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Synthesis and structural chemistry of arene-ruthenium half-sandwich complexes bearing an oxazolinyl–carbene ligand

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Abstract

Reaction of a series of directly connected oxazoline–imidazolium salts with silver(I) oxide and subsequent transmetallation with $[Ru(p\text{-cymene})Cl_2]_2$ and anion exchange with KPF_6 cleanly gave the corresponding 2-oxazolinyl-(*N*-mesityl)imidazolidene(chloro)ruthenium(II) half-sandwich complexes $[RuCl(oxcarb)(p\text{-cymene})]PF_6$, two derivatives of which were characterized by X-ray diffraction. Abstraction of the chloro ligand furnished the dicationic aqua complexes $[Ru(H_2O)(oxcarb)(p\text{-cymene})](PF_6)_2$ which possess a similar coordination geometry. The syntheses were found to be highly diastereoselective, since only one diastereoisomer could be observed in all ruthenium complexes upon reaction of the chiral enantiopure oxazoline–imidazolium salts. Their potential as transfer hydrogenation and Lewis acid catalysts has been probed.

Keywords: *N*-heterocyclic carbene; Oxazoline; Ruthenium; Arene complex; Chiral complexes

1. Introduction

Although the first transition metal complexes with *N*-heterocyclic carbenes (NHCs) were reported by Öfele [1] and Wanzlick and Schönherr [2] as early as 1968, the area only progressed slowly until the isolation of the first free imidazol-2-ylidene carbene by Arduengo et al. [3]. By the mid 1990's, Herrmann et al. showed the potential of NHCs as useful spectator ligands in the preparation of very efficient homogeneous catalysts [4–6]. Since then, a rapid development of this area has occurred and NHC ligands have been widely employed in the design of new catalysts for a wide variety of reactions, in part replacing the use of phosphines as ancillary ligands [7].

Given this potential for applications in homogeneous catalysis, the design of chiral *N*-heterocyclic carbenes for use in stereoselective catalytic transformations provided an additional dimension to this field of ligand design. Whereas the first examples of chiral NHC-based complexes were reported by Herrmann et al. [8] and Enders et al. [9] in 1996–1997, the first catalysts which were truly efficient in asymmetric catalysis were described by Burgess and co-workers [10]. Since then, the area has expanded dramatically, several efficient chiral NHC catalysts have been described and these have been reviewed very recently [11].

One straightforward and efficient method to develop chiral catalysts based on *N*-heterocyclic carbene ligands as stereodirecting units is the coupling between an *N*-heterocyclic carbene ring and an oxazoline unit [10,12,13]. Chiral oxazoline ligands have been widely used in asymmetric catalysis [14] with excellent results, in

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particular in Cu based Lewis acid catalysis [15]. They combine the virtue of relative rigidity of the heterocycle with a location of the stereocentre adjacent to the N-donor atom and thus an almost ideal orientation of the stereodirecting substitutent.

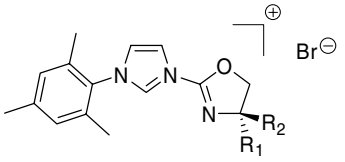
We recently reported a new strategy to obtain oxazoline–carbene ligand precursors, based on the direct linkage between both heterocycles, and these have been successfully coordinated to palladium [16], rhodium [12,17] and copper [18]. Several cationic rhodium complexes, in particular, proved to be highly enantioselective catalysts for the hydrosilylation of prochiral dialkyl ketones [12]. Given these results, we decided to extend the coordination chemistry of the new ligands to other metals such ruthenium and now report the preparation and characterization of a series of new oxazolinyl-carbene-Ru(arene) complexes. The crystal structures of several of these compounds are also described in this work.

2. Results and discussion

2.1. Synthesis of the oxazolinyl–imidazolium salts as ligand precursors and its coordination to ruthenium

The 1-(oxazolinyl)-3-mesitylimidazolium bromide salts labelled as **1a–c** (Scheme 1) were obtained in high yield by direct linkage between 1-mesitylimidazole and the corresponding bromooxazoline unit as previously reported [19].

The coordination of the ligand precursors **1a–c** to ruthenium could not be achieved by the use of an external base. We therefore turned to a strategy based on the use of a transmetallation by means of a silver *N*-heterocyclic carbene complex. This method has proved to be useful in the preparation of a variety of NHC-complexes [20]. Stirring the imidazolium salt with an excess of Ag_2O in dichloromethane at room temperature afforded the corresponding silver *N*-heterocyclic carbene complex. Whilst previous studies have shown that these silver complexes can be isolated as white powders [16], we used them in situ after filtering through Celite to remove the unreacted silver oxide. The addition of $[Ru(p\text{-cymene})Cl_2]_2$ to the carbene-silver solution immediately gave a white suspension of silver bromide and the desired arene ruthenium(II) complexes



$R_1 = R_2 = Me$ **1a**

$R_1 = t$Bu; $R_2 = H$ **1b**

$R_1 = i$Pr; $R_2 = H$ **1c**

Scheme 1. Oxazoline-NHC (“oxcarbH”) ligand precursors **1a–c**.

