



HAL
open science

Functionalized-1,3,4-oxadiazole ligands for the ruthenium-catalyzed Lemieux-Johnson type oxidation of olefins and alkynes in water

Shaima Hkiri, Soufiane Touil, Ali Samarat, David Sémeril

► To cite this version:

Shaima Hkiri, Soufiane Touil, Ali Samarat, David Sémeril. Functionalized-1,3,4-oxadiazole ligands for the ruthenium-catalyzed Lemieux-Johnson type oxidation of olefins and alkynes in water. *Molecular Catalysis*, 2022, 517, pp.112014. 10.1016/j.mcat.2021.112014 . hal-03813565

HAL Id: hal-03813565

<https://hal.science/hal-03813565>

Submitted on 13 Oct 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Functionalized-1,3,4-oxadiazole ligands for the ruthenium-catalyzed Lemieux-Johnson type oxidation of olefins and alkynes in water

Shaima Hkiri,^{a,b} Soufiane Touil,^b Ali Samarat,^b David Sémeril^{*a}

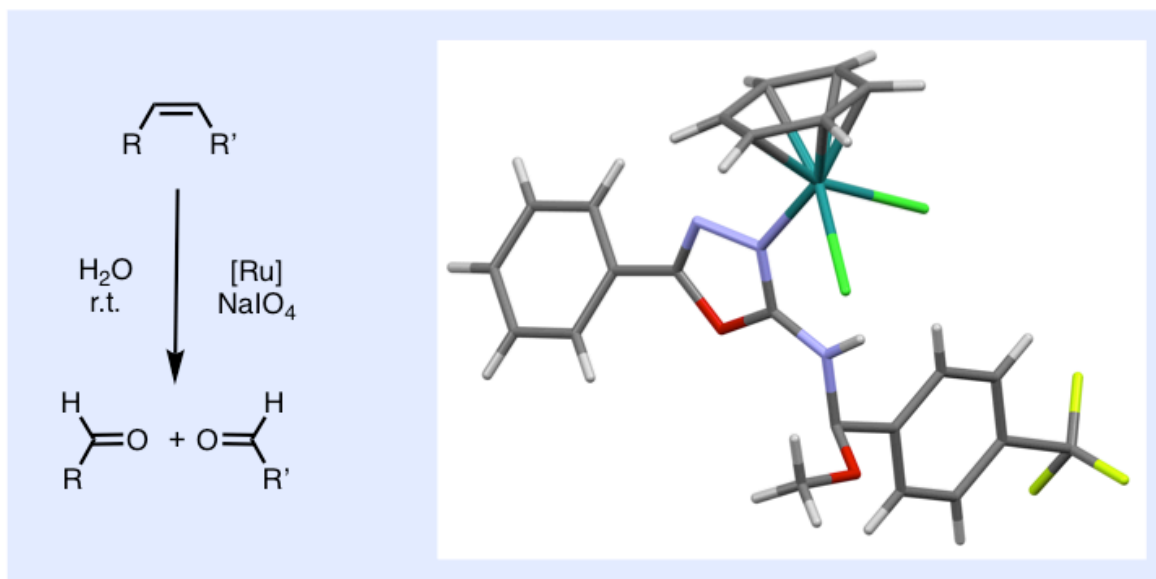
- a. University of Strasbourg, Synthèse Organométallique et Catalyse, UMR-CNRS 7177, 4 rue Blaise Pascal, 67008 Strasbourg, France; E-mail: dsemeril@unistra.fr
- b. University of Carthage, Faculty of Sciences of Bizerte, LR18ES11, Laboratory of Hetero-Organic Compounds and Nanostructured Materials, 7021, Bizerte, Tunisia

