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Synthesis of bis-oxazoline-ruthenium(II)-arene complexes. Combined catalytic isomerisation and Claisen rearrangement of bis-allyl ether

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Abstract

Bis-oxazolines **1a**–**c** and 2-benzothiazol-2-ylmethyl-benzooxazole (**1d**) (N–N) react with $[RuCl_2(p\text{-cymene})]_2$ in polar solvent with NH_4BF_4 or NH_4PF_6 and lead to ionic arene-ruthenium complexes $[RuCl(N–N)(p\text{-cymene})]^+X^-$ (**3a**–**d**) in quantitative yields. These complexes are easily deprotonated on the bridging methylene group and their electrochemical study shows the subtle influence of the substituents on the electron richness of the ruthenium atom. Complex **3b** in the presence of both 1,3-bis(2,6-diisopropylphenyl)imidazolinium chloride **6** and Cs_2CO_3 (1/1/2) catalyses the selective transformation of bis-allyl ether into γ,δ-unsaturated aldehyde via successive alkene isomerisation and Claisen rearrangement.

Keywords: Bis-oxazoline-ruthenium complexes; Alkene isomerisation; Claisen rearrangement; Imidazolinium salt; Allyl ether in catalysis

1. Introduction

During the last decade, the use of ruthenium catalysts for fine chemistry has seen rapid developments [1]. They have not only contributed to increase the performance of known, useful reactions such as the catalytic alkene metathesis [2], but also have led to innovative reactions such as the functionalisation of inert C–H bonds [3], the selective formation of C–C bonds via the selective coupling of functional unsaturated substrates [4] or the anti-Markovnikov addition to alkynes via vinylidene intermediates [5]. Moreover, ruthenium catalysts are currently at the centre of environment tolerant processes including atom-saving reactions [6]. This fast growing utilisation of ruthenium catalysts for the discovery of selective synthetic methods requires new ruthenium catalyst precursors that are continuously designed in parallel to the evaluation of their basic properties for catalysis: ligand lability, proton capture or release and redox potentials. In addition, new trends in metal catalysis involve the use of ionic liquids for the catalyst recovery and recycling [7] and the transfer of catalysis in these ionic media requires well-defined ionic catalyst precursors that are produced.

In the course of our current studies on combined catalytic reactions such as the selective isomerisation of alkene followed by Claisen rearrangement [8], it was found that the three component combination of a ruthenium precursor, a sterically hindered imidazolinium and cesium carbonate led to an efficient catalytic system. This motivated the search for new ionic ruthenium complexes containing, at the same time a labile ligand, in order to in situ generate a coordinatively unsaturated species, and an electron releasing bidentate group able to stabilise this species. We have thus explored the coordination to ruthenium moieties of easily synthesised bis-oxazoline molecules, as they have

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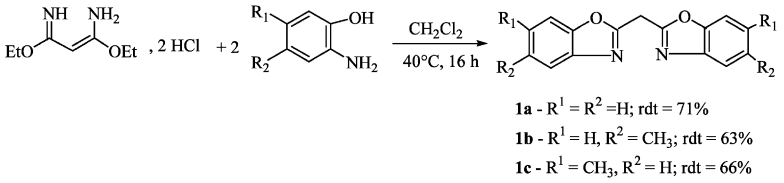
been previously shown to tune the properties of metal catalysts [9,10], and as their optically active versions stabilise various metal systems active in enantioselective catalysis [11]. On the other hand, bis-oxazoline-metal complexes containing a methylene group bridging the heterocyclic rings were considered as they offer potential for complex modification by successive deprotonation/alkylation reactions.

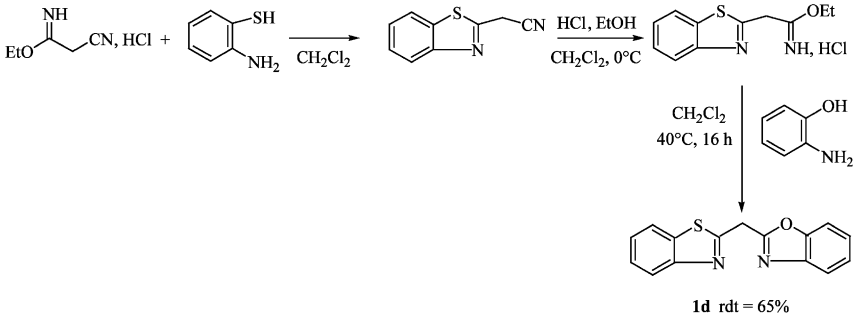
We now report the preparation of a series of new ionic bis-oxazoline-ruthenium and one 2-benzothiazol-2-yl-methyl-benzooxazol-ruthenium complexes containing a labile arene ligand, their selective deprotonation into neutral bidentate nitrogen complexes, and the preliminary result of the use of one them, with the cooperative action of imidazolinium salt and cesium carbonate, as catalyst precursor for tandem allyl to vinyl isomerisation and Claisen rearrangement to selectively transform a bis-allyl ether into a γ,δ-unsaturated aldehyde.