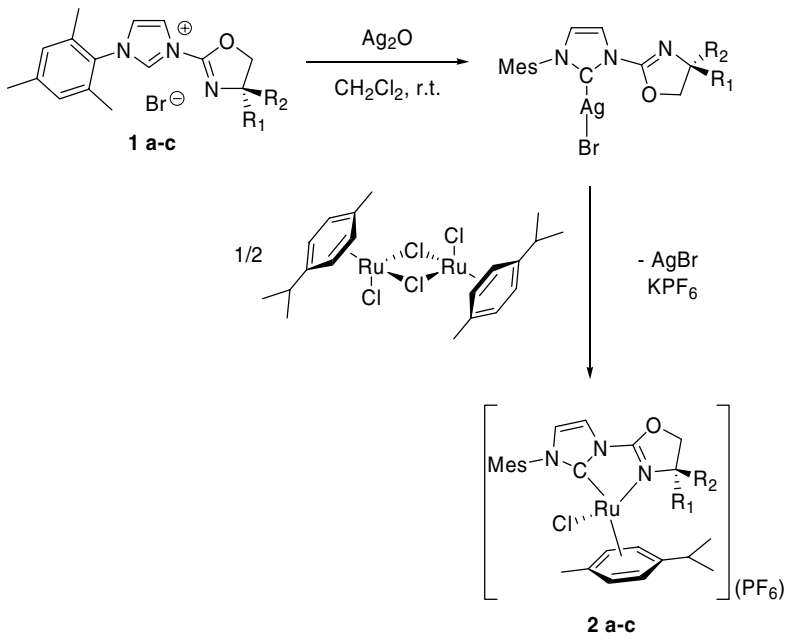
(Scheme 2). The 1-(oxazolinyl)-3-mesitylimidazolylidene (oxcarb) complexes **2a–c** (Scheme 2) were purified by column chromatography using silica gel. Elution with a mixture at 50% (v/v) dichloromethane–acetone and KPF_6, gave the cationic ruthenium(II) complexes as air and moisture stable solids. The new ruthenium complexes were characterized by NMR and mass spectroscopy, and gave satisfactory elemental analyses.

All of the complexes are chiral since the ruthenium atom is a stereocentre itself. In the case of compound **2a**, which bears an achiral ligand, two enantiomers (*R* and *S*) are possible. On the other hand, complexes **2b** and **2c** have two stereocentres (the ruthenium atom and the oxazoline unit) and thus two out of four (2^2) possible diastereomers can be obtained, since the chirality of the oxazoline unit is fixed. These are expected to have different chemical and physical properties, and should be readily detectable by NMR spectroscopy. However, we only observed the ^1H and ^{13}C NMR signals of one of the two diastereoisomers in the reaction mixture. Both compounds were therefore isolated in enantio- and diastereomerically pure form. We note that several related ruthenium (η^6-*p*-cymene) complexes with bidentate PN or NN [21] donor ligands have been reported, however, in these cases mixtures of two diastereomers were obtained [22]. Complexes of chiral imidazolylidene ligands with a stereogenic center at the metal atom have been previously prepared by Enders et al. and in these particular cases, a mixture of diastereoisomers was observed [23].

The expected bidentate coordination of the ligand was confirmed by NMR spectroscopy, the most characteristic data of the ^{13}C NMR spectra being the signals attributed to the metallated carbene-carbon (187.2 ppm for **2a**, 188.0 ppm for **2b** and 188.6 ppm for **2c**) in the typical high-frequency region where the carbene carbons of other NHC–Ru coordinated complexes resonate [23b–25]. In the ^1H NMR spectra, the signals due to aromatic protons of the *p*-cymene ligand appear as broad signals in all cases as a consequence of the internal rotation about the C_t-Ru axis (C_t = central point of the *p*-cymene ring). The coordination of the oxazoline ring is confirmed by a shift of the NCO resonances in comparison with the ligand precursor (e.g., δ(**1a**) = 148.8 ppm and δ(**2a**) = 158.0 ppm). Positive ion ES analyses of the isolated compounds in MeOH displayed the respective molecular ion peaks (*m*/*z* $[M]^+$ (554.1) for **2a**, $[M]^+$ (582.0) for **2b** and $[M]^+$ (568.0) for **2c**).

The details of the molecular structures of complexes **2a** and **2b** have been established by X-ray diffraction studies; suitable crystals of both cationic compounds were obtained by layering concentrated solutions in dichloromethane with hexanes and allowing slow diffusion at room temperature. The molecular structures of complexes **2a** and **2b** are displayed in Figs. 1 and 2, respectively, along with selected bond lengths and angles.

Both molecular structures show the ruthenium atom in a distorted tetrahedral coordination. As in solution, only one diastereoisomer was observed for complex **2b**. In the



Scheme 2. Synthesis of the arene ruthenium(II) complexes **2a**–**c**.

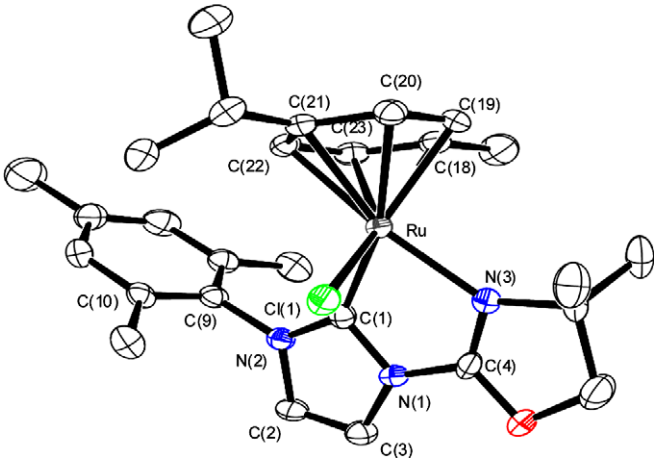


Fig. 1. Molecular structure of **2a**. Hydrogen atoms and the counterion (PF_6^-) are omitted for clarity. Selected bond lengths (Å) and angles (°): Ru–C(1) 2.038 (3), Ru–N(3) 2.125(2), Ru–Cl(1) 2.420(1), Ru–C(18) 2.210(3), Ru–C(19) 2.238(3), Ru–C(20) 2.244(3), Ru–C(21) 2.248(3) Ru–C(22) 2.205(3), Ru–C(23) 2.155(3); and Cl(1)–Ru–C(1) 83.91(7), C(1)–Ru–N(3) 76.6(1), C(1)–N(1)–C(4)–N(3) 2.1 (3), C(10)–C(9)–N(2)–C(2) 89.3 (3).

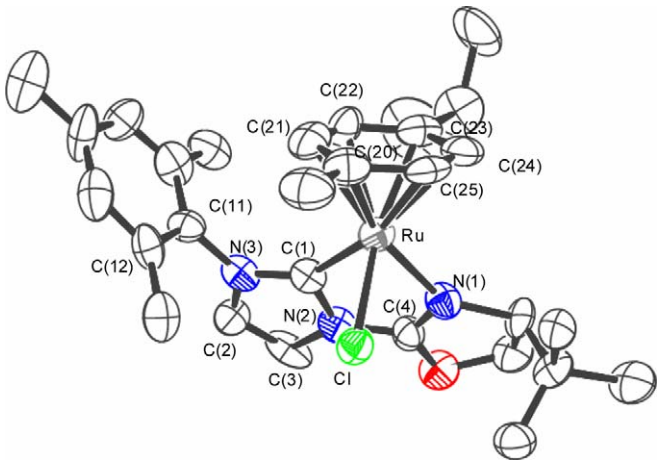


Fig. 2. Molecular structure of **2b**. Hydrogen atoms and the counterion (PF_6^-) are omitted for clarity. Selected bond lengths (Å) and angles (°): Ru–C(1) 2.03(2), Ru–N(1) 2.17(2), Ru–C(20) 2.20(2), Ru–C(21) 2.17(2), Ru–C(22) 2.11(2), Ru–C(23) 2.18(2), Ru–C(24) 2.22(2), Ru–C(25) 2.23(2); and C(1)–Ru–N(1) 76.0(6), Cl–Ru–N(1) 86.2(3), C(1)–N(2)–C(4)–N(1) 0(2) C(12)–C(11)–N(3)–C(2) 83(2).

molecular structure of **2b**, the chloro ligand was found to adopt the same orientation as the *t*Bu substituent, probably due to steric repulsion between the later and the *p*-cymene ligand. In both cases, the imidazol and the oxazoline rings are almost coplanar, as is reflected in the corresponding dihedral angles (dihedral angle for **2a**: C(1)–N(1)–C(4)–N(3) 2.1°; dihedral angle for **2b**: C(1)–N(2)–C(4)–N(1) 0°). The mesityl ring is orientated almost orthogonally to the imidazolyl ring in complex **2a**, whereas it slightly deviates from this orientation in complex **2b** (dihedral angle for **2a**: C(10)–C(9)–N(2)–C(2) 89.3°; dihedral angle for **2b**: C(12)–C(11)–N(3)–C(2) 83°). The Ru–$C_{carbene}$ distances (2.038 Å (**2a**) and 2.03 Å (**2b**)) lie in the typical range for NHC–Ru complexes [24,25].

It is noteworthy that the bite angles of the chelating oxazolinyl-carbene ligands in complexes **2a** and **2b** (76.6° and 76.0°, respectively) are very similar to those observed for other metal compounds with these and related ligands [16,17]. This is due to the rigidity of the ligand backbone, the structure of which barely varies upon coordination to a metal centre. For the rhodium complexes with distorted trigonal bipyramidal geometry, the C–Rh–N bite angles lie between 77.47° and 77.49°, while for the Rh(I) cationic complexes with square-planar geometry, these angles were

Table 1
Catalytic transfer hydrogenation using complex **2a** as catalyst[a]

Entry	Substrate	Additive	Time (h)	GC yield (%)
1	Acetophenone	–	24	10
2	Acetophenone	$AgPF_6$	9	32
3	Acetophenone	$AgPF_6$	24	99
4	2-Octanone	$AgPF_6$	24	84
5	Pinacolone	$AgPF_6$	24	0

[a] *Conditions*: substrate/catalyst (**2a**)/base (KOH), 100/1/5 in 10 mL *i*PrOH at reflux temperature. Yield determined by GC using internal standard.

found to be in the range of 78.7–78.2° [17]. On the other hand, the chelating angle in the square-planar Pd(II) complex [$PdCl_2$(Me$_2$-oxcarb)] is 79.2° [16].

Complex **2a** showed moderate activity in the transfer hydrogenation of ketones to the corresponding secondary alcohols from *i*PrOH/KOH at 82 °C [26]. Good conversion was achieved in 24 h using acetophenone and 2-octanone as substrates (see Table 1). However, the reaction failed with sterically more demanding substrates such as pinacolone. The formation of a dicationic species as active catalyst seems to be crucial since the use of complex **2a** without adding a silver salt gave very poor yields. On the other hand, the chiral complex **2b** did not show any activity in this test even using other bases such as *t*BuOK or K_2CO_3. All attempts towards using complex **2b** in other asymmetric catalyses, such as the hydrogenation of ketones or isomerization of allylic alcohols, were unsuccessful. Since Lewis acid complexes may be catalytically very active in C–C coupling reactions such as the Diels–Alder reaction, we decided to carry out the latter with chiral complex **2c** using methyl acrylate or acrolein and cyclopentadiene [27]. Although the system displayed high activity in the coupling reaction, we did not observe any significant stereoselectivity in the formation of the reaction products. Using methyl acrylate as substrate, a yield of 70% was obtained after 24 h at room temperature using 1.0 mol% catalyst **2c** and $AgPF_6$ as additive (*endo*/*exo* 83/17). Acrolein gave a complete conversion under the same conditions and an *endo*/*exo* ratio of 75/25 was observed.

2.2. Synthesis of the dicationic species *3a* and *3b*

The dicationic complexes **3a** and **3b** (Scheme 3) were readily obtained from complexes **2a** and **2b**, respectively, by adding a silver salt to a solution of the latter in dichloromethane. The mixture was stirred at room temperature and under exclusion of light and the silver chloride formed in the process was separated by filtration through Celite under inert atmosphere. The salts of the dicationic complexes were recrystallized and the aqua complex derivatives obtained in high yield as crystalline orange solids. We believe that the coordination of H_2O to the complex may come from traces of water contained in the solvents used, or in the manipulation of the solutions during the crystallization workup. An electron-deficient 16-electron species may be generated in the initial formation of the products, which is converted into the corresponding THF or H_2O adducts in the presence of any of them. In our case only the H_2O adduct was isolated.

The 18 electron complexes, which were obtained by this procedure, were characterized by NMR and mass spectroscopy. As expected, both the ^{1}H and the ^{13}C NMR spectra, show very similar resonance patterns to those of the neutral complexes **2a** and **2b**. Again, the most characteristic feature in the ^{13}C NMR spectra is the signal due to the metallated

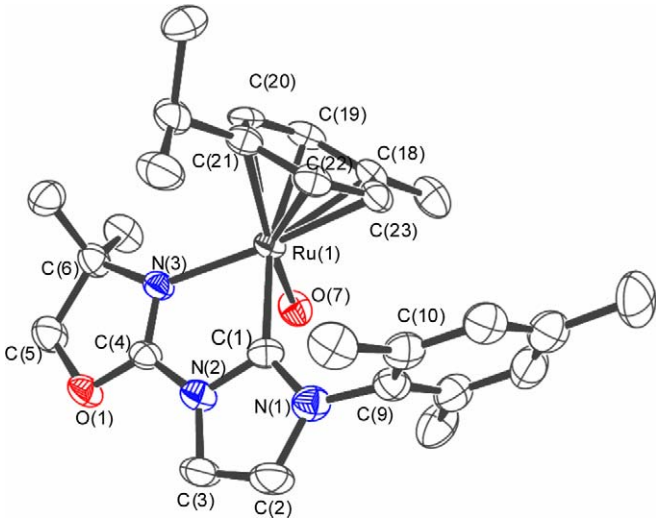
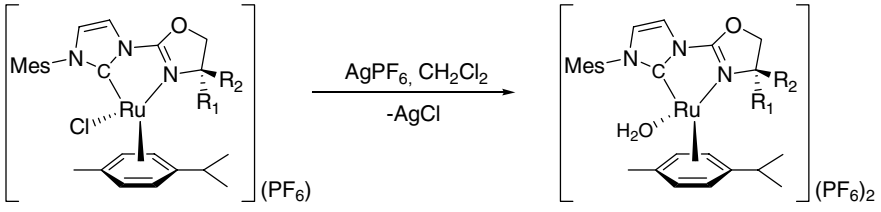


Fig. 3. X-ray molecular structure of **3a**. Hydrogen atoms and counterion (PF_6^-) are omitted for clarity. Selected bond lengths (Å) and angles (°): Ru(1)–C(1) 2.045(4), Ru(1)–N(3) 2.121(3), Ru(1)–O(7) 2.169(3), Ru(1)–C(22) 2.178(4), Ru(1)–C(23) 2.200(4), Ru(1)–C(21) 2.214(4), Ru(1)–C(18) 2.220(4) Ru(1)–C(20) 2.235(4), Ru(1)–C(19) 2.235(4), C(1)–Ru(1)–N(3) 76.0(2), C(1)–Ru(1)–O(7) 85.7(2), C(1)–N(2)–C(4)–N(3) 4.6(6), C(2)–N(1)–C(9)–C(10) 87.9(6).



2a, R_1=R_2=Me
2b, R_1=^{t}Bu, R_2=H

3a-b

Scheme 3. Synthesis of dicationic ruthenium(arene) complexes.

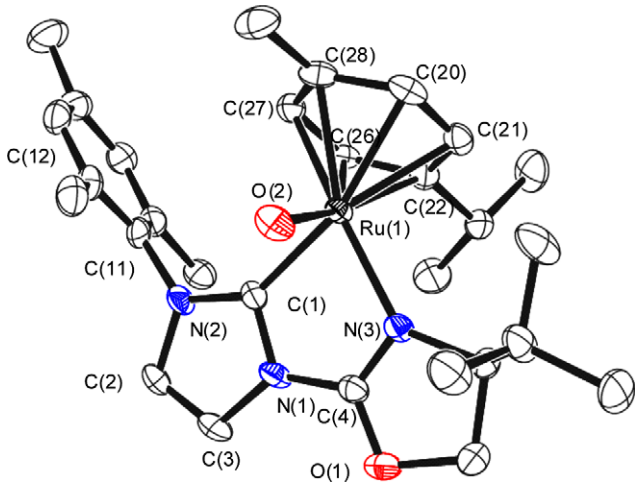


Fig. 4. X-ray molecular structure of **3b**. Hydrogen atoms and counterion (PF_6^-) are omitted for clarity. Selected bond lengths (Å) and angles (°): Ru(1)–C(1) 2.037(5), Ru(1)–O(2) 2.147(4), Ru(1)–N(3) 2.148(4), Ru(1)–C(26) 2.175(5), Ru(1)–C(22) 2.192(6), Ru(1)–C(27) 2.207(6), Ru(1)–C(28) 2.232(5) Ru(1)–C(21) 2.243(6), Ru(1)–C(20) 2.251(5); and C(1)–Ru(1)–O(2), 85.6(2), C(1)–Ru(1)–N(3) 76.0(2), C(1)–N(1)–C(4)–N(3) 4(1), C(12)–C(11)–N(2)–C(2) 106.3(7).

carbene carbon atom, which is observed in the typical frequency region (184.4 ppm for **3a** and 185.2 ppm for **3b**). To unequivocally confirm the molecular structure of these complex dications, single crystals of **3a** and **3b** were grown by slow diffusion of THF/Et_2O mixtures. The gross features of the molecular structures of both complexes, **3a** and **3b** (Figs. 3 and 4, respectively), are virtually identical to those of complexes **2a** and **2b**. The ruthenium atom is again in a distorted tetrahedral environment and the coordination sphere is now completed by coordination of a molecule of water.

The imidazol and oxazoline heterocycles are almost coplanar, whilst the mesityl unit slightly deviates from the orthogonal orientation to the imidazol ring (dihedral angle for **3a**: C(10)–C(9)–N(1)–C(7) 96.8; dihedral angle for **3b**: C(12)–C(11)–N(2)–C(2) 106.2) in both cases. The bite angles of the oxazolinyl-carbene ligands in the dicationic species **3a** and **3b** are very similar to those observed previously in complexes containing these chelating ligands and the Ru–$C_{carbene}$ distances of 2.045 and 2.037 Å lie in the expected range.

3. Conclusions

In this study, we report the first ruthenium complexes bearing the oxazolinyl-carbene ligands which we recently introduced to asymmetric catalysis. Using the silver carbene route, these new complexes were readily accessible and could be fully characterized and converted to the corresponding cationic species. Their potential as catalysts for transfer hydrogenations and Lewis acid catalyzed Diels–Alder reactions has been probed and has established their limitations. Work towards extending this study to other types of ruthenium complexes, which are suitable as precatalysts for stereoselective catalytic transformations is under way.

4. Experimental

4.1. General procedures

The ligand precursors **1a**–**c** [12,16] and the metal complex [Ru(*p*-cymene)Cl_2]$_2$ [28] were prepared as previously described. All manipulations were performed under an inert gas atmosphere using standard Schlenk techniques. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance NMR spectrometer at 300 and 75 MHz, respectively, and were referenced using the residual proton solvent peak. Assignments are based on COSY and DEPT experiments. The elemental analyses and electrospray mass spectra were performed by the analytical services of the Heidelberg Chemistry Department. All other reagents were used as received from commercial suppliers.

4.2. Transmetallation reactions, general procedure

A suspension of the ligand precursor (1 equiv.) and silver oxide (0.5 equiv.) was stirred at room temperature for 2 h. The product mixture was then filtered through Celite to remove the unreacted silver oxide and [Ru(*p*-cymene)Cl_2]$_2$ (0.5 equiv) was added to the solution. The white precipitate of silver halide, which formed immediately, was again removed by filtration through Celite after having stirring the suspension overnight. The filtrate solution was subsequently concentrated under reduced pressure, and the precipitate, which was formed in the process, was dissolved in dichloromethane and purified by column chromatography.

4.3. Synthesis of *2a*

The transmetallation procedure was carried out as described above at room temperature in dichloromethane with 1-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-3-mesitylimidazolium bromide (**1a**, 238 mg, 0.65 mmol), silver oxide (75.7 mg, 0.33 mmol) and [Ru(*p*-cymene)Cl_2]$_2$ (200 mg, 0.33 mmol). Elution with dichloromethane/acetone (1/1) and KPF_6 afforded the separation of an orange band that contained **2a** (350 mg, 80% yield). Suitable crystals for X-ray diffraction were obtained by layering concentrated solutions of the compound in dichloromethane with hexanes and allowing slow diffusion at room temperature. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.58 (d, $^3J_{H-H} = 2.4$ Hz, 1H, CH_{imid}), 7.20, 7.12 (s, 2H, $CH_{mesityl}$), 7.08 (d, $^3J_{H-H} = 2.4$ Hz, 1H, CH_{imid}), 5.36, 5.30, 5.14, 4.98 (br s, 4H, $(CH_3)_2CHC_6H_4(CH_3)$-*p*), 4.91, 4.70 (d, $^2J_{H-H} = 8.4$ Hz, 2H, $CH_{2oxazoline}$), 2.54 (m, 1H, $(CH_3)_2CHC_6H_4(CH_3)$-*p*), 2.45 (s, 3H, CH_{3para}), 2.23, 2.20 (s, 6H, CH_{3ortho}), 1.98 (s, 3H, $(CH_3)_2CHC_6H_4(CH_3)$-*p*), 1.70, 1.58 (s, 6H, $CH_{3oxazoline}$), 1.11–1.04 (dd, 6H, $(CH_3)_2CHC_6H_4(CH_3)$-*p*).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 300 MHz): δ 187.2 (C–Ru), 158.0 (NCO), 141.3, 136.3, 135.7, 134.0 ($C_{mesytil}$), 129.9, 129.6 ($CH_{mesityl}$), 125.5, 117.8 (CH_{imid}), 88.5 ($CH_{p\text{-cymene}}$), 85.5 ($CH_{2oxazoline}$), 84.1 ($CH_{p\text{-cymene}}$), 68.5 ($C_{4oxazoline}$), 31.4 (($CH_3)_2CHC_6H_4(CH_3)$-*p*), 27.9, 27.6 ($CH_{3oxazoline}$), 22.8 (CH_{3para}), 21.8, 21.3 (($CH_3)_2CHC_6H_4(CH_3)$-*p*), 19.0 (CH_{3ortho}), 18.9 (($CH_3)_2CHC_6H_4(CH_3)$-*p*), 18.0 (($CH_3)_2CHC_6H_4(CH_3)$-*p*). Anal. Calc. for $C_{27}H_{35}N_3OClRuPF_6$ (699.07): C, 46.39; H, 5.05; N, 6.01. Found: C, 46.20; H, 5.03; N, 5.34%. MS(FAB) *m*/*z* (%): 554.1 (70) [LRu(*p*-cymene)Cl]$^+$, 518.0 (20) [LRu(*p*-cymene)]$^+$. $\nu_{C=N}$ = 1660.8 cm^{-1}.

4.4. Synthesis of **2b**

In an analogous manner to the preparation of **2a**, transmetallation was carried out at room temperature using dichloromethane as solvent with 1-(4(*S*)-*tert*-butyl-4,5-dihydrooxazol-2-yl)-3-mesitylimidazolium bromide (**1b**, 96 mg, 0.244 mmol), silver oxide (28.3 mg, 0.122 mmol) and [Ru(*p*-cymene)Cl_2]$_2$ (75 mg, 0.122 mmol). Column chromatography using dichloromethane/acetone (1/1) and KPF_6 afforded the separation of an orange band that contained **2b** (120 mg, 67% yield). X-ray quality crystals were grown by slow diffusion from dichloromethane/methanol/hexanes. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.59 (d, $^3J_{H-H}$ = 2.2 Hz, 1H, CH_{imid}), 7.19, 7.10 (s, 2H, $CH_{mesityl}$), 7.06 (d, $^3J_{H-H}$ = 2.2 Hz, 1H, CH_{imid}), 5.38, 5.31 (d, 2H, ($CH_3)_2CHC_6H_4(CH_3)$-*p*), 5.13, 4.90 (br s, 2H, ($CH_3)_2CHC_6H_4(CH_3)$-*p*), 5.16 (dd, 1H, $CH_{oxazoline}$), 4.97, 4.36 (dd, $^2J_{H-H}$ = 9.1 Hz, $^3J_{H-H}$ = 3.9 Hz, 2H, $CH_{2oxazoline}$), 2.49 (m, 1H, ($CH_3)_2CHC_6H_4(CH_3)$-*p*), 2.43 (s, 3H, CH_{3para}), 2.25, 2.23 (s, 6H, CH_{3ortho}), 2.17 (s, 3H, ($CH_3)_2CHC_6H_4(CH_3)$-*p*), 1.16 (s, 9H, $C(CH_3)_3$), 1.05, 0.97 (d, 6H, ($CH_3)_2CHC_6H_4(CH_3)$-*p*). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 300 MHz): δ 188.3 (C–Ru), 159.5 (NCO), 141.3, 136.8, 135.5, 134.1 ($C_{mesytil}$), 130.1, 129.4 ($CH_{mesityl}$), 125.7, 118.3 (CH_{imid}), 75.5 ($CH_{2oxazoline}$), 65.9 ($CH_{oxazoline}$), 35.6 ($C(CH_3)_3$), 31.0 (($CH_3)_2CHC_6H_4(CH_3)$-*p*), 25.9 ($C(CH_3)_3$), 22.5, 21.8 (($CH_3)_2CHC_6H_4(CH_3)$-*p*), 21.2 (CH_{3para}), 18.6 (2C, 1C ($CH_3)_2CHC_6H_4(CH_3)$-*p*, 1C CH_{3ortho}), 17.9 (CH_{3ortho}). Anal. Calc. for $C_{29}H_{39}N_3OClRuPF_6$ (727.13): C, 47.90; H, 5.41; N, 5.78. Found: C, 47.75; H, 5.54; N, 5.51%. MS(FAB) *m*/*z* (%): 582.0 (70) [LRu(*p*-cymene)Cl]$^+$, 547.1 (6) [LRu(*p*-cymene)]$^+$, 412.0 (20) [LRu]$^+$. $\nu_{C=N}$ = 1666.9 cm^{-1}.

4.5. Synthesis of **2c**

The transmetallation was carried out in dichloromethane at reflux with 1-(4(*S*)-*iso*-propyl-4,5-dihydrooxazol-2-yl)-3-mesitylimidazolium bromide (**1c**, 123 mg, 0.33 mmol), silver oxide (37.8 mg, 0.16 mmol) and [Ru(*p*-cymene)Cl_2]$_2$ (100 mg, 0.16 mmol). Elution with CH_2Cl_2/acetone (1/1) and KPF_6 afforded the separation of an orange band that contained **2c**. Complex **2c** was obtained in a moderate yield (110 mg, 48%) by precipitation from a dichloromethane/Et_2O solution. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.58 (d, $^3J_{H-H}$ = 2.1 Hz, 1H, CH_{imid}), 7.19, 7.10 (s, 2H, $CH_{mesityl}$), 7.07 (d, $^3J_{H-H}$ = 2.1 Hz, 1H, CH_{imid}), 5.39–4.48 (m, 7H, 4H ($CH_3)_2CHC_6H_4(CH_3)$-*p*, 2H $CH_{2oxazoline}$, 1H $CH_{oxazoline}$), 2.44 (s, 4H, 1H ($CH_3)_2CHC_6H_4(CH_3)$-*p*, 3H CH_{3para}), 2.33 (m, 1H, $CH(CH_3)_2$), 2.21 (s, 6H, CH_{3ortho}), 1.95 (s, 3H, ($CH_3)_2CHC_6H_4(CH_3)$-*p*), 1.13–0.93 (m, 12H, 6H ($CH_3)_2CHC_6H_4(CH_3)$-*p*, 6H $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 300 MHz): δ 188.6 (C–Ru), 158.9 (NCO), 141.2, 136.6, 135.6, 134.1 ($C_{mesytil}$), 130.0, 129.4 ($CH_{mesityl}$), 125.6, 117.9 (CH_{imid}), 108.5, 99.91 ($C_{p\text{-cymene}}$), 89.1 ($CH_{p\text{-cymene}}$), 85.9 ($CH_{2oxazoline}$), 85.7 ($CH_{oxazoline}$), 85.3 ($CH_{p\text{-cymene}}$), 76.1, 70.1 ($CH_{p\text{-cymene}}$), 31.1 (($CH_3)_2CHC_6H_4(CH_3)$-*p*), 30.3 ($CH(CH_3)_2$), 23.0, 21.3 ($CH(CH_3)_2$), 21.2, 19.4, 18.8, 18.7 (4C, 3C $CH_{3mesityl}$, 1C ($CH_3)_2CHC_6H_4(CH_3)$-*p*), 17.8, 16.1 (($CH_3)_2CHC_6H_4(CH_3)$-*p*). Anal. Calc. for $C_{28}H_{39}N_3O_2ClRuPF_6$ (731.12): C, 46.00; H, 5.38; N, 5.75. Found: C, 45.97; H, 5.20; N, 5.57%. MS(FAB) *m*/*z* (%): 568.0 (71) [LRu(*p*-cymene)Cl]$^+$, 533.0 (10) [LRu(*p*-cymene)]$^+$, 398.0 (10) [LRu]$^+$. $\nu_{C=N}$ = 1667.2 cm^{-1}.

4.6. Synthesis of **3a**

To an orange solution of **2a** (20 mg, 0.029 mmol) in distilled dichloromethane (5 mL) solid $AgPF_6$ was added (15 mg, 0.058 mmol, 2 equiv). The mixture was stirred at room temperature under exclusion of light for 3 h. A white precipitate (silver halide), which had formed, was separated by filtration through Celite, and the solvent of the filtrate was subsequently removed in vacuo to give complex **3a** as an orange microcrystalline solid (19 mg, 86%). Suitable crystals for an X-ray diffraction study were obtained by slow diffusion from a mixture THF/Et_2O under exposure to air. ^1H NMR (CD_2Cl_2, 300 MHz): δ 7.71 (d, $^3J_{H-H}$ = 2.2 Hz, 1H, CH_{imid}), 7.33 (d, $^3J_{H-H}$ = 2.2 Hz, 1H, CH_{imid}), 7.29, 7.32 (br s, 2H, $CH_{mesityl}$), 5.72, 5.57, 5.43, 5.10 (d, 4H, ($CH_3)_2CHC_6H_4(CH_3)$-*p*), 5.01, 4.88 (d, $^2J_{H-H}$ = 8.4 Hz, 2H, $CH_{2oxazoline}$), 2.53 (s, 3H, CH_{3para}), 2.39 (m, 1H, ($CH_3)_2CHC_6H_4(CH_3)$-*p*), 2.27, 2.13 (s, 6H, CH_{3ortho}), 1.91 (s, 3H, ($CH_3)_2CHC_6H_4(CH_3)$-*p*), 1.78, 1.75 (s, 6H, $CH_{3oxazoline}$), 1.09–1.05 (dd, 6H, ($CH_3)_2CHC_6H_4(CH_3)$-*p*). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 300 MHz): δ 184.4 (C–Ru), 160.2 (NCO), 142.1, 135.3, 135.0, 133.6 ($C_{mesytil}$), 130.2, 130.1 ($CH_{mesityl}$), 126.8, 118.4 (CH_{imid}), 88.9 ($CH_{p\text{-cymene}}$), 86.2 ($CH_{2oxazoline}$), 83.3 ($CH_{p\text{-cymene}}$), 68.1 ($C_{4oxazoline}$), 31.3 (($CH_3)_2CHC_6H_4(CH_3)$-*p*), 28.3, 26.2 ($CH_{3oxazoline}$), 22.4 (CH_{3para}), 21.5, 21.0 (($CH_3)_2CHC_6H_4(CH_3)$-*p*), 18.5, 17.8 (CH_{3ortho}), 17.8 (($CH_3)_2CHC_6H_4(CH_3)$-*p*). MS(FAB) *m*/*z* (%): 553.9 (12) [LRu(*p*-cymene)Cl]$^+$, 518.0 (48) [LRu(*p*-cymene)]$^+$, 381.9 (45) [LRu]$^+$. $\nu_{C=N}$ = 1651.2 cm^{-1}.

