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A Ferrocenyl-Benzo-Fused Imidazolylidene Complex of Ruthenium as Redox-Switchable Catalyst for the Transfer Hydrogenation of Ketones and Imines

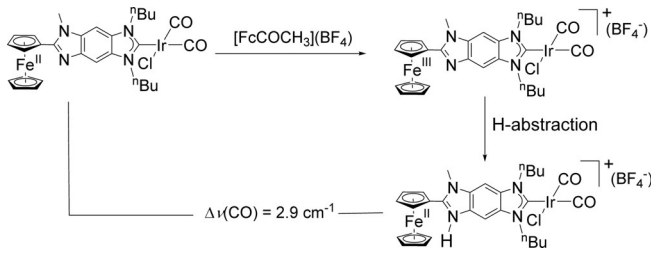
Susana Ibáñez, Macarena Poyatos,* and Eduardo Peris*[a]

A ferrocenyl-benzo-fused imidazolylidene complex of Ru^{II} was prepared and fully characterized. In the presence of acetylferrocenium tetrafluoroborate this complex can be oxidized to generate a complex with a cationic ligand. The neutral complex can be recovered by reducing the oxidized cationic compound with cobaltocene. The activity of the neutral and oxidized complexes was tested in the transfer hydrogenation of ketones and imines, using isopropyl alcohol as the hydrogen source. The neutral complex is very active in the reduction of all tested substrates, whereas the oxidized species shows low activity in the reduction of ketones. The rate of the reduction of hexaphenone could be modulated by addition of subsequent amounts of oxidant and reductant. The addition of acetylferrocenium tetrafluoroborate caused a decrease in the catalytic activity, whereas the addition of cobaltocene restored the activity. The catalytic activity shown by both catalysts in the reduction of *N*-benzylideneaniline was 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 owing to their great chemical versatility a large number of *N*-heterocyclic carbene ligands (NHCs) containing redox-active moieties have been recently reported,[5] although their use in homogeneous catalysis has been 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 resulting from the protonation of the ferrocenyl–imidazolylidene (Fe^{2+}) ligand



Scheme 1. Oxidation and further hydrogen abstraction of the ferrocenyl-benzo-fused imidazolylidene Ir^{I} complex.

(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 electron-donating character of the ligand was quantified as 2.9 cm^{-1}, considering the shift in the ν_{av}(CO) of the related [IrCl(Fc-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.

Based on these previous findings, we now report the preparation of a ruthenium(II) complex with a ferrocenyl-benzo-

[a] Dr. S. Ibáñez, Dr. M. Poyatos, Prof. Dr. E. Peris
Institute of Advanced Materials (INAM)
Universitat Jaume I
Avda. Sos Baynat., E-12071-Castellón (Spain)
E-mail: eperis@uji.es
poyatosd@uji.es

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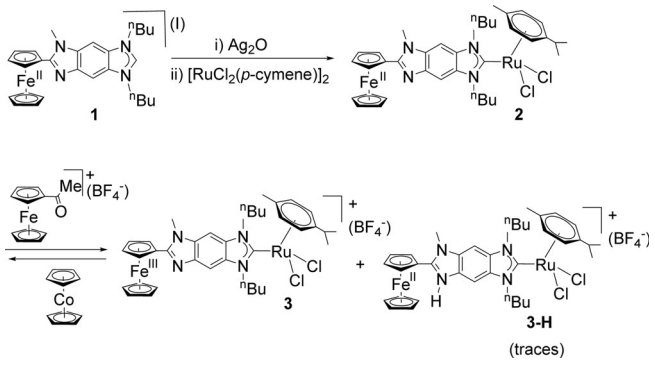
fused imidazolylidene ligand. The complex was characterized and its electrochemical behavior was fully analyzed. The redox-switchable properties of this new complex are described in the reduction of ketones and imines by transfer hydrogenation using isopropyl alcohol as a hydrogen source.

Results and Discussion

The synthesis of the ferrocenyl–imidazolylidene ruthenium(II) complex **2** is displayed in Scheme 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**.

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

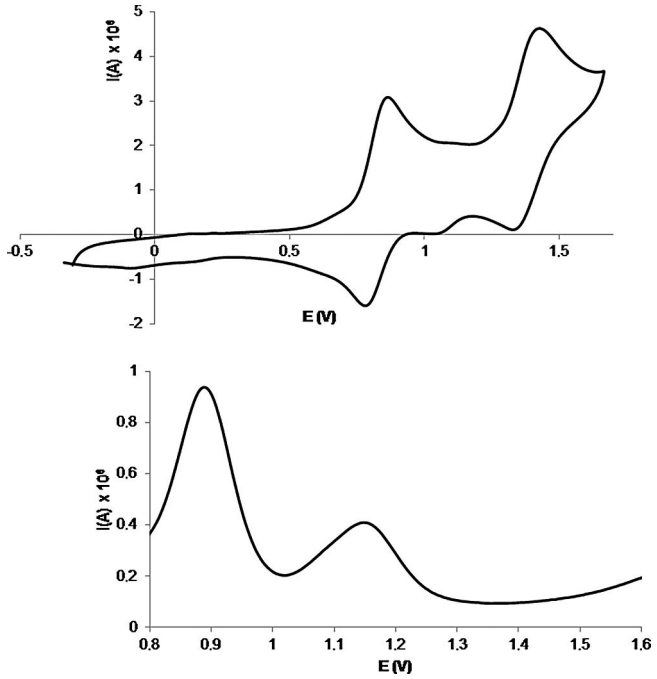


Figure 1. CV diagram (above) and relevant section of the differential pulse analysis of complex **2** (below). Measurements performed on a 1 mM solution of the analyte in dry CH_2Cl_2 with 0.1 M $[NBu_4][PF_6]$ as the supporting electrolyte, 100 mV s^{-1} scan rate, Fc/Fc^{+} used as standard with $E_{1/2}(Fc/Fc^{+})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

The molecular structure of complex **2** is displayed in Figure 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 length is 2.087(8) Å. The plane of the tricyclic carbene ligand deviates from that of the substituted Cp ring of the ferrocenyl fragment by an angle of 23.88°. The two N–C bond lengths of the imidazolyl ring bound to the ferrocenyl moiety are different, in agreement with the existence of a double and a single C–N bond (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

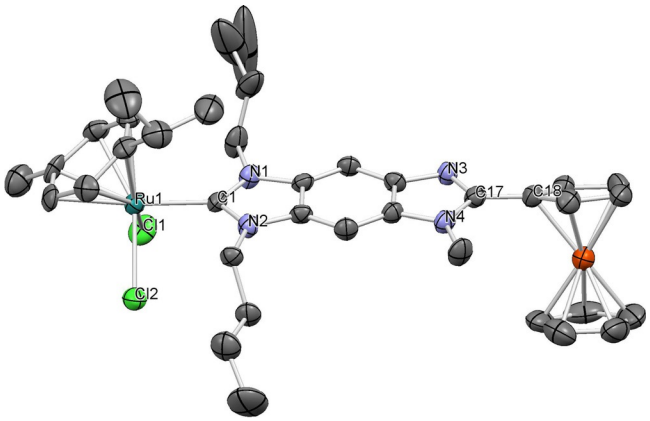


Figure 2. Molecular structure of complex **2**. Ellipsoids at 50% of probability. Hydrogen atoms and solvent ($CHCl_3$) are omitted for clarity. Selected bond lengths (Å) and angles (°): Ru(1)–C(1) 2.087(8), Ru(1)–Cl(1) 2.410(2), Ru(1)–Cl(2) 2.430(2), C(1)–N(1) 1.336(10), C(1)–N(2) 1.364(11), C(17)–C(18) 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).

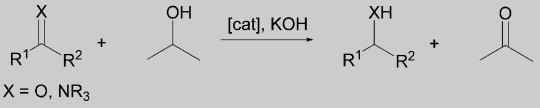
the substituted and unsubstituted Cp rings. This distance, together with the eclipsed orientation of the Cp rings, is consistent with the presence of a Fe^{II} center at the ferrocenyl moiety.[9]

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 isopropyl alcohol as a 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 the loss of the arene ligand is the slowest step of the process,[14a] therefore, strong electron-donating ancillary ligands (which should favor this loss) may enhance the activity of the catalyst. On the contrary, poor electron-donating 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.

The results of the reduction of a series of ketones and imines in isopropyl alcohol using **2** as the catalyst are shown in Table 1. To determine if the oxidation of the ferrocenyl ligand could have an effect on the catalytic outcome of the process, the reactions were also performed under the same reaction conditions, but with the addition of acetylferrocenium tetrafluoroborate. We used the optimized reaction conditions that we have obtained in some previously published works.[15] The reactions were performed using 0.5 mol% catalyst loading (same amount of oxidant, if needed), in isopropyl alcohol at 80 °C 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.

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



X = O, NR_3

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 °C for 2 h. [b] Yields determined by GC using anisole (0.5 mmol) as an internal standard.

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. It shows that the addition of the oxidant not only produces a lower yield of the product, but also decelerates the reaction, 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 have kinetic reasons rather than reasons related to the stability of both, **2** and **3**. Notably, the yields shown in Figure 3 and Table 1 are significantly different, but this owed 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.

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 80 °C using **2** (0,5 mol%). We chose this substrate because it gave us the largest difference in catalytic activity between **2** and **3** (com-

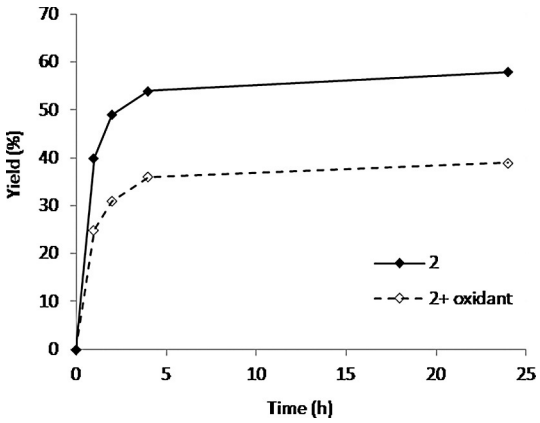


Figure 3. Time-dependent reaction profile of the transfer hydrogenation of cyclohexanone. Reaction conditions as those described in Table 1. Oxidant = acetylferrocenium tetrafluoroborate.

pare 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 is shown in Figure 4. After one hour (50% yield) acetylferrocenium tetrafluoroborate (1 equiv.) 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 equiv.) restored the activity of the catalyst, as expected for the regeneration of the neutral catalyst **2** from the reduction of **3**. Although the recovery of the activity of the catalyst was not complete, we attributed the attenuated activity to partial decomposition of the catalyst caused by the successive removing of aliquots during the study, which made us interrupt the reaction for a period of time by cooling the mixture and restoring the temperature after each measurement.

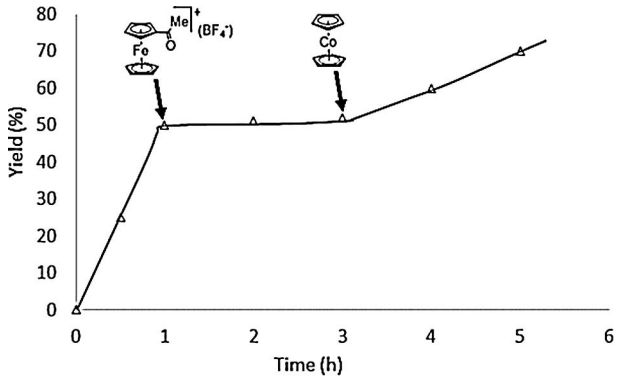


Figure 4. Time-dependent reaction profile of the reduction of hexanophenone by transfer hydrogenation. The arrows indicate the addition of acetylferrocenium tetrafluoroborate (1 equiv.) and cobaltocene (1.1 equiv.). The reactions were performed by using 0.5 mol% of catalyst, at 80 °C, under the same reaction conditions as those described in Table 1. Yields calculated by GC using anisole as a standard.

Conclusions

We prepared and fully characterized a new ferrocenyl-benzofused 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. If 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, whereas 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 imine, the activity of the neutral complex was similar to that shown by its oxidized partner. Our work adds a new example to the rare cases of 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 ionization mass spectra (ESI–MS) were recorded on a Micromass Quatro LC instrument; nitrogen was employed as drying and nebulizing gas. Elemental analyses were performed on a TruSpec Micro Series. Electrochemical studies were performed 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 mV s^{-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 RT 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 RT 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, $CDCl_3$): $\delta = 7.71$ (s, 1H, CH_{Ph}), 7.18 (s, 1H, CH_{Ph}), 5.50 (d, $^3J_{H,H} = 5.0$ Hz, 2H, $CH_{p\text{-}cym}$), 5.11 (d, $^3J_{H,H} = 5.0$ 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, $^3J_{H,H} = 5.0$ Hz, 6H, $CH_{3\ isop\ p\text{-}cym}$), 1.05 (t, $^3J_{H,H} = 15.0$ Hz, 3H, $NCH_2CH_2CH_2CH_3$), 1.01 ppm (t, $^3J_{H,H} = 15.0$ Hz, 3H, $NCH_2CH_2CH_2CH_3$). ^{13}C NMR (126 MHz, $CDCl_3$): $\delta = 188.0$ (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 ($NCH_2CH_2CH_2CH_3$), 50.2 ($NCH_2CH_2CH_2CH_3$), 32.2 ($NCH_2CH_2CH_2CH_3$), 32.1 ($NCH_2CH_2CH_2CH_3$), 31.9 (NCH_3), 30.8 ($CH_{isop\,p\text{-}cym}$), 22.7 ($CH_{3\,isop\,p\text{-}cym}$), 20.6 ($NCH_2CH_2CH_2CH_3$), 18.7 ($CH_{3\,p\text{-}cym}$), 14.2 ($NCH_2CH_2CH_2CH_3$), 14.1 ppm ($NCH_2CH_2CH_2CH_3$). ESI–MS (20 V, *m/z*): 739.3 $[M-Cl]^+$. 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 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. ESI–MS (20 V, *m/z*): 370.0 $[M\text{-}Cl+H]^{2+}$. ESI–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 RT 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%.

General procedure for the transfer hydrogenation catalytic experiment

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 evacuated and filled with nitrogen three times. Isopropyl alcohol (2 mL) and the corresponding ketone or imine (0.5 mmol) were added, and the mixture was stirred at 80 °C 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 evacuated and filled with nitrogen three times. Isopropyl alcohol (2 mL) and hexanophenone (0.5 mmol) were added, and the resulting mixture stirred at 80 °C for 1 h. The oxidant, acetylferrocenium tetrafluoroborate (0.0025 mmol), was then added and the resulting mixture was stirred at 80 °C for 2 h. After this time, the reductant, cobaltocene (0.00275 mmol), was added to the reaction vessel and the resulting mixture was stirred at 80 °C. Aliquots were extracted at the desired times, and analysed by GC using anisole (0.5 mmol) as internal standard.

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Keywords: carbene ligands · ligand design · oxidation · ruthenium · hydrogenation

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