1a - $R^1 = R^2 = H$; rdt = 71%

1b - $R^1 = H$, $R^2 = CH_3$; rdt = 63%

1c - $R^1 = CH_3$, $R^2 = H$; rdt = 66%



1d rdt = 65%

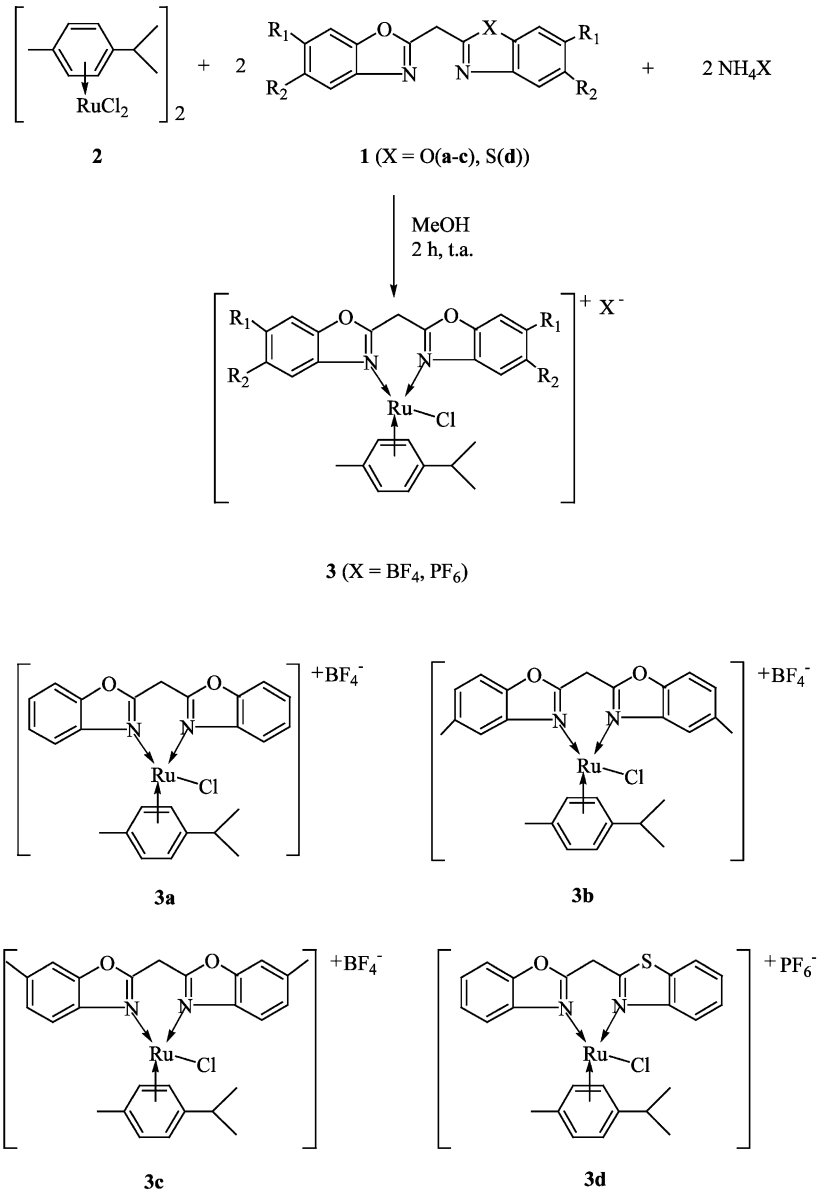
(1)