4.7. Synthesis of **3b**

As described for **3a**, complex **3b** was obtained by adding $AgPF_6$ (15 mg, 0.058 mmol, 2 equiv.) to a solution of **2b** (20 mg, 0.028 mmol) in distilled dichloromethane. The mix-

Table 2
Crystallographic data of **2a**, **2b** and **3a**, **3b**

	2a	**2b**	**3a**	**3b**
Empirical formula	$C_{28}H_{37}Cl_3F_6N_3OPRu$	$C_{30}H_{43}ClF_6N_3O_2PRu$	$C_{35}H_{53}F_{12}N_3O_4P_2Ru$	$C_{37}H_{57}F_{12}N_3O_4P_2Ru$
M_w	784.00	759.16	970.81	998.87
Crystal system	Monoclinic	Hexagonal	Triclinic	Monoclinic
Space group	$P2_1/c$	$P6_1$	$P\bar{1}$	$P2_1$
a (Å)	10.710(1)	10.392(5)	14.043(1)	10.867(1)
b (Å)	25.309(4)	10.392(5)	16.401(1)	13.932(1)
c (Å)	12.414(2)	55.599(5)	19.846(1)	14.544(1)
α (°)	90	90	89.18(1)	90
β (°)	103.33(2)	90	80.75(1)	92.11(1)
γ (°)	90	120	68.50(1)	90
V (Å^3)	3274.6(9)	5200(4)	4192.8(2)	2200.4(1)
Z	4	6	4	2
Reflections collected	9549	4274	24349	11648
Absorption coefficient (mm^{-1})	0.834	0.638	0.544	0.521
Goodness-of-fit	0.935	0.988	1.051	0.991
Final R_1	0.046	0.069	0.071	0.078
Reflections with [$I > 2\delta(I)$]	5728	2638	14636	9010
wR_2	0.094	0.197	0.229	0.172
Flack parameter	–	0.07(8)	–	−0.04(4)

ture was stirred at room temperature in the absence of light and the white precipitate, which had formed, was filtered through Celite. After removing the volatiles, the desired complex was obtained as an orange solid (15 mg, 64%). Suitable crystals for X-ray diffraction were obtained by slow diffusion from a mixture THF/Et_2O under exposure to air. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 7.64 (d, $^3J_{H-H}$ = 2.2 Hz, 1H, CH_{imid}), 7.24 (br s, 1H, $CH_{mesityl}$), 7.24 (d, $^3J_{H-H}$ = 2.2 Hz, 1H, CH_{imid}), 7.22 (br s, 1H, $CH_{mesityl}$), 5.69, 5.64, 5.24, 4.96 (d, $^3J_{H-H}$ = 6.3 Hz, 4H, $(CH_3)_2CHC_6H_4(CH_3)$-*p*), 5.15–5.12 (m, 2H, 1H $CH_{2oxazoline}$, 1H $CH_{oxazoline}$), 4.46 (dd, $^2J_{H-H}$ = 8.4 Hz, $^3J_{H-H}$ = 5.1 Hz, 1H, $CH_{2oxazoline}$), 2.48 (m, 1H, $(CH_3)_2CHC_6H_4(CH_3)$-*p*), 2.46 (s, 3H, CH_{3para}), 2.22, 2.15 (s, 6H, CH_{3ortho}), 1.93 (s, 3H, $(CH_3)_2CHC_6H_4(CH_3)$-*p*), 1.16 (s, 9H, $C(CH_3)_3$), 1.01, 0.96 (d, 6H, $(CH_3)_2CHC_6H_4(CH_3)$-*p*). ^{13}C{^{1}H} NMR ($CDCl_3$, 300 MHz): δ 185.2 (C–Ru), 161.6 (NCO), 141.8, 135.9, 135.0, 131.5 ($C_{mesytil}$), 130.1, 129.7 ($CH_{mesityl}$), 126.8, 118.7 (CH_{imid}), 77.3 ($CH_{p\text{-cymene}}$), 74.3 ($CH_{2oxazoline}$), 67.7 ($CH_{p\text{-cymene}}$), 65.6 ($CH_{oxazoline}$), 35.2 ($C(CH_3)_3$), 30.9 ($(CH_3)_2CHC_6H_4(CH_3)$-*p*), 25.3 ($C(CH_3)_3$), 22.6, 21.0 ($(CH_3)_2CHC_6H_4(CH_3)$-*p*), 20.9 (CH_{3para}), 18.0 ($(CH_3)_2CHC_6H_4(CH_3)$-*p*), 17.7, 15.0 (CH_{3ortho}). MS(FAB) *m/z* (%): 566.3 (88) [LRu(*p*-cymene)H_2OH]$^+$, 546.3 (90) [LRu(*p*-cymene)]$^+$. $\nu_{C=N}$ = 1661.6 cm^{-1}.

4.8. X-ray diffraction study of **2a**, **2b**, **3a** and **3b**

The crystal data were collected on a Nonius Kappa CCD diffractometer at −100 °C and transferred to a DEC Alpha workstation; for all subsequent calculations the Nonius OPENMOLEN package was used [29]. The structures were solved using direct methods with absorption corrections being part of the scaling procedure of the data reductions. After refinement of the heavy atoms, difference Fourier maps revealed the maxima of residual electron density close to the positions expected for the hydrogen atoms; they were introduced as fixed contributors in the structure factor calculations with fixed coordinates (C–H: 0.95 Å) and isotropic temperature factors (B(H) = 1.3 B_{eqv} (C) Å^2) but not refined. Full least-square refinements on F^2. A final difference map revealed no significant maxima of electron density. The scattering factor coefficients and the anomalous dispersion coefficients were taken from Ref. [30]. Crystal data and experimental details for **2a**, **2b**, **3a** and **3b** are given in Table 2.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 295099–295102. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax: +(44) 1223 336 033, e-mail: deposit@ccdc.cam.ac.uk.

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