru(1)-C(7) 2.256(5), Ru(1)-C(34) 2.101(5), C(3)-O(3) 1.335(6). Right: ORTEP drawing of **[4c]$^+$**. Displacement ellipsoids are at the 30% probability level. H-atoms have been omitted for clarity, except H(3) and H(6). Selected bond lengths (Å): Ru(1)-C(1) 1.876(8), Ru(1)-C(2) 1.901(9), Ru(1)-C(3) 2.319(7), Ru(1)-C(4) 2.262(7), Ru(1)-C(5) 2.240(7), Ru(1)-C(6) 2.221(7), Ru(1)-C(7) 2.271(8), Ru(1)-C(34) 2.109(7), C(3)-O(3) 1.339(9).

Finally, with the aim of allowing the coordination of the pyridine to the metal centre, complex **4d[CF_3SO_3]** has been irradiated with a UV lamp. The photolytic removal of one terminal CO led to the formation of the chelated complex **6d[CF_3SO_3]** in good yield (Scheme 3).



Scheme 3. Photolytic removal of terminal CO.

The IR spectrum shows the disappearance of the two absorptions due to the CO stretching of **4d[CF_3SO_3]**, and the appearance of a unique band at 1967 cm^{-1} (**6d[CF_3SO_3]**). Carbene resonance, in ^{13}C NMR spectrum, is shifted to lower fields (δ 185.63 ppm (**6d[CF_3SO_3]**) vs δ 166.07 ppm (**4d[CF_3SO_3]**).

The X-Ray molecular structure of **6d[CF_3SO_3]** further supports the characterization performed in solution (Figure 3) and consists of a Ru center coordinated to a η^5-cyclopentadienyl ligand, a terminal CO and a chelating NHC ligand bonded to Ru *via* the carbene and the N-atom of the pyridine side group. The Ru(1)-Cp distances [2.216(7)- 2.302(8) Å, average 2.248(16) Å] are comparable to those reported above for **[4a]$^+$** and **[4c]$^+$** and analogous Ru-complexes containing protonated cyclopentadienone ligands.[18d, 23] As in the case of **[4a]$^+$** and **[4c]$^+$**, the C(3)-O(3) interaction [1.338(9) Å] is a single bond, in view of the presence of a H atom on the oxygen, which is involved in H-bond with the triflate anion.

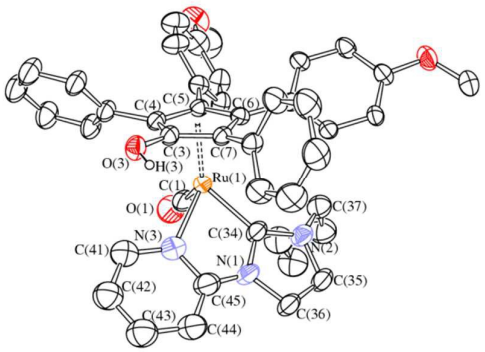


Figure 3. ORTEP drawing of **6d[CF_3SO_3]**. Displacement ellipsoids are at the 30% probability level. H-atoms have been omitted for clarity, except H(3). Selected bond lengths (Å): Ru(1)-C(1) 1.860(9), Ru(1)-C(3) 2.302(8), Ru(1)-C(4) 2.237(7), Ru(1)-C(5) 2.216(7), Ru(1)-C(6) 2.236(7), Ru(1)-C(7) 2.251(7), Ru(1)-C(34) 2.030(7), Ru(1)-N(3) 2.127(10), C(3)-O(3) 1.338(9).

It is worth mentioning that UV irradiation (3 h) of the neutral complexes **3a** and **3d** leaves the reactant unaltered indicating that the formal oxidation of Ru complex, upon protonation, favor the CO removal. The same result was surprisingly obtained with the cationic complexes **4a[CF_3SO_3]** and **5a[CF_3SO_3]**, for which CO release was expected (16 h of irradiation in ^{i}PrOH). Nonetheless irradiating **4a[CF_3SO_3]** and **5a[CF_3SO_3]**, in the presence of a trapping agent such as pyridine, the formation of the complexes **7[CF_3SO_3]** and **8[CF_3SO_3]** was finally observed (Figure 4) actually demonstrating that the CO release occurs in the cationic complexes. Indeed neutral complex **3a** did not lose CO under UV irradiation even in the presence of pyridine. It is thus likely that, in the case of cationic complexes, without the help of pyridine the removal of CO is an equilibrium in which ruthenium-CO bond is reformed at the end of the reaction leading to the recovery of the precursors **4a[CF_3SO_3]** and **5a[CF_3SO_3]**.

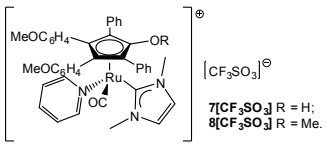


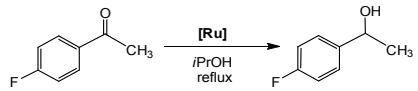
Figure 4. Molecular structure of **7[CF_3SO_3]** and **8[CF_3SO_3]**.

Formation of **7[CF_3SO_3]** and **8[CF_3SO_3]** is evidenced by the disappearance of the two carbonyl stretching bands associated to **4a[CF_3SO_3]** (2037, 1985 cm^{-1}) and **5a[CF_3SO_3]** (2045, 1995 cm^{-1}), with the concomitant appearance of a single band associated with the new complex **7[CF_3SO_3]** (1943 cm^{-1}) and **8[CF_3SO_3]** (1948 cm^{-1}) (Figure 4). Complexes **7[CF_3SO_3]** and **8[CF_3SO_3]** have been found in mixture with other species and their characterization was not complete. However the bathochromic shift observed in IR spectra is in agreement with the replacement of a strong π ligand with a σ N-donor ligand such as pyridine. Furthermore ESI-MS analyses performed on complexes **7[CF_3SO_3]** and **8[CF_3SO_3]** showed the presence of the molecular ions.

Catalytic transfer hydrogenation

The Ru complexes **3a-d**, **4a-d[X]** [(X = Cl, BF_4, NO_3, CF_3SO_3)] and **5a,d[CF_3SO_3]** were evaluated as catalyst precursors under transfer hydrogenation conditions *i.e.* refluxing ^{i}PrOH as hydrogen source employing 4-fluoroacetophenone as model substrate. Catalytic runs were performed to investigate the role of different additives in the activation of **3a-d**, to compare the catalytic activity of the ruthenium(0) complexes **3a-d** with the corresponding ruthenium(II) cationic complexes **4a-d[X]** and **5a,d[CF_3SO_3]** and finally to evaluate the influence of a pyridine substituent on the NHC side chain. Results are reported in Table 1: in all cases selectivity is complete and conversion corresponds to yield unless otherwise stated.

Table 1. Catalytic transfer hydrogenation of 4-fluoroacetophenone.[a]



entry	[Ru]	additive	conversion (%) 8 h	conversion (%) 24 h
1	**3a**	---	0	0
2	**3b**	---	0	0
3	**3c**	---	0	0
4	**3d**	---	0	0
5	**3a**	CAN[b]	25	61
6	**3a**[c]	CAN[b]	0	27
7	**3b**	CAN[b]	10	87
8	**3c**	CAN[b]	10	25
9	**3d**	CAN[b]	0	9
10	**3a**	$NaIO_4$[d]	0	0
11	**3a**	BQ[d]	25	55
12	**4a[CF_3SO_3]**	---	58	93
13	**4a[CF_3SO_3]**[c]	---	5	29
14	**4a[CF_3SO_3]**[e]	---	64	87
15	**4a[CF_3SO_3]**	KO^{t}Bu[d]	14	35
16	**4a[BF_4]**	---	41	71
17	**4a[Cl]**	---	16	24
18	**3a**	CF_3SO_3H[d]	32	>99[f]
19	**3a**	H_2SO_4[d]	45	92
20	**3a**	HNO_3[d]	60	65
21	**4b[CF_3SO_3]**	---	9	60
22	**4c[CF_3SO_3]**	---	35	46[g]
23	**4d[CF_3SO_3]**	---	84	>99
24	**4d[Cl]**	---	0	5
25	**4d[BF_4]**	---	37	40
26	**3d**	CF_3SO_3H[d]	84	>99[f]
27	**3d**	H_2SO_4[d]	76	86
28	**3d**	HNO_3[d]	0	36
29	**5a[CF_3SO_3]**	---	28	64
30	**5d[CF_3SO_3]**	---	10	13
31	**6d[CF_3SO_3]**	---	0	5
32	**HCF_3SO_3**	---	0	0

[a]General conditions: Ruthenium complex (5 mol% Ru), *i*PrOH (3 mL), reflux; conversions determined by ^{19}F NMR spectroscopy; [b]CAN 1 mol equiv. per ruthenium center; [c]catalyst loading reduced to 1 mol% Ru; [d]$NaIO_4$, BQ (benzoquinone), KO^{t}Bu and acids: 1 mol equiv. per ruthenium center; [e]recycling test; [f]yield ~70% the co-product arising from the acid catalyzed etherification of 4-fluoroacetophenol with the solvent 2-propanol; [g] yield ~ 35% the coproduct was not identified.

The neutral complexes **3a-d** did not present any catalytic activity in the absence of additives (entry 1-4), as well as by adding $NaIO_4$ (entry 10). However, we found that the addition of one equivalent of CAN (entry 5-9) results in the formation of active intermediates, likely deriving from the release of one CO ligand, favoured by oxidation as discussed in the previous section. In fact the use of benzoquinone, as oxidant additive under the same conditions (entry 11), activates the catalyst even though leading to a slightly lower conversion if compared with CAN.

Reduction of the catalyst loading to 1 mol% (**3a**) increases the induction time halving the conversion in 24 h (entry 5 vs 6). In general pre-catalysts **3a-d** resemble the behaviour of the triazolylidene ruthenium(0) congener, namely the dicarbonyl-(η^4-3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone)(1,3-dimethyl-4-phenyl-1,2,3-triazol-ylidene)ruthenium, previously tested as hydrogen transfer catalyst.[24]

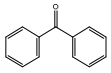
The oxidation state of the metal center appears to be the key point in order to activate the catalyst and indeed, better conversions are reached with the pre-catalysts **4a-d[X]** [(X = Cl, BF_4, NO_3, CF_3SO_3) (entries 12, 13, 16, 17, 21-25)]. A recycling test has been performed with **4a[CF_3SO_3]**, the catalyst can be reused although a slight decrease in conversion from 93 to 87% was observed after 24 h (entry 14). Noteworthy also the counterion shows to influence the catalytic activity, and $CF_3SO_3^-$ provides the best results: for example we observed complete conversion within 24 h in the case of **4a[CF_3SO_3]** and **4d[CF_3SO_3]** (entries 12, 23). Furthermore the latter pyridine-functionalized catalyst **4d[CF_3SO_3]** shows a faster activation if compared with **4a[CF_3SO_3]** (conversion of 84% and 58% respectively in 8 h). On the other hand, catalytic activity is suppressed in the case of **4a[Cl]** and **4d[Cl]** (entry 17, 24), possibly due to the coordinating ability of Cl^- counterion; on the contrary **4a[BF_4]** and **4d[BF_4]** give intermediate results (entry 16, 25).

The *in situ* addition of various acids such as HCF_3SO_3, H_2SO_4 and HNO_3 to **3a** and **3d** (entries 18-20, 26-28) produces, in the case of triflic acid, similar conversions as for the corresponding preformed catalysts (*e.g.* entry 23, **4d[CF_3SO_3]** vs entry 26, **3d** + CF_3SO_3H *in situ*). However, a lower selectivity is observed due to the acid catalyzed etherification of 4-fluorobenzylalcohol and isopropanol. Best *in situ* performances are accomplished by sulfuric acid (entries 19, 27), which gives much better results than HNO_3 (entry 20, 28), confirming the detrimental effect of the coordination ability of counterions. A base, such as KO^tBu, has a negative effect on the reaction (entry 15), likely due to deactivation of the pre-catalyst by deprotonation. Finally a blank experiment performed with HCF_3SO_3 in refluxing isopropanol rule out an exclusive role of the acid itself in the catalytic activity (entry 32).

With the aim of evaluating the role of the hydroxyl group in the catalytic reaction methylated complexes **5a[CF_3SO_3]** and **5d[CF_3SO_3]** have been also tested as catalysts (entry 29 and 30). Quite surprisingly, the methylated complex **5a[CF_3SO_3]** shows a remarkable catalytic activity although in the absence of the acidic OH. Worst performances came from the pyridine-functionalized methylated complex **5d[CF_3SO_3]**, probably due to a deactivation pathway associated with the formation of stable species in the chelated form. Indeed, no conversion is observed when the chelated cationic complex **6d[CF_3SO_3]** is employed as pre-catalyst (entry 31).

The substrate scope has been also evaluated extending the reactivity of **3a**, **4a[CF_3SO_3]** and **4d[CF_3SO_3]** as hydrogen transfer catalysts to acetophenone, benzophenone and benzaldehyde. Data are reported in Table 2. All the substrates are converted to the corresponding alcohol by activated **3a** and by the cationic complex **4a[CF_3SO_3]**. As expected the catalysts are much more active in the case of benzaldehyde (entry 7 and 9), since aldehydes are substrates more prone to reduction than ketones. Additionally, the scale of activity is consistent with the electron withdrawing properties of the ketones examined. Again, **4d[CF_3SO_3]** (entry 3, 6, 9) shows a faster activation. As an example, benzaldehyde reaches complete conversion within 4 h, that becomes 8 h in the case of **4a[CF_3SO_3]** (entry 9[c] vs 8).

Table 2. Catalytic transfer hydrogenation.[a]

entry	substrate	[Ru]	Additive[b]	Conv. (%) 8 h	Conv. (%) 24 h
1		**3a**	CAN	10	77
2		**4a[CF_3SO_3]**	---	15	68
3		**4d[CF_3SO_3]**	---	45	48
4		**3a**	CAN	0	42
5		**4a[CF_3SO_3]**	---	0	36
6		**4d[CF_3SO_3]**	---	42	43
7		**3a**	CAN	31	39
8		**4a[CF_3SO_3]**	---	>99	
9		**4d[CF_3SO_3]**	---	>99%[c]	

[a]Reaction conditions: [Ru] = 5 mol%, iPrOH (3mL), reflux. Conversions determined by GC; [b]CAN 1 mol equiv. per ruthenium center; c) Complete conversion is reached within 4 h.

Mechanistic insight

On the basis of the results described above, we can draw some considerations regarding the active catalytic species. First of all, the trapping experiments with pyridine (see cyclization of **4d[CF_3SO_3]** to **6d[CF_3SO_3]**, Scheme 3 and complexes **7[CF_3SO_3]** and **8[CF_3SO_3]**, Figure 4) demonstrates that CO release is involved in the activation, leaving unaltered the Ru-carbene bond. Indeed, all the crude products of catalytic reactions have been analyzed by IR and NMR spectroscopy and only in a couple of cases traces of Shvo catalyst, which would results from NHC ligand release, were visible in NMR spectra, accompanied by a very bright yellow color of the solution typical of Shvo complex.[18] Furthermore, an outer sphere mechanism is likely to be followed, in that the complex $[CpRu(CO)_2][CF_3SO_3]$, obtained by reaction between $[Cp_2Ru_2(CO)_4]$ with AgOTf, did not present any catalytic activity, supporting the role of hydroxycyclopentadienyl complex as a bifunctional catalyst. Noteworthy, in the case of **4d[CF_3SO_3]** the pyridine itself can be involved in the catalytic cycle as a cooperative ligand through the formation of the active catalyst **A** in which an hydride and two different acid hydrogens should be available for the hydrogen transfer. (Figure 5).

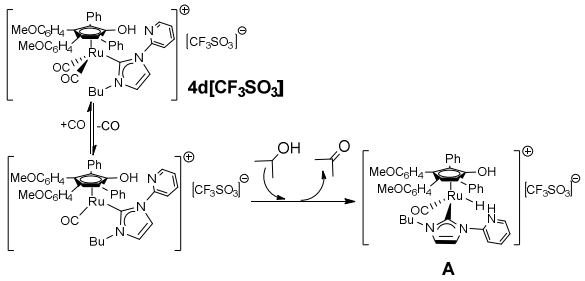


Figure 5. Proposed activation of the pre-catalyst **4d[CF_3SO_3]**.

Indeed, **4d[CF_3SO_3]** results to be the best pre-catalyst. Furthermore from the crude reaction mixture at the end of the reaction some resonances in the ^{1}H-NMR spectrum are detected in the hydride region: a singlet at δ -10.18 ppm is presumably associated with monomeric Ru-H species, while the signal at δ -14.95 ppm falls in the region of bridging hydrides (Ru-H-Ru). Even though we were not able to isolate these hydride species, in analogy with what observed in the synthesis of Shvo catalyst (δ RuHRu -18.80 ppm for the dimeric specie and δ -9.37 ppm for the monomeric one),[18d, 23] the formation of active hydride complexes containing the NHC ligand in place of a terminal CO reasonably occurs.

Labeling experiments on the reduction of 4-fluoroacetophenone with **4a[CF_3SO_3]** and **4d[CF_3SO_3]** in isopropanol-d_8 (see ESI for reaction conditions and spectra) lead to the formation of the corresponding deuterated alcohol further confirming the role of isopropanol as hydrogen source as well as the action of the catalysts in its activation.

With regard to **4c[CF_3SO_3]**, which in our experiments leads to the worst conversion after 24h and lower selectivity (Table 1, entry 22), its molecular structure (Figure 2, right side) evidences an hydrogen bond between the hydroxycyclopentadienyl ligand and the –OH group in the NHC side chain. Furthermore **4c[CF_3SO_3]**, upon CO release, would be prone to an intramolecular dehydrogenation, probably leading to the formation of an inactive catalyst. By comparing the behavior of **4c[CF_3SO_3]** with that of an iridium complex containing the NHC hydroxymethyl ligand which

lead to the formation of an [Ir(Cp*)(I)(NHC-CH_2C=O)] complex upon oxidation and cyclometallation[25] we can propose a similar reactivity for our ruthenium complex in agreement with the ν(CO) and ν(C=O) bands found at 1950 cm^{-1} and 1723 cm^{-1}.

Concerning monodentate NHC complexes **4a-c[X]** (X = Cl, BF_4, NO_3, CF_3SO_3) due to the absence of a *N*-containing side group able to be protonated, the active catalytic species has to be different from the proposed intermediate **A**. Once a vacant coordination site is formed by CO removal, proton abstraction from ^{i}PrOH should be performed by the counteranion $CF_3SO_3^-$ as external base, or by the oxygen of the -OH group (or -OMe group) on the catalyst itself, but at present we do not have any evidence to support such hypothesis.

Experimental

General

Solvents: dichloromethane (CH_2Cl_2), tetrahydrofuran (THF), diethyl ether (Et_2O), petroleum ether referring to a fraction of bp 60-80 °C, acetonitrile (CH_3CN) were dried and distilled prior to use. Acetone has been degassed and stored under inert atmosphere on molecular sieves. Other solvents such as ethylacetate (EtOAc), chloroform, ethanol (EtOH), methanol (MeOH), heptane, hexane, 2-propanol, $CDCl_3$, D_2O, CD_3CN (Sigma Aldrich) have been employed without further purification. Reagents: triruthenium-dodecacarbonil ($Ru_3(CO)_{12}$) (Strem), methyl iodide, silver oxide, 1-methylimidazole, 1-chlorobutane, 1-butylimidazole, 1-chloroethanol, 1,3 diphenylacetone, 4,4'dimethoxybenzil (Alfa Aesar), 2-bromopyridine, 4-fluoroacetophenone, acetophenone, benzophenone, benzaldehyde, dodecane, trifluoromethanesulfonic acid, tetrafluoroboric acid diethyl ether complex (Sigma Aldrich), chloridric, nitric and sulfuric acid, methyl trifluoromethanesulfonate, pyridine, cerium ammonium nitrate (CAN), benzoquinone, sodium periodate have been employed as purchased. 1,3-dimethylimidazolium iodide (**1a**),[26] 1-methyl-3-butyl-imidazolium chloride (**1b**), 1-methyl-3-(2-hydroxyethyl)imidazolium chloride (**1c**),[27] 1-butyl-3-(2-pyridinyl)-imidazolium bromide (**1d**)[28], 3,4-Bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone,[29] dicarbonyl(η^4-3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone) ruthenium dimer,[30] dicarbonyl-η^4-3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone)-1,3(dimethyl)-imidazol-2-ylidene)ruthenium (**3a**), dicarbonyl-η^4-3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone)-1-methyl-3-butyl-imidazol-2-ylidene)ruthenium (**3b**), dicarbonyl-η^4-3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-

dienone)-1-methyl-3-butyl-imidazol-2-ylidene)ruthenium (**3c**),[20] have been prepared as previously reported. The prepared derivatives were characterized by spectroscopic methods. The NMR spectra were recorded using Varian Inova 300 (^{1}H, 300.1; ^{13}C, 75.5 MHz), Varian Mercury Plus VX 400 (^{1}H, 399.9; ^{13}C, 100.6 MHz), Varian Inova 600 (^{1}H, 599.7; ^{13}C, 150.8 MHz) spectrometers at 298 K; chemical shifts were referenced internally to residual solvent peaks. Full ^{1}H- and ^{13}C-NMR assignments were done, when necessary, by gHSQC and gHMBC NMR experiments using standard Varian pulse sequences. Infrared spectra were recorded at 298 K on a Perkin-Elmer Spectrum 2000 FT-IR spectrophotometer. ESI-MS spectra were recorded on Waters Micromass ZQ 4000 with samples dissolved in MeOH or CH_3CN. Elemental analyses were performed on a Thermo-Quest Flash 1112 Series EA instrument. The conversions were monitored by GC analysis (Agilent Technologies 7890A GC system) and ^{19}F-NMR. UV irradiation was performed by using a commercial Hg lamp (365 nm, 125 W).

Synthesis of dicarbonyl-η^4-3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone) 1-(butyl-3-(2-pyridinyl)-imidazol-2-ylidene)ruthenium (3d)

A mixture of 1-butyl-3-(2-pyridinyl)-1H-imidazolium bromide (**1d**) 0.094g (0.33mmol), Ag_2O 0.092g (0.40mmol) and dicarbonyl(η^4-3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone) ruthenium dimer (**2**) 0.200g (0.16mmol) in dry CH_2Cl_2 were stirred in the dark under inert atmosphere at room temperature for 1h. Upon filtration on a celite pad and removal of the solvent the quantitative formation of the dicarbonyl-η^4-3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone) 1-(butyl-3-(2-pyridinyl)-imidazol-2-ylidene)ruthenium (**3d**) was verified by ^{1}H-NMR, ^{13}C-NMR, ESI-MS and X-Ray crystal structure. Suitable crystals were obtained by slow diffusion from toluene/hexane double layer ^{1}H-NMR (599.7 MHz, $CDCl_3$) δ (ppm): 8.36 (dd, 1H, CH_{py}), 7.60 (m, 4H, CH_{aryl}), 7.04-6.97 (m, 10H, CH_{aryl} + 1H, CH_{py} + 2H, CH_{NHC}), , 6.60-6.55 (m, 4H, CH_{aryl} + 1H, CH_{py}), 3.67 (s, 6H, -OCH_3), 3.54 (t, 2H, NCH_2), 1.46 (m, 2H, -CH_2CH_2-), 1.04 (m, 2H, -CH_2CH_3), 0.75 (t, 3H, -CH_3); ^{13}C-{^{1}H}NMR (150.8 MHz, $CDCl_3$) δ (ppm): 201.77 (CO), 173.20 ($C_{carbene}$), 168.22 (C_1=O, Cp), 158.41 (-*C*OCH_3), 152.16 (C_{ipso}), 148.11 (CH_{py}), 138.40 (CH_{py}), 135.17 (Cq_{aryl}), 133.45 (CH_{aryl}), 129.49 (CH_{aryl}), 127.43 (CH_{aryl}), 125.28 (Cq_{aryl}), 124.85 (CH_{aryl}), 124.54 (CH_{NHC}), 123.89 (CH_{py}), 122.43(CH_{NHC}), 121.82 (CH_{py}), 112.76 (CH_{aryl}), 103.10 ($C_{2,5}$, Cp), 79.69 ($C_{3,4}$, Cp), 54.98 (-OCH_3), 50.72 (NCH_2), 33.08, 19.41 (-CH_2CH_2), 14.11 (-CH_3); IR (CH_2Cl_2) ν(CO): 2008 cm^{-1}, 1949 cm^{-1}, ν(C=O) 1583 cm^{-1}, ν(C=C) 1609 cm^{-1}, 1518 cm^{-1}. ESI-MS (m/z) (+) = 804 [M+H]$^+$; 826 [M + Na] $^+$. Anal. Calcd (%) for $C_{45}H_{39}N_3O_5Ru$: C, 67.23; H, 4.89; N, 5.23. Found: C, 67.21; H, 4.87; N, 5.24.

Synthesis of [Dicarbonyl-η^5-3,4-bis(4-methoxyphenyl)-2,5-diphenylhydroxycyclopentadienyl)(1,3-dimethylimidazol-2-ylidene)ruthenium]trifluoromethanesulfonate (4a[CF_3SO_3])

Dicarbonyl-η^4-3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone)(1,3-dimethylimidazol-2-ylidene)ruthenium complex (**3a**) 0.100g (0.143mmol) was dissolved in 10 mL of CH_2Cl_2 under inert atmosphere. 1.2 equivalent of HCF_3SO_3 (solution at 0.98% in CH_2Cl_2) 1.55mL (0.172mmol) were subsequently added. The reaction mixture was stirred for 10 minutes at room temperature, then the solvent was removed under vacuum and the crude washed twice with 10 ml of Et_2O. The slightly brown solid obtained was identified as **4a[CF_3SO_3]** by IR, ^{1}H-NMR, ^{13}C-NMR, ^{19}F-NMR, ESI-MS. The yield was quantitative and suitable crystals for X-Ray diffraction analysis were prepared by toluene/hexane double layer. ^{1}H-NMR (599.7 MHz, $CDCl_3$) δ (ppm): 7.43 (m, 4H, CH_{aryl}), 7.27-7.01 (m, 10H, CH_{aryl}), 6.97 (s, 2H, CH_{NHC}), 6.65 (m, 4H, CH_{aryl}), 3.71 (s, 6H, -OCH_3), 3.27 (s, 6H, $NCH_{3,NHC}$); ^{13}C-{^{1}H}NMR (150.8 MHz, $CDCl_3$) δ (ppm): 199.64 (CO), 161.35 ($C_{carbene}$), 159.88 (-*C*OCH_3), 142.77 (C-OH, Cp), 133.86 (CH_{aryl}), 130.93 (CH_{aryl}), 129.07 (CH_{aryl}), 125.27 (Cq_{aryl}), 128.38 (Cq_{aryl}), 125.97 (CH_{aryl}), 121.40 (CH_{NHC}), 113.81 (CH_{aryl}), 104.85 ($C_{2,5}$, Cp), 87.90 ($C_{3,4}$, Cp), 55.55 (-OCH_3), 39.23 ($CH_{3,NHC}$). ^{19}F-NMR (282.4 MHz, $CDCl_3$) δ (ppm): -78.34 (CF_3SO_3). IR (CH_2Cl_2) ν(CO): 2037 cm^{-1}, 1985 cm^{-1}, ν(C=C) 1611 cm^{-1}, 1520 cm^{-1}. ESI-MS (m/z) (+) = 699 [M]$^+$; 149 [M]$^-$. Anal. Calcd (%) for $C_{39}H_{33}F_3N_2O_8RuS$: C, 55.18; H, 3.92; N, 3.30. Found: C, 55.14; H, 3.90; N, 3.32.

Synthesis of [Dicarbonyl-η5-3,4-bis(4-methoxyphenyl)-2,5-diphenylhydroxycyclopentadienyl)(1,3-dimethylimidazol-2-ylidene)ruthenium]chloride (4a[Cl])

Dicarbonyl-η^4-3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone)(1,3-dimethylimidazol-2-ylidene)ruthenium complex (**3a**) 0.023g (0.0330 mmol) was dissolved in 5 mL of CH_2Cl_2 under inert atmosphere. Two equivalent of HCl (aqueous solution at 37%, 0.005 mL, 0.0660 mmol) were subsequently added. The reaction mixture was stirred for 2h at room temperature, then the solvent was removed under vacuum and the crude washed twice with 10 ml of Et_2O . The slightly brown solid identified as **4a[Cl]** by IR, ^{1}H-NMR, ^{13}C-NMR, ESI-MS obtained in quantitative yield. ^{1}H-NMR (599.7 MHz, $CDCl_3$) δ (ppm): 7.57 (m, 4H, CH_{aryl}), 7.23-7.03 (m, 10H, CH_{aryl}), 6.93 (s, 2H, CH_{NHC}), 6.65 (m, 4H, CH_{aryl}), 3.71 (s, 6H, -OCH_3), 3.03 (s, 6H, $NCH_{3,NHC}$); ^{13}C-{^{1}H}NMR (150.8 MHz, $CDCl_3$) δ (ppm): 199.79 (CO), 162.42 ($C_{carbene}$), 159.24 (-*C*OCH_3), 144.52 (C-OH, Cp), 133.47 (CH_{aryl}), 130.95 (CH_{aryl}), 128.60 (CH_{aryl}), 128.18 (Cq_{aryl}), 125.35 (CH_{aryl}), 121.60 (CH_{NHC}), 113.24 (CH_{aryl}), 104.55 ($C_{2,5}$, Cp), 86.61 ($C_{3,4}$, Cp), 55.09 (-OCH_3), 39.22 ($CH_{3,NHC}$). IR (CH_2Cl_2) ν(CO): 2033 cm^{-1}, 1981 cm^{-1}, ν(C=C) 1611 cm^{-1}, 1520 cm^{-1}. ESI-MS (m/z) (+) = 699 [M]$^+$. Anal. Calcd (%) for $C_{38}H_{33}ClN_2O_5Ru$: C, 62.11; H, 4.53; N, 3.81. Found: C, 62.13; H, 4.55; N, 3.79.

Synthesis of [Dicarbonyl-η^5-3,4-bis(4-methoxyphenyl)-2,5-diphenylhydroxycyclopentadienyl)(1,3-dimethylimidazol-2-ylidene)ruthenium]tetrafluoroborato (4a[BF_4])

Dicarbonyl-η^4-3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone)(1,3-dimethylimidazol-2-ylidene)ruthenium complex (**3a**) 0.050g (0.072mmol) was dissolved in 10mL of CH_2Cl_2 under inert atmosphere. 1.2 equivalent of tetrafluoroboric acid diethyl ether complex

(0.012mL, 0.086mmol) were subsequently added. The reaction mixture was stirred for 1h at room temperature, then the solvent was removed under vacuum and the crude washed twice with 10 ml of Et_2O. The slightly brown solid identified as **4a[BF_4]** by IR, ^{1}H-NMR, ^{13}C-NMR, ^{19}F-NMR was obtained in quantitative yield. ^{1}H-NMR (599.7 MHz, $CDCl_3$) δ (ppm): 7.42 (m, 4H, CH_{aryl}), 7.31-7.03 (m, 10H, CH_{aryl}), 7.05 (s, 2H, CH_{NHC}), 6.68 (m, 4H, CH_{aryl}), 3.74 (s, 6H, -OCH_3), 3.29 (s, 6H, $NCH_{3,NHC}$); ^{13}C-{^{1}H}NMR (150.8 MHz, $CDCl_3$) δ (ppm): 199.06 (CO), 160.82 ($C_{carbene}$), 159.57 (-*C*OCH_3), 141.82 (C-OH, Cp), 133.43 (CH_{aryl}), 130.40 (CH_{aryl}), 128.80 (CH_{aryl}), 128.78 (C_{aryl}), 127.89 (C_{aryl}), 125.74 (CH_{aryl}), 120.80 (CH_{NHC}), 113.47 (CH_{aryl}), 104.31 ($C_{2,5}$, Cp), 87.51 ($C_{3,4}$, Cp), 55.15 (-OCH_3), 38.75 ($CH_{3,NHC}$); ^{19}F-NMR (282.4 MHz, $CDCl_3$) δ (ppm): -152.01 (BF_4). IR (CH_2Cl_2) ν(CO): 2038 cm^{-1}, 1987 cm^{-1}, ν(C=C) 1611 cm^{-1}, 1520 cm^{-1}. Anal. Calcd (%) for $C_{38}H_{33}BF_4N_2O_5Ru$: C, 58.09; H, 4.20; N, 3.57. Found: C, 58.11; H, 4.17; N, 3.58.

Synthesis of [Dicarbonyl-η^5-3,4-bis(4-methoxyphenyl)-2,5-diphenylhydroxycyclopentadienyl)(1-methyl-3-butyl-imidazol-2-ylidene)ruthenium]trifluoromethanesulfonate (4b[CF_3SO_3])

Dicarbonyl-η^4-3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone)(1-methyl-3-butyl-imidazol-2-ylidene)ruthenium complex (**3b**) 0.100g (0.135mmol) was dissolved in 10mL of CH_2Cl_2 under inert atmosphere. 1.2 equivalent of HCF_3SO_3 (solution at 0.98% in CH_2Cl_2 1.39 mL, 0.157mmol) were subsequently added. The reaction mixture was stirred for 1h at room temperature, then the solvent was removed under vacuum and the crude washed twice with 10 ml of Et_2O. The slightly brown solid identified as **4b[CF_3SO_3]** by IR, ^{1}H-NMR, ^{13}C-NMR and ^{19}F-NMR was obtained in quantitative yield. ^{1}H-NMR (599.7 MHz, $CDCl_3$) δ (ppm): 7.44 (m, 4H, CH_{aryl}), 7.28-7.02 (m, 10H, CH_{aryl}), 7.05 (2H, CH_{NHC}), 6.66 (m, 4H, CH_{aryl}), 3.72 (s, 6H, -OCH_3), 3.70(m, 2H, -NCH_2), 3.32 (s, 3H, $NCH_{3,\ NHC}$), 1.49 (m, 2H, -CH_2CH_2-), 0.97 (m, 2H, -CH_2CH_3), 0.77 (m, 3H, -CH_3); ^{13}C-{^{1}H}NMR (150.8 MHz, $CDCl_3$) δ (ppm): 199.27 (CO), 160.57 ($C_{carbene}$), 159.47 (-*C*OCH_3), 142.83 (C-OH, Cp), 133.43 (CH_{aryl}), 130.55 (CH_{aryl}), 128.60 (CH_{aryl}), 128.09 (C_{aryl}), 126.24 (C_{aryl}), 123.02 (CH_{aryl}), 121.01 (CH_{NHC}), 113.39 (CH_{aryl}), 104.42 ($C_{2,5}$, Cp), 87.45 ($C_{3,4}$, Cp), 55.13(-OCH_3), 50.81 (-NCH_2), 38.91 (-NCH_3), 32.97 (-CH_2CH_2-), 19.48 (-CH_2CH_3), 13.65(-CH_3); ^{19}F-NMR (282.4 MHz, $CDCl_3$) δ (ppm): -78.37. IR (CH_2Cl_2) ν(CO): 2035 cm^{-1}, 1984 cm^{-1}, ν(C=C) 1610 cm^{-1}, 1520 cm^{-1}. ESI-MS (m/z) (+) = 741[M]$^+$, 149 [M]$^-$. Anal. Calcd (%) for $C_{42}H_{39}F_3N_2O_8RuS$: C, 56.62; H, 4.38; N, 3.15. Found: C, 56.59; H, 4.37; N, 3.16.

Synthesis of [Dicarbonyl-η^5-3,4-bis(4-methoxyphenyl)-2,5-diphenylhydroxycyclopentadienyl)(1-methyl-3-(2-hydroxyethyl-imidazol-2-ylidene)ruthenium]trifluoromethanesulfonate (4c[CF_3SO_3])

Dicarbonyl-η^4-3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone)(1-methyl-3-(2-hydroxyethyl-imidazol-2-ylidene)ruthenium complex (**3c**) 0.050g (0.069mmol) was dissolved in 10 mL of CH_2Cl_2 under inert atmosphere. 1.2 equivalent of HCF_3SO_3 (solution at 0.98% in CH_2Cl_2 0.73 mL, 0.082mmol) were subsequently added. The reaction mixture was stirred for 1h at room temperature, then the solvent was removed under vacuum and the crude washed twice with 10 ml of Et_2O. The slightly brown solid identified as **4c[CF_3SO_3]** by IR, ^{1}H-NMR, ^{13}C-NMR, ^{19}F-NMR, ESI-MS was obtained in quantitative yield. Suitable crystals for X-Ray diffraction analysis were prepared by slow diffusion from CH_2Cl_2/Et_2O double layer. ^{1}H-NMR (399.9 MHz, $CDCl_3$) δ (ppm): 7.46 (m, 4H, CH_{aryl}), 7.30-7.03 (m, 10H, CH_{aryl}), 7.40 (s, 1H, CH_{NHC}), 7.01 (s, 1H, CH_{NHC}), 6.68 (m, 4H, CH_{aryl}), CH_2 not detected, (m, 2H,-NCH_2), 3.73 (s, 6H, -OCH_3), 3.24 (s, 3H, -NCH_3); ^{13}C-NMR (100.6 MHz, $CDCl_3$) δ (ppm): 206.97 (CO), 162.98 ($C_{carbene}$), 159.58 (-*C*OCH_3), 142.23 (C-OH, Cp), 133.41 (CH_{aryl}), 130.49 (CH_{aryl}), 128.84 (CH_{aryl}) 128.62 (C_{aryl}), 126.08 (C_{aryl}), 123.02 (CH_{aryl}), 120.75 (CH_{NHC}), 113.48 (CH_{aryl}), C_{aryl}, Cp not detected,, 58.43 (-NCH_2) , 55.14 (-OCH_3), 51.82 (-CH_2OH), 38.45 (-NCH_3); ^{19}F-NMR (282.4 MHz, $CDCl_3$) δ (ppm): -78.37. IR (CH_2Cl_2) ν(CO): 2038 cm^{-1}, 1988 cm^{-1}, ν(C=C) 1610 cm^{-1}, 1520 cm^{-1}. ESI-MS (m/z) (+) = 729 [M]$^+$, 149 [M]$^-$ Anal. Calcd (%) for $C_{40}H_{35}F_3N_2O_9RuS$: C, 54.67; H, 3.85; N, 3.19. Found: C, 54.68; H, 3.83; N, 3.22.

Synthesis of [Dicarbonyl-η^5-3,4-bis(4-methoxyphenyl)-2,5-diphenylhydroxycyclopentadienyl)(1-butyl-3-(2-pyridinyl)-imidazol-2-ylidene)ruthenium]trifluoromethanesulfonate (4d[CF_3SO_3])

Dicarbonyl-η^4-3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone)(1-butyl-3-(2-pyridinyl)-imidazol-2-ylidene)ruthenium complex (**3d**) 0.100g (0.124mmol) was dissolved in 10mL of CH_2Cl_2 under inert atmosphere. 1.2equivalent of HCF_3SO_3 (solution at 0.98% in CH_2Cl_2 1.35mL, 0.149mmol) were subsequently added. The reaction mixture was stirred for 15 minutes at room temperature, then the solvent was removed under vacuum and the crude washed twice with 10 ml of Et_2O. The slightly orange solid identified as **4d[CF_3SO_3]** by IR, ^{1}H-NMR, ^{13}C-NMR, ^{19}F-NMR, ESI-MS was obtained in quantitative yield. ^{1}H-NMR (599.7 MHz, CD_3CN) δ (ppm): 7.88 (m, 1H, CH_{py}), 7.38 (m, 1H, CH_{py}), 7.34 (m, 1H, CH_{py}), 7.28 (d, 1H, CH_{NHC}), 7.25 (d, 1H, CH_{NHC}), 7.23 (m, 1H, CH_{py}), 7.17-6.99 (m, 10H, CH_{aryl}), 6.78 (m, 4H, CH_{aryl}), 6.48 (m, 4H, CH_{aryl}), 3.70 (t, 2H, NCH_2), 3.68 (s, 6H, -OCH_3), 1.72 (m, 2H, -*CH*$_2$$CH_2$-), 1.19 (m, 2H, -*CH*$_2$$CH_3$), 0.88 (t, 3H, -$CH_3$); ^{13}C-{^{1}H}NMR (150.8 MHz, CD_3CN) δ (ppm): 199.59 (CO), 166.73 ($C_{carbene}$), 160.80 (-*C*OCH_3), 149.27 (C_{ipso}), 147.43 (CH_{py}), 144.94 (CH_{py}), 136.56 (C_1-OH, Cp), 134.52-114.29 (C_{aryl}), 127.93 (CH_{NHC}), 125.71 (CH_{py}), 125.13(CH_{py}), 121.95 (CH_{NHC}), 104.10($C_{2,5}$, Cp), 94.05 ($C_{3,4}$, Cp), 55.98 (-OCH_3), 52.87 (-NCH_2), 33.72 (-*C*H_2CH_2), 20.42 (-*C*H_2CH_3), 13.93 (-CH_3); ^{19}F-NMR (282.4 MHz, CD_3CN) δ (ppm): -79.33 (CF_3SO_3). IR (CH_2Cl_2) ν(CO): 2041 cm^{-1}, 1991 cm^{-1}, ν(C=C) 1610 cm^{-1}, 1520 cm^{-1}. ESI-MS (m/z) (+) = 804 [M]$^+$, 149 [M]$^-$. Anal. Calcd (%) for $C_{46}H_{40}F_3N_3O_8RuS$: C, 57.91; H, 4.23; N, 4.41. Found: C, 57.89; H, 4.22; N, 4.38.

Synthesis of [Dicarbonyl-η^5-3,4-bis(4-methoxyphenyl)-2,5-diphenylhydroxycyclopentadienyl)(1-butyl-3-(2-pyridinyl)-imidazol-2-ylidene)ruthenium]chloride (4d[Cl])

Dicarbonyl-η^4-3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone)(1-butyl-3-(2-pyridinyl)-

imidazol-2-ylidene)ruthenium complex (**3d**) 0.025g (0.031mmol) was dissolved in 5 mL of CH_2Cl_2 under inert atmosphere. Two equivalent of HCl (aqueous solution at 37%, 0.005mL, 0.061mmol) were subsequently added. The reaction mixture was stirred for 1h at room temperature, then the solvent was removed under vacuum and the crude washed twice with 10 ml of Et_2O. The slightly brown solid identified as **4d[Cl]** by IR, ^{1}H-NMR, ^{13}C-NMR obtained in quantitative yield. ^{1}H-NMR (599.7 MHz, CD_3CN) δ (ppm): 8.10 (m, 1H, CH_{py}), 7.69 (m, 1H, CH_{py}), 7.48 (d, 2H, CH_{NHC}), 7.45 (d, 2H, CH_{NHC}), 7.41-7.19 (m, 10H, CH_{aryl} + 2H, CH_{py}), 6.98 (m, 4H, CH_{aryl}), 6.65 (m, 4H, CH_{aryl}), 3.68 (t, 2H, -NCH_2), 3.69 (s, 6H, -OCH_3), 1.70 (m, 2H, -C$H_2$$CH_2$-), 1.14 (m, 2H, -C$H_2$$CH_3$), 0.84 (t, 3H, -$CH_3$); ^{13}C-{^{1}H}NMR (150.8 MHz, CD_3CN) δ (ppm): 199.73 (CO), 166.09 ($C_{carbene}$), 160.67 (-$C$$OCH_3$), 150.34 ($C_{ipso}$), 147.87 ($CH_{py}$), 143.52 ($CH_{py}$), 136.47 ($C_1$-OH, Cp), 134.62-114.23 (C_{aryl} + CH_{py}), 124.71 (CH_{NHC}), 122.13 (CH_{NHC}), 102.43 ($C_{2,5}$, Cp), 87.44 ($C_{3,4}$, Cp), 55.95 (-OCH_3), 52.65 (-NCH_2), 33.24 (-$C$$H_2$$CH_2$), 20.40 (-$CH_2$$CH_3$), 13.93 (-$CH_3$); IR ($CH_2Cl_2$) ν(CO): 2041cm^{-1}, 1992 cm^{-1}, ν(C=C) 1609 cm^{-1}, 1521 cm^{-1}. Anal. Calcd (%) for $C_{45}H_{39}ClN_3O_5Ru$: C, 64.43; H, 4.69; N, 5.01. Found: C, 64.40; H, 4.66; N, 5.02.

Synthesis of [Dicarbonyl-η^5-3,4-bis(4-methoxyphenyl)-2,5-diphenylhydroxycyclopentadienyl)(1-butyl-3-(2-pyridinyl)-imidazol-2-ylidene)ruthenium]tetrafluoroborate (4d[BF_4])

Dicarbonyl-η^4-3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone)(1-butyl-3-(2-pyridinyl)-imidazol-2-ylidene)ruthenium complex (**3d**) 0.050 g (0.062 mmol) was dissolved in 5 mL of CH_2Cl_2 under inert atmosphere. 1.2 equivalent of tetrafluoroboric acid diethyl ether complex (0.012mL, 0.086mmol) were subsequently added. The reaction mixture was stirred for 1h at room temperature, then the solvent was removed under vacuum and the crude washed twice with 10 ml of Et_2O. The slightly brown solid identified as **4d[BF_4]** by IR, ^{1}H-NMR, ^{19}F-NMR, ^{13}C-NMR, ESI-MS was obtained in quantitative yield. ^{1}H-NMR (599.7 MHz, CD_3CN) δ (ppm): 7.95 (m, 1H, CH_{py}), 7.49-7.16 (m, 10H, CH_{aryl} + 3H, CH_{py} + 2H, CH_{NHC}), 6.98 (m, 4H, CH_{aryl}), 6.69 (m, 4H, CH_{aryl}), 3.69 (s, 6H, -OCH_3), 3.67 (t, 2H, NCH_2), 1.75 (m, 2H, -C$H_2$$CH_2$-), 1.25 (m, 2H, -C$H_2$$CH_3$), 0.79 (t, 3H, -$CH_3$); ^{13}C-{^{1}H}NMR (150.8 MHz, CD_3CN) δ (ppm): 199.65 (CO), 166.30 ($C_{carbene}$), 160.78 (-$C$$OCH_3$), 151.52 ($C_{ipso}$), 149.07 ($CH_{py}$), 142.05 ($CH_{py}$), 134.63 ($C_1$-OH, Cp), 134.06-114.30 (C_{aryl}), 126.82 (CH_{NHC}), 124.74 (CH_{py}), 124.25 (CH_{py}), 122.20 (CH_{NHC}), 104.16($C_{2,5}$, Cp), 87.35 ($C_{3,4}$, Cp), 56.00 (-OCH_3), 52.84 (NCH_2), 33.21 (-$C$$H_2$$CH_2$-), 20.55 (-$C$$H_2$$CH_3$), 13.91 (-$CH_3$); ^{19}F-NMR (282.4 MHz, CD_3CN) δ (ppm): -151.63 (BF_4). IR (CH_2Cl_2) ν(CO): 2041 cm^{-1}, 1992 cm^{-1}, ν(C=C) 1609 cm^{-1}, 1521 cm^{-1}. Anal. Calcd (%) for $C_{45}H_{39}BF_4N_3O_5Ru$: C, 60.66; H, 4.41; N, 4.71. Found: C, 60.63; H, 4.40; N, 4.69.

Synthesis of [Dicarbonyl-η^5-3,4-bis(4-methoxyphenyl)-2,5-diphenylmethoxycyclopentadienyl)(1,3-dimethyl-imidazol-2-ylidene)ruthenium]trifluoromethanesulfonate (5a[CF_3SO_3])

Dicarbonyl-η^4-3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone)(1,3-dimethylimidazol-2-ylidene)ruthenium complex (**3a**) 0.100g (0.143mmol) was dissolved in 10 mL of CH_2Cl_2 under inert atmosphere. Three equivalent of $MeCF_3SO_3$ (0.048mL, 0.429 mmol) were subsequently added. The reaction mixture was stirred for 1h at room temperature, then the solvent was removed under vacuum and the crude washed twice with 10 ml of Et_2O. The slightly brown solid identified as **5a[CF_3SO_3]** by IR, ^{1}H-NMR, ^{13}C-NMR, ^{19}F-NMR, ESI-MS was obtained in quantitative yield. ^{1}H-NMR (599.7 MHz, CD_3CN) δ (ppm): 7.40-7.31 (m, 10H, CH_{aryl}), 7.13 (s, 2H, CH_{NHC}), 7.04 (m, 4H, CH_{aryl}), 6.66 (m, 4H, CH_{aryl}), 3.68 (s, 6H, -OCH_3), 3.43 (s, 6H, NCH_3), 2.99 (s, 3H, -OCH_3); ^{13}C-NMR (150.8 MHz, CD_3CN) δ (ppm): 199.52 (CO), 161.90 ($C_{carbene}$), 160.59 (-$C$$OCH_3$), 141.45 (C-$OCH_3$, Cp), 134.53 ($CH_{aryl}$), 132.34 ($CH_{aryl}$), 129.66 ($CH_{aryl}$), 129.28 ($C_{aryl}$), 128.24 ($C_{aryl}$), 126.22 ($CH_{aryl}$), 121.71 ($CH_{NHC}$), 114.04 ($CH_{aryl}$), 104.86 ($C_{2,5}$, Cp), 93.24 ($C_{3,4}$, Cp), 62.47 (-$OCH_3$, Cp), 55.87 (-$OCH_3$), 39.71 (-$NCH_3$); ^{19}F-NMR (282.4 MHz, CD_3CN) δ (ppm): -78.23. IR (CH_2Cl_2) ν(CO): 2045 cm^{-1}, 1995 cm^{-1}; ν(C=C) 1610 cm^{-1}, 1521 cm^{-1}. ESI-MS (m/z) (+) = 713 [M]$^+$; 149 [M]$^-$. Anal. Calcd (%) for $C_{40}H_{35}F_3N_2O_8RuS$: C, 55.68; H, 4.09; N 3.25. Found: C, 55.65; H, 4.07; N 3.27.

Synthesis of [Dicarbonyl-η^5-3,4-bis(4-methoxyphenyl)-2,5-diphenylmethoxycyclopentadienyl1-butyl-3-(2-pyridinyl)-imidazol-2-ylidene)ruthenium]trifluoromethanesulfonate (5d[CF_3SO_3])

Dicarbonyl-η^4-3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone)(1-butyl-3-(2-pyridinyl)-imidazol-2-ylidene)ruthenium complex (**3d**) 0.050g (0.072mmol) was dissolved in 10 mL of CH_2Cl_2 under inert atmosphere. Three equivalent of $MeCF_3SO_3$ (0.023mL, 0.216mmol) were subsequently added. The reaction mixture was stirred for 1h at room temperature, then the solvent was removed under vacuum and the crude washed twice with 10 ml of Et_2O. The slightly brown solid identified as **5d[CF_3SO_3]** by IR and ESI-MS was obtained in quantitative yield. . ^{1}H-NMR (599.7 MHz, CD_3CN) δ (ppm): 8.47 (m, 1H, CH_{py}), 7.87 (m, 1H, CH_{py}), 7.71 (m, 1H, CH_{py}), 7.65 (d, 1H, CH_{NHC}), 7.56 (d, 1H, CH_{NHC}), 7.46-6.59 (m, 18H, CH_{aryl} + 1H, CH_{py}), 3.69 (s, 6H, -OCH_3), 3.63 (t, 2H, NCH_2), 3.15 (s, 6H, -OCH_3, Cp), 1.52 (m, 2H, -C$H_2$$CH_2$-), 1.11 (m, 2H, -C$H_2$$CH_3$), 0.77 (t, 3H, -$CH_3$); ^{13}C-{^{1}H}NMR (150.8 MHz, CD_3CN) δ (ppm): 199.85 (CO), 167.40 ($C_{carbene}$), 160.61 (-$C$$OCH_3$), 150.52 ($C_{ipso}$), 149.56 ($CH_{py}$), 145.70 ($CH_{py}$), 140.66 ($C_1$-$OCH_3$, Cp), 134.60-114.14 ($C_{aryl}$), 127.56 ($CH_{NHC}$), 124.19 ($CH_{py}$), 121.64 ($CH_{py}$), 120.73 ($CH_{NHC}$), C_{aryl}, Cp not detected, 63.36 (-OCH_3, Cp), 55.93 (-OCH_3), 52.14 (-NCH_2), 33.04 (-$C$$H_2$$CH_2$), 20.15 (-$C$$H_2$$CH_3$), 14.01 (-$CH_3$); ^{19}F-NMR (282.4 MHz, CD_3CN) δ (ppm): -79.32 (CF_3SO_3). IR (CH_2Cl_2) ν(CO): 2045 cm^{-1}, 1996 cm^{-1}, ν(C=C) 1611 cm^{-1}, 1520 cm^{-1}. ESI-MS (m/z) (+) = 818 [M]$^+$; 149 [M]$^-$. Anal. Calcd (%) for $C_{47}H_{42}F_3N_3O_8RuS$: C, 58.32; H, 4.34; N, 4.34. Found: C, 58.30; H, 4.32; N, 4.35.

Synthesis of [Carbonyl-η^5-3,4-bis(4-methoxyphenyl)-2,5-diphenylmethoxycyclopentadienyl)(1-butyl-3-(2-pyridinyl)-imidazol-2-ylidene)ruthenium]trifluoromethanesulfonate (6d[CF_3SO_3])

[Dicarbonyl-η^5-3,4-bis(4-methoxyphenyl)-2,5-diphenylhydroxycyclopentadienyl)(1-butyl-3-(2-pyridinyl)-imidazol-2-ylidene)ruthenium]trifluoromethanesulfonate

(**4d[CF_3SO_3]**) was dissolved in 25 mL of ^{i}PrOH. The reaction mixture was irradiated under stirring for 3h, then the solvent was removed under vacuum and the crude washed twice with 20 mL of hexane. The brown solid was identified as 6 and obtained with an yield of 78 %. **6d[CF_3SO_3]** has been completely characterized by IR, ^{1}H-NMR, ^{13}C-NMR, ^{19}F-NMR, ESI-MS. Suitable crystals for X-Ray diffraction analysis were prepared by slow diffusion from CH_2Cl_2/hexane double layer. ^{1}H-NMR (599.7 MHz, $CDCl_3$) δ (ppm): 8.33 (d, 1H, CH_{py}), 8.27 (m, 1H, CH_{py}), 8.09 (m, 1H, CH_{py}), 7.04 (m, 4H, CH_{aryl}), 7.30-6.66 (m, 2H, CH_{NHC}+ 10H, CHaryl), 3.86 (m, 2H, NCH_2), 3.79 (s, 3H, -OCH_3), 3.74 (s, 3H, -OCH_3), 1.47 (m, 2H, -CH_2CH_2), 0.97 (m, 2H, -CH_2CH_3), 0.72 (t, 3H, -CH_3); ^{13}C-{^{1}H}NMR (150.8 MHz, $CDCl_3$) δ (ppm): 199.57 (CO), 185.63 ($C_{carbene}$), 159.30, 159.08 (-$COCH_3$), 154.60 (C_{ipso}), 153.34 (CH_{py}), 141.53 (C_1-OH, Cp), 138.08 (CH_{py}), 133.31-112.74 (C_{aryl} + CH_{NHC}), 97.38 ($C_{2,5}$, Cp), 84.34 ($C_{3,4}$, Cp), 55.21 (-OCH_3), 50.67 (NCH_2), 32.66, 19.35 (-CH_2CH_2), 13.56 (-CH_3); ^{19}F-NMR (282.4 MHz, CD_3CN) δ (ppm): -78.19 (CF_3SO_3); IR (CH_2Cl_2) ν(CO): 1967 cm^{-1}, ν(C=C) 1609 cm^{-1}, 1521 cm^{-1}; ESI-MS (m/z) (+) = 776 [M]$^{+}$, 149 [M]$^{-}$. Anal. Calcd (%) for $C_{45}H_{40}F_3N_3O_7RuS$: C, 58.37; H, 4.36; N, 4.54. Found: C, 58.35; H, 4.35; N, 4.51.

Synthesis of [Carbonyl-pyridin-η^5-3,4-bis(4-methoxyphenyl)-2,5-diphenylhydroxycyclopentadienyl)(1,3-dimethylimidazol-2-ylidene)ruthenium] trifluoromethanesulfonate (7[CF_3SO_3])

[Dicarbonyl-η^5-3,4-bis(4-methoxyphenyl)-2,5-diphenylhydroxycyclopentadienyl)(1,3-dimethylimidazol-2-ylidene)ruthenium]trifluoromethanesulfonate (**4a[CF_3SO_3]**) 0.060g (0.071mmol) and pyridine 0.023mL (0.283mmol) were dissolved in ^{i}PrOH (25 mL). The reaction mixture was irradiated under stirring for 6h and **7[CF_3SO_3]** identified from the reaction mixture by IR and ESI-MS. IR (CH_2Cl_2) ν(CO): 1943 cm^{-1}, ν(C=C) 1610 cm^{-1},1520 cm^{-1}. ESI-MS (m/z) (+) (CH_3CN) = 671 [M-py]$^{+}$, 643 [M-py-CO]$^{+}$

Synthesis of [Carbonyl-pyridin-η^5-3,4-bis(4-methoxyphenyl)-2,5-diphenylmethoxycyclopentadienyl)(1,3-dimethylimidazol-2-ylidene)ruthenium] trifluoromethanesulfonate (8[CF_3SO_3])

[Dicarbonyl-η^5-3,4-bis(4-methoxyphenyl)-2,5-diphenylmethoxycyclopentadienyl)(1,3-dimethyl-imidazol-2-ylidene)ruthenium]trifluoromethanesulfonato (**5a[CF_3SO_3]**) 0.050g (0.058mmol) and pyridine 0.023mL (0.232mmol) were dissolved in toluene (25 mL). The reaction mixture was irradiated under stirring for 18h and **8[CF_3SO_3]** identified from the reaction mixture by IR and ESI-MS. IR (CH_2Cl_2) ν(CO): 1948 cm^{-1}, ν(C=C) 1610 cm^{-1},1520 cm^{-1}. ESI-MS (m/z) (+) (MeOH) = 764 [M]$^{+}$; 149 [M]$^{-}$

General procedure for transfer hydrogenation

Complex (15 μmol, 5% mol), additive (1 eq. when needed) and *i*PrOH (3 mL) were stirred at reflux for 15 min. Then 4-fluoroacetophenone (36 μL, 300 μmol) was added and samples were taken at regular intervals. Aliquots (ca. 0.05mL) were diluted with $CDCl_3$ (0.5 mL) and conversions were determined by ^{19}F-NMR spectroscopy and GC analysis.

X-ray Crystallography.

Crystal data and collection details for **3d·0.5CH_2Cl_2**, **[4a][CF_3SO_3]·0.5toluene**, **[4c][CF_3SO_3]·$CHCl_3$** and **[6d][CF_3SO_3]** are reported in Table S1. The diffraction experiments were carried out on a Bruker APEX II diffractometer equipped with a CCD detector using Mo–Kα radiation. Data were corrected for Lorentz polarization and absorption effects (empirical absorption correction SADABS).[31] Structures were solved by direct methods and refined by full-matrix least-squares based on all data using F^2.[32] All hydrogen atoms were fixed at calculated positions and refined by a riding model, unless otherwise stated. All non-hydrogen atoms were refined with anisotropic displacement parameters.

3d·0.5CH_2Cl_2: The asymmetric unit of the unit cell contains one **3d** complex (on a general position) and half of a CH_2Cl_2 molecule disordered over two symmetry related (by 2) positions. The disordered solvent molecule has been refined isotropically. The crystals are non-merohedrally twinned. The TwinRotMat routine of PLATON[33] was used to determine the twinning matrix and to write the reflection data file (.hkl) containing the two twin components. Refinement was performed using the instruction HKLF 5 in SHELXL and one BASF parameter (0.291(8) after refinement). The Bu-group of the **3d** complex is disordered over two positions and has been refined isotropically using one occupancy factor per disordered group. Similar *U* restraints (SIMU line in SHELXL; s.u. 0.01) have been applied to C, N and O atoms. Restraints to bond distances were applied as follow (s.u. 0.02): 1.53 Å for C–C in the disordered Bu-group of **3d**; 1.75 Å for C–Cl in CH_2Cl_2. The Ph-rings have been constrained to fit regular hexagons (AFIX 66 line in SHELXL).

[4a][CF_3SO_3]·0.5toluene: The asymmetric unit of the unit cell contains two cations, two anions and one toluene molecule (all located in general positions). The H-atoms bonded to the O-atoms have been located in the Fourier map and refined using the 1.5 fold U_{iso} value of the parent atoms. The O-H distances have been restrained to 0.89 Å (s.u. 0.01). Similar *U* restraints (SIMU line in SHELXL; s.u. 0.01) have been applied to C and F atoms. The F-atoms have been restrained to isotropic behaviour (ISOR line in SHELXL, s.u. 0.01).

[4c][CF_3SO_3]·$CHCl_3$: The asymmetric unit of the unit cell contains two cations, two anions and two $CHCl_3$ molecules (all located in general positions). One $CHCl_3$ molecule is disordered over two positions and has been refined using one occupancy parameter per disordered group. The H-atoms bonded to the O-atoms have been initially located in the Fourier map and, then, refined by a riding model. The F-atoms have been restrained to isotropic behaviour (ISOR line in SHELXL, s.u. 0.01).

[6d][CF_3SO_3]: The asymmetric unit of the unit cell contains one cation and one anion (all located in general positions). The F and O atoms of the $CF_3SO_3^-$ anion are disordered and, thus, have been split and refined using one occupancy parameter per disordered group. The chelating NHC ligand in the cation is disordered and, thus, it has been split into two postions and refined using one occupancy parameter per disordered group.

The H-atoms bonded to the O-atoms have been initially located in the Fourier map and, then, refined by a riding model. Similar *U* restraints (SIMU line in SHELXL; s.u. 0.01) have been applied to C, N, F and O atoms. The C, N, O and F atoms of the disordered groups have been restrained to isotropic behaviour (ISOR line in SHELXL, s.u. 0.01). The Ph-rings have been constrained to fit regular hexagons (AFIX 66 line in SHELXL). Restraints to bond distances were applied as follow (s.u. 0.02): 1.53 Å for C–C in the Bu-group; 1.43 Å for $C(sp^3)$–O; 1.34 Å for $C(sp^2)$–O.

Conclusions

A series of cationic hydroxy- or methoxy-cyclopentadienyl ruthenium(II) *N*-heterocyclic carbene complexes have been prepared in quantitative yield upon protonation with strong acids or methylation with $MeCF_3SO_3$ of neutral ruthenium(0) complexes containing both the non-innocent cyclopentadienone ligand and variously functionalized NHCs. These novel complexes have been successfully employed as selective catalysts in transfer hydrogenation. The reaction is general and several substrates such as various ketones and aldehydes can be selectively reduced to the corresponding alcohol. The catalytic activity can thus be tuned by the proper choice of both substituents on NHC ligand and counterions. Neutral Ru(0) complexes **3a-d** need an oxidizing agent such as CAN or benzoquinone in order to be activated, while the corresponding cationic complexes **4a-d[X]** (X = Cl, BF_4, NO_3, CF_3SO_3) and **5a,d[CF_3SO_3]**, formally containing a Ru(II) center are more prone to release a CO ligand and do not need any additives to be activated. In the cationic complexes the counterion plays a non-innocent role and $CF_3SO_3^-$ showed the best outcome due to its coordinating ability.

Noteworthy the insertion of a pyridine substituent on the NHC side chain further improves the catalytic activity due to the presence of a second cooperative ligand containing a basic nitrogen.

With regard to the reaction mechanism CO release and its key role in the catalyst activation was demonstrated by trapping experiment with pyridine as well as by the UV-mediated formation of the chelated complex **6d[CF_3SO_3]**. Hydride species has been identified in the reaction mixture of the pyridine functionalized complex **4d[CF_3SO_3]** and the cooperative function of nitrogen- (pyridine in **4d[X]** and **5d[CF_3SO_3]**) and oxygen-containing ($CF_3SO_3^-$ or -OH and -OMe in **4a-c[X]** and **5a[CF_3SO_3]**) moieties with the vacancy on ruthenium prone to accept an hydride species has been drawn as consideration in order to explain ^{i}PrOH activation and subsequent active catalyst formation.

The versatility of NHC ligands which can be variously functionalized, together with the presence of the non-innocent cyclopentadienone open the way to the rational design of novel metal-ligand bifunctional catalysts liable to heterogenization and tunable solubility.

Acknowledgements

Authors wish to thank the University of Bologna and the FARB Project "Catalytic transformation of biomass-derived materials into high added-value chemicals", 2014-2015.

Notes and references

1 For reviews, see: a) F. E. Hahn and M. C. Jahnke, *Angew. Chem. Int. Ed.,* 2008, **47**, 3122; b) M. Melaimi, M. Soleilhavoup and G. Bertrand, *Angew. Chem. Int. Ed.,* 2010, **49**, 8810. c) L. Benhamou, E. Chardon, G. Lavigne, S. Bellemin-Laponnaz and V. Cesar, *Chem. Rev.*, 2011, **111**, 2705. d) L. A. Schaper, S. J. Hock, W. A. Herrmann and F. E. Kühn, *Angew. Chem. Int. Ed*., 2013, **52**, 270.

2 For selected reviews, see: a) D. Bourissou, O. Guerret, F. P. Gabbai and G. Bertrand, *Chem. Rev.,* 2000, **100**, 39; b) W. A. Herrmann, *Angew. Chem. Int. Ed.,* 2002, **41**, 1290; c) C. M. Crudden and D. P. Allen, *Coord. Chem. Rev*., 2004, **248**, 2247; d) M. Poyatos, J. A. Mata and E. Peris, *Chem. Rev.,* 2009, **109**, 3677; e) O. Schuster, L. Yang, H. G. Raubenheimer and M. Albrecht, *Chem. Rev.,* 2009, **109**, 3445; f) L. Mercs and M. Albrecht, *Chem. Soc. Rev*., 2010, **39**, 1903; (g) M. N. Hopkinson, C. Richter, M. Schedler and F. Glorius, *Nature*, 2014, **510**, 485; (h) S. P. Nolan, N-Heterocyclic Carbenes: Effective Tools for Organometallic Synthesis, 2014, Wiley VCH.

3 a) C. Samojlowicz, M. Bieniek and K. Grela, *Chem. Rev.,* 2009, **109**, 3708; b) S. Monfette and D. E. Fogg, *Chem. Rev.,* 2009, **109**, 3783; c) G. C. Vougioukalakis and R. H. Grubbs, *Chem. Rev.,* 2010, **110**, 1746.

4 a) E. A. B. Kantchev, C. J. O'Brien and M. G. Organ, *Angew. Chem. Int. Ed.,* 2007, **46**, 2768; b) G. C. Fortman, and S. P. Nolan, *Chem. Soc. Rev.,* 2011, **40**, 5151.

5 For examples, see: a) R. Corberan and E. Peris, *Organometallics,* 2008, **27**, 1954; b) A. Savini, G. Bellachioma, G. Ciancaleoni, C. Zuccaccia, D. Zuccaccia and A. Macchioni, *Chem. Commun.,* 2010, **46**, 9218; c) A. Petronilho, J. A. Woods, H. Mueller-Bunz, S. Bernhard and M. Albrecht, *Chem. Eur. J.,* 2014, **20**, 15775.

6 a) A. Fürstner and P. W. Davies, *Angew. Chem. Int. Ed.,* 2007, **46**, 3410; b) N. Marion and S. P. Nolan, *Chem. Soc. Rev.,* 2008, **37**, 1776; c) A. S. K. Hashmi, *Angew. Chem. Int. Ed.,* 2008, **47**, 6754.

7 a) S. Diez-Gonzalez, N. Marion and S. P. Nolan, *Chem. Rev.,* 2009, **109**, 3612; b) H. D. Velazquez and F. Verpoort, *Chem. Soc. Rev.,* 2012, **41**, 7032.

8 a) J. Witt, A. Pothig, F. E. Kuhn and W. Baratta, *Organometallics,* 2013, **32**, 4042; b) N. Gurbuz, E. O. Ozcan, I. Ozdemir, B. Cetinkaya, O. Sahin and O. Buyukgungor, *Dalton Trans*., 2012, **41**, 2330; c) S. Horn, C. Gandolfi and M. Albrecht, *Eur. J. Inorg. Chem*., 2011, 2863; d) S. Kuwata, and T. Ikariya, *Chem. Eur. J*., 2011, **17**, 3542; e) W. W. N. O, A. J. Lough and R. H. Morris, *Organometallics,* 2012, **31**, 2137.

9 a) C. Gandolfi, M. Heckenroth, A. Neels, G. Laurenczy and M. Albrecht, *Organometallics,* 2009, **28**, 5112; b) T. Wang, C. Pranckevicius, C. L. Lund, M. J. Sgro and D. W. Stephan, *Organometallics* 2013, **32**, 2168; c) B. Bagh and D. W. Stephan, *Dalton Trans.* 2014, **43**, 15638; via transfer hydrogenation: d) S. Horn and M. Albrecht *Chem. Commun.* 2011, **47**, 8802.

10 E. Fogler, E. Balaraman, Y. Ben-David, G. Leitus, L. J. W. Shimon and D. Milstein, *Organometallics,* 2011, **30**, 3826.

11 a) S. Urban, B. Beiring, N. Ortega, D. Paul and F. Glorius, *J. Am. Chem. Soc.,* 2012, **134**, 1541; b) J. Wysocki, N. Ortega and F. Glorius, *Angew. Chem. Int. Ed*., 2014, **53**, 8751.

12 B. Kang, Z. Fu and S. H. Hong, *J. Am. Chem. Soc*., 2013, **135**, 11704.
13 I. S. Makarov and R. Madsen*, J. Org. Chem*., 2013, **78**, 6593.
14 J. Balogh, A. M. Z. Slawin and S. P. Nolan, *Organometallics,* 2012, **31**, 3259.
15 a) A. Prades, E. Peris and M. Albrecht, *Organometallics,* 2011, **30**, 1162; b) A. Solvhoj and R. Madsen, *Organometallics,* 2011, **30**, 6044; c) D. Canseco-Gonzalez and M. Albrecht, *Dalton Trans*., 2013, **42**, 7424; d) M. Delgado-Rebollo, D. Canseco-Gonzalez, M. Hollering, H. Müller-Bunz and M. Albrecht, *Dalton Trans*. 2014, **43**, 4462; e) B. Bagh, A. M. McKinty, A. J. Lough and D. W. Stephan, *Dalton Trans*., 2014, **43**, 12842.
16 L. Bernet, R. Larlempuia, W. Ghattas, H. Mueller-Bunz, L. Vigara, A. Llobet and M. Albrecht, *Chem. Commun*., 2011, **47**, 8058.
17 a) J. A. Cabeza, M. Damonte and E. Perez-Carreno, *Organometallics,* 2012, **31**, 8355; b) J. A. Cabeza, M. Damonte, P. Garcia-Alvarez and E. Perez-Carreno, *Chem. Commun*. 2013, **49**, 2813; c) C. E. Ellul, M. F. Mahon, O. Saker and M. K. *Angew. Chem. Int. Ed*., 2007, **46**, 6343; d) L. Benhamou, J. Wolf, V. Cesar, A. Labande, R. Poli, N. Lugan, and G. Lavigne, *Organometallics,* 2009, **28**, 6981.
18 a) M. C. Warner, C. P. Casey and J.-E. Backvall, *Top. Organomet. Chem.,* 2011, **37**, 85; b) B. L. Conley, M. K. Pennington-Boggio, E. Boz and T. J. Williams, *Chem. Rev.,* 2010, **110**, 2294; c) T. Pasini, G. Solinas, V. Zanotti, S. Albonetti, F. Cavani, A. Vaccari, A. Mazzanti, S. Ranieri and R. Mazzoni, *Dalton Trans.*, 2014, **43**, 10224. d) C. Cesari, L. Sambri, S. Zacchini, V. Zanotti and R. Mazzoni *Organometallics* 2014, **33**, 2814 and reference cited therein.
19 H. Ohara, W. W. N. O, A. J. Lough and R. H. Morris, *Dalton Trans.*, 2012, **41**, 8797.
20 C. Cesari, S. Conti, S. Zacchini, V. Zanotti, M. C. Cassani and R. Mazzoni, *Dalton Trans*., 2014, **43**, 17240.
21 H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen and R. Taylor, *J. Chem. Soc., Perkin Trans.*, 1987, **2**, S1-S19.
22 J. A. Cabeza and P. Garcia-Alvarez, *Chem. Soc. Rev.*, 2011, **40**, 5389.
23 a) Y. Shvo, D. Czarkie, Y. Rahamim and D. F. Chodosh, *J. Am. Chem. Soc.*, 1986, **108**, 7400; b) C. P. Casey, S. W. Singer, D. R. Powell, R. K. Hayashi and M. Kavana, *J. Am. Chem. Soc.*, 2001, **123**, 1090; c) L. K. Thalen, D. Zhao, J.–B. Sortais, J. Paetzold, C. Hoben and J.-E. Backwall, *Chem. –Eur. J.*, 2009, **15**, 3402.
24 C. Cesari, R. Mazzoni, H. Müller-Bunz and M. Albrecht, *J. Organomet. Chem*., 2015, **793**, 256.
25 M. Benìtez, E. Mas-Marzà, J. A. Mata and E. Peris, *Chem*.–*Eur. J*., 2011, **17**, 10453.
26 a) A. M. Oertel, V. Ritleng, L. Burr, C. Harwig and M. J. Chetcuti, *Organometallics,* 2011, **30**, 6685; b) L. B. Benac, E. M. Burgess, L. Burr and A. J. Arduengo, *Organic Syntheses, Coll*., 1990, **7**, 195; 1986, **64**, 92.
27 L. C. Branco, J. N. Rosa, J. J. Moura Ramos and C. A. M. Afonso, *Chem. Eur. J.*, 2002, **8**, 3671.
28 J. A. Loch, M. Albrecht, E. Peris, J. Mata, J. W. Faller and R. H. Crabtree, *Organometallics* 2002, **21**, 700.
29 M. Boiani, A. Baschieri, C. Cesari, R. Mazzoni, S. Stagni, S. Zacchini and L. Sambri, *New. J. Chem*. 2012, **36**, 1469.
30 Y. Mum, D. Czarkle, Y. Rahamlm and Y. Shvo, *Organometallics*, 1985, **4**, 1461.
31 G. M. Sheldrick, *SADABS*, Program for empirical absorption correction, University of Göttingen, Germany, 1996.
32 G. M. Sheldrick, *SHELX97*, Program for crystal structure determination, University of Göttingen, Germany, 1997.
33 A. L. Spek, PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, 2005.