Abstract

Three arene-ruthenium(II) complexes bearing alkyloxy(5-phenyl-1,3,4-oxadiazol-2-ylamino)(4-trifluoromethylphenyl)methyl ligands were quantitatively obtained through the reaction of (*E*)-1-(4-trifluoromethylphenyl)-*N*-(5-phenyl-1,3,4-oxadiazol-2-yl)-methanimine with the ruthenium precursor $[\text{RuCl}_2(\eta^6\text{-}p\text{-cymene})]_2$ in a mixture of the corresponding alcohol and CH_2Cl_2 at 50°C. The obtained complexes were fully characterized by elemental analysis, infrared, NMR and mass spectrometry. Solid-state structures confirmed the coordination of the 1,3,4-oxadiazole moiety to the ruthenium center *via* their electronically enriched nitrogen atom at position 3 in the aromatic ring. These complexes were evaluated as precatalysts in the Lemieux-Johnson type oxidative cleavage of olefins and alkynes in water at room temperature with NaIO_4 as oxidizing agent. Good to full conversions of olefins into the corresponding aldehydes were measured, but low catalytic activity was observed in the case of alkynes. In order to get more insight into the mechanism, three analogue arene-ruthenium complexes were synthesized and tested in the oxidative cleavage of styrene. The latter tests clearly demonstrated the importance of the hemilabile alkyloxy groups, which may form more stable (*N,O*)-chelate intermediates and increase the efficiency of the *cis*-dioxo-ruthenium(VI) catalyst.

Keywords: 1,3,4-oxadiazole, ruthenium catalysis, Lemieux-Johnson oxidation, hemilabile ligand, (*N,O*)-chelate

Graphical abstract



Introduction

Lemieux-Johnson type oxidative cleavage of olefins^[1] is an efficient way to prepare aldehydes, safer than through ozonolysis. Initially using osmium complexes as catalysts,^[2] such double bond cleavage can be also achieved with cobalt,^[3] copper,^[4] gold,^[5] iron,^[6] molybdenum,^[7] nickel,^[8] palladium,^[9] titanium^[10] or vanadium^[11] based catalysts. These reactions often proceed with low catalytic activities and selectivities and side reactions such as epoxidation, dihydroxylation and allylic oxidation could be observed.

Recently, ruthenium complexes received much interest due to their large range of oxidation states (-2 to +8) and their ability to improve the chemoselectivity of such oxidative cleavages towards formation of aldehydes. Although ruthenium(III) trichloride was found to be effective for the oxidation of unsaturated hydrocarbons to carbonyl compounds,^[12] several complexes with polydentate ligands have been also studied. Let us cite, for example, the use of complexes containing bisphosphine ligands such as 1,3-bis(diphenylphosphino)propane (dpp) in $[\text{RuCl}(\text{dpp})_2]\text{ClO}_4$, *trans*- $[\text{RuCl}_2(\text{dpp})_2]$ ^[13] or $[\text{RuCl}_2(\kappa\text{-PPh}_2\text{-}\eta^6\text{-arene})]$ complexes, in which the aromatic side arm of the phosphine is tethered to the metal.^[14] However, the coordinating atom of choice was found to be the nitrogen atom in the form of one-^[15] or two-electrons donor ligands, often incorporated in polydentate frameworks containing as other coordinating atoms one or two additional nitrogens,^[16] carbon,^[17] oxygen or sulfur^[18] atoms. For instance, the pincer $[\text{RuBr}_2(\text{CO})(\text{CNC})]$ complex (CNC = 2,6-bis(butylimidazol-2-ylidene)-pyridine) (**A**; Figure 1) associated with NaIO_4 was employed by Peris *and coll.* in the oxidative cleavage of olefins, high yields were obtained for cyclic olefin like norbornene or 1-methylcyclohexene in 24 h with 1 mol % of catalyst.^[19] The group of Bera reported the synthesis of a (C,N)-chelate ruthenium complex containing a π -conjugated imidazo[1,2-a][1,8]naphthyridine-based abnormal N-heterocyclic carbene (**B**; Figure 1), which displayed important chemoselectivity and catalytic activity towards the Lemieux-Johnson oxidation of highly functionalized sugars and amino acids.^[20] The air stable cyclometalated ruthenium(II) benzhydrazone complex **C** (Figure 1) was employed by Ramesh *and coll.* in the cleavage of various olefins with NaIO_4 as oxidant in a water/organic solvent mixture, allowing a quasi full conversion within only 30 min at room temperature with a catalyst loading of 0.5 mol %.^[21] A water-soluble $[\text{Ru}(\text{terPy})(\text{MeCN})_3](\text{PF}_6)_2$ complex (**D** with terPy = terpyridine; Figure 1), was reported by Maiti *et coll.* for such oxidation to furnish aldehydes or ketones in high yields using 1 mol % of metal with NaIO_4 in 12 h at room temperature.^[22] Half sandwich

