Imidazolium Salts of Ruthenium Anionic Cyclopentadienone Complexes: Ion Pair for Bifunctional Catalysis in Ionic Liquids

Imidazolium salts of ruthenium anionic cyclopentadienone complexes: ion pair for bifunctional catalysis in ionic liquids

Cristiana Cesari, Andrea Cingolani, Martina Teti, Alessandro Messori, Stefano Zacchini, Valerio Zanotti* and Rita Mazzoni*

Abstract

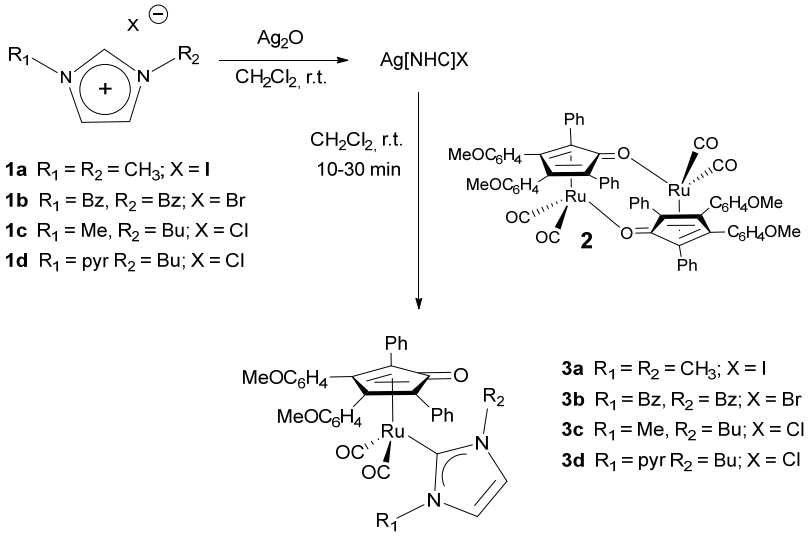
The reactivity of the dinuclear complex dicarbonyl(η^4-3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone (**2**) with imidazolium salts has been studied using a library of variously functionalized imidazolium salts, and leading to a class of ruthenium anionic complexes of the type [dicarbonyl(η^4-3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone)(halide)Ru][1,3-disubsittuted-imidazolium] (**4**) in the form of ion pair with imidazolium. The reaction is clean, general and quantitative and the complexes formed are stable to air and moisture both in the solid state and in solution. The ionic complexes **4** show affinity for ionic liquids and represent stable precursors of a catalytic active species, likely similar to those generate from Shvo catalyst, a well-established homogeneous bifunctional catalyst for hydrogen transfer. Our approach allows the use of green ionic liquids (IL) as solvents, providing better control of catalytic reactions involving **4**, and easier catalyst recycle. IL-supported ionic pair catalysts exhibit interesting catalytic activity (up to >99% of conversion) in the transfer hydrogenation of a model compound such as 4-fluoroacetophenone. The IL-supported redox catalysts can be also recycled exploiting the biphasic nature of the system. The synthetic method here discussed represents a novelty within the field of IL-supportation and is potentially useful for the heterogenization of the catalysts.

Introduction

Over the past decade, ionic liquids (ILs) have gained wide recognition in the field of green organic synthesis in that they can act as environmentally benign solvents and also support various chemical processes.[1] Initially introduced as alternative green reaction media in organic synthesis because of their unique properties (e.g. low volatility, non-flammability, thermal and chemical stability,

controlled miscibility), ILs have had a revolutionary impact in a number of fields including: analytical chemistry, electrochemistry, polymer chemistry, nanotechnology and biotechnology, energy[2] and catalysis.[3] Reactions which have been successfully performed in ILs include hydrogenation and oxidation.[3] However, redox reactions mediated by bifunctional catalysts, such as homogeneous transfer hydrogenation[4] and dehydrogenation, which are of great interest, particularly in the field of bio-refinery,[5] have been scarcely investigated with respect to the use of ILs.

In previous works, ruthenium complexes that combine cyclopentadienone and NHC ligands have been described together with their properties as redox bifunctional catalysts. [7] Their preparation is recalled in Scheme 1. The imidazolium salts (e.g. compounds **1a-d**), which are precursors of NHC ligands, can be easily functionalized, providing an effective way to control the steric and electronic properties, and the solubility of the resulting NHCs complexes. Furthermore, by design of proper substituents, the NHC ligand itself is potentially able to cooperate with the metal and behave as non-innocent species.[7b,8]



Scheme 1 Synthesis of cyclopentadienone imidazolylidene ruthenium(0) complexes **3a–d**.

During our study on the reactivity of imidazolium salts with the dinuclear ruthenium carbonyl cyclopentadienone **2**, aimed at obtaining new ruthenium NHC complexes, we observed the formation of a novel class of anionic Ru complexes behaving as ILs. Anionic complexes bearing an imidazolium as counterion are uncommon in the literature, even though they might have interesting properties and,

in a few cases, have been exploited in catalysis,[9] and medicinal chemistry.[10] To the best of our knowledge, they have never been employed in transfer hydrogenation. On the other hand, several ionic tagged complexes have been designed in order to obtain catalysts soluble in ionic liquids for ILs-supported catalysis, resulting in simplified procedures for separation of the products and catalyst reuse.[11]

Herein we report on the synthesis and characterization of a class of ion paired ruthenium complexes **4**, consisting in the anion $[Ru(CO)_2\{C_5(C_6H_4OMe)_2(Ph)_2{=}O\}(X)]^-$ (X = halide or trifluoromethanesulfornate) and cation $[R_1ImR_2]^+$ ($[R_1ImR_2]^+$ = disubstituted imidazolium), soluble in ionic liquids such as [BMIM][PF_6] (BMIM = 1-n-butyl-3-methylimidazolium). The easy and quantitative synthetic approach for obtaining complexes **4** was extended to a number of variously encumbered and functionalized imidazolium salts, resulting in the formation of a family of complexes potentially good candidates for biphasic catalytic applications in ILs. Catalytic activity and recycling ability of the ILs-supported catalysts on the reduction of 4-fluoroacetophenone are presented and discussed.

Results and discussion

Synthesis and structures of ruthenium complexes

The reactivity of the dinuclear complex **2** with imidazolium salts has been explored using a library of variously functionalized imidazolium salts, prepared according to literature procedures (Figure 1).