2. Results and discussion

The symmetrical bis-oxazolines **1a**–**c** and the unsymmetrical 2-benzothiazol-2-ylmethyl-benzooxazole (**1d**) were easily made according to literature [12] from the corresponding 2-aminophenols and 2-aminothiophenol in 60–70% yield (Eq. (1)). They were reacted with the ruthenium source $[RuCl_2(p\text{-cymene})]_2$ (**2**) [13], a complex leading to well-defined arene-ruthenium(II) complexes with bidentate ligands [14], and of which the arene can be easily selectively removed from the metal either by smooth heating or on UV–vis light irradiation [15]. The binuclear precursor $[RuCl_2(p\text{-cymene})]_2$ and two equivalents of bis-oxazolines **1a**–**d** were stirred in a polar solvent, methanol, in order to favour the ionic dissociation of one Ru–Cl bond, and in the presence of $NH_4^+BF_4^-$ or $NH_4^+PF_6^-$ to introduce a non-coordinating escorting anion. After 2 h of stirring at room temperature, the bis-oxazoline **1** was completely transformed and the orange–brown complexes **3** were obtained in excellent yields: **3a** (98%), **3b** (94%), **3c** (97%) and **3d** (98%) (Scheme 1).

The complexes **3a**–**d** were characterised by ^{1}H- and ^{13}C-NMR. The ^{1}H-NMR spectra revealed that coordination of the bis-oxazoline with respect to the free molecule undergoes a strong shift of the methylene bridging protons from a singlet at 4.1 ppm for **1a** to an AB system centred at 5.3 ppm for **3a**. Indeed, the four complexes **3** offer a well-defined AB system with $J_{(HA,HB)}$ value of 19–20 Hz for the methylene bridging protons as one of them is facing the chloride and the other one the arene group. The chiral complex **3d** does not introduce any difference in the system except the dissymmetry brought by the two different heterocyclic rings.

The complexes **3** are easily deprotonated on treatment with K_2CO_3 in dichloromethane at room temperature. Thus, the neutral brown complexes **4a** (98%) and **4b** (87%) were obtained directly from **3a** and **3b**. The ^{1}H-NMR spectrum shows the disappearance of the methylene AB system to the benefit of the –CH= singlet (4.75 ppm). The spectrum of **4b** shows the equivalence of the



Scheme 1.

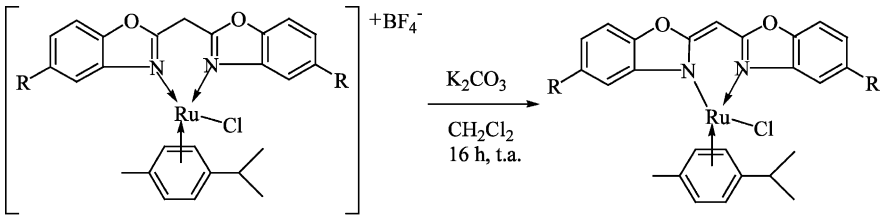
two oxazoline rings $MeC_6H_3(O)(N)$ compatible with an electron delocalisation on the whole bidentate ligand (Eq. (2)).

3. Electrochemical studies

The cyclic voltammetry study of complexes **3**–**4** was undertaken in order to give information on the modulation of the electron density brought by various bis-oxazoline ligands. The data were obtained from complex solution (10^{-4} M) in dry and degassed dichloromethane in the presence of the electrolyte Bu_4NPF_6 (0.1 M) and the potentials were measured with respect to the reversible ferrocene/ferrocenium couple as internal standard. The results are gathered in Table 1.

The cyclic voltammograms of all complexes show an irreversible reduction wave at 100 mV s^{-1}. The cathodic potential values show that the reference complex **3a** is reduced at −1.207 V (vs. Cp_2Fe) and that this value is decreased, as expected, by the introduction of methyl groups on the bis-oxazoline rings. However, the introduction of methyl group at 5 and 5′ positions of **3c** is more efficient to increase the electron-density at the metal site and thus to decrease the cathodic potential rather than at 6 and 6′ positions: **3c**: −1.410, **3b**: −1.326 V.

The comparison of the **3a** and **3d** cathodic potentials shows that the substitution of only one oxygen atom by



(2)

3

a : R = H
b : R = Me

4a-b

a sulfur atom drastically decreases the potential by 0.3 V. We can thus expect that the benzothiazol derivatives are more suitable to stabilise high oxidation state of ruthenium complexes or to favour oxidative addition or coupling reaction intermediates.

The cyclic voltammogram of the neutral complex **4a** shows only a slight decrease of the potential (−1.333 V) with respect to **3a** (−1.207 V) and thus it is noteworthy that the deprotonation has a similar effect as the introduction of methyl groups at 6 and 6′ positions of the chelating ligands (**3b**: −1.326 V).

4. Catalytic tandem isomerisation/Claisen reaction of bis-allyl ether

In the course of catalytic alkene metathesis reactions, it was recently found that ruthenium(II) complexes containing an electron-rich, bulky imidazolinylidene ligands were active catalysts for preliminary allyl to vinyl isomerisation [16]. We also have shown that $[RuCl_2(p\text{-cymene})]_2$ but more efficiently $Ru_3(CO)_{12}$ in the presence of both imidazolinium salt and Cs_2CO_3, enables homoallyl to allyl and allyl to vinyl isomerisation of unsaturated ethers, thus in situ affording precursors for Claisen rearrangement [8]. These observations added to the already rich chemistry of heterocyclic carbenes and of their precursors as stable carbenes or as key ligands in metal complex catalysts [17]. They also motivated the search of new ruthenium sources, to be associated to imidazolinium salts, for alkene isomerisation thus allowing another consecutive selective reaction. Thus the complex **3b**, of medium cathodic potential, was evaluated in the catalytic transformation of the mixed bis-allyl ether **5**.

When the ether **5** in toluene was heated with 5 mol% of complex **3b** for 16 h at 120 °C, no transformation was observed. By contrast, when the ether **5** was added to the in situ prepared catalyst by combination of **3b** (5 mol%), 1,3-bis(2,6-diisopropylphenyl)imidazolinium chloride **6** and Cs_2CO_3 in the ratio 1/1/2 in 6 ml of toluene at reflux a transformation occurred. The cesium carbonate was used as an attempt to modify the imidazolinium salt and to in situ generate the electron releasing bulky imidazolinylidene carbene ligand [8,18] and it was shown that imidazolinium salt with Cs_2CO_3 and $[RuCl_2(p\text{-cymene})]_2$ on prolonged heating lead to RuX_2(carbene)(arene) complex [19]. After 16h at 120 °C with the above three component catalyst, the ether **5** was completely transformed into the unsaturated aldehyde **7** which was isolated in 73% yield [20] (Eq. (3)).

This two step, one-pot transformation can be explained by the initial and preferential isomerisation of the non-substituted allyl group into a vinyl group leading to intermadiate **8** followed by thermal Claisen rearrangement.

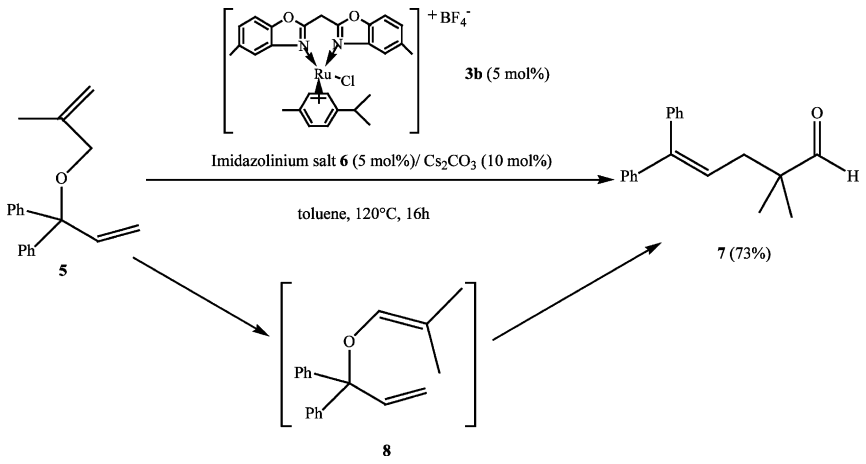
Table 1
Cyclic voltammetry of complexes **3**–**4** [a]

Complex	E (pc) (V vs. $FeCp_2$) (V)
3a	−1.207
3b	−1.326
3c	−1.410
3d	−1.532
4a	−1.333

[a] Solution of complexes **3**–**4** (10^{-4} M) in dry and degassed dichloromethane, Bu_4NPF_6 (0.1 M), internal standard: reversible ferrocene/ferrocenium couple, cyclic voltammetry at 100 mV s^{-1}.

5. Conclusion

The above results show that simple bis-oxazolines can be used to give access in high yield to new bis-oxazoline-ruthenium-arene complexes with easily deprotonated methylene bridges. Electrochemical studies show the fine tuning of the substituents of the chelating ligand to modulate the electron-richness of the ruthenium site. One of these complexes **3b** was shown, in the presence of the suitable imidazolinium salt and Cs_2CO_3, to catalyse the tandem isomerisation/Claisen rearrangement, thus allowing the one-pot transformation of a bis-allyl ether into γ,δ-unsaturated aldehydes.



(3)

6. Experimental

Diethyl ether was dried by refluxing over purple Na–benzophenone under Ar, while CH_2Cl_2 was purified over CaH_2. Methanol was used without further purification and degassed before use. The reactions described were carried out under nitrogen; however, once isolated as pure solids, the compounds are air-stable and further precautions for their storage are not necessary.

^{1}H-NMR spectra were obtained using a Bruker spectrometer operating at 200 MHz in $CDCl_3$ or CD_2Cl_2 unless stated otherwise; chemical shifts were recorded in ppm (referenced to residual protons in the NMR solvents). IR spectra were recorded in KBr pellets using a Nicolet 205 FT-IR. UV–vis spectra were recorded on a KONTRON UVIKON 941 spectrometer in diluted CH_2Cl_2 (ca. 10^{-4} mol l^{-1}). Microanalysis was performed by the Centre Régional de Mesures Physiques de l'Ouest in Rennes (France) and by the Service Central d'Analyses du CNRS (Vernaison, France). Electrochemical experiments were carried out in a three-electrode, one-compartment cell equipped with a Pt disk working electrode, a Pt wire auxiliary electrode, and a saturated NaCl calomel electrode (SSCE); all measurements were based on ferrocene as internal reference. An AUTOLAB PGSTAT 30 polarographic analyser was used to collect cyclic voltammetric data.

6.1. Preparation of [RuCl(bis(oxazoline))(p-cymene)][BF_4 or PF_6] (**3a–d**)

A solution of bis-oxazoline ligands **1** (two equivalents) in MeOH (10 ml) was added to $[RuCl_2(p\text{-cymene})]_2$ (one equivalent) and NH_4BF_4 or NH_4PF_6 (two equivalents), and the resulting suspension was stirred at room temperature (r.t.) for 2 h. An orange–brown solution was obtained, which was then evaporated and the crude residue dissolved in CH_2Cl_2. Filtration through celite gave a brown solution, which was evaporated, and the crude complex was washed with Et_2O (2×15 ml) and dried under vacuum. The scale and the yield for individual complexes are shown below.

6.2. [RuCl(bis(2-benzoxazolyl)methane)(p-cymene)][BF_4] (**3a**)

Complex **3a** was prepared from $[RuCl_2(p\text{-cymene})]_2$ (100 mg, 0.163 mmol), bis(2-benzoxalyl)methane (81 mg, 0.32 mmol), and NH_4BF_4 (34 mg, 0.32 mmol) and isolated in 95 mg yield (98%). Anal. Calc. for $C_{25}H_{24}BClF_4N_2O_2Ru$: C, 49.40; H, 3.98; N, 4.61. Found: C, 49.07; H, 3.91; N, 4.58%. ^{1}H-NMR: δ 1.25 (d, 6H, $J = 6.9$ Hz, $CH(CH_3)_2$), 2.20 (s, 3H, $CH_3C_6H_4$), 2.95 (sept, 1H, $J = 6.9$ Hz, $CH(CH_3)_2$), 4.85 (d(AB), 1 H, $J_{AB} = 20.5$ Hz, CH_2), 5.75 (d(AB), 1 H, $J_{AB} = 20.5$ Hz, CH_2), 5.90 (d(AB), 2 H, $J_{AB} = 6.3$ Hz, C_6H_4 *p*-cymene), 6.00 (d(AB), 2 H, $J_{AB} = 6.3$ Hz, C_6H_4 *p*-cymene) 7.50–7.91 (m, 8H, $2C_6H_4$). ^{13}C-NMR: δ 18.5 (MeC_6H_4), 22.5 ($CHMe_2$), 28.1 (CH_2), 31.3 ($CHMe_2$), 82.8 and 83.8 (4*C*H *p*-cymene), 100.1 and 107.4 (2*C p*-cymene), 112.3, 119.5, 126.4, 127.6 (4*C*H arom), 138.9, 150.3 (2*C* arom), 160.1 (2*C*=N). IR (cm^{-1}): 1162 (ν B–F), 1539 (ν C=C), 1578 (ν C=N), 1609 (ν C=N). UV: λ (nm) (ε, 1 mol^{-1} cm^{-1}): 393 (4000), 279 (7658), 273 (8610), (230 (9025). Electrochemistry (100 mV s^{-1}): E (Pc) = −1.207 V versus $FeCp_2$.

6.3. [RuCl(6,6′-dimethylbis(2-benzoxazolyl)methane)(p-cymene)][BF_4] (**3b**)

Complex **3b** was prepared from $[RuCl_2(p\text{-cymene})]_2$ (100 mg, 0.163 mmol), 6,6′-dimethylbis(2-benzoxalyl)methane (91 mg, 0.32 mmol), and NH_4BF_4 (34 mg, 0.32 mmol) and isolated in 97 mg yield (94%). Anal. Calc. for $C_{27}H_{28}BClF_4N_2O_2Ru$: C, 51.00; H, 4.44; N,

4.41; Cl, 5.58. Found: C, 50.72; H, 4.65; N, 4.48; Cl, 5.84%. ^{1}H-NMR: δ 1.25 (d, 6H, $J = 6.9$ Hz, CH(CH_3)$_2$), 2.15 (s, 3H, CH_3C$_6$H$_4$), 2.55 (s, 6H, 2 *Me*C$_6$H$_3$), 2.95 (sept, 1H, $J = 6.9$ Hz, C*H*(CH$_3$)$_2$), 4.75 (d(AB), 1H, $J_{AB} = 20.5$ Hz, CH_2), 5.80 (d(AB), 1H, $J_{AB} = 20.5$ Hz, CH2), 5.85 (d(AB), 2H, $J_{AB} = 6.2$ Hz, C$_6H_4$ *p*-cymene), 5.95 (d(AB), 2H $J_{AB} = 6.2$ Hz, C$_6H_4$ *p*-cymene) 7.28–7.70 (m, 6H, 2C$_6H_3$). ^{13}C-NMR: δ 18.6 (*Me*C$_6$H$_4$), 21.9 (2 *Me*C$_6$H$_3$), 22.7 (CH*Me*$_2$), 28.2 (*C*H$_2$), 31.4 (*C*HMe$_2$), 83.3 and 83.5 (4*C*H *p*-cymene), 100.5 and 107.1 (2*C p*-cymene), 111.7, 119.3, 128.9 (3*C*H arom), 136.8, 139.3, 148.7 (3*C* arom), 160.0 (2*C*=N). IR (cm^{-1}): 1167 (ν B–F), 1539 (ν C=C), 1578 (ν C=N), 1619 (ν C=N). UV: λ (nm) (ε, 1 mol^{-1} cm^{-1}): 397 (7293), 281 (1489). Electrochemistry (100 mV s^{-1}): E (Pc) = −1.326 V versus FeCp$_2$.

6.4. [RuCl(5,5′-dimethylbis(2-benzoxazolyl)methane)(p-cymene)][BF4] (3c)

Complex **3c** was prepared from [RuCl$_2$(*p*-cymene)]$_2$ (100 mg, 0.163 mmol), 5,5′-dimethylbis(2-benzoxalyl)methane (91 mg, 0.32 mmol), and NH_4BF_4 (34 mg, 0.32 mmol) and isolated in 109 mg yield (97%). ^{1}H-NMR: δ 1.24 (d, 6H, $J = 6.7$ Hz, CH(CH_3)$_2$), 2.22 (s, 3H, CH_3C$_6$H$_4$), 2.55 (s, 6H, 2 *Me*C$_6$H$_3$), 2.82 (sept, 1H, $J = 6.9$ Hz, C*H*(CH$_3$)$_2$), 4.90 (d(AB), 1H, $J_{AB} = 19.2$ Hz, CH_2), 5.30 (d(AB), 1H, $J_{AB} = 19.2$ Hz, CH_2), 5.80 (d(AB), 2 H, $J_{AB} = 5.9$ Hz, C$_6H_4$ *p*-cymene), 5.88 (d(AB), 2H $J_{AB} = 5.9$ Hz, C$_6H_4$ *p*-cymene) 7.36–7.73 (m, 6H, 2C$_6H_3$). ^{13}C-NMR: δ 18.7 (*Me*C$_6$H$_4$), 21.8 (2 *Me*C$_6$H$_3$), 22.7 (CH*Me*$_2$), 28.4 (*C*H$_2$), 31.3 (*C*HMe$_2$), 83.3 and 83.6 (4*C*H *p*-cymene), 100.5 and 107.0 (2*C p*-cymene), 112.2, 118.8, 127.7 (3*C*H arom), 136.9, 138.5, 150.6 (3*C* arom), 159.6 (2*C*=N). IR (cm^{-1}): 1167 (ν B–F), 1539 (ν C=C), 1578 (ν C=N), 1619 (ν C=N). UV: λ (nm) (ε, 1 mol^{-1} cm^{-1}): 396 (2062), 280 (1480). Electrochemistry (100 mV s^{-1}): E (Pc) = −1.410 V versus FeCp$_2$.

6.5. [RuCl(2-benzothiazol-2-ylmethyl-benzoxazol)(p-cymene)][PF6] (3d)

Complex **3d** was prepared from [RuCl$_2$(*p*-cymene)]$_2$ (100 mg, 0.163 mmol), 2-benzothiazol-2-ylmethyl-benzoxazol (87 mg, 0.32 mmol), and NH_4PF_6 (53 mg, 0.32 mmol) and isolated in 97 mg yield (98%). Anal. Calc. for $C_{25}H_{24}ClF_6N_2ORuS$: C, 44.03; H, 3.55; N, 4.11; Cl, 5.20. Found: C, 44.08; H, 3.39; N, 3.98; Cl, 5.25%. ^{1}H-NMR: δ 1.05 (d, 3H, $J = 6.9$ Hz, CH(CH_3)$_2$), 1.25 (d, 3H, $J = 6.9$ Hz, CH(CH_3)$_2$), 2.18 (s, 3H, CH_3C$_6$H$_4$), 2.80 (sept, 1H, $J = 6.9$ Hz, C*H*(CH$_3$)$_2$), 5.01 (d(AB), 1H, $J_{AB} = 19.3$ Hz, CH_2), 5.20 (d(AB), 1H, $J_{AB} = 19.2$ Hz, CH_2), 5.71 (d(AB), 2 H, $J_{AB} = 6.0$ Hz, C$_6H_4$ *p*-cymene), 5.93 (d(AB), 2H $J_{AB} = 6.0$ Hz, C$_6H_4$ *p*-cymene) 7.15–7.74 (m, 5H, 2C$_6H_4$), 7.84–7.97 (m, 5H, 2C$_6H_4$), 8.56–8.61 (m, 1H, 2C$_6H_4$). ^{13}C-NMR: δ 18.6 (*Me*C$_6$H$_4$), 22.4, 22.7 (CH*Me*$_2$), 31.6 (*C*H$_2$), 32.2 (*C*HMe$_2$), 82.2, 83.5, 83.6, 85.0 (4*C*H *p*-cymene), 100.5 and 107.5 (2*C p*-cymene), 112.3, 119.6, 122.7, 125.0, 126.2, 127.7, 127.9 (*C*H arom), 132.5, 135.8, 138.3, 142.6 (*C* arom), 160.3, 164.3 (2*C*=N). IR (cm^{-1}): 1162 (ν P–F), 1539 (ν C=C), 1578 (ν C=N), 1609 (ν C=N). UV: λ (nm) (ε, 1 mol^{-1} cm^{-1}): 412 (1390), 280 (10 167), 273 (11 233), 240 (17 612). Electrochemistry (100 mV s^{-1}): E (Pc) = −1.532 V versus FeCp$_2$.

6.6. Preparation of RuCl(2-(3H-benzoxazol-2-ylidenemethyl)benzoxazole))(p-cymene) (4a–b)

A solution of complex **3a** or **3b** (one equivalent) in CH_2Cl_2 (10 ml) was added to K_2CO_3 (three equivalents), and the resulting suspension was stirred at r.t. for one night. A brown solution was obtained, which was then filtered through celite to remove salts, then evaporated. The crude complex was washed with Et_2O (2 × 15 ml) and dried under vacuum.