[RuCl(L₂)(η⁶-*p*-cymene)]PF₆ (**E**; L₂ = 2-phenyl-1H-imidazo[4,5-*f*][1,10]phenanthroline; Figure 1), in which the presence of the imidazole moiety was found to be useful for the activation of the oxidant and for the generation of the active species, was employed by Pratihari *et coll.* for the selective oxidative cleavage of carbon-carbon multiple bonds to aldehydes in the presence of *tert*-butyl hydroperoxide.^[23] Recently, Albrecht *and coll.* explored the dynamic donor ability of the *N,N'*-bis(pyridylidene)oxalamide (bisPYA) ligand in the cationic [RuCl(bisPYA)(η⁶-*p*-cymene)]PF₆ complex (**F**; Figure 1) for Lemieux-Johnson oxidation of olefins allowing turnover frequencies up to 650.000 mol(styrene) mol(**F**)⁻¹ h⁻¹ at room temperature.^[24]

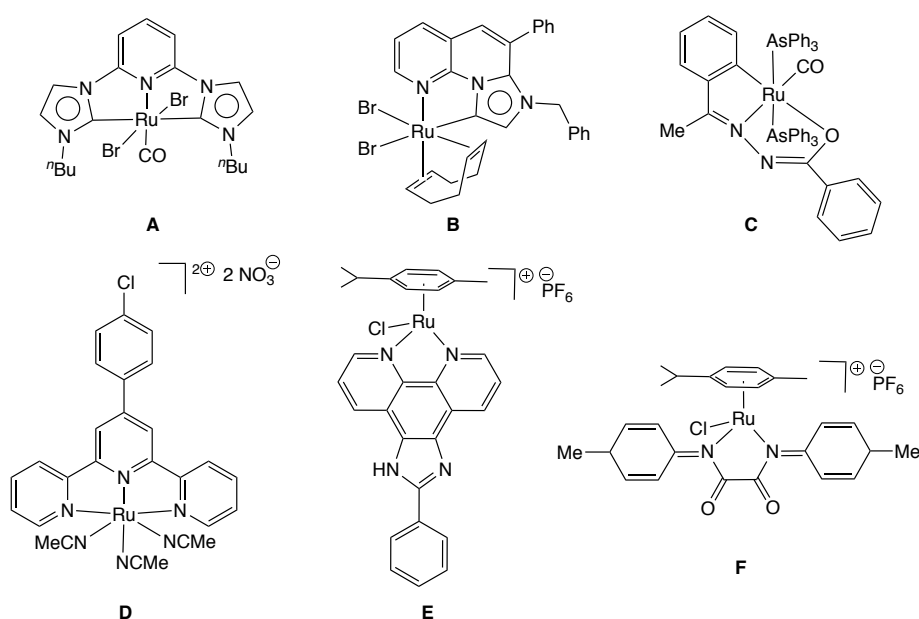


Figure 1. Examples of reported nitrogenated ruthenium complexes (**A-F**) employed in the oxidative cleavage of olefins.