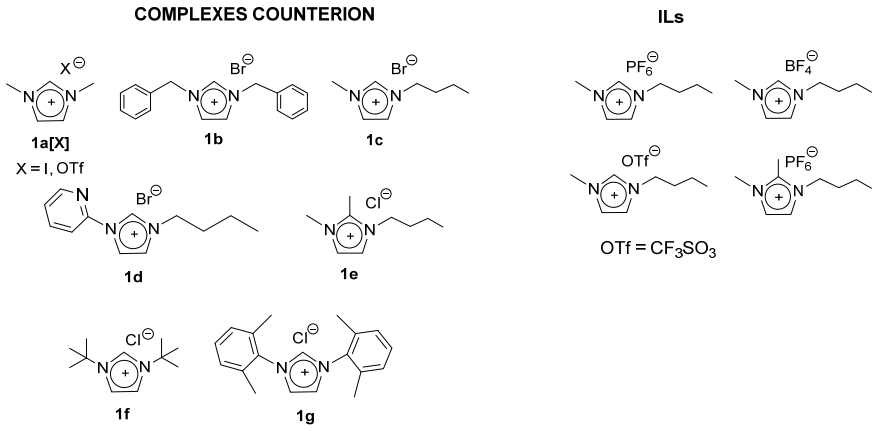
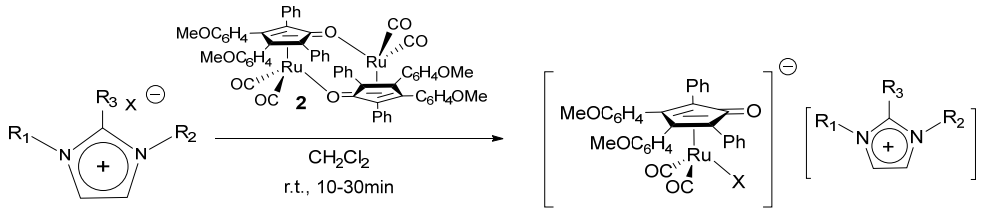


Figure 1 Imidazolium salts employed in this work: complexes counterion and Ionic Liquids (ILs).

Imidazolium salts **1a–g** were reacted directly with the dimeric precursor dicarbonyl(η^4-3,4-bis-(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone) (**2**). A quantitative and instantaneous reaction leads to the formation of the ionic pairs **4a–g** consisting of the imidazolium cation and Ru(0) anionic complexes (Scheme 2). These latter are obtained upon the coordination of the imidazolium counterion X^- (X = Cl, Br, I, SO_3CF_3) to the 16 electron ruthenium mononuclear intermediate, which is generated as soon as the dimer is dissolved in organic solvents such as CH_2Cl_2.



1a[X] $R_1 = R_2 = CH_3$; R_3=H; X = I, CF_3SO_3
1b R_1 = Bz, R_2 = Bz; R_3=H; X = Br
1c R_1 = Me, R_2 = Bu; R_3=H; X = Br
1d R_1 = pyr, R_2 = Bu; R_3=H; X = Br
1e R_1 = Me, R_2 = Bu; R_3=Me; X = Cl
1f R_1 = ^{t}Bu, R_2 = ^{t}Bu; R_3=H; X = Cl
1g R_1 = 2,5-$C_6H_3(Me)_2$, R_2 = 2,5-$C_6H_3(Me)_2$; X = Cl

4a[X] $R_1 = R_2 = CH_3$; R_3=H; X = I, CF_3SO_3
4b R_1 = Bz, R_2 = Bz; R_3=H; X = Br
4c R_1 = Me, R_2 = Bu; R_3=H; X = Br
4d R_1 = pyr, R_2 = Bu; R_3=H; X = Br
4e R_1 = Me, R_2 = Bu; R_3=Me; X = Cl
4f R_1 = ^{t}Bu, R_2 = ^{t}Bu; R_3=H; X = Cl
4g R_1 = 2,5-$C_6H_3(Me)_2$, R_2 = 2,5-$C_6H_3(Me)_2$; X = Cl

Scheme 2 Synthesis of cyclopentadienone ruthenium(0) complexes ion paired to imidazolium salts **4a–g**.

The reaction outcome has to be compared to that shown in Scheme 1: in the absence of the transmetallation step provided by the silver NHC intermediate, the imidazolium salts act as a source of halide instead of carbene ligand, generating complexes **4** in the place of **3**. It is also worth noting that complex **4a[I],** upon treatment with Ag_2O in CH_2Cl_2 solution, converts to **3a** by transmetallation, and that precipitation of AgI is observed, as expected.

The reaction shown in Scheme 2 has a general character, involving both bulky and not-hindered imidazolium salts, and is tolerant to functional groups, in that it also occurs in the presence of pyridine (**1d** to **4d**). It proceeds with the halide anion of the starting imidazolium salt, as well as with trifluoromethanesulfonate. On the other hand, the reaction does not occur with NTf_2^- (bis(trifluoromethylsulfonyl)imide) as counterion, probably due to its peculiar coordination properties.[12] The synthesis of **4a–g** can be followed by IR spectroscopy, observing the lowering in νCO stretching frequencies (e.g. **4a**: ν(CO) = 2004, 1945 cm^{-1} vs. **2**: 2018, 1967 cm^{-1}), which is

consistent with the anionic nature of the complexes. This observation is confirmed by the C=O distance in the X-Ray diffraction structures of **4e** and **4f** [1.240(3) and 1.227(8) Å, respectively]. An η^4 coordination of the cyclopentadienone is thus reasonable and the negative charge on the metal together with the π-donor nature of chloride and congeners allow more back-bonding toward the CO ligands (Figure 2 and 3). ESI-MS data show the molecular anion $[Ru(CO)_2\{C_5(C_6H_4OMe)_2(Ph)_2=O\}(X)]^-$ and the molecular cation $[R_1ImR_2]^+$ (see experimental).

The solid state structures of **4e** and **4f** are composed of $[\{2,5\text{-}Ph_2\text{-}3,4\text{-}(p\text{-}MeO\text{-}C_6H_4)_2(\eta^4\text{-}C_4C{=}O)\}Ru(CO)_2Cl]^-$ complex anions and imidazolium $[1\text{-}R\text{-}3\text{-}R'\text{-}C_3N_2H_2R'']^+$ (R = Me, R' = ^{n}Bu, R'' = Me **4e**; R = ^{t}Bu, R' = ^{t}Bu, R'' = H **4f**) cations. The cations display structures similar to those previously reported with other anions.[13] The molecular structures of the $[\{2,5\text{-}Ph_2\text{-}3.4\text{-}(p\text{-}MeO\text{-}C_6H_4)_2(\eta^4\text{-}C_4C{=}O)\}Ru(CO)_2Cl]^-$ anions are closely related to the neutral $\{2,5\text{-}Ph_2\text{-}3.4\text{-}(p\text{-}MeO\text{-}C_6H_4)_2(\eta^4\text{-}C_4C{=}O)\}Ru(CO)_2(L)$ (L = NHC carbene ligand) complexes, for what concerns the coordination of the cyclopentadienone ligand.[6,7] In particular, the Ru(1)-C(3) distance [2.485(2) and 2.502(7) Å for **4e** and **4f**, respectively] is significantly longer than Ru(1)-C(4-7) [2.179(2)-2.262(2) Å, average 2.210(4) Å for **4e**; 2.149(7)-2.267(6) Å, average 2.213(12) Å for **4f**] as previously found in other complexes where the cyclopentadienone ligand is essentially η^4-coordinated to Ru.[14] For comparison, the same Ru-C contact is shortened to 2.32-2.34 Å in the case of Ru-complexes containing η^5-cyclopentadienone derived ligands.[7,15] In agreement with the above η^4-coordination, the C(3)-O(3) contact [1.240(3) and 1.227(8) Å] is essentially a double bond.

It must be remarked that in the solid state structure of **4f**, a C-H···O inter-molecular contact is present involving the C(41)-H(41) group of the imidazolium cation and the O(3) atom of the cyclopentadienone ligand of the anion [C(41)-H(41) 0.93 Å, H(41)···O(3) 2.49 Å, C(41)···O(3) 3.381(9) Å, <C(41)H(41)O(3) 159.8° for **4f**; see Figure S17 in Supporting Information. The most relevant bond lengths and angles relative to the structures of **4e** and **4f** are summarized in Table 1.

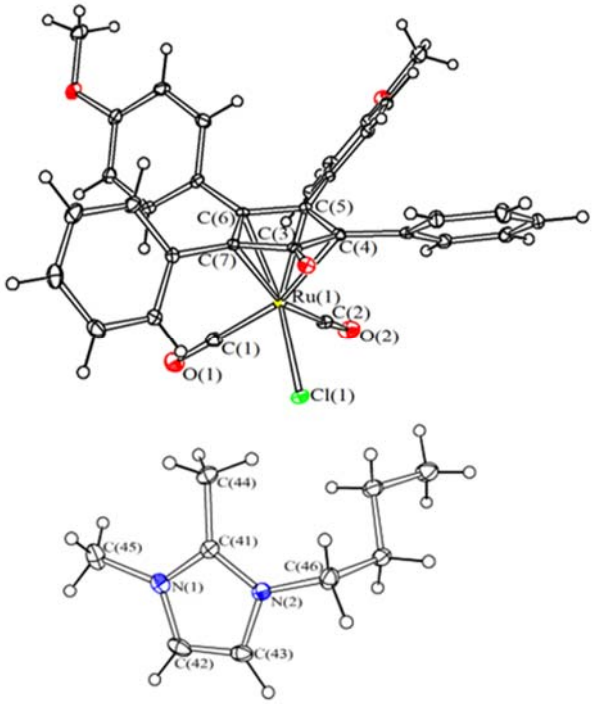


Figure 2 ORTEP drawing of the cation and anion of **4e**. Displacement ellipsoids are at the 30% probability level.

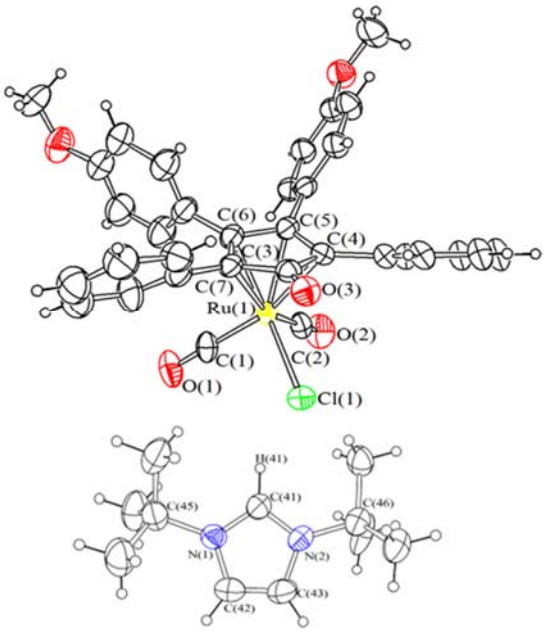


Figure 3 ORTEP drawing of the cation and anion of **4f**. Displacement ellipsoids are at the 30% probability level.

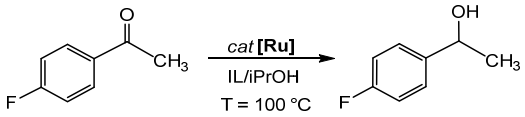
Table 1 Selected bond lengths (Å) and angles (deg) for **4e** and **4f**.

	4e	**4f**
Ru(1)-C(1)	1.876(2	1.866(8)
Ru(1)-C(2)	1.884(2)	1.873(8)
Ru(1)-Cl(1)	2.4519(6)	2.4464(17)
Ru(1)-C(3)	2.485(2)	2.502(7)
Ru(1)-C(4)	2.262(2)	2.253(6)
Ru(1)-C(5)	2.192(2)	2.186(7)
Ru(1)-C(6)	2.179(2)	2.149(7)
Ru(1)-C(7)	2.209(2)	2.267(6)
C(1)-O(1)	1.145(3)	1.155(8)
C(2)-O(2)	1.147(3)	1.158(8)
C(3)-O(3)	1.240(3)	1.227(8)
C(3)-C(4)	1.477(3)	1.495(9)
C(4)-C(5)	1.444(3)	1.438(9)
C(5)-C(6)	1.431(3)	1.443(9)
C(6)-C(7)	1.450(3)	1.450(9)
C(7)-C(3)	1.471(3)	1.461(9)
C(41)-N(1)	1.334(3)	1.324(8)
C(41)-N(2)	1.337(3)	1.298(8)
N(1)-C(42)	1.374(4)	1.351(9)
N(2)-C(43)	1.387(3)	1.370(10)
C(42)-C(43)	1.337(4)	1.302(12)
C(41)-C(44)	1.474(3)	-
O(3)-C(3)-C(4)	127.9(2)	128.0(6)
O(3)-C(3)-C(7)	127.0(2)	127.2(6)
C(7)-C(3)-C(4)	104.86(18)	104.4(6)
C(3)-C(4)-C(5)	107.72(19)	108.5(6)
C(4)-C(5)-C(6)	108.71(19)	108.0(6)
C(5)-C(6)-C(7)	107.76(19)	107.9(6)
C(6)-C(7)-C(3)	108.03(19)	109.3(6)
N(1)-C(41)-N(2)	107.9(2	110.1(6)
C(41)-N(2)-C(43)	108.2(2)	107.4(7)
C(41)-N(1)-C(42)	109.2(2)	106.2(6)
N(2)-C(43)-C(42)	107.5(2)	107.0(7)
N(1)-C(42)-C(43)	107.1(2)	109.2(8)

Catalytic transfer hydrogenation

The ruthenium complexes **4a[I]** and **4a[CF_3SO_3]** have been evaluated as catalyst precursors using ionic liquids as reaction solvents under transfer hydrogenation conditions (*i.e.* employing ^{i}PrOH as hydrogen source and 4-fluoroacetophenone as model substrate). The reaction products, extracted from the crude with diethyl ether, have been analyzed by gas chromatography (GC). Preliminary catalytic runs have been performed in order to investigate the catalytic activity of the ruthenium ionic complexes in non-conventional media; results and comparison with the neutral ruthenium complex **3a** in ionic liquid [BMIM][PF_6] are reported in Table 2.

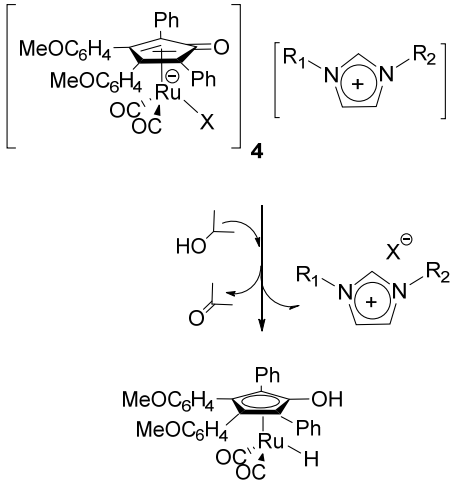
Table 2. Catalytic transfer hydrogenation of 4-fluoroacetophenone.[a]



entry	[Ru]	solvent (IL)	Conversion 3h (%)	Conversion 6h (%)	Conversion 24h (%)
1	**3a**	[BMIM][PF_6]	0	0	0
2	**4a[I]**	[BMIM][PF_6]	49	69	75
3	**4a[CF_3SO_3]**	[BMIM][PF_6]	45	63	72
4	**4a[I]**	[BMIM][BF_4]	33	54	57
5	**4a[I]**	[BDMIM][PF_6]	53	75	81
6	**4a[I]**	[BMIM][OTf][b]	50	67	73
7	**4a[I][c]**	-	27	53	78
8	**4a[CF_3SO_3][c]**	-	23	40	76

[a]General conditions: Ruthenium complex (5 mol% Ru), ionic liquid (2 mL), *i*PrOH (2 mL), T = 100°C; conversions determined by ^{19}F NMR spectroscopy. The reaction is selective, thus conversion of the ketone corresponds to the yield of the alcohol; [b] OTf = CF_3SO_3; [c] Reaction performed in absence of IL: ruthenium complex (5 mol% Ru), *i*PrOH (4 mL), reflux.

The neutral complex **3a** did not show any catalytic activity even in ionic liquid media (entry 1), as already stated in the case of the organic solvent 2-propanol.[7] By contrast, the ionic complexes **4** show a good catalytic activity. This behavior might be explained by the fact that the neutral complexes **3** need to release a CO ligand in order to generate a 16 electron unsaturated species, which is supposed to be the active catalytic intermediate, and this step is not easily accomplished.[7] Conversely, in the anionic complexes **4** the release of iodide or $CF_3SO_3^-$, as imidazolium counterion, would more easily lead to the formation of the 16 electron active species, able to perform the hydrogen transfer from iPrOH to the substrate 4-fluoroacetophenone (Scheme 3).



Scheme 3 Proposed activation of ionic complexes **4**.

Therefore, the catalytic mechanism is likely to be similar to that of the Shvo catalyst[16] with the advantage of a possible recover and reuse of the catalyst immobilized in the ionic liquid phase.

The catalytic activity of the ionic complexes **4a[I]** and **4a[CF_3SO_3]**, containing different imidazolium counterions, have been found similar, (entries 2, 3), suggesting that there is no or little influence of the coordination ability of the counterion in the pre-catalyst activation.

With the aim of understanding the role of the ionic liquid, some catalytic runs have been carried out employing also [BMIM][BF_4], [BDMIM][PF_6] and [BMIM][OTf] as reaction solvents. Under the same hydrogen transfer conditions, the catalytic activity increases in the following order: [BMIM][BF_4] < [BMIM][OTf] ~ [BMIM][PF_6] (entry 2, 4 and 6). The lower conversion observed in

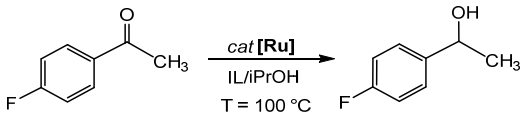
the case of [BMIM][BF_4] is probably due to the physical properties of the IL, which in turn, depend on the nature of both cation and anion.[3] Purity of the ionic liquid is also fundamental, in that traces of halide or nitrogen ligands, such as unreacted imidazoles, would poison the catalyst with a serious drop, often shutdown, of the catalytic activity.

Furthermore, the nature of the cationic part of the ionic liquid employed as solvent has some influence on the catalytic performance, as shown by comparison of the reactions with **4a[I]** as catalyst, in [BDMIM][PF_6] (BDMIM = 1-butyl-2,3 - dimethylimidazolium) (75% conversion, entry 5 Table 2) vs. [BMIM][PF_6], (69% conversion, entry 2).

As control experiments complexes **4a[I]** and **4a[CF_3SO_3]** have been also tested in the absence of ILs (entry 7 and 8 in Table 2). Both catalysts are indeed activated even at lower temperature (reflux of 2-propanol), leading to a conversion of 78% and 76% respectively after 24h. This behavior confirms that the activation can be reasonably ascribed to iodide or $CF_3SO_3^-$ release (Scheme 3).

In Table 3 is summarized the catalytic activity of Ru complexes **4g** and **4e**, containing imidazolium counteranions, with different steric encumbrance. Comparison of **4g** (entry 2, Table 3) and **4a[I]** (entry 2, Table 2), suggests a negligible role of the steric demand of the imidazolium substituents. On the other hand, a significant improvement of the catalytic activity is observed with **4e**, which, among the complexes of type **4**, is the only one displaying the NC(Me)N moiety in the imidazolium cation. This observation suggests a possible detrimental role of the acidic NC(H)N group present in the complexes **4a** and **4g**.

Table 3. Catalytic transfer hydrogenation of 4-fluoroacetophenone.[a]



entry	[Ru]	solvent (ILs)	Conversion 3h (%)	Conversion 6h (%)	Conversion 24h (%)
1	**4g**	[BDMIM][PF_6]	60	68	75
2	**4g**	[BMIM][PF_6]	71	87	88
3	**4e**	[BDMIM][PF_6]	85	94	>99
4	**4e**	[BMIM][PF_6]	89	93	>99
5	**4e**	[BMIM][OTf][b]	73	92	>99

[a]General conditions: Ruthenium complex (5 mol% Ru), ionic liquid (2 mL), *i*PrOH (2 mL), T = 100°C; conversions determined by ^{19}F NMR spectroscopy. The reaction is selective, thus conversion of the ketone corresponds to the yield of the alcohol. [b] OTf = CF_3SO_3.

Catalyst 4e recycle experiments

As previously mentioned, one possible advantage associated to the use of ILs as reaction media is the easy recovery of the catalyst and its reuse, which, in the case of Ru catalysts, is a most desirable target. Therefore, based on the catalytic results above described, recovery and recycle of the best performing catalyst **4e** have been investigated using different work up strategies. In particular, two methods have been designed (method A and B).

Table 4. Catalyst **4e** recycle with different work up strategies.[a]

entry	Recycling method	Number of cycle	solvent (ILs)	Conversion 24h (%)
1	**---**	1	[BDMIM][PF_6]	>99
2	**A**	2	[BDMIM][PF_6]	17
3	**---**	1	[BMIM][OTf][b]	>99
4	**A**	2	[BMIM][OTf][b]	32
5	**A**	3	[BMIM][OTf][b]	9
6	**---**	1	[BDMIM][PF_6]	>99
7	**B**	2	[BDMIM][PF_6]	60

[a]General conditions: Ruthenium complex (5 mol% Ru), ionic liquid (2 mL), *i*PrOH (2 mL), T = 100°C; conversions determined by ^{19}F NMR spectroscopy. The reaction is selective, thus conversion of the ketone corresponds to the yield of the alcohol. [b] OTf = CF_3SO_3.

The work up for the method **A** consists, at the end of the reaction, in extraction of the IL with hexane, a solvent which is immiscible with ILs and, in principle, unable to dissolve the catalyst. Results reported in Table 4 for method **A** (entry 2, 4 and 5) show a significant drop of the conversions both in [BDMIM][PF_6] or [BMIM][OTf] as ILs. This behavior is probably ascribable to some loss of the catalyst during the extraction, due to partial solubility of the catalyst in 2-propanol. In order to avoid this problem, an alternative approach (method **B**) has been investigated. In this case the work up and catalyst recycle is based on removal of 2-propanol, substrate and product by distillation under vacuum at 50 °C for 2h, followed by addition of fresh 2-propanol and substrate to the remaining solution containing the catalyst. The method **B** also avoids catalyst deactivation due to accidental exposition to water or oxygen, occurring more frequently by using the method **A**.

Indeed, best results in the terms of recycling have been obtained with catalyst **4e** in both [BDMIM][PF_6] and [BMIM][PF_6] (Figure 4, green and blu bars). Results reported in Figure 4 correspond to conversions after the 3 h reaction. A shorter reaction time (compared to 6 or 24 h, see Table 2) has been considered in order to evidence the decrease of conversions and yields after each cycle. For the sake of comparison, these experiments have been also repeated for catalysts **4a[I]** and **4g,** (Figure 4 red and yellow bars, respectively). Resulting data further demonstrate the influence of imidazolium counterion on both catalytic activity and recycling ability.

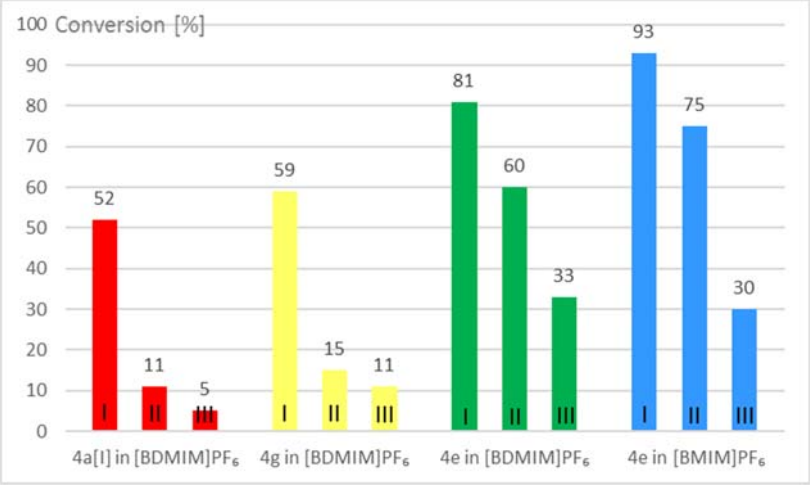


Figure 4. Screening of the recycles with method **B**, reaction time: 3h, the numbers of the cycles are denoted by Roman numerals.

Conclusion

The direct and straightforward reaction of the dinuclear ruthenium complex dicarbonyl(η^4-3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone (**2**) with a series of variously functionalized imidazolium salts afforded a class of anionic ruthenium cyclopentadienone complexes paired with imidazolium as counterions of type $[Ru(CO)_2\{C_5(C_6H_4OMe)_2(Ph)_2{=}O\}(X)]^-$ ($[imidazolium]^+$) (X = halide or trifluoromethanesulfonate)] (**4**). The reaction is clean, general and quantitative and the products are stable to air and moisture both in the solid state and in solution. All the complexes obtained have been characterized by means of IR, NMR and ESI-MS techniques and, when possible, with X-ray diffraction studies. Exploiting the affinity of complexes **4** for ionic liquids, their catalytic activity, in hydrogen transfer, has been investigated in ionic liquids such as [BMIM][PF_6], [BDMIM][PF_6] and [BMIM][OTf], with good results: the IL-immobilized catalysts **4** are active in the catalytic reduction of 4-fluoroacetophenone. The use of ionic liquids (imidazolium salts) as reaction media gives the opportunity to work under biphasic reaction conditions, favoring catalyst recovery and giving an overall greener character to the reaction. Recycling experiments demonstrate that, at the end of the reaction, different work up methods of the reaction mixture are feasible. The most effective recycle conditions (method **B**), consisting in the removal of the isopropanol and the reaction products by evaporation under vacuum, allows to maintain high activity of the catalyst **4e** in [BMIM][PF_6] or [BDMIM][PF_6]. Experiments demonstrate that the catalyst remains active in the ionic liquid environment, until the introduction of a further portion of substrate and co-solvent, starting a new catalytic run.

Experimental Section

Materials and procedures. 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, toluene, $CDCl_3$, D_2O, CD_3CN (Sigma Aldrich) have been employed without further

purification. Reagents: triruthenium-dodecacarbonil ($Ru_3(CO)_{12}$) (Strem), methyl iodide, methyl bromide, bromidric and chloridric acid, silver oxide, 1-methylimidazole, 1,3 diphenylacetone, benzyl bromide, benzyl chloride, paraformaldehyde, *tert*-butylamine, 2,6-dimethylaniline, 2,6-diisopropylaniline, glyoxal, acetic acid, 2,4,6-trimethylaniline, (Sigma Aldrich), 4,4'dimethoxybenzil (Alfa Aesar) have been employed as purchased.