6.7. RuCl(2-(3H-benzoxazol-2-ylidenemethyl)benzoxazole))(p-cymene) (4a)

Complex **4a** was prepared from complex **3a** (50 mg, 0.082 mmol), K_2CO_3 (34 mg, 0.247 mmol) and isolated in 42 mg yield (98%). ^{1}H-NMR: δ 1.15 (d, 6H, $J = 6.9$ Hz, CH*Me*$_2$), 2.37 (s, 3H, *Me*C$_6$H$_4$), 2.43 (sept, 1H, $J = 6.9$ Hz, C*H*Me$_2$), 4.75 (s, 1H, C*H*), 5.40 (d(AB), 2H, $J_{AB} = 6.2$ Hz, C$_6H_4$ *p*-cymene), 5.55 (d(AB), 2H $J_{AB} = 6.2$ Hz, C$_6H_4$ *p*-cymene) 6.95–7.40 (m, 8H, 2C$_6H_4$). ^{13}C-NMR: δ 18.9 (*Me*C$_6$H$_4$), 22.7 (CH*Me*$_2$), 30.7 (*C*HMe$_2$), 77.2 (C=*C*H–C=N), 82.3, 82.6 (4*C*H *p*-cymene), 97.3 and 99.9 (2*C p*-cymene), 108.9, 115.0, 120.9, 124.0, 138.6, 149.9 (*C*H arom), 158.3 (C=CH–*C*=N), 165.2 (C=CH–*C*=N). Electrochemistry (100 mV s^{-1}): E (Pc) = −1333 V versus FeCp$_2$.

6.8. RuCl(5-methyl-2-(5-methyl-3H-benzooxazol-2-ylidenemethyl)benzoxazole))(p-cymene) (4b)

Complex **4b** was prepared from complex **3b** (55 mg, 0.086 mmol), K_2CO_3 (49 mg, 0.35 mmol) in 41 mg yield (87%). ^{1}H-NMR: δ 1.12 (d, 6H, $J = 6.9$ Hz, CH*Me*$_2$), 2.40 (s, 3H, CH_3C$_6$H$_4$), 2.45 (s, 6H, *Me*C$_6$H$_3$), 2.47 (sept, 1H, $J = 6.9$ Hz, C*H*Me$_2$), 4.72 (s, 1H, C*H*), 5.41 (d(AB), 2 H, $J_{AB} = 6.2$ Hz, C$_6H_4$ *p*-cymene), 5.47 (d(AB), 2H $J_{AB} = 6.2$ Hz, C$_6H_4$ *p*-cymene) 6.79–6.86 (m, 2H, MeC$_6H_3$), 7.05–7.18 (m, 4H, 2 MeC$_6H_3$). ^{13}C-NMR: δ 19.0 (*Me*C$_6$H$_4$), 21.8 (*Me*C$_6$H$_3$), 22.4 (CH*Me*$_2$), 31.1 (*C*HMe$_2$), 58.2 (C=*C*H–C=N), 82.8, 82.9 (4*C*H *p*-cymene), 99.9 and 103.5 (2*C p*-cymene), 108.6, 115.8, 122.0 (*C*H arom), 134.2, 143.8, 148.5 (*C* arom), 159.8 (C=CH–*C*=N), 165.7 (C=CH–*C*=N).

6.9. Catalytic reaction

Bis-allyl ether **5** (100 mg, 0.4 mmol) was added to the catalyst solution containing the complex **3b** (10.4 mg, 5 mol%), 1,3-bis(2,6-diisopropylphenyl)imidazolinium chloride ($Im((^{i}Pr)_2Ph)_2^+Cl^-$) [21] **6** (8.4 mg, 5 mol%) and cesium carbonate (12.4 mg, 10 mol%) in $C_6H_5CH_3$ (6 ml). The reaction mixture was heated 16 h at 120 °C and then cooled down. The resulting brown solution was evaporated and the gummy oil obtained was then dissolved in heptane (10 ml), filtered and the solution evaporated. The crude was flash chromatographied over silica gel (eluent: $Et_2O/C_7H_{16} = 1/20$) to afford 73 mg (73% yield) of the aldehyde **7**.

6.10. 2,2-Dimethyl-5,5-diphenyl-pent-4-enal (7)

^{1}H-NMR: δ 1.12 (s, 6H, C(CHO)Me_2), 2.39 (d, 2H, $J = 7.6$ Hz, $(Ph)_2C{=}CHCH_2$), 6.08 (t, 1H, $J = 7.6$ Hz, $(Ph)_2C{=}CHCH_2$), 7.18–7.49 (m, 10H, 2 × Ph), 9.48 (s, 1H, CHO). ^{13}C-NMR: δ 21.2 (2 × CH_3), 36.6 ($(Ph)_2C{=}CHCH_2$), 46.5 ($C(CHO)Me_2$), 123.6 ($(Ph)_2C{=}CHCH_2$), 127.0, 127.1, 128.0, 128.2, 129.7 (C arom), 139.5, 142.2 (2 × C arom quat), 144.3 ($(Ph)_2C{=}CHCH_2$), 205.5 (CHO). MS (EI): m/z (%) = 264 (3) [M^+], 193 (34), 180 (71), 178 (24), 165 (21), 115 (100), 103 (16), 91 (50), 32 (76).

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