In this context, we now report the ability of *N*-[alkyloxy(4-trifluoromethyl-phenyl)methyl]-5-phenyl-1,3,4-oxadiazol-2-amines, hemilabile ligands (**L**), to coordinate to a ruthenium precursor *via* their 1,3,4-oxadiazole aromatic ring and to form complexes of the general formula [RuCl₂(L)(η⁶-*p*-cymene)] (**Figure 2**). The ability of these complexes to form (*N,O*)-chelates as active species was investigated into the ruthenium-catalyzed oxidative cleavage of olefins and alkynes.

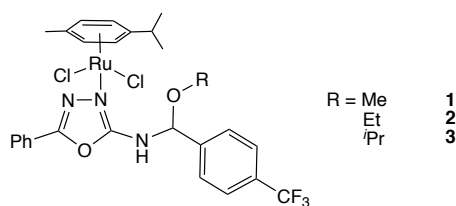
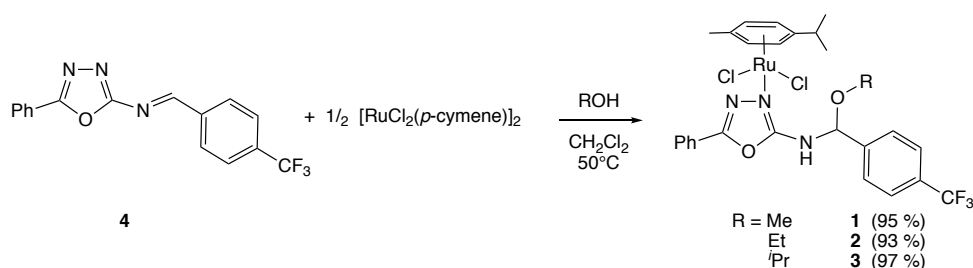


Figure 2. Ruthenium complexes (**1-3**) employed in this study.

Results and discussion

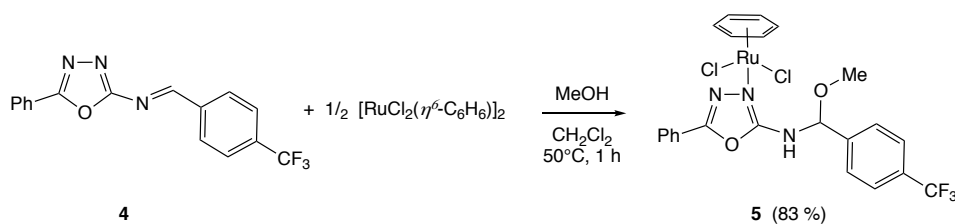
Preparation of ruthenium complexes

The arene-ruthenium(II) complexes **1-3** were obtained in 93-97 % yields, by heating at 50°C the (*E*)-1-(4-trifluoromethylphenyl)-*N*-(5-phenyl-1,3,4-oxadiazol-2-yl)-methanimine (**4**) with the metal precursor $[\text{RuCl}_2(\eta^6\text{-}p\text{-cymene})]_2$ (Ru/**4** stoichiometry of 1:1) in a mixture of CH_2Cl_2 and the corresponding alcohol, namely methanol, ethanol and *iso*-propanol (Scheme 1). The air- and moisture-stable ruthenium complexes **1-3** were fully characterized by infrared, multinuclear NMR spectroscopy (^1H , ^{13}C and ^{19}F), mass spectrometry and elemental analysis (see the Experimental section). Their ^1H NMR spectra show the presence of two new doublets at around 5.80 and 8.40 ppm corresponding to the CHOR and NH moieties, respectively. The ^{19}F NMR spectra display an up field shift of 1 ppm with regard to the imine **4**. Infrared measurements show the disappearance of the C=N band of the substrate and a shifts of the stretching vibrations $\nu(\text{C}=\text{N})$ of the oxadiazole ring towards higher wave numbers by 30-50 cm^{-1} in the complexes, which reveals the coordination of a nitrogen atom to the ruthenium center. The confirmation the coordination of the *N*-[alkyloxy(4-trifluoromethylphenyl)methyl]-5-phenyl-1,3,4-oxadiazol-2-amines ligands to the ruthenium precursor was further unambiguously confirmed by the mass spectra analyses, which show peaks corresponding to $[\text{M} - \text{Cl}]^+$ and $[\text{M} + \text{Na}]^+$ cations with the expected isotopic profiles.



