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FULL PAPER

A ferrocenyl-benzo-fused imidazolylidene complex of ruthenium as redox-switchable catalyst for the transfer hydrogenation of ketones and imines

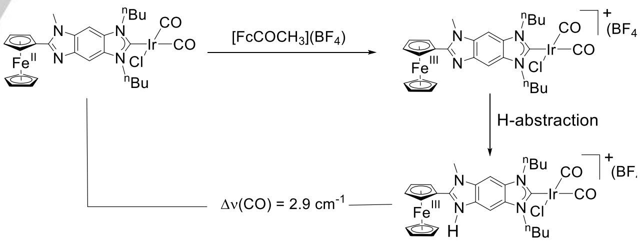
Susana Ibáñez,[a] Macarena Poyatos*[a] and Eduardo Peris*[a]

Abstract: A ferrocenyl-benzo-fused-imidazolylidene complex of Ru(II) was prepared and fully characterized. In the presence of acetylferrocenium tetrafluoroborate this complex can be oxidised generating a complex with a cationic ligand. The neutral complex can be recovered by reducing the oxidised cationic compound with cobaltocene. The activity of the neutral and oxidized complexes was tested in the transfer hydrogenation of ketones and imines, using *i*-PrOH as hydrogen source. While the neutral complex is very active in the reduction of all substrates, the oxidized species shows low activity in the reduction of ketones. The rate of the reduction of acetophenone could be modulated by addition of subsequent amounts of oxidant and reductant. The addition of acetylferrocenium tetrafluoroborate caused a decrease in the catalytic activity, while the addition of cobaltocene restored the activity. The catalytic activity shown by both catalysts in the reduction of N-benzylideneaniline is similar.

Introduction

'Switchable catalysts' are normally defined as all those catalysts that are able to switch their activities by applying certain types of stimuli, such as light, pH, redox processes or changes of reaction conditions.[1] Among this type of catalysts, those containing redox-switchable ligands have been thoroughly studied. Redox active ligands are sources of electrons that normally allow the metal retaining its original oxidation state,[2] while facilitating the tuning of the electron richness of the ligand and the bound metal.[3] The participation of a redox active ligand in a catalytic process, may be by accepting or releasing electrons, or by actively forming or breaking covalent bonds.[4] Probably due to their great chemical versatility, during the last decade a large number of N-heterocyclic carbene ligands (NHCs) containing redox active moieties have been reported,[5] although their use in homogeneous catalysis is still relatively rare.[6]

We recently described a redox-switchable benzo-fused-imidazolylidene ligand, which was coordinated to iridium (I) and gold (I).[7] From the experimental and computational analysis of the ligand and some coordinated compounds, we concluded that the oxidation of the ligand with acetylferrocenium tetrafluoroborate afforded the corresponding oxidized (Fe^{3+}) species, together with a minor product product resulting from the protonation of the ferrocenyl-imidazolylidene (Fe^{2+}) ligand (Scheme 1). The minor protonated species was presumably formed as a consequence of the hydrogen abstraction from the produced cationic radical generated by the oxidation of the ferrocenyl-imidazolylidene ligand. The two resulting cationic ligands, which can be regarded as the product of the oxidation of the starting ferrocenyl-imidazolylidene, reduced the electron richness of the metal, as a consequence of the diminished electron donor character of the cationic ligands compared to the neutral one. This change in the electrondonating character of the ligand was quantified as 2.9 cm^{-1}, considering the shift in the $\nu_{av}(CO)$ of the related $[IrCl(Fc\text{-}NHC)(CO)_2]$ complexes (with Fc-NHC = ferrocenyl-imidazolylidene, or its related cationic forms). This subtle, yet not negligible, electron-donor shift, was found to be very useful for preparing a redox-switchable gold catalyst for the cyclization of alkynes with furans. For this reaction, it was observed that the activity of the neutral gold complex was negligible, but it could be switched on by adding an oxidant that transformed the gold complex into a very active catalyst.



Scheme 1. Oxidation and further hydrogen abstraction of the ferrocenyl-benzo-fused imidazolylidene Ir(I) complex

Based on this previous findings, we now report the preparation of a ruthenium (II) complex with a ferrocenyl-benzo-fused-imidazolylidene ligand. The full characterization and the electrochemical behavior of this complex will be fully analyzed. The redox-switchable properties of this new complex will be described in the reduction of ketones and imines by transfer hydrogenation using isopropanol as hydrogen source.