1,3-dimethylimidazolium iodide (**1a[I]**),[17] 1,3-dimethylimidazolium trifluoromethanesulfonate (**1a[OTf]**), 1,3-dibenzylimidazolium bromide (**1b**),[18] 1-methyl-3-butyl-imidazolium bromide (**1c**),[19] 1-butyl-3-(2-pyridinyl)-imidazolium bromide (**1d**),[20] 1-butyl-2,3-dimethylimidazolium chloride (**1e**),[21] 1,3-di-*tert*-butylimidazolium chloride (**1f**),[22], N,N′-bis(2,6-dimethylphenyl)-1,4-diaza-1,3-butadiene, 1,3-bis(2,6-dimethylphenyl)imidazolium chloride (**1g**),[23] 3,4-Bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone,[24] dicarbonyl(η^4-3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone) ruthenium dimer (**2**),[25] have been prepared as previously reported. 1-methyl-3-butyl-imidazolium hexafluorophosphate ([BMIM][PF_6]), 1-methyl-3-butyl-imidazolium tetrafluoroborate ([BMIM]BF_4), 1-methyl-3-butyl-imidazolium triflate ([BMIM][OTf]), 1-butyl-2,3-dimethylimidazolium hexafluorophosphate ([BDMIM][PF_6]) with a certificate purity for catalytic application where purchased from Sigma Aldrich.

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.

Synthesis of [dicarbonyl-η^4-3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone)halogenide][1R$_1$-3R$_2$ imidazolium] ruthenium complexes (4)

Imidazolium salts (**1**), were reacted with dicarbonyl(η^4-3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone) ruthenium dimer (**2**) (0.5 eq. vs. imidazolium salts). The reaction mixture was stirred at room temperature until the end of the reaction, followed by IR spectroscopy. Upon precipitation with hexane, the yellow solid were obtained in quantitative yield by filtration and identified as [dicarbonyl-η^4-3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone)halogenide][1R$_1$-3R$_2$ imidazolium] ruthenium complexes (**4**) by ^{1}H-NMR, ^{13}C-NMR, IR, ESI-MS and X-Ray crystal structure when suitable crystals were available. Complexes **4** are stable to air, in organic solvents and in the presence of water.

[dicarbonyl(η^4-3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone)(iodine)ruthenium][1,3-dimethylimidazolium] (4a[I]): 1,3-dimethylimidazolium iodide (**1a**) 0.011 g (0.0499 mmol), **2** 0.030 g (0.0249 mmol), CH_2Cl_2, room temperature, 1h. The yellow solid obtained was identified as **4a[I]**. Suitable crystals for X-Ray diffraction has been obtained by toluene/hexane double layer. Complex **4a[I]** has been analyzed by IR, ^{1}H-NMR, ^{13}C-NMR, ESI-MS and X-Ray diffraction. ^{1}H-NMR (599.7 MHz, $CDCl_3$): δ 10.16(s, NCHN), 7.59 (d, 4H, CH_{aryl}), 7.15-6.98 (m, 10H, CH_{aryl}), 6.87 (s, 2H, CH_{im}), 7.57 (d, 4H, CH_{aryl}), 3.71 (s, 6H, NCH_3), 3.58 (s, 6H, -OCH_3). ^{13}C-NMR (150.8 MHz, $CDCl_3$, g-HSQC, g-HMBC, DEPT): δ 200.99 (CO), 172.11 (C=O, Cp), 158.39 (-$COCH_3$), 138.96 (NCHN), 135.21-112.65 (C_{aryl}), 122.55 (CH_{im}), 100.08 ($C_{2,5}$, Cp), 81.40 ($C_{3,4}$, Cp), 53.41 (-OCH_3), 36.55 (NCH_3). IR (CH_2Cl_2, cm^{-1}): 2004, 1944 (ν_{CO}); 1580 ($\nu_{C=O}$), 1604, 1518 ($\nu_{C=C}$). ESI-MS (m/z) (+): 97 [M]$^+$; (-): 729 [M]$^-$. Anal. Calcd (%) for $C_{38}H_{33}IN_2O_5Ru$: C, 55.28; H, 4.03; N, 3.39. Found: C, 55.26; H, 4.00; N, 3.41.

[dicarbonyl(η^4-3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone)(trifluoromethanesulfonate)ruthenium][1,3-dimethylimidazolium] (4a[OTf]): 1,3-dimethylimidazolium trifluoromethanesulfonate (**1a[OTf]**) 0.012 g (0.0499 mmol), **2** 0.030 g (0.0249 mmol), CH_2Cl_2, room temperature, 2h. The yellow solid obtained was identified as **4a[OTf]**.

Complex **4[OTf]** has been analyzed by IR, ^{1}H-NMR, ^{13}C-NMR, ^{19}F-NMR, ESI-MS. ^{1}H-NMR (599.7 MHz, $CDCl_3$): δ 9.71 (s, NCHN), 7.57 (d, 4H, CH_{aryl}), 7.22-6.96 (m, 10H, CH_{aryl}), 7.18 (s, 2H, CH_{im}), 6.55 (d, 4H, CH_{aryl}), 3.80 (s, 6H, NCH_3), 3.69 (s, 6H, -OCH_3). ^{13}C-NMR (150.8 MHz, $CDCl_3$): δ 201.08 (CO), 172.14 (C=O, Cp), 158.37 (-$COCH_3$), 138.24 (NCHN), 135.20-112.64 (C_{aryl}), 122.85 (CH_{im}), 100.24 ($C_{2,5}$, Cp), 81.34 ($C_{3,4}$, Cp), 54.99 (-OCH_3), 36.63 (NCH_3). ^{19}F-NMR (282.4 MHz, $CDCl_3$): δ -78.61 (s, 3F). IR (CH_2Cl_2, cm^{-1}): 2004, 1944 (ν_{CO}); 1579 ($\nu_{C=O}$), 1604, 1518 ($\nu_{C=C}$). ESI-MS (m/z) (+): 97 $[M]^+$; (-): 751 $[M]^-$. Anal. Calcd (%) for $C_{39}H_{33}F_3N_2O_8RuS$: C, 55.25; H, 3.92; N, 3.30. Found: C, 55.21; H, 3.89; N, 3.31.

[dicarbonyl(η^4-3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone)(bromine)ruthenium] [1,3-dibenzylimidazolium] (4b): 1,3-dibenzylimidazolium bromide (**1b**) 0.011 g (0.0332 mmol), **2** 0.020 g (0.0166 mmol), CH_2Cl_2, room temperature, 30 min. The yellow solid obtained was identified as **4b**. Complex **4b** has been analyzed by IR, ^{1}H-NMR, ^{13}C-NMR, ESI-MS. ^{1}H-NMR (599.7 MHz, $CDCl_3$): δ 10.65 (s, NC*H*N), 7.65 (d, 4H, CH_{aryl}), 7.35-6.96 (m, 20H, CH_{aryl}), 6.71 (s, 2H, CH_{im}), 6.56 (d, 4H, CH_{aryl}), 5.08 (s, 4H, CH_2Ph), 3.70 (s, 6H, -OCH_3). ^{13}C-NMR (150.8 MHz, $CDCl_3$): δ 200.84 (CO), 171.24 (C=O, Cp), 158.41 (-$COCH_3$), 139.76 (NCHN), 134.94-112.66 (C_{aryl}), 120.48 (CH_{im}), 99.47 ($C_{2,5}$, Cp), 81.98 ($C_{3,4}$, Cp), 55.00 (-OCH_3), 53.41 (CH_2Ph). IR (CH_2Cl_2, cm^{-1}): 2006, 1945 (ν_{CO}); 1580 ($\nu_{C=O}$), 1605, 1517 ($\nu_{C=C}$). ESI-MS (m/z) (+): 249 $[M]^+$; (-): 683 $[M]^-$. Anal. Calcd (%) for $C_{50}H_{41}BrN_2O_5Ru$: C, 64.52; H, 4.44; N, 3.00. Found: C, 64.55; H, 4.42; N, 2.99.

[dicarbonyl(η^4-3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone)(bromine)ruthenium][1- butyl-3-methylimidazolium] (4c): 1-butyl-3-metylimidazolium bromide (**1c**) 0.005 g (0.0332 mmol), **2** 0.020 g (0.0166 mmol), CH_2Cl_2, room temperature, 30 min. The yellow solid obtained was identified as **4c**. Complex **4c** has been analyzed by IR, ^{1}H-NMR, ^{13}C-NMR, ESI-MS. ^{1}H-NMR (599.7 MHz, $CDCl_3$): δ 10.05 (s, NC*H*N), 7.61 (d, 4H, CH_{aryl}), 7.62-6.95 (m, 10H, CH_{aryl}), 6.88 (s, 2H, CH_{im}), 6.56 (d, 4H, CH_{aryl}), 3.90 (t, 2H, NCH_2), 3.70 (s, 6H, -OCH_3), 3.54 (s, 3H, -NCH_3), 1.64, 1.22 (m, 2H, -CH_2CH_2-), 0.88 (t, 3H, -CH_3). ^{13}C-NMR (150.8 MHz,

$CDCl_3$): δ 200.96 (CO), 171.50 (C=O, Cp), 158.37 (-$COCH_3$), 135.21 (NCHN), 133.18-112.63 (C_{aryl}, CH_{im}), 99.63 ($C_{2,5}$, Cp), 81.66 ($C_{3,4}$, Cp), 55.01 (-OCH_3), 49.43 (-NCH_2), 36.24 (-NCH_3), 31.91, 19.42 (-CH_2CH_2-), 13.46 (-CH_3). IR (CH_2Cl_2, cm^{-1}): 2005, 1944 (ν_{CO}); 1581 ($\nu_{C=O}$), 1605, 1517 ($\nu_{C=C}$). ESI-MS (m/z) (+): 139 $[M]^+$; (-): 683 $[M]^-$. Anal. Calcd (%) for $C_{41}H_{39}BrN_2O_5Ru$: C, 59.91; H, 4.77; N, 3.40. Found: C, 59.94; H, 4.80; N, 3.40.

[dicarbonyl(η^4-3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone)(chloro)ruthenium][1-(butyl-3-(2-pyridinyl)-imidazolium] (4d): 1-(butyl-3-(2-pyridinyl)-imidazolium (**4d**) 0,034 g (0,17 mmol), **2** 0,10 g (0,08 mmol), CH_2Cl_2, room temperature, 1h. The yellow solid obtained was identified as **4d**. Complex **4d** has been analyzed by IR, ^{1}H-NMR, ^{13}C-NMR, ESI-MS. ^{1}H-NMR (599.7 MHz, $CDCl_3$): δ 11.12 (s, NC*H*N), 8.34 (dd, 1H, CH_{py}), 8.28 (1H, CH_{py}), 8.07 (1H, CH_{py}), 7.66-6.55 (CH_{aryl}, CH_{im}), 3.70 (s, 6H, -OCH_3), 3.68 (t, 2H, NCH_2) 1.58, 1.12 (m, 4H, -CH_2CH_2-), 0.86 (t, 3H, -CH_3). ^{13}C-NMR (150.8 MHz, $CDCl_3$): δ 200.91 (CO), 171.13 (C=O, Cp), 158.38 (-*C*OCH_3), 147.95-112.62 ($C_{aryl,py}$), 137.80 (-NCHN-), 124.70 (CH_{im}), 120.07 (CH_{im}), 99.91 ($C_{2,5}$, Cp), 82.36 ($C_{3,4}$, Cp), 55.00 (–OCH_3), 49.54 (NCH_2), 31.48, 19.37 (–CH_2CH_2), 13.56 (–CH_3). IR (CH_2Cl_2, cm^{-1}): 2006, 1945 (ν_{CO}), 1577 cm^{-1} ($\nu_{C=O}$), 1602, 1518 ($\nu_{C=C}$). ESI-MS (m/z) (+): 202 $[M]^+$; (-):683 $[M]^-$. Anal. Calcd (%) for Anal. Calcd (%) for $C_{45}H_{40}BrN_3O_5Ru$: C, 50.85; H, 4.52; N, 4.75. Found: C, 50.92; H, 4.56; N, 4.73.

[dicarbonyl(η^4-3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone)(bromine)ruthenium] [1- butyl 2,3-dimethylimidazolium] (4e): 1-butyl-2,3-dimethylimidazolium chloride (**1e**) 0.031 g (0.166 mmol), **2** 0.100 g (0.083 mmol), CH_2Cl_2, room temperature, 1h. The yellow solid obtained was identified as **4e**. Suitable crystals for X-Ray diffraction has been obtained by dichlorometane/hexane double layer. Complex **4e** has been analyzed by IR, ^{1}H-NMR, ^{13}C-NMR, ESI-MS. ^{1}H-NMR (599.7 MHz, $CDCl_3$): δ 7.53 (d, 4H, CH_{aryl}), 7.09-6.91 ($CH_{aryl,}$ CH_{im}), 6.54 (d, 4H, CH_{aryl}), 3.81 (t, 2H, NCH_2), 3.68 (s, 6H, -OCH_3), 3.46 (s, 3H, -NCH_3), 2.27 (s, 3H, -NC(CH_3)N), 1.52, 1.25 (m, 4H, -CH_2CH_2-), 0.90 (t, 3H, -CH_3). ^{13}C-NMR (150.8 MHz, $CDCl_3$): δ 201.42 (CO), 170.13 (C=O, Cp), 158.31 (-$COCH_3$), 143.38 (N*C*(CH_3)N), 135.11-

112.58 (C_{aryl}), 123.14, 120.45 (CH_{im}), 99.85 ($C_{2,5}$, Cp), 81.36 ($C_{3,4}$, Cp), 54.96 (-OCH_3), 48.27 (-NCH_2), 31.56 (-NCH_3), 35.70, 19.50 (-CH_2CH_2-), 13.46 (-CH_3), 10.16 (-CH_3), 10.16 (NC(*C*H_3)N). IR (CH_2Cl_2, cm^{-1}): 2001, 1938 (ν_{CO}); 1591 ($\nu_{C=O}$), 1607, 1517 ($\nu_{C=C}$). ESI-MS (m/z) (+): 153 $[M]^+$; (-): 637 $[M]^-$. Anal. Calcd (%) for $C_{42}H_{41}ClN_2O_5Ru$: C, 63.83; H, 5.23; N, 3.54. Found: C, 63.85; H, 5.25; N, 3.56.

[dicarbonyl(η^4-3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone)(chloro)ruthenium][1,3- di-*tert*-butylimidazolium] (4f): 1,3-di-*tert*-butylimidazolium chloride (**1f**) 0.010 g (0.0499 mmol), **2** 0.030 g (0.0249 mmol), CH_2Cl_2, room temperature, 1h. The yellow solid obtained was identified as **4f**. Suitable crystals for X-Ray diffraction has been obtained by $CDCl_3$/petroleum ether double layer. Complex **4f** has been analyzed by IR, ^{1}H-NMR, ^{13}C-NMR, ESI-MS and X-Ray diffraction. ^{1}H-NMR (599.7 MHz, $CDCl_3$): δ 9.80 (s, NCHN), 7.60 (d, 4H, CH_{aryl}), 7.34-6.92 (C_{aryl}), 7.34 (s, 2H, CH_{Im}), 6.51 (d, 4H, CH_{aryl}), 3.66 (s, 6H, -OCH_3), 1.57 (s, 18H, CH_{3tBu}). ^{13}C-NMR (150.8 MHz, $CDCl_3$): δ 201.75 (CO), 171.16 (C=O, Cp), 158.16 (-$COCH_3$), 134.16 (NCHN), 135.32-112.45 (C_{aryl}), 119.49 (CH_{im}), 100.20 ($C_{2,5}$, Cp), 82.65 ($C_{3,4}$, Cp), 60.50 ($C_{q,tBu}$), 54.91 (-OCH_3), 30.02 ($CH_{3,tBu}$). IR (CH_2Cl_2, cm^{-1}): 2001, 1938 (ν_{CO}); 1578 ($\nu_{C=O}$), 1607, 1518 ($\nu_{C=C}$). ESI-MS (m/z) (+): 180 $[M]^+$; (-): 638 $[M]^-$. Anal. Calcd (%) for $C_{44}H_{45}ClN_2O_5Ru$: C, 70.19; H, 5.99; N, 3.42. Found: C, 70.21; H, 6.01; N, 3.44.

[dicarbonyl(η^4-3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone)(chloro)ruthenium][1,3-bis(2,6-dimethylphenyl)imidazolium] (4g): 1,3-bis(2,6-dimethylphenyl)imidazolium chloride (**1g**) 0.052 g (0.166 mmol), **2** 0.100 g (0.083 mmol), CH_2Cl_2, room temperature, 1h. The beige solid obtained was identified as **4g**. Complex **4g** has been analyzed by IR, ^{1}H-NMR, ^{13}C-NMR, ESI-MS. ^{1}H-NMR (599.7 MHz, $CDCl_3$): δ 9.95 (s, NCHN), 7.58 (s, 2H, CH_{Im}), 7.46-6.51 (CH_{aryl}), 3.68 (s, 6H, -OCH_3), 2.16 (s, 12H, -CH_3). ^{13}C-NMR (150.8 MHz, $CDCl_3$): δ 201.58 (CO), 170.59 (C=O, Cp), 158.16 (-$COCH_3$), 137.09 (NCHN), 134.55-112.49 (C_{aryl}), 126.96 (CH_{im}), 99.92 ($C_{2,5}$, Cp), 81.01 ($C_{3,4}$, Cp), 54.85 (-OCH_3), 17.71 (CH_3). IR (CH_2Cl_2, cm^{-1}): 2000,

1937 (ν_{CO}); 1591 ($\nu_{C=O}$), 1607, 1517 ($\nu_{C=C}$). ESI-MS (m/z) (+): 277 $[M]^+$; 637 $[M]^-$. Anal. Calcd (%) for $C_{52}H_{45}ClN_2O_5Ru$: C, 68.30; H, 4.96; N, 3.06. Found: C, 68.32; H, 4.98; N, 3.08.

General method for hydrogenation

Ruthenium ionic complex (15 μmol, 5% mol) was dissolved in a mixture of ionic liquid (2 mL) and *i*PrOH (2 mL) in a 10 mL two neck-flask and stirred at 100°C for 10 min. Then 4-fluoroacetophenone (36 μL, 300 μmol) was added and samples were taken at regular intervals. Aliquots (ca. 0.05 mL) were diluted with $CDCl_3$ (0.5 mL) and conversions were determined by ^{19}F-NMR spectroscopy.

X-Ray diffraction studies

Crystal data and collection details for **4e** and **4f·0.5CH$_2$Cl$_2$** are reported in Table S1. The diffraction experiments were carried out on a Bruker APEX II diffractometer equipped with a PHOTON100 detector (**4e**) or a CCD detector (**4f·0.5CH$_2$Cl$_2$**) using Mo–Kα radiation. Data were corrected for Lorentz polarization and absorption effects (empirical absorption correction SADABS).[26] Structures were solved by direct methods and refined by full-matrix least-squares based on all data using F^2.[27] All hydrogen atoms were fixed at calculated positions and refined by a riding model. All non-hydrogen atoms were refined with anisotropic displacement parameters.

4e: The asymmetric unit of the unit cell contains one anion and one cation (located on general positions). One p-MeO-C_6H_4 group in the anion is disordered. Disordered groups have been split into two positions and refined using one occupancy factor per disordered group. The C and O atoms of the disordered groups have been restrained to have similar *U* parameters (SIMU line in SHELXL; s.u. 0.01) and isotropic like behavior (ISOR line in SHELXL, s.u. 0.01). The disordered aromatic rings have been constrained to fit regular hexagons (AFIX 66 line in SHELXL).

4f·0.5CH$_2$Cl$_2$: The asymmetric unit of the unit cell contains one anion and one cation (located on general positions), as well as half of a CH_2Cl_2 molecule disordered over four positions two by two related by a 2-fold axis. The CH_2Cl_2 molecule has been refined isotropically. One Ph and one p-MeO-C_6H_4 group in the anion and one ^{t}Bu substituent in the cation are disordered. Disordered groups have

been split into two positions and refined using one occupancy factor per disordered group. Similar *U* restraints (SIMU line in SHELXL; s.u. 0.01) have been applied to C and O atoms. Some of the C and O atoms of the disordered groups have been restrained to isotropic behaviour (ISOR line in SHELXL, s.u. 0.005). The disordered aromatic rings have been constrained to fit regular hexagons (AFIX 66 line in SHELXL). Restraints to bond distances were applied as follow (s.u. 0.01): 1.75 Å for C–Cl in CH_2Cl_2.

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Table of contents

Biscarbonyl cyclopentadienone ruthenium complexes ion paired with variously functionalized imidazolium salts are suitable as bifunctional catalysts for transfer hydrogenation on a model compound, such as 4-fluoroacetophenone, in ionic liquid media. The biphasic system allows recovery and recycle of the catalyst.