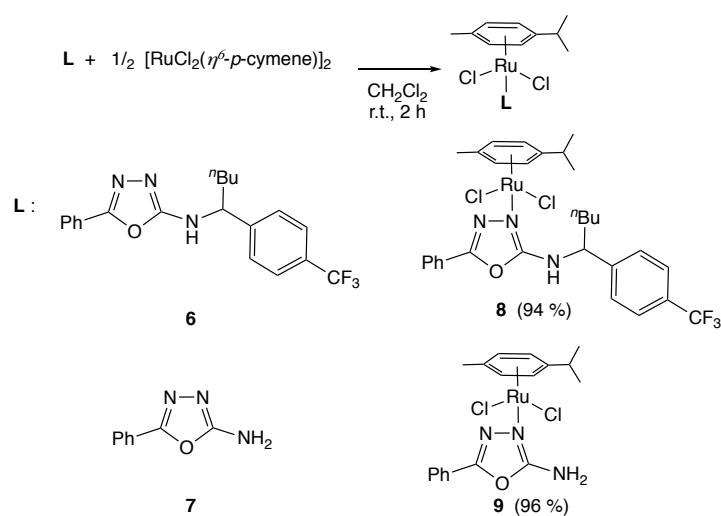
Scheme 1. Synthesis of ruthenium complexes **1-3**.

Similarly, complex **5** was obtained in 83 % yield from imine **4** and the ruthenium precursor $[\text{RuCl}_2(\eta^6\text{-C}_6\text{H}_6)]_2$ (Ru/**4** stoichiometry of 1:1) in a mixture of CH_2Cl_2 and methanol (Scheme 2). Its spectroscopic data are close to those measured for the related complex **1** (see the Experimental section). The presence of the coordinated η^6 -benzene was confirmed by the ^1H and ^{13}C NMR spectroscopy, which exhibited singlets at 5.85 (integrating for 6 protons) and 84.86 ppm, respectively.



Scheme 2. Synthesis of ruthenium complex **5**.

Finally, the arene-ruthenium complexes **8** and **9** were quantitatively obtained by reacting *N*-[butyl(4-trifluoromethyl-phenyl)methyl]-5-phenyl-1,3,4-oxadiazol-2-amine (**6**) or 5-phenyl-1,3,4-oxadiazol-2-amine (**7**), respectively, with $[\text{RuCl}_2(\eta^6\text{-}p\text{-cymene})]_2$ (Ru/**L** stoichiometry of 1:1) in CH_2Cl_2 at room temperature for 2 h (Scheme 3). The orange/red ruthenium complexes **8** and **9** were fully characterized by various spectroscopic techniques (see the Experimental section). In particular, the mass spectra exhibited peaks corresponding to $[\text{M} - \text{Cl}]^+$ and $[\text{M} + \text{Na}]^+$ cations with the expected isotopic profiles.



Scheme 3. Synthesis of ruthenium complexes **8** and **9**.

We have previously reported natural bond orbital charge analyses carried out on 5-phenyl-1,3,4-oxadiazol-2-ylamine derivatives. The calculations revealed that the presence of an amine substituent induced a polarization of the aromatic ring with a more basic nitrogen atom at position 3 in the oxadiazole. Consequently, the coordination of such 1,3,4-oxadiazole derivatives occurred through the above-mentioned nitrogen atom as illustrated by several X-ray crystallographic structure of ruthenium^[25] complexes. In the present family of ruthenium complexes **1-3**, **5**, **8** