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Ru^{II}, Ir^{III} and Os^{II} mesoionic carbene complexes: efficient catalysts for transfer hydrogenation of selected functionalities†‡

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Pyridine-appended triazolylidene donors have been recently used as ligands in various homogeneous catalytic processes. We present here a new pyrimidine substituted triazolium salt which was prepared and used in the coordination to Ru^{II} and Os^{II}. The new triazolium salt and the obtained complexes were characterized by multinuclear NMR spectroscopy. The molecular composition of the mentioned compounds was confirmed by positive ion electrospray ionization (ESI+) mass spectra. The new pyrimidyl containing complexes, as well as the related pyridyl-triazolylidene containing complexes, were applied in transfer hydrogenation reactions of carbonyls, alkenes, imines and nitroarenes. The pyrimidyl containing complexes reveal an over-all better activity in comparison to their pyridine bearing analogues. The studies of electronic effects of the ligands, as well as mechanistic insights for the reduction of nitrobenzene with three selected precatalysts are presented.

Introduction

The transfer hydrogenation reaction promoted by metal-complexes is currently one of the most commonly investigated homogeneous hydrogenation processes.[1] This reaction is highly appealing for several reasons. It does not require hazardous gaseous hydrogen and pressurized reactors, and it employs cheap and sustainable solvents as the source of hydrogen, to name just a few. The wide range of functional groups that can be reduced by transfer hydrogenation is noteworthy. These include carbonyl, olefin, imine, nitrile, and nitro compounds. The need to develop simple and sustainable reaction conditions that require only low catalyst loadings is currently emerging in developing new catalysts and catalytic systems.

In the last two decades N-heterocyclic carbenes (NHCs) have been developed as a powerful class of ligands. Despite being used in nearly every field of modern chemical sciences, without a doubt NHCs have most dramatically affected organometallic chemistry and catalysis. Owing to their strong σ-donation ability, air and moisture stability, high structural variability, as well as low toxicity, they have become viable alternatives to widely used phosphines in many catalytic processes. Today, a vast number of transformations are known to proceed only with NHC-based catalysts.[2] 1,2,3-Triazol-5-ylidenes are a prominent subclass of NHCs possessing a mesoionic carbene (MIC) structure. Due to a lower heteroatom stabilization and mesoionic character, MICs are among one of the best σ-donors among the NHCs.[3] The highly efficient and modular nature of click reaction that is generally used to access 1,2,3-triazol-5-ylidenes makes the design and preparation of diverse libraries of these ligands extremely easy.[4] Complexes bearing triazolylidenes are increasingly used in homogeneous metal-based catalysis, as well as for photophysical and biochemical purposes.[4d] Many catalytic systems of this type have been studied, showing comparable or even better efficiency in comparison to the majority of their NHC analogues.[5] Metal complexes of MIC ligands have been used as catalysts among others in olefin metathesis,[6] oxidations,[7] reductions,[8] click reactions,[9] and C–C/C–N bond formation reactions.[10]

Recently, three series of complexes consisting of pyridine appended triazolylidenes as ligands with ruthenium(II), iridium(III) and osmium(II) were reported and they were successfully used in transfer hydrogenation of selected carbonyl substrates (Scheme 1).[11] All complexes have shown remarkable activity even at very low catalyst loadings with several different substrates investigated. The ruthenium(II) complexes were also used in oxidation of primary and secondary alcohols.[7d]

Encouraged by these results, we were prompted to test the activity of these complexes also for transfer hydrogenation of substrates bearing other functional groups. In particular, we

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† Dedicated to Prof. Bernhard Lippert on the occasion of his 70th birthday.

‡ Electronic supplementary information (ESI) available. See DOI: 10.1039/c6dt01324d

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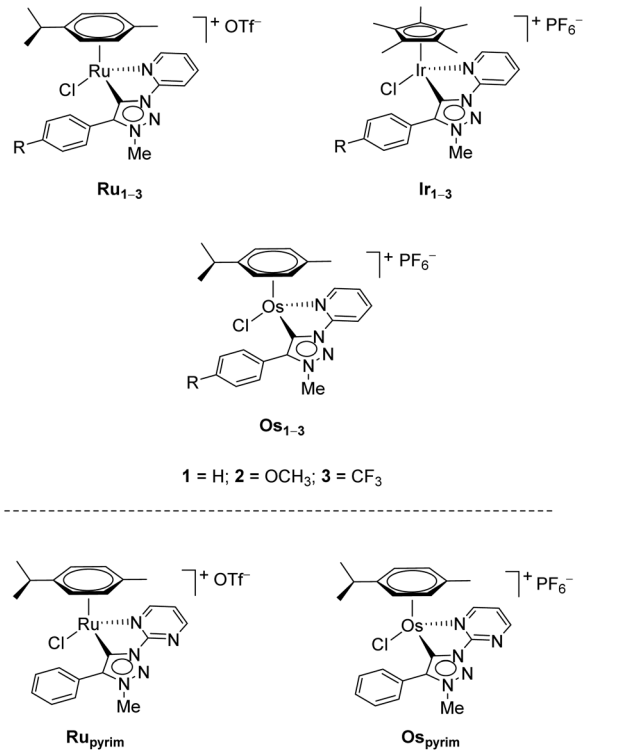


Scheme 1 The Ru^{II}, Os^{II} and Ir^{III} pyridine-appended MIC complexes (up),[11] and Ru^{II} and Os^{II} pyrimidine-appended MIC complexes (bottom) used in this work.

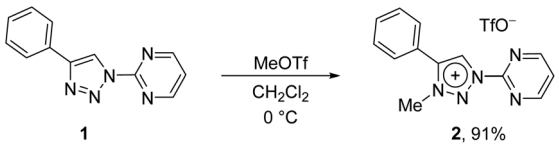
were interested in different carbonyl, olefin, imine, and nitroarene substrates.

In addition to the pyridine-appended MICs, we decided to design novel MICs that are functionalized with a pyrimidine ring. The starting 1-(2-pyrimidyl)-functionalized triazolium salt was prepared in excellent yields and purity and used to construct the corresponding Ru(II) and Os(II) complexes (Scheme 1). The coordination was achieved by a transmetallation protocol and the corresponding complexes were characterized by ^{1}H, ^{13}C and ^{15}N NMR spectroscopy and high resolution mass spectrometry. Unfortunately, the preparation of the Ir(III) analogue failed. The two pyrimidine-appended MIC complexes of Ru(II) and Os(II) and the previously reported[7d,11] pyridine-appended MICs of Ru(II), Ir(III), and Os(II), shown in Scheme 1, were used in transfer hydrogenation of the above mentioned functionalities. This is also the first report on pyrimidine-appended triazolium salts, the corresponding MICs and their transition metal complexes. Some mechanistic insights into the reduction of nitrobenzene with the three selected complexes are presented.