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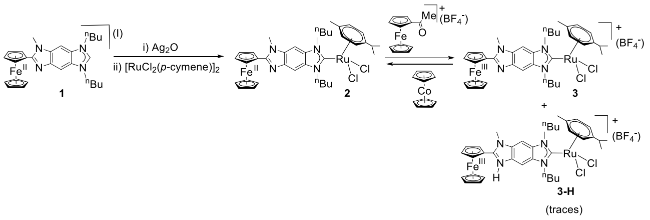
Results and Discussion

Scheme 2 displays the synthetic procedure to synthesize the ferrocenyl-imidazolylidene ruthenium (II) complex **2**. The reaction of the ferrocenyl-imidazolium iodide **1** with silver oxide afforded the corresponding Fc-NHC-Ag(I) complex, which reacted *in situ* with $[RuCl_2(p\text{-cymene})]_2$ to afford the ferrocenyl-imidazolylidene ruthenium (II) complex **2** in 70 % yield. Complex **2** was characterized by NMR spectroscopy and mass spectrometry, and gave satisfactory elemental analysis. As a diagnostic of the formation of the Fc-NHC-Ru complex, the ^{13}C NMR spectrum of **2** displayed the characteristic resonance of the carbene carbon at 188.0 ppm.



Scheme 2. Synthesis of Ru(II)-based complexes **3** and **3-H**

In order to see if we could isolate the product of the oxidation of the ferrocenyl fragment of this new ruthenium complex, we oxidized complex **2** with acetylferrocenium tetrafluoroborate at room temperature in dichloromethane. The addition of the oxidant produced an immediate darkening of the brownish solution. The reaction produced the quantitative formation of acetylferrocene, which could be separated by washing with diethyl ether the crude solid resulting from the reaction. The resulting paramagnetic dark brown solid was analyzed by elemental analysis and mass spectroscopy. The ^{1}H NMR spectrum of **3** showed the broad signals expected for a paramagnetic compound. The mass spectrum revealed a small peak at m/z 370.0, which is consistent with the presence of a dicationic species resulting from the loss of a chloride ligand in **3-H** (see Scheme 2). These results are consistent with our previously reported findings, which indicated that the oxidized species may slowly evolve to a protonated species resulting from the hydrogen abstraction from the produced radical cationic species. Although we do not have a clear explanation for the formation of this protonated species, we know that the presence of traces of H_2O is favoring the process. In any case, the reduction of **3** with cobaltocene allowed the quantitative recovery of the neutral complex **2**, therefore suggesting that if **3-H** had formed, it would only be present in a trace amount.

The study of the electrochemical properties of **2** was carried out by performing the cyclic voltammetry (CV) and differential pulse voltammetry (DPV) experiments (Figure 1). Both experiments were carried out in dichloromethane, with $[NBu_4](PF_6)$ as electrolyte, and using ferrocene as reference ($E_{1/2}$ (Fc/Fc^+) = 0.46 V *vs.* SCE). The cyclic voltammetry revealed two quasi-reversible redox events at 0.89 and 1.15 V, attributed to the oxidations occurring at the Fe and Ru centers, respectively. The value of the redox potential for the Ru^{2+}/Ru^{3+} couple is in the higher region of the redox potentials shown by other related $[RuCl_2(NHC)(p\text{-cymene})]$ complexes (typically ranging between 1.00-1.15 V),[8] thus suggesting that the oxidation of the ferrocenyl-based ligand influences the redox potential of ruthenium center.

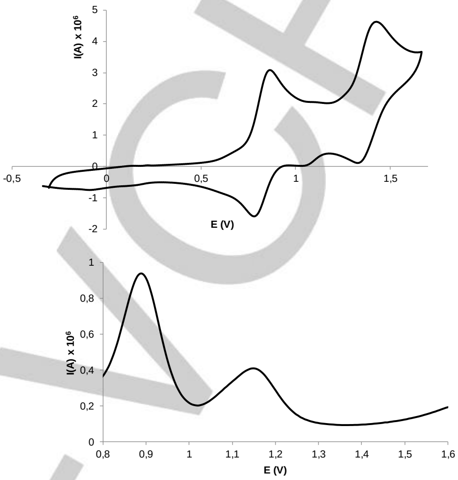


Figure 1. Cyclic voltammetry diagram (above) and relevant section of the differential pulse analysis of complex **2** (below). Measurements performed on a 1 mM solution of the analyte in dry CH_2Cl_2 with 0.1 M $[NBu_4][PF_6]$ as the supporting electrolyte, 100 mV/s scan rate, Fc/Fc+ used as standard with $E_{1/2}$ (Fc/Fc^+) = 0.46 V vs. SCE.

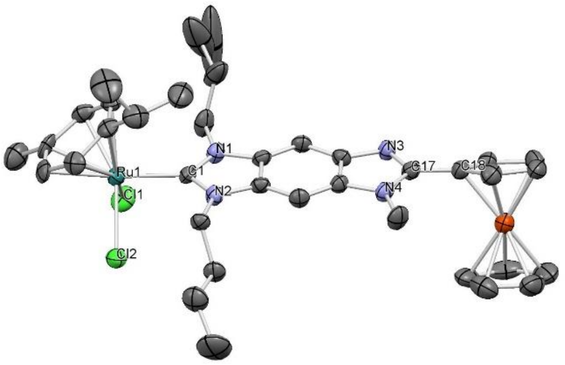


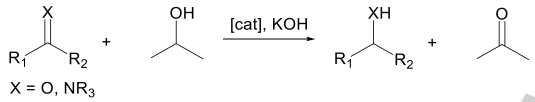
Figure 2. Molecular structure of complex **2**. Ellipsoids at 50 % of probability. Hydrogen atoms and solvent ($CHCl_3$) omitted for clarity. Selected bond distances (Å) and angles (º): Ru(1)-C(1) 2.087(8), Ru(1)-Cl(1) 2.410(2), Ru(1)-Cl(2) 2.430(2), C(1)-N(1) 1.336(10), C(1)-N(2) 1.364(11), C(17)-C(18) 1.454(12) N(4)-C(17) 1.380(10), N(3)-C(17) 1.311(11), C(1)-Ru(1)-Cl(1) 88.5(2), C(1)-Ru(1)-Cl(2) 90.7(2).

Figure 2 shows the molecular structure of complex **2**. The structure consists of a ferrocenyl-benzo-fused imidazolylidene ligand coordinated to a ruthenium center, which completes its coordination sphere with a *p*-cymene and two chloride ligands. The Ru-$C_{carbene}$ bond distance is 2.087(8) Å. The plane of the tricyclic-carbene ligand deviates from the substituted Cp ring of the ferrocenyl fragment by an angle of 23.88º. The two N-C distances of the imidazolyl ring bound to the ferrocenyl moiety are different, in agreement with the existence of a double and a single

C-N bonds (1.311(11) and 1.380(10) Å, respectively). The distance of the iron center to the centroids of the Cp rings is 1.659 Å, for both the substituted and unsubstituted Cp rings. This distance, together with the eclipsed orientation of the Cp rings, is consistent with the presence of a Fe(II) center at the ferrocenyl moiety.[9]

In order to study the catalytic redox-switchable abilities of complex **2**, we decided to test its catalytic activity in the reduction of ketones and imines by transfer hydrogenation using isopropanol as hydrogen source.[10] We did not find any examples in which redox-switchable catalysts were used in this important reaction. The earliest examples of Ru-NHC catalysts for this type of processes date from 2002[11] and 2003,[12] and since then a large number of NHC-containing catalysts have proven great activity in this reaction.[13] For Ru(arene)(NHC) catalysts detailed studies on the mechanistic pathway of the process have been published[14] It has been proposed that loss of the arene ligand is the slowest step of the process,[14a] therefore strong electrondonating ancillary ligands (which should favour this loss) may enhance the activity of the catalyst. On the contrary, poor electrondonating ligands, as the ones resulting from the oxidation of one of the ligands present in the coordination sphere of the complex, may reduce the activity of the catalyst.

Table 1. Transfer hydrogenation of ketones and imines using complex **2**[a]



Entry	Substrate	Catalyst	Yield(%)[b]
1	acetophenone	**2**	94
2	acetophenone	**2** + oxidant	24
3	cyclohexanone	**2**	75
4	cyclohexanone	**2** + oxidant	66
5	hexanophenone	**2**	94
6	hexanophenone	**2** + oxidant	20
7	2-acetonaphthone	**2**	60
8	2-acetonaphthone	**2** + oxidant	6
9	4-bromoacetophenone	**2**	68
10	4-bromoacetophenone	**2** + oxidant	51
11	4-methoxyacetophenone	**2**	40
12	4-methoxyacetophenone	**2** + oxidant	18
13	N-benzylideneaniline	**2**	85
14	N-benzylideneaniline	**2** + oxidant	81

[a] Reaction conditions: 0.5 mmol ketone or imine, 0.05 mmol KOH, 0.5 mol% of complex **2**, 0.5 mol% of acetylferrocenium tetrafluoroborate (oxidant) and 2 mL of isopropanol at 80 ºC for 2 h. [b] Yields determined by GC using anisole (0.5 mmol) as internal standard.

Table 1 shows the results that we obtained for the reduction of several ketones and imines in isopropanol using **2** as catalyst. In order to determine if the oxidation of the ferrocenyl ligand could have an effect on the catalytic outcome of the process, the reactions were also carried out under the same reaction conditions, but with the addition of acetylferrocenium tetrafluoroborate. We used the optimized reaction conditions that we used in some previously published works.[15] The reactions were carried out using a 0.5 mol % of catalyst loading (same amount of oxidant, when needed), in isopropanol at 80ºC for two hours, in the presence of KOH. As can be seen from the results shown in Table 1, catalyst **2** produced good to excellent yields of the final reduced products.

The addition of the oxidant clearly reduced the activity of the catalyst in the reduction of the ketones. This reduced activity turned into a significant inhibition for the cases of the reduction of acetophenone, hexanophenone and 2-acetonaphtone. Interestingly, for the reaction of N-benzylideneaniline, the activity of the neutral complex **2** was similar to the activity of the reaction carried out in the presence of an oxidant. This result is particularly relevant, because it indicates that the oxidized complex maintains its abilities to reduce imines, while reduces its activity in the reduction of carbonyl compounds, therefore suggesting that the system may be used for the selective reduction of imine functional groups in those cases where imines and carbonyl groups are present.

In order to get a more detailed insight about the effect of the addition of the oxidant in the reaction medium, we decided to monitor the reduction of cyclohexanone. The reaction profile is depicted in Figure 3. As can be seen from this profile, the addition of the oxidant not only produces a lower yield of the product, but also decelerates the reaction, therefore indicating that the higher activity of the neutral catalyst (**2**) is maintained all along the reaction course. This result suggests that the differences in activity are due to kinetic reasons rather to reasons related to the stability of both, **2** and **3**. It is noteworthy to point out that the yields shown in Figure 3 and Table 1 are significantly different, but this is mainly due to the fact that the monitoring of this reaction required interrupting the reaction at the selected reaction times for taking the aliquots, and this has an effect in reducing the reaction rates.

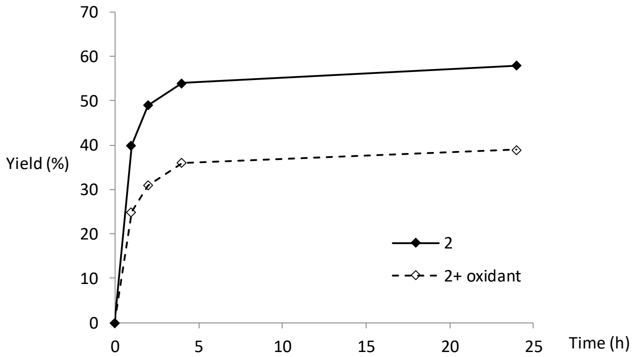


Figure 3. Time-dependent reaction profile of the transfer hydrogenation of cyclohexanone. Reaction conditions as those described in Table 1. Oxidant = acetylferrocenium tetrafluoroborate.

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Based on the observation that **2** and **3** catalyzed the reduction of ketones at different constant rates, we decided to study if we could modulate the activity of the catalyst over the course of the reaction. We monitored the reduction of hexanophenone to 1-phenylhexanol in *i*PrOH at 80ºC using **2** (0,5 mol%). We chose this substrate because it was the one to give us the largest difference in catalytic activity when **2** or **3** were used (compare entries 5 and 6 in Table 1). The reaction was monitored by gas chromatography (GC) by taking aliquots at the selected times. The result of the study can be observed in Figure 4. After one hour (50% yield) acetylferrocenium tetrafluoroborate (1 equivalent) was added. This addition produced the deceleration of the reaction, which after two more hours did not show any measurable advance. Further addition of cobaltocene (1.1 equivalens), restored the activity of the catalyst, as expected for the regeneration of the neutral catalyst **2** from the reduction of **3**. Although we observed that the recovery of the activity of the catalyst was not complete, we attributed the attenuated activity to partial decomposition of the catalyst due to the successive removing of aliquots in the performance of the study, which made us interrupt the reaction for a period of time by cooling the mixture and restoring the temperature after each measurement.

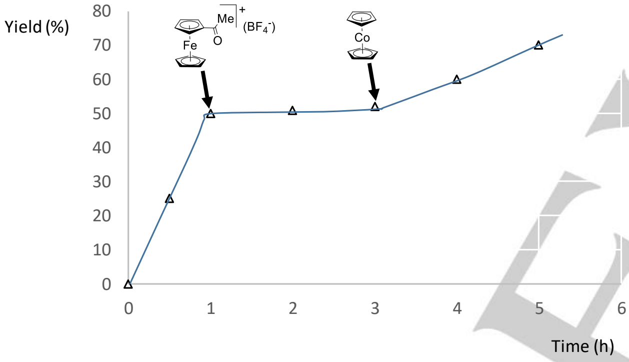

Figure 4. Time dependent reaction profile of the reduction of hexanophenone by transfer hydrogenation. The arrows indicate the addition t of acetylferrocenium tetrafluoroborate (1 equivalnet) or cobaltocene (1.1 equivalents). The reactions were carried out using 0.5 mol% of catalyst, at 80ºC, under the same reaction conditions as those described in Table 1. Yields calculated by GC using anisole as standard.

Conclusions

In summary, we prepared and fully characterized a new ferrocenyl-benzo-fused imidazolylidene complex of ruthenium. The reaction of this complex with acetylferrocenium tetrafluoroborate afforded the product from the oxidation of the ferrocenyl group to ferrocenium (**3**), although this compound may contain some small amounts of **3-H**, which can be regarded as the protonated analogue of **2**. The cationic nature of the ligand (in **3** makes the electron density at the ruthenium center be lower than the electron density of the same metal at the mother complex **2**. Interestingly, the reaction of **3** with cobaltocene allows the quantitative recovery of **2**, therefore indicating the full reversibility of the process.

The catalytic activity of the ruthenium complex **2** was tested in the reduction of ketones and imines by the transfer hydrogenation methodology. The complex showed good to excellent activity in the transfer hydrogenation of a wide variety of ketones and one imine. When the activity of the complex was compared with the activity of the *in situ* generated oxidized catalyst **3**, a clear inhibition of the activity was observed for the cases in which the substrates contained carbonyl groups. This allowed the modulation of the activity of the catalyst by successively adding acetylferrocenium tetrafluoroborate and cobaltocene. The addition of acetylferrocenium tetrafluoroborate interrupted the advance of the reaction, while the addition of cobaltocene restored the catalytic activity. This result expands upon the relatively few examples known of reversibly switching catalysts, and to the best of our knowledge, this is the first one to be used in the well-known reduction of ketones by transfer hydrogenation. For the case of the imine, the activity of the neutral complex was similar to that shown by its oxidized partner. All in all, our work represents a new example among the very rare cases of known NHC-based redox switchable catalysts.

Experimental Section

General considerations. Compound **1**[7] and acetylferrocenium tetrafluoroborate,[16] were prepared according to the method reported in the literature. All other reagents were used as received from commercial suppliers. NMR spectra were recorded on a Varian Innova 500 MHz, using $CDCl_3$ as solvent. Electrospray mass spectra (ESI-MS) were recorded on a Micromass Quatro LC instrument; nitrogen was employed as drying and nebulizing gas. Elemental analyses were carried out on a TruSpec Micro Series. Electrochemical studies were carried out by using an Autolab Potentiostat (Model PGSTAT101) using a three-electrode cell. The cell was equipped with platinum working and counter electrodes, as well as a silver wire reference electrode. In all experiments, $[NBu_4](PF_6)$ (0.1 M in dry dichloromethane) was used as the supporting electrolyte with analyte concentration of approximately 1 mM. Measurements were performed at 50 mVs^{-1} scan rates. All redox potentials were referenced to the Fc/Fc^+ couple as internal standard with $E_{1/2}(Fc/Fc^+)$ *vs*. SCE = +0.46 V.

Synthesis of complex 2. A suspension of the ferrocene-based imidazolium salt **1** (100 mg, 0.17 mmol) and Ag_2O (19.63 mg, 0.08 mmol) in dichloromethane, was stirred at room temperature overnight. Then, $[RuCl_2(p\text{-cymene})]_2$ (51.34 mg, 0.08 mmol) was added. Immediately, the formation of a white precipitate was observed. To complete the reaction, the suspension was stirred at room temperature for 7 h and then filtered through a pad of Celite. The solution was concentrated nearly to dryness and diethyl ether (5 mL) was added to precipitate the complex, which was collected by filtration and further washed with diethyl ether. Complex **2** was isolated as a brown solid. Yield: 92.8 mg, 70 %. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.71 (s, 1H, CH_{Ph}), 7.18 (s, 1H, CH_{Ph}), 5.50 (d, $^{3}J_{H,H}$ = 5.0 Hz, 2H, $CH_{p\text{-cym}}$), 5.11 (d, $^{3}J_{H,H}$ =5.0 Hz, 2H, $CH_{p\text{-cym}}$), 4.99-4.95 (m, 4H, 2H $NCH_2CH_2CH_2CH_3$ and 2H, CH_{Cp}), 4.52 (s, 2H, CH_{Cp}), 4.37-4.29 (m, 2H $NCH_2CH_2CH_2CH_3$), 4.23 (s, 5H CH_{Cp}), 4.10 (s, 3H NCH_3), 3.09-2.94 (m, 1H, $CH_{isop\ p\text{-cym}}$), 2.31-2.10 (m, 4H, $NCH_2CH_2CH_2CH_3$), 1.97 (s, 3H, $CH_{3\ p\text{-cym}}$), 1.75-1.62 (m, 4H, $NCH_2CH_2CH_2CH_3$), 1.28 (d, $^{3}J_{H,H}$ = 5.0 Hz, 6H, $CH_{3\ isop\ p\text{-cym}}$), 1.05 (t, $^{3}J_{H,H}$ = 15.0 Hz, 3H, $NCH_2CH_2CH_2CH_3$), 1.01 (t, $^{3}J_{H,H}$ = 15.0 Hz, 3H, $NCH_2CH_2CH_2CH_3$). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 188.0 (Ru-$C_{carbene}$), 155.7 (NCN), 140.1 ($C_{q\ Ph}$), 134.3 ($C_{q\ Ph}$), 132.7 ($C_{q\ Ph}$), 132.4 ($C_{q\ Ph}$), 109.3 ($C_{q\ p\text{-cym}}$), 99.8 ($C_{q\ p\text{-cym}}$), 99.6 (CH_{Ph}), 89.6 (CH_{Ph}), 86.9 ($CH_{p\text{-cym}}$), 83.0 ($CH_{p\text{-cym}}$), 73.8 ($C_{q\ Cp}$), 70.4 (CH_{Cp}), 69.8 (CH_{Cp}), 69.2 (CH_{Cp}), 50.4 ($N\mathit{C}H_2CH_2CH_2CH_3$), 50.2 ($N\mathit{C}H_2CH_2CH_2CH_3$), 32.2 ($NCH_2\mathit{C}H_2CH_2CH_3$), 32.1 ($NCH_2\mathit{C}H_2CH_2CH_3$), 31.9 ($N\mathit{C}H_3$), 30.8 ($\mathit{C}H_{isop\ p\text{-}cym}$), 22.7 ($\mathit{C}H_{3\ isop\ p\text{-}cym}$), 20.6 ($NCH_2CH_2\mathit{C}H_2CH_3$), 18.7 ($\mathit{C}H_{3\ p\text{-}cym}$), 14.2 ($NCH_2CH_2CH_2\mathit{C}H_3$), 14.1 ($NCH_2CH_2CH_2\mathit{C}H_3$). Electrospray MS (20 V, *m/z*): 739.3 $[M\text{-}Cl]^+$. Anal. Calcd. for $C_{37}H_{46}N_4Cl_2FeRu{\cdot}H_2O$ (792.62): C, 56.07; H, 6.10; N, 7.07. Found: C, 55.95; H, 6.09; N, 7.08.

Oxidation of complex 2, synthesis of complex 3. Complex **2** (20 mg, 0.03 mmol) and acetylferrocenium tetrafluoroborate (8.13 mg, 0.03 mmol) were placed together in a Schleck tube. The tube was evacuated and filled with nitrogen three times. The solids were dissolved in dry dichloromethane (10 mL) and the resulting mixture stirred at room temperature for 2 h. The solution was then concentrated nearly to dryness and dry diethyl ether (5 mL) was added. The brown solid so formed was washed three times with dry diethyl ether in order to remove the formed acetylferrocene, which is soluble in diethyl ether. Complex **3** was isolated, along with **3**-**H**, as a brown solid. Yield: 20.2 mg, 91%. Anal. Calcd. for $C_{37}H_{46}N_4Cl_2RuFeBF_4$ (861.41): C, 51.59; H, 5.38; N, 6.50. Found: C, 51.48; H, 5.42; N, 6.22. Electrospray MS (20 V, *m/z*): 370.0 $[M\text{-}Cl{+}H]^{2+}$. Electrospray MS negative mode (20 V, *m/z*): 87.3 $[BF_4]^-$.

Reduction of complex 3, recovery of complex 2. Complex **3** (10 mg, 0.01 mmol) and cobaltocene (2.19 mg, 0.01 mmol) were placed together in a Schleck tube. The tube was evacuated and filled with nitrogen three times. The solids were dissolved in dry dichloromethane (5 mL) and the resulting mixture stirred at room temperature for 1 h. The solution was then concentrated nearly to dryness and dry diethyl ether (5 mL) was added. The brown solid so formed was washed three times with dry diethyl ether. The filtrate was concentrated under reduced pressure affording the desired product. The spectroscopic data were in agreement with those described above for complex **2**. Yield: 8.5 mg, 95%.

Catalytic experiments

General procedure for the transfer hydrogenation. Complex **2** (0.0025 mmol) and KOH (0.05 mmol) were placed in a Schlenk tube fitted with a Teflon cap. The tube was then degassed and filled with nitrogen three times. Isopropanol (2 mL) and the corresponding ketone or imine (0.5 mmol) were added, and the mixture was stirred at 80 ºC for 2 h. Yields were determined by GC analyses using anisole (0.5 mmol) as internal standard. Some of the products were identified according to commercially available samples: 1-phenylethanol, cyclohexanol, α-methyl-2-naphtalenemethanol, 4-bromo-α-methylbenzyl alcohol, 4-methoxy-α-methylbenzyl alcohol and N-benzylaniline. The spectroscopic features of 1-phenylhexan-1-ol were obtained from the literature.[17]

Redox-switching experiments using complex 2. Complex **2** (0.0025 mmol) and KOH (0.05 mmol) were placed together in a Schlenk tube fitted with a Teflon cap. The tube was degassed and filled with nitrogen three times. Isopropanol (2 mL) and hexanophenone (0.5 mmol) were added, and the resulting mixture stirred at 80ºC for 1h. The oxidant, acetylferrocenium tetrafluoroborate (0.0025 mmol), was then added and the resulting mixture was stirred at 80ºC for 2h. After this time, the reductant, cobaltocene (0.00275 mmol), was added to the reaction vessel and the resulting mixture was stirred at 80ºC. Aliquots were extracted at the desired times, and analysed by GC using anisole (0.5 mmol) as internal standard.

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Keywords: N-Heterocyclic carbenes • Ruthenium • Transfer hydrogenation • redox-switchable • Ferrocene

[1] V. Blanco, D. A. Leigh and V. Marcos, *Chem. Soc. Rev.* **2015**, *44*, 5341-5370
[2] O. R. Luca and R. H. Crabtree, *Chem. Soc. Rev.* **2013**, *42*, 1440-1459.
[3] A. M. Allgeier and C. A. Mirkin, *Angew. Chem. Int. Ed.* **1998**, *37*, 894-908.
[4] a) V. Lyaskovskyy and B. de Bruin, *ACS Catal.* **2012**, *2*, 270-279; b) B. de Bruin, *Eur. J. Inorg. Chem.* **2012**, 340-342.
[5] a) U. Siemeling, C. Faerber, M. Leibold, C. Bruhn, P. Muecke, R. F. Winter, B. Sarkar, M. von Hopffgarten and G. Frenking, *Eur. J. Inorg. Chem.* **2009**, 4607-4612; b) U. Siemeling, C. Faerber and C. Bruhn, *Chem. Commun.* **2009**, 98-100; c) D. M. Khramov, E. L. Rosen, V. M. Lynch and C. W. Bielawski, *Angew. Chem. Int. Ed.* **2008**, *47*, 2267-2270; d) A. G. Tennyson, R. J. Ono, T. W. Hudnall, D. M. Khramov, J. A. V. Er, J. W. Kamplain, V. M. Lynch, J. L. Sessler and C. W. Bielawski, *Chem. Eur. J.* **2010**, *16*, 304-315; e) K. Arumugam, J. Chang, V. M. Lynch and C. W. Bielawski, *Organometallics* **2013**, *32*, 4334-4341; f) A. Labande, N. Debono, A. Sournia-Saquet, J.-C. Daran and R. Poli, *Dalton Trans.* **2013**, *42*, 6531-6537; g) A. Labande, J.-C. Daran, N. J. Long, A. J. P. White and R. Poli, *New J. Chem.* **2011**, *35*, 2162-2168; h) B. Bildstein, *J. Organomet. Chem.* **2001**, *617*, 28-38; i) B. Bildstein, M. Malaun, H. Kopacka, K. Wurst, M. Mitterbock, K. H. Ongania, G. Opromolla and P. Zanello, *Organometallics* **1999**, *18*, 4325-4336; j) B. Bildstein, M. Malaun H. Kopacka, K. H. Ongania and K. Wurst, *J. Organomet. Chem.* **1999**, *572*, 177-187; k) B. Bildstein, M. Malaun, H. Kopacka, K. H. Ongania and K. Wurst, *J. Organomet. Chem.* **1998**, *552*, 45-61; l) N. Debono, J.-C. Daran, R. Poli and A. Labande, *Polyhedron* **2015**, *86*, 57-63; m) L. Bechki and T. Lanez, *Asian J. Chem.* **2010**, *22*, 5523-5527.
[6] a) M. Sussner and H. Plenio, *Angew. Chem. Int. Ed.* **2005**, *44*, 6885-6888; b) K. Arumugam, C. D. Varnado, S. Sproules, V. M. Lynch and C. W. Bielawski, *Chem. Eur. J.* **2013**, *19*, 10866-10875; c) C. D. Varnado, Jr., E. L. Rosen, M. S. Collins, V. M. Lynch and C. W. Bielawski, *Dalton Trans* **2013**, *42*, 13251-13264; d) L. Hettmanczyk, S. Manck, C. Hoyer, S. Hohloch and B. Sarkar, *Chem. Commun.* **2015**, *51*, 10949-10952; e) E. L. Rosen, C. D. Varnado, A. G. Tennyson, D. M. Khramov, J. W. Kamplain, D. H. Sung, P. T. Cresswell, V. M. Lynch and C. W. Bielawski, *Organometallics* **2009**, *28*, 6695-6706; f) A. G. Tennyson, V. M. Lynch and C. W. Bielawski, *J. Am. Chem. Soc.* **2010**, *132*, 9420-9429.
[7] S. Ibanez, M. Poyatos, L. N. Dawe, D. Gusev and E. Peris, *Organometallics* **2016**, *35*, 2747-2758.
[8] L. Mercs, A. Neels and M. Albrecht, *Dalton Trans.* **2008**, 5570-5576.
[9] a) R. Martinez and A. Tiripicchio, *Acta Crystallogr. Sect. C-Cryst. Struct. Commun.* **1990**, *46*, 202-205; b) X. C. Wang, Y. P. Tian, Y. H. Kan, C. Y. Zuo, J. Y. Wu, B. K. Jin, H. P. Zhou, J. X. Yang, S. Y. Zhang, X. T. Tao and M. H. Jiang, *Dalton Trans.* **2009**, 4096-4103; c) T. Y. Dong, B. R. Huang, S. M. Peng, G. H. Lee and M. Y. Chiang, *J. Organomet. Chem.* **2002**, *659*, 125-132; d) N. J. Mammano, A. Zalkin, A. Landers and A. L. Rheingold, *Inorg. Chem.* **1977**, *16*, 297-300.
[10] D. Wang and D. Astruc, *Chem. Rev.* **2015**, *115*, 6621-6686.
[11] A. A. Danopoulos, S. Winston and W. B. Motherwell, *Chem. Commun.* **2002**, 1376-1377.
[12] M. Poyatos, J. A. Mata, E. Falomir, R. H. Crabtree and E. Peris, *Organometallics* **2003**, *22*, 1110-1114.

[13] V. Dragutan, I. Dragutan, L. Delaude and A. Demonceau, *Coord. Chem. Rev.* **2007**, *251*, 765-794.

[14] a) J. DePasquale, M. Kumar, M. Zeller and E. T. Papish, *Organometallics* **2013**, *32*, 966-979; b) W. W. N. O, A. J. Lough and R. H. Morris, *Organometallics* **2011**, *30*, 1236-1252.

[15] S. Ruiz-Botella and E. Peris, *Chem. Eur. J.* **2015**, *21*, 15263-15271.

[16] N. G. Connelly and W. E. Geiger, *Chem. Rev.* **1996**, *96*, 877-910.

[17] M. Victoria Jimenez, J. Fernandez-Tornos, F. Javier Modrego, J. J. Perez-Torrente and L. A. Oro, *Chem. Eur. J.* **2015**, *21*, 17877-17889.

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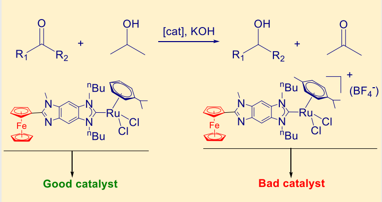
FULL PAPER

A ferrocenyl-benzo-fused-imidazolylidene complex of Ru(II) was used as a redox-switchable catalyst in the transfer hydrogenation of ketones and imines. The activity of the catalyst significantly decreases in the presence of an oxidant.



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