Results and discussion

Ligand synthesis and coordination

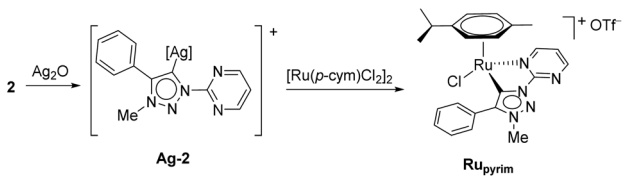
In contrast to earlier reports of unselective methylation of pyridyl-triazoles,[12] some of us have recently reported a selective route to generate only $N_{Triazole}$ methylated pyridyl-triazolium salts.[13] Some of these salts have already been successfully used to generate ruthenium(II), osmium(II) and iridium(III) complexes.[7d,11] Inspired by these reports, we designed and prepared an analogous derivative, that has a pyrimidine ring attached directly to the triazole nitrogen atom N1 (Scheme 2). The starting triazole **1** was prepared by copper-catalyzed cycloaddition of phenylacetylene with 2-azidopyrimidine (tetrazolo [1,5-*a*]pyrimidine) as reported previously.[14] The methylation into **2** was achieved by mixing the triazole with MeOTf in dry dichloromethane at 0 °C for 24 h (Scheme 2). Triazolium salt **2** was isolated as a triflate salt in 91% yield. In analogy to 1-(2-pyridyl)-1,2,3-triazoles,[13] 1-(2-pyrimidyl)-1,2,3-triazole **1** could be selectively alkylated with MeOTf at triazole nitrogen N3 with no need of pyrimidine ring protection.



Scheme 2 The synthesis of triazolium salt **2**.

Next, the coordination ability of triazolium salt **2** towards Ru(II), Ir(III) and Os(II) was examined. To this end, we chose the already established transmetalation protocol *via* the intermediate carbenic silver(I) complex, shown in Scheme 3.[15]

The triazolium salt **2** was stirred with Ag_2O and in dry acetonitrile at room temperature for 4 days (Scheme 3). The formation of complex **Ag-2** was suggested by the disappearance of the triazolium proton H-5 from the ^{1}H NMR spectral analysis in DMSO-d_6. Due to the general instability of such silver complexes, we were unable to obtain more experimental data for its structure. Subsequently, **Ag-2** was subjected to transmetalation without previous isolation employing $[Ru(p\text{-cym})Cl_2]_2$ as a ruthenium source (Scheme 3). The reaction progress was monitored by TLC analysis. The pure complex $\mathbf{Ru_{pyrim}}$ was isolated as a triflate salt after 2 hours by simple three-step filtration–solvent evaporation–crystallization workup in 85% yield (Table 1). For the preparation of $\mathbf{Os_{pyrim}}$, which involved transmetalation with the Os^{II} precursor $[Os(p\text{-cym})Cl_2]_2$ the reaction mixture had to be stirred for a prolonged time of 3 days. The complex $\mathbf{Os_{pyrim}}$ was isolated in the pure form as a PF_6 salt in a moderate yield of 53% (Table 1). Unfortunately, we were unable to prepare the Ir^{III} analogue. After the addition of $[IrCp^*Cl_2]_2$ to the reaction mixture of the triazolium salt **2**



Scheme 3 The ruthenation of **2** *via* transmetalation.

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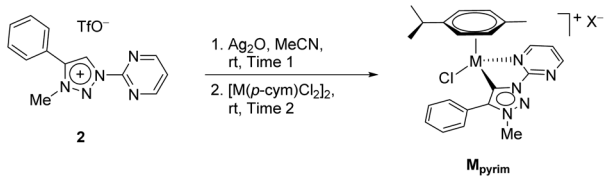
Table 1 The synthesis of $\mathbf{Ru_{pyrim}}$ and $\mathbf{Os_{pyrim}}$ complexes



M = Ru, X = OTf
M = Os, X = PF_6

Entry	Time 1 (days)	Time 2 (h)	Product	Yield[a] (%)
1	4	2	$\mathbf{Ru_{pyrim}}$	85
2	4	72	$\mathbf{Os_{pyrim}}$	53

[a] Isolated pure product.

and Ag_2O in acetonitrile, no pure product could be isolated. Instead a mixture of products was isolated. The use of a base such as Cs_2CO_3 or heating of the reaction mixture did not lead to any improvement. Even though we could identify the product in the mass spectrum of the crude reaction mixture (see the ESI‡), attempts to purify it led to its decomposition. Although it is not clear at this stage as to why the product decomposes at the purification stage, we think that it does not survive either the filtration through Celite, or the salt metathesis with KPF_6 that is necessary for its purification.

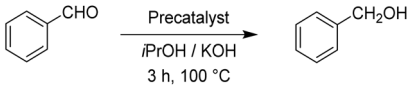
Transfer hydrogenation catalysis

After having the two complexes $\mathbf{Ru_{pyrim}}$ and $\mathbf{Os_{pyrim}}$ prepared, we examined their activity in transfer hydrogenation catalysis. In this context we also tested some Ru^{II}, Ir^{III} and Os^{II} complexes from our previous reports, which were already used for carbonyl group reduction.[11] As the model reaction we examined the reduction of benzaldehyde to benzyl alcohol. After testing at room temperature, 60 °C and 80 °C, we observed that the best conversions are obtained at 100 °C. Hence, all transfer hydrogenation reactions (other than nitrobenzene) were carried out at 100 °C. The results for benzaldehyde are presented in Table 2.

The reduction of benzaldehyde under the applied reaction conditions proceeds smoothly with all tested complexes. Applying 0.5 mol% of the precatalysts, as well as with only 0.01 mol%, the reduction occurred with full conversion of the starting material, reflecting in a TON of about 10 000. This is comparable to known ruthenium(II)–NHC complexes[16] and in line with the activity of their pyridyl-MIC analogues.[11] To investigate further the catalytic performance of the $\mathbf{Ru_{pyrim}}$ and $\mathbf{Os_{pyrim}}$, acetophenone was used as a substrate. Ketones in general are known to be more challenging substrates than aldehydes for the reduction. The results are outlined in Table 3.

Whereas the reduction of acetophenone with the ruthenium complex $\mathbf{Ru_{pyrim}}$ at the precatalyst loadings of 0.5 mol% gave full conversion of acetophenone to 1-phenylethanol, the osmium complex $\mathbf{Os_{pyrim}}$ gave only 70% of the reduced substrate. By using 0.01 mol%, the pyrimidine analogue $\mathbf{Ru_{pyrim}}$

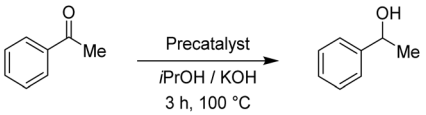
Table 2 The transfer hydrogenation of benzaldehyde[a]



Precatalyst	Conv.[b] (%)	Precatalyst	Conv.[b] (%)	Precatalyst	Conv.[b] (%)
Precatalyst loading: 0.5 mol%					
$\mathbf{Ru_1}$ [c]	>99	$\mathbf{Ir_1}$ [c]	>99	$\mathbf{Os_1}$ [c]	>99
$\mathbf{Ru_2}$ [c]	>99	$\mathbf{Ir_2}$ [c]	>99	$\mathbf{Os_2}$ [c]	>99
$\mathbf{Ru_3}$ [c]	>99	$\mathbf{Ir_3}$ [c]	>99	$\mathbf{Os_3}$ [c]	>99
$\mathbf{Ru_{pyrim}}$	>99			$\mathbf{Os_{pyrim}}$	>99
Precatalyst loading: 0.01 mol%					
$\mathbf{Ru_1}$ [c]	>99	$\mathbf{Ir_1}$ [c]	>99	$\mathbf{Os_1}$ [c]	>99
$\mathbf{Ru_2}$ [c]	>99	$\mathbf{Ir_2}$ [c]	>99	$\mathbf{Os_2}$ [c]	>99
$\mathbf{Ru_3}$ [c]	>99	$\mathbf{Ir_3}$ [c]	>99	$\mathbf{Os_3}$ [c]	>99
$\mathbf{Ru_{pyrim}}$	>99			$\mathbf{Os_{pyrim}}$	>99

[a] General reaction conditions: benzaldehyde (0.5 mmol), precatalyst, KOH (0.085 mmol), iPrOH (4 mL), 100 °C for 3 h. [b] Conversion determined by ^1H NMR spectroscopy using hexamethylbenzene as an internal standard. [c] Data collected from ref. 11.

Table 3 The reduction of acetophenone[a]



Precatalyst	Conv.[b] (%)	Precatalyst	Conv.[b] (%)	Precatalyst	Conv.[b] (%)
Precatalyst loading: 0.5 mol%					
$\mathbf{Ru_1}$ [c]	>99	$\mathbf{Ir_1}$ [c]	88	$\mathbf{Os_1}$ [c]	76
$\mathbf{Ru_2}$ [c]	>99	$\mathbf{Ir_2}$ [c]	71	$\mathbf{Os_2}$ [c]	88
$\mathbf{Ru_3}$ [c]	>99	$\mathbf{Ir_3}$ [c]	92	$\mathbf{Os_3}$ [c]	65
$\mathbf{Ru_{pyrim}}$	>99			$\mathbf{Os_{pyrim}}$	70
Precatalyst loading: 0.01 mol%					
$\mathbf{Ru_1}$ [c]	80				
$\mathbf{Ru_2}$ [c]	89				
$\mathbf{Ru_3}$ [c]	60				
$\mathbf{Ru_{pyrim}}$	94				

[a] General reaction conditions: acetophenone (0.5 mmol), precatalyst, KOH (0.085 mmol), iPrOH (4 mL), 100 °C for 3 h. [b] Conversion determined by ^1H NMR spectroscopy using hexamethylbenzene as an internal standard. [c] Data collected from ref. 11.

has shown the best activity amongst all tested precatalysts. With 0.5 mol% of the $\mathbf{Ru_2}$ precatalyst, we were able to isolate the product in 85% yield (conversion >99%). Prompted by very good overall results with acetophenone we decided to continue with a more sterically hindered substrate, benzophenone. The results are collected in Table 4.

Benzophenone was fully converted into diphenylmethanol with the $\mathbf{Ru_{pyrim}}$ precatalyst at 0.5 mol%. The same complex gave an excellent 93% conversion also at 0.1 mol% precatalyst loading, which is the best performance for all tested compounds. With 0.1 mol% of the $\mathbf{Ru_1}$ precatalyst, we were able to isolate the product in 60% yield (conversion 69%, Table 4). On the other hand $\mathbf{Os_{pyrim}}$ gave only 72% conversion by employing

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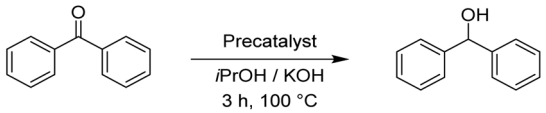
Table 4 The reduction of benzophenone[a]



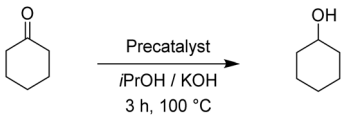
Precatalyst	Conv.[b] (%)	Precatalyst	Conv.[b] (%)	Precatalyst	Conv.[b] (%)
Precatalyst loading: 0.5 mol%					
Ru$_1$[c]	>99	**Ir$_1$**[c]	65	**Os$_1$**[c]	68
Ru$_2$[c]	>99	**Ir$_2$**[c]	55	**Os$_2$**[c]	88
Ru$_3$[c]	>99	**Ir$_3$**[c]	85	**Os$_3$**[c]	25
Ru$_{pyrim}$	>99			**Os$_{pyrim}$**	72
Precatalyst loading: 0.1 mol%					
Ru$_1$[c]	69				
Ru$_2$[c]	90				
Ru$_3$[c]	59				
Ru$_{pyrim}$	93				

[a] General reaction conditions: benzophenone (0.5 mmol), precatalyst, KOH (0.085 mmol), iPrOH (4 mL), 100 °C for 3 h. [b] Conversion determined by ^{1}H NMR spectroscopy using hexamethylbenzene as an internal standard. [c] Data collected from ref. 11.

0.5 mol% of the precatalyst. This result is in line with other Os(II) complexes **Os$_{1-3}$**. To finish, we conducted the reduction of cyclohexanone as a representative of an aliphatic substrate. The results are summarized in Table 5.

The two pyrimidyl-MIC complexes **Ru$_{pyrim}$** and **Os$_{pyrim}$** have shown the best activity for the transfer hydrogenation of cyclohexanone into cyclohexanol. Employing either 0.5 mol% or 0.1 mol% of the precatalyst resulted in an excellent overall activity. The **Ru$_{pyrim}$** gave a very good 78% conversion also by using only 0.05 mol% of the precatalyst. Good results of the complexes **Ru$_{pyrim}$** and **Os$_{pyrim}$** in the transfer hydrogenation

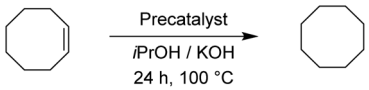
Table 5 The reduction of cyclohexanone[a]



Precatalyst	Conv.[c] (%)	Precatalyst	Conv.[c] (%)	Precatalyst	Conv.[c] (%)
Precatalyst loading: 0.5 mol%					
Ru$_1$[d]	>99	**Ir$_1$**[d]	86	**Os$_1$**[d]	>99
Ru$_2$[d]	>99	**Ir$_2$**[d]	75	**Os$_2$**[d]	>99
Ru$_3$[d]	>99	**Ir$_3$**[d]	92	**Os$_3$**[d]	91
Ru$_{pyrim}$	>99			**Os$_{pyrim}$**	>99
Precatalyst loading: 0.1 mol%					
Ru$_1$[d]	79			**Os$_1$**[d]	62
Ru$_2$[d]	94			**Os$_2$**[d]	76
Ru$_3$[d]	72			**Os$_3$**[d]	50
Ru$_{pyrim}$	>99, 78[b]			**Os$_{pyrim}$**	94

[a] General reaction conditions: cyclohexanone (0.5 mmol), precatalyst, KOH (0.085 mmol), iPrOH (4 mL), 100 °C for 3 h. [b] Precatalyst (0.05 mol%). [c] Conversion determined by ^{1}H NMR spectroscopy using hexamethylbenzene as an internal standard. [d] Data collected from ref. 11.

Table 6 The reduction of cyclooctene[a]



Precatalyst	Conv.[b] (%)	Precatalyst	Conv.[b] (%)	Precatalyst	Conv.[b] (%)
Precatalyst loading: 1.0 mol%					
Ru$_1$	>99	**Ir$_1$**	73	**Os$_1$**	84
Ru$_2$	>99	**Ir$_2$**	60	**Os$_2$**	93
Ru$_3$	>99	**Ir$_3$**	80	**Os$_3$**	59
Ru$_{pyrim}$	>99			**Os$_{pyrim}$**	89
Precatalyst loading: 0.5 mol%					
Ru$_1$	79				
Ru$_2$	94				
Ru$_3$	72				
Ru$_{pyrim}$	87				

[a] General reaction conditions: cyclooctene (0.5 mmol), precatalyst, KOH (0.085 mmol), iPrOH (4 mL), 100 °C for 24 h. [b] Conversion determined by ^{1}H NMR spectroscopy using hexamethylbenzene as an internal standard.

of the carbonyl group prompted us to test other functional groups. We started with olefin substrates: cyclooctene, methylstyrene and *trans*-stilbene. The results for the reduction of cyclooctene are presented in Table 6.

For the reduction of cyclooctene, we used similar reaction conditions as mentioned above. A mixture of cyclooctene, the selected precatalyst and KOH in iPrOH was stirred under an inert atmosphere at 100 °C for 24 h. By using 1.0 mol% of ruthenium-based precatalysts we observed full conversions into cyclooctane with all four tested complexes. Also with the iridium and osmium analogues, the conversions were very good. Scaling down to 0.5 mol% of Ru(II) complexes, we could still reach excellent conversions, better than those described for already known similar systems.[17] The best performance was seen with **Ru$_2$**, bearing the 4-methoxyphenyl donor group at the triazole, which is in line with the results for the reduction of carbonyls. Excellent performance in the reduction of cyclooctene encouraged us to try other such substrates. We took *trans*-β-methylstyrene and applied the same reaction conditions as for cyclooctene. The results are summarized in Table 7.

In comparison to cyclooctene, *trans*-β-methylstyrene proved to be a more challenging substrate. With the exception of the Os(II) representatives, the complexes still performed very well. Nonetheless, our catalysts have shown similar or better performance in this reduction than the previously reported examples.[17] The ligand effect trends were similar to the previous observations. For the Ru(II) complexes the electron-donating substituents at the triazole ring worked better, whereas the Ir(III) complexes preferred electron withdrawing groups.[11] Furthermore, we investigated the transfer hydrogenation of *trans*-stilbene, a sterically more hindered alkene. The results from Table 8 confirm the reduction of *trans*-stilbene into 1,2-diphenylethane as more demanding for our catalytic system, which has been also reported for other such systems.[17]

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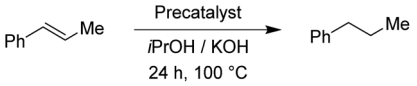
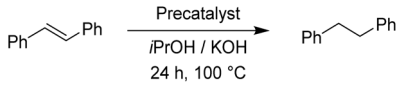
Table 7 The transfer hydrogenation of *trans*-β-methylstyrene[a]



Precatalyst	Conv.[b] (%)	Precatalyst	Conv.[b] (%)	Precatalyst	Conv.[b] (%)
Precatalyst loading: 1.0 mol%					
Ru$_1$	65	**Ir$_1$**	62	**Os$_1$**	8
Ru$_2$	75	**Ir$_2$**	58	**Os$_2$**	6
Ru$_3$	56	**Ir$_3$**	67	**Os$_3$**	4
Ru$_{pyrim}$	78			**Os$_{pyrim}$**	0
Precatalyst loading: 0.5 mol%					
Ru$_1$	45				
Ir$_1$	25				
Os$_1$	4				

[a] General reaction conditions: *trans*-β-methylstyrene (0.5 mmol), precatalyst, KOH (0.085 mmol), iPrOH (4 mL), 100 °C for 24 h. [b] Conversion determined by ^{1}H NMR spectroscopy using 4-bromobenzaldehyde as an internal standard.

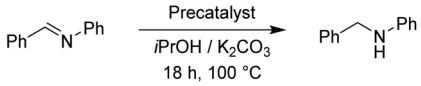
Table 8 The transfer hydrogenation of *trans*-stilbene[a]



Precatalyst	Conv.[b] (%)	Precatalyst	Conv.[b] (%)	Precatalyst	Conv.[b] (%)
Precatalyst loading: 1.0 mol%					
Ru$_1$	30	**Ir$_1$**	9	**Os$_1$**	15
Ru$_2$	41	**Ir$_2$**	11	**Os$_2$**	16
Ru$_3$	28	**Ir$_3$**	13	**Os$_3$**	4
Ru$_{pyrim}$	13			**Os$_{pyrim}$**	8

[a] General reaction conditions: *trans*-stilbene (0.5 mmol), precatalyst, KOH (0.085 mmol), iPrOH (4 mL), 100 °C for 24 h. [b] Conversion determined by ^{1}H NMR spectroscopy using hexamethylbenzene as an internal standard.

Table 9 The transfer hydrogenation of *N*-benzylideneaniline[a]



Precatalyst	Conv.[b] (%)	Precatalyst	Conv.[b] (%)	Precatalyst	Conv.[b] (%)
Precatalyst loading: 1.0 mol%					
Ru$_1$	>99	**Ir$_1$**	50	**Os$_1$**	19
Ru$_2$	>99	**Ir$_2$**	23	**Os$_2$**	18
Ru$_3$	>99	**Ir$_3$**	17	**Os$_3$**	17
Ru$_{pyrim}$	>99			**Os$_{pyrim}$**	30
Precatalyst loading: 0.5 mol%					
Ru$_1$	71				
Ru$_2$	87				
Ru$_3$	60				
Ru$_{pyrim}$	90				

[a] General reaction conditions: *N*-benzylideneaniline (0.5 mmol), precatalyst, K_2CO_3 (0.025 mmol), iPrOH (4 mL), 100 °C for 18 h. [b] Conversion determined by ^{1}H NMR spectroscopy using hexamethylbenzene as an internal standard.

Table 10 Cyclohexenone reduction[a]

Precatalyst	Conv.[b] (%)	Precatalyst	Conv.[b] (%)	Precatalyst	Conv.[b] (%)
Ru$_1$	0/100	**Ir$_1$**	21/79	**Os$_1$**	67/33
Ru$_2$	8/92	**Ir$_2$**	31/69	**Os$_2$**	83/17
Ru$_3$	0/100	**Ir$_3$**	42/58	**Os$_3$**	64/36
Ru$_{pyrim}$	0/100			**Os$_{pyrim}$**	30/70

[a] Reaction conditions: cyclohexenone (0.5 mmol), catalyst (0.5 mol%), KOH (0.1 mmol), isopropanol (4 mL), 100 °C, 20 h reflux. [b] Conversion determined by ^{1}H NMR spectroscopy using hexamethylbenzene as an internal standard; >99% conversion of starting meterials: ketone/alcohol product ratio.

To continue we took an imine substrate and selected *N*-benzylideneaniline.[18] We employed both K_2CO_3 as well as KOH as bases and stirred the reaction mixture for 18 h at 100 °C. Both bases delivered similar conversions. The results are collected in Table 9.

With 1.0 mol% precatalyst loading the ruthenium-based precatalysts converted the *N*-benzylideneaniline into *N*-benzylaniline fully. Also by using 0.5 mol% the same complexes gave an excellent overall conversion. The **Ru$_{pyrim}$** performed best, but also the **Ru$_2$** showed excellent activity, confirming the ligand effects for the Ru(II) complex series. On the other hand the Ir(III) and Os(II) precatalysts were less active for the reduction of this type of substrates. The activity of our complexes is comparable to the previously reported ruthenium catalyst in the transfer hydrogenation of *N*-benzylideneaniline.[18] We also tested the reduction of cyclohexenone as an example of an α,β-unsaturated carbonyl. Whereas conversions were high for all tested precatalysts (Table 10), only **Os$_2$** displayed relatively high selectivity towards selective reduction of the C=C bond over the C=O bond.

To conclude, we tested the transfer hydrogenation of the nitro group. Recently, an efficient transfer hydrogenation catalytic system for the reduction of nitroarenes into anilines was reported and was based on Ru(II) and Ir(III) MIC precatalysts.[8a] We carried out an initial screening with nitrobenzene as a substrate, applying 1.5 mol% of the precatalysts and 0.5 equiv. of KOH in iPrOH at 80 °C.[8a] Azobenzene and azoxybenzene were expected as the side products. The results are presented in Table 11. The screening showed a catalyst dependent conversion, as well as product distribution. In contrast to the previously tested functional groups, the Ir(III) precatalysts were the most active of all the tested complexes, affording aniline as the major product. The Ru(II) complexes gave good conversion into aniline and azoxybenzene with only minute amounts of azobenzene. Once again the pyrimidine analogue **Ru$_{pyrim}$** showed

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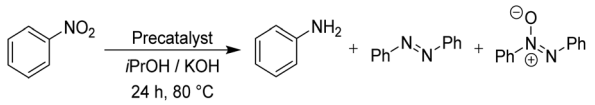
Table 11 The transfer hydrogenation of nitrobenzene[a]



Precatalyst	Aniline[b]	Starting nitro[b]	Azo[b]	Azoxy[b]
Precatalyst loading: 1.5 mol%				
Ru$_1$	50	10	10	30
Ru$_2$	56	26	4	14
Ru$_3$	32	40	0	28
Ru$_{pyrim}$	71	0	12	17
Ir$_1$	93	0	7	0
Ir$_2$	85	0	11	4
Ir$_3$	>99	0	0	0
Os$_1$	50	31	0	19
Os$_2$	83	0	3	14
Os$_3$	50	35	0	15
Os$_{pyrim}$	80	0	3	17
Precatalyst loading: 5.0 mol%				
Ru$_1$	>99	0	0	0
Ru$_2$	>99	0	0	0
Ru$_3$	>99	0	0	0
Ru$_{pyrim}$	>99	0	0	0
Ir$_1$	97	0	3	0
Ir$_2$	93	0	7	0
Ir$_3$	>99	0	0	0
Os$_1$	64	36	0	0
Os$_2$	87	10	0	3
Os$_3$	60	40	0	0
Os$_{pyrim}$	>99	0	0	0

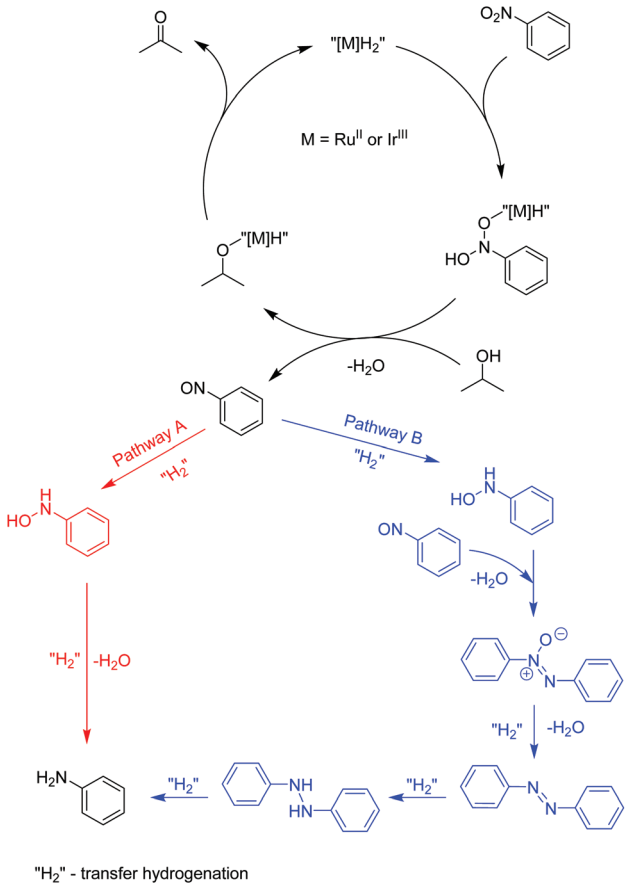
[a] General reaction conditions: nitrobenzene (0.5 mmol), precatalyst, KOH (0.21 mmol), iPrOH (4 mL), 80 °C for 24 h. [b] Conversion in % determined by GC using hexadecane as an internal standard.

superior activity. The Os(II) complexes performed similar to the Ru(II) analogues, giving slightly higher conversions. The best performance was seen for **Os$_2$**, where aniline was the main product.

As was previously observed,[8a] when employing 5.0 mol% of the precatalysts, we observed a drastic improvement in catalytic activity. The best results were seen with all four Ru(II) complexes, giving full conversion of nitrobenzene into aniline. The Ir(III) analogues performed very similarly. On the other hand, the Os(II) complexes were less active, except for **Os$_{pyrim}$**, which yielded aniline quantitatively.

Mechanistic studies

Recently, a mechanistic study for a similar catalytic system was reported[8a] where a two-pathway mechanism was postulated based on two previous literature reports.[19] The mechanism is outlined in Scheme 4. The metal complex is converted into hydrides "[M]H$_2$" in basic iPrOH. Next, nitrosobenzene is formed, which can be reduced into aniline through two different pathways. Route A proceeds through *N*-phenylhydroxyamine giving aniline directly. In contrast, path B involves an azoxybenzene intermediate, which gets converted to azobenzene before being reduced to aniline. To determine the reaction pathways for each of the complex families, we ran a time-dependent screening of the product formation. With the



Scheme 4 The postulated mechanism for the transfer hydrogenation of nitrobenzene.[8a,19]

chosen precatalysts, we carried out the reduction of nitrobenzene under catalytic conditions with 1.5 mol% loading and analysed aliquots over time. The resulting data are represented in Fig. 1. With ruthenium complex **Ru$_1$** 54% conversion into aniline was observed after 32 h at 80 °C. While the amount of nitrobenzene decreased over time, the amounts of azoxybenzene and aniline increased. The formation of aniline, as well as azoxybenzene correlated well with the consumption of the starting nitrobenzene. Only minor amounts of azobenzene were traced after 32 h. The results point to pathway B. The iridium complex **Ir$_3$** gave 84% conversion to aniline after 24 h with the amount of azoxybenzene less than 18%. The consumption of nitrobenzene correlates very well with the formation of aniline. These results indicate more preference for path A. With **Os$_2$** 74% conversion into aniline was observed with no azobenzene as a side product. The amount of aniline correlates very well with the consumption of nitrobenzene. The conversion into azoxybenzene was below 8% and quite constant after 24 h. This indicates the preference for pathway A.

For the transfer hydrogenation of the nitro functional group we chose four additional substrates: 2-, 3- and 4-nitroanisole, as well as 1-chloro-2-nitrobenzene. We selected **Os$_2$** and **Ir$_3$** as the precatalysts and conducted the transfer hydrogen-

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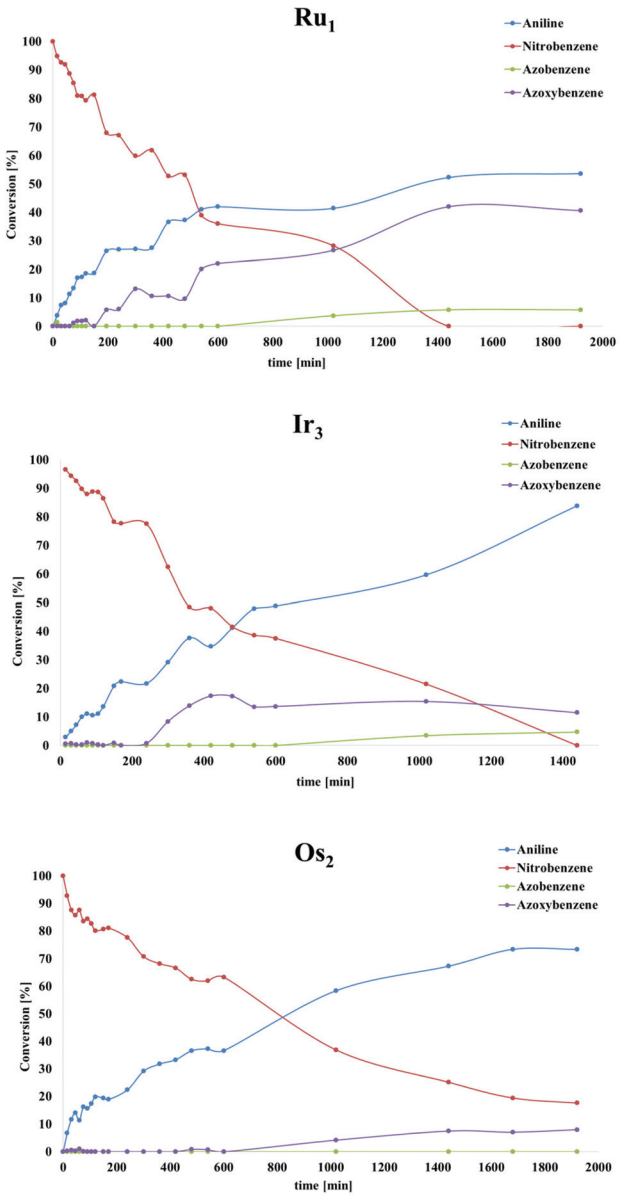

Fig. 1 Time-dependence screening for the selected complexes Ru_1, Ir_3 and Os_2.

ation with 1.5 mol% precatalyst loading. Each of the four substrates was stirred with 0.5 equiv. of KOH in iPrOH at 80 °C for 24 h (Table 12). 2-Nitroanisole was converted with both tested complexes into *o*-anisidine as the only product. The conversions were 65% and 54%, respectively. Both complexes catalysed the reduction of 3-nitroanisole into *m*-anisidine very well. Ir_3 gave full conversion into the amino product. The reduction of 4-nitroanisole into *p*-anisidine proceeded with both complexes, however, giving lower conversions. By using the complex Ir_3, 1-chloro-2-nitrobenzene was fully converted into 2-chloroaniline. In contrast, Os_2 gave only 58% of the aniline derivative after 24 h. Overall, the Ir(III) complex Ir_3 was more active in the transfer hydrogenation catalysis of the selected nitro substrates. Surprisingly no azo- or azoxy-side products

Table 12 The transfer hydrogenation reduction of four selected nitroarenes[a]

Precatalyst	Amino[b]	Nitro[b]	Azo[b]	Azoxy[b]
2-Nitroanisole				
Ir_3	65	35	0	0
Os_2	54	46	0	0
3-Nitroanisole				
Ir_3	100	0	0	0
Os_2	75	25	0	0
4-Nitroanisole				
Ir_3	54	46	0	0
Os_2	18	82	0	0
1-Chloro-2-nitrobenzene				
Ir_3	100	0	0	0
Os_2	58	42	0	0

[a] General reaction conditions: nitro substrate (0.5 mmol), precatalyst (1.5 mol%), KOH (0.21 mmol), iPrOH (4 mL), 80 °C for 24 h. [b] Conversion in % determined by GC using hexadecane as an internal standard.

were detected. For the reduction of cyclohexene and for the reduction of nitrobenzene, we performed the Hg-poisoning test by adding Hg during the catalysis. The addition of Hg had no effect on the yield or the rate of formation of the catalytic products. Hence, we believe that catalysis in the present case is likely homogeneous.

Conclusions

The scope of the pyridine-functionalized triazolylidene complexes of ruthenium, iridium and osmium as precatalysts for transfer hydrogenation was investigated. We have also presented the synthesis of the 1-(2-pyrimidyl)-functionalized triazolium salt and used it as a precursor for the carbenic ligand for coordination to ruthenium(II) and osmium(II). This is the first report of a pyrimidine-appended triazolium salt and also the first examples of ruthenium and osmium complexes with such MIC ligands. All tested complexes are very efficient (pre-)catalysts for the reduction of several functional groups such as carbonyls, alkenes, imines and also nitroarenes. We demonstrated that in general the additional nitrogen atom of the pyrimidine ring is beneficial in terms of catalytic activity. The two pyrimidine-functionalized complexes have shown a better conversion in comparison to pyridine analogues, except for the reduction of C=C double bond substrates. The ruthenium and osmium complexes having triazolylidene ligands substituted with an electron-donating group performed better, whereas for the iridium complexes the effects were the opposite: complexes with electron-withdrawing groups are superior catalysts. In the final part we have shown some mechanistic studies for the reduction of nitrobenzene with three selected precatalysts, one for each metal (ruthenium, iridium and osmium). The Cp*–Ir-containing pre-catalysts presented here deliver better conversions for the conversion of C=O groups and comparable conversion for the reduction of C=C compared to the reported Cp*–Ir complexes with NHC ligands.[2l]

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On the other hand, the Cp*–Ir-containing complexes deliver more aniline through the reduction of nitrobenzene compared to related complexes.[8a] These results are important to understand the behaviour of the complexes during the catalysis. The results also show the potential of the tested complexes with chelating pyridyl- and pyrimidyl-triazolylidenes in the transfer hydrogenation of several functionalities, such as the carbonyl group, C=C double bond, imine and also the nitro group. The newly synthesized pyrimidyl-triazolylidenes might be useful ligands for generating both homo- and heterodinuclear complexes.

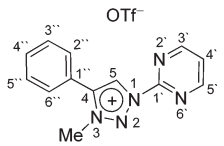
Experimental section

Materials and physical methods

The reagents and solvents were used as obtained from commercial sources (Sigma-Aldrich, Fluka, Alfa Aesar). Acetonitrile was dried over 3 Å molecular sieves, and dichloromethane over 4 Å molecular sieves. For methylation reactions dry glassware and solvents were used. Triazole **1** was prepared as described in the literature.[14] NMR spectra were recorded with a Bruker Avance 300, Bruker Avance III 500 (Ljubljana) and Jeol ECS 400 (Berlin) spectrometers. Proton and carbon spectra were referenced to $Si(CH_3)_4$ as the internal standard. Some ^{13}C chemical shifts were determined relative to the ^{13}C signal of the solvent DMSO-d_6 (39.5 ppm). ^{19}F NMR and ^{31}P NMR spectra were referenced to CCl_3F and 85% phosphoric acid, respectively, as external standards at $\delta = 0$. The nitrogen chemical shifts were extracted from ^1H–^{15}N HMBC spectra with 20 Hz digital resolution in the indirect dimension. ^{15}N chemical shifts are rounded to integer numbers because of the digital resolution limits of the experiment. The reported ^{15}N chemical shifts were extracted from ^1H–^{15}N HMBC spectra (with 20 Hz digital resolution in the indirect dimension) with respect to external 90% CH_3NO_2 in $CDCl_3$ and converted to the δ ^{15}N (liq. NH_3) = 0 ppm scale using the relationship: δ ^{15}N (CH_3NO_2) = δ ^{15}N (liq. NH_3) + 380.5 ppm. Chemical shifts are given on the δ scale (ppm). Coupling constants (J) are given in hertz. The multiplicities are indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), sept (septet), m (multiplet) and br (broadened). Assignments of proton, carbon and nitrogen resonances were performed by standard 2D NMR techniques (^1H–^1H COSY, ^1H–^{13}C HSQC, ^1H–^{13}C HMBC, and ^1H–^{15}N HMBC). The numbering used for the assignment of NMR signals is as follows: 1,2,3-triazole ring, simple figures; pyridine ring, primed figures; phenyl ring, double-primed figures (C-1″ is attached to the 1,2,3-triazole ring). An Agilent 6224 time-of-flight (TOF) mass spectrometer equipped with a double orthogonal electrospray source at atmospheric pressure ionization (ESI) coupled to an Agilent 1260 HLPC and an Agilent 6210 ESI-TOF spectrometer were used for recording HRMS spectra. Elemental analysis was performed with a Perkin-Elmer 2400 Series II CHNS/O Analyzer. IR spectra were obtained with a Perkin-Elmer Spectrum 100, equipped with a Specac Golden Gate Diamond ATR as a solid sample support. Melting points were determined on a Kofler micro hot stage instrument. The reactions were monitored by TLC on TLC-CARD silica gel, 220–440 mesh. ^1H NMR spectra of benzyl alcohol, 1-phenylethanol, diphenylmethanol, cyclohexanol and cyclooctane were compared with those of the authentic samples (Tables 2–6). Propylbenzene[20] (Table 7), 1,2-diphenylethane[21] (Table 8) and *N*-benzylaniline[22] (Table 9) were identified by comparison of their ^1H NMR spectral data with the literature reports. GC-MS analysis was performed on a Varian Saturn 2100C (column: Varian factory four capillary column VF-5 ms; temperature: 50 to 250 °C, heating rate 20 K min^{-1}). The calibration was done as follows: we collected the GC analyses of all the products, using pure samples. We obtained ret. times and also factors for calculating the areas of the GC peaks into conversions, percent yields. Ret. times (min): 6.22 (aniline), 7.36 (nitrobenzene), 11.21 (azobenzene), 12.42 (azoxybenzene); 5.63 (2-anisidine), 6.86 (2-nitroanisole); 5.29 (2-chloroaniline), 6.17 (2-chloronitrobenzene); 6.11 (3-anisidine), 6.73 (3-nitroanisole); 5.96 (4-anisidine), 7.22 (4-nitroanisole). Catalytic reactions were carried out using Schlenk tubes and a pressure-vessel. All catalytic reactions were performed at least in duplicate.

Synthesis of the ligand

Pyrimidyl-triazole **1** in dry CH_2Cl_2 was purged with dry argon and stirred on an ice-bath at 0 °C for a few minutes. MeOTf was added *via* syringe and the reaction mixture was stirred for 30 min at 0 °C and then 24 h at room temperature. The reaction mixture was concentrated using a rotary evaporator and the residue was column chromatographed on silica gel using a mixture of CH_2Cl_2 and MeOH (10 : 1) as the eluent ($R_f \approx 0.3$). Re-crystallization from EtOAc–light petroleum afforded analytically pure triazolium salts **2OTf**. Quantities used in the above procedure, analytical and spectral data of **2OTf** are given below.



2

3-Methyl-4-phenyl-1-(pyrimidin-2-yl)-1*H*-1,2,3-triazolium trifluoromethanesulphonate (2OTf). Triazole **1** (223.2 mg, 1.00 mmol), CH_2Cl_2 (3 mL), MeOTf (180.4 mg, 1.10 mmol, 0.12 mL). White solid (350.7 g, 91%). R_f (CH_2Cl_2 : MeOH = 10 : 1) = 0.3. Mp 154–156 °C. IR: 3119, 3093, 2972, 1612, 1589, 1424, 1399, 1264, 1228, 1145, 1031, 830, 772, 762, 697, 635 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ = 4.48 (s, 3H, CH_3-trz), 7.72–7.70 (m, 3H, H-3″, H-5″, H-4″), 7.87 (dd, J = 7.5, 2.0 Hz, 2H, H-2″, H-6″), 7.99 (t, J = 4.8 Hz, 1H, H-5′), 9.22 (d, J = 4.9 Hz, 2H, H-6′, H-4′), 10.04 (s, 1H, H-5). ^{13}C NMR (126 MHz, DMSO-d_6): δ = 39.8 (CH_3-trz), 122.3 (C-1″), 124.4 (C-5′), 127.2 (C-5), 129.4 (C-3″, C-5″), 129.6 (C-2″, C-6″), 131.7 (C-4″), 143.5 (C-4), 152.2 (C-2′), 160.5 (C-6′, C-4′). ^{15}N NMR (51 MHz, DMSO-d_6): δ = 245 (N-3), 255 (N-1), 270 (N-1′, N-3′),

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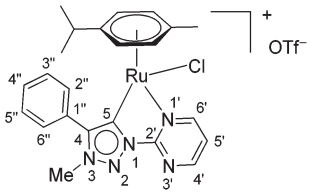
340 (N-2). ^{19}F NMR (471 MHz, DMSO-d_6): δ = −77.8 (s, 3F, OTf). HRMS (ESI+): calcd for $C_{13}H_{12}N_5^+$ $[M]^+$ 238.1087, found 238.1088. Anal. calcd for $C_{14}H_{12}F_3N_5O_3S$: C 43.41, H 3.12, N 18.08; found: C 43.12, H 3.29, N 18.51.

Synthesis of complexes

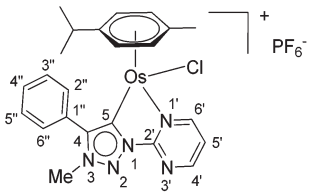
Ruthenium complex Ru_{pyrim}. A mixture of a triazolium salt **2OTf** and Ag_2O in acetonitrile was purged with argon and stirred in the absence of light at room temperature for 4 days. After the addition of $[Ru(\eta^6\text{-}p\text{-cym})Cl_2]_2$ the stirring was continued for 2 hours. The reaction mixture was filtered through Celite. The solvent was removed *in vacuo* and the residue was crystallized from chloroform (1–2 mL) with slow addition of hexane to give the pure $\mathbf{Ru_{pyrim}}$. For quantities used, and analytical and spectral data of $\mathbf{Ru_{pyrim}PF_6}$, see below.



$\mathbf{Ru_{pyrim}}$

3-Methyl-4-phenyl-1-(pyrimidin-2-yl)-1*H*-1,2,3-triazolium chloro(*p*-cymene)ruthenium(II) trifluoromethanesulphonate ($\mathbf{Ru_{pyrim}OTf}$). Triazolium salt **2OTf** (38.7 mg, 0.10 mmol), Ag_2O (34.5 mg, 0.15 mmol), acetonitrile (4 mL), time 1 = 4 days, $[Ru(\eta^6\text{-}p\text{-cym})Cl_2]_2$ (30.6 mg, 0.05 mmol). Yellow solid (58.0 mg, 81%). R_f (CH_2Cl_2 : MeOH = 10 : 1) = 0.8. Mp 71–73 °C. IR: 2965, 1611, 1555, 1472, 1258, 1222, 1151, 1028, 803, 775, 710, 636 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.98 (d, J = 7.0 Hz, 3H, $(CH_3)_2CH$), 1.08 (d, J = 6.9 Hz, 3H, $(CH_3)_2CH$), 2.04 (s, 3H, CH_3^{Cym}), 2.54 (septet, J = 6.9 Hz, 1H, $(CH_3)_2CH$), 4.34 (s, 3H, CH_3–N-3), 5.21 (dd, J = 6.2, 0.7 Hz, 1H, ArH^{Cym}), 5.58 (dd, J = 6.2, 0.8 Hz, 1H, ArH^{Cym}), 5.67 (t, J = 6.4 Hz, 2H, ArH^{Cym}), 7.72–7.71 (m, 3H, H-3″, H-4″, H-5″), 7.83–7.81 (m, 3H, H-5′, H-2″, H-6″), 8.96 (dd, J = 4.8, 2.0 Hz, 1H, H-4′ or H-6′), 9.84 (dd, J = 5.7, 2.0 Hz, 1H, H-6′ or H-4′). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 18.9 (CH_3^{Cym}), 21.7 ($(CH_3)_2CH$), 22.7 ($(CH_3)_2CH$), 31.2 ($(CH_3)_2CH$), 38.7 (CH_3–N-3), 83.5 (Ar^{Cym}), 85.7 (Ar^{Cym}), 88.3 (Ar^{Cym}), 89.9 (Ar^{Cym}), 104.2 (Ar^{Cym}), 110.4 (Ar^{Cym}), 123.3 (C-5′), 125.9 (C-1″), 129.8 (C-3″, C-5″), 130.5 (C-2″, C-6″), 131.6 (C-4″), 147.7 (C-4), 155.0 (C-2′), 160.0 (C-4′ or C-6′), 166.5 (C-6′ or C-4′), 170.7 (C-5). ^{15}N NMR (51 MHz, DMSO-d_6): δ = 218 (N-1′ or N-3′), 242 (N-3), 268 (N-3′ or N-1′), 339 (N-2). ^{19}F NMR (471 MHz, DMSO-d_6): δ = −78.3 (s, 3F, OTf). HRMS (ESI+): calcd for $C_{23}H_{25}ClN_5Ru^+$ $[M]^+$ = 508.0842, found 508.0834.

Osmium complex Os_{pyrim}. Triazolium salt **2OTf** was mixed with Ag_2O and KCl and stirred in dry acetonitrile under a nitrogen atmosphere (in the absence of air), in the absence of light, at room temperature for 4 days. Later $[Os(p\text{-cym})Cl_2]_2$ was added and the mixture was stirred for an additional 3 days under a nitrogen atmosphere, in the absence of light at room temperature. The reaction mixture was filtered over Celite and washed with dichloromethane. All the solvents were removed *in vacuo*. The residue was dissolved in methanol (10 mL), KPF_6 was added (10 equiv.) and the mixture was stirred for 10 minutes. Then water was added (100 mL). An orange precipitate was collected after 10 minutes of stirring by filtration and dried at room temperature. Pure $\mathbf{Os_{pyrim}PF_6}$ was obtained and fully characterized. For quantities used, and analytical and spectral data of $\mathbf{Os_{pyrim}PF_6}$, see below.



$\mathbf{Os_{pyrim}}$

3-Methyl-4-phenyl-1-(pyrimidin-2-yl)-1*H*-1,2,3-triazolium chloro(*p*-cymene)osmium(II) hexafluorophosphate(V) ($\mathbf{Os_{pyrim}PF_6}$). Triazolium salt **2OTf** (77.4 mg, 0.20 mmol), Ag_2O (162.4 mg, 0.70 mmol), KCl (149.2 mg, 2.0 mmol), MeCN (10 mL), $[Os(p\text{-cym})Cl_2]_2$ (79.1 mg, 0.10 mmol). Red-brown solid (70.3 mg, 53%). ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C, TMS): δ = 0.90 (d, J = 7.0 Hz, 3H, $(CH_3)_2CH$), 0.93 (d, J = 6.9 Hz, 3H, $(CH_3)_2CH$), 2.06 (s, 3H, CH_3^{Cym}), 2.32 (septet, J = 6.9 Hz, $(CH_3)_2CH$), 4.24 (s, 3H, CH_3–N-3), 5.11 (d, J = 5.7 Hz, 1H, ArH^{Cym}), 5.44 (d, J = 5.7 Hz, 1H, ArH^{Cym}), 5.51 (bs, 2H, ArH^{Cym}), 7.63 (bs, 6H, H-5′, H-2″, H-3″, H-4″, H-5″, H-6″), 8.93 (dd, J = 4.8, 2.0 Hz, 1H, H-4′ or H-6′), 9.40 (dd, J = 5.8, 2.0 Hz, 1H, H-6′ or H-4′). ^{13}C NMR (100 MHz, CD_2Cl_2, 25 °C, TMS): δ = 17.8 (CH_3^{Cym}), 20.8 ($(CH_3)_2CH$), 22.0 ($(CH_3)_2CH$), 30.4 ($(CH_3)_2CH$), 38.1 (CH_3–N-3), 73.0 (Ar^{Cym}), 76.4 (Ar^{Cym}), 78.7 (Ar^{Cym}), 81.3 (Ar^{Cym}), 89.7 (Ar^{Cym}), 103.5 (Ar^{Cym}), 122.7 (C-5′), 124.1 (C-3″, C-5″), 124.8 (C-1″), 129.0 (C-2″, C-6″), 129.6, 130.8 (C-4″), 146.5 (C-4), 150.6 (C-2′), 159.6 (C-4′ or C-6′), 165.0 (C-6′ or C-4′). ^{15}N NMR (41 MHz CD_2Cl_2): δ = 196 (N-1′ or N-3′), 244 (N-3), 336 (N-2). ^{19}F NMR (377 MHz, CD_2Cl_2): δ = −72.7 (d, J = 712 Hz, 6F, PF_6). ^{31}P NMR (162 MHz, CD_2Cl_2): δ = −144.5 (sept, J = 712 Hz, 1P, PF_6). HRMS (ESI+): calcd for $C_{24}H_{26}ClN_4Os^+$ $[M]^+$ = 598.1413, found 598.1422.

General procedure for the catalysed transfer hydrogenation

Carbonyl group. The selected substrate (0.5 mmol), KOH (0.085 mmol), iso-propanol (4 mL) and the chosen precatalyst were mixed in a Schlenk tube under a nitrogen atmosphere. The reaction mixtures were stirred at 100 °C for 3 hours. The solvent was then removed *in vacuo* and the residue was analysed by ^{1}H NMR spectroscopy, using hexamethylbenzene as an internal standard, to identify products and determine conversions indicated in Tables 2–5.

Olefin group. The selected substrate (0.5 mmol), KOH (0.085 mmol), iso-propanol (4 mL) and the chosen precatalyst were mixed in a Schlenk tube under a nitrogen atmosphere. The reaction mixtures were stirred at 100 °C for 24 hours. The solvent was then removed *in vacuo* and the residue was analysed by ^{1}H NMR spectroscopy, using hexamethylbenzene (for *trans*-stilbene) or 4-bromobenzaldehyde (for *trans*-β-methyl-

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styrene and cyclooctene) as an internal standard, to identify products and determine conversions indicated in Tables 6–8.

Imine group. *N*-Benzylideneaniline (0.5 mmol), K_2CO_3 (0.025 mmol), iso-propanol (4 mL) and the chosen precatalyst were mixed in a Schlenk tube under a nitrogen atmosphere. The reaction mixtures were stirred at 100 °C for 18 hours. The solvent was then removed *in vacuo* and the residue was analysed by ^{1}H NMR spectroscopy, using hexamethylbenzene as an internal standard, to identify products and determine conversions indicated in Table 9.

Nitro group. The selected substrate (0.5 mmol), KOH (0.21 mmol), iso-propanol (4 mL) and the chosen precatalyst were mixed in a Schlenk tube under a nitrogen atmosphere. The reaction mixtures were stirred at 80 °C for 24 hours. The crude reaction mixture was diluted with ethyl acetate and subjected to GC to identify products and determine conversion indicated in Tables 10 and 11. Hexadecane was used as an internal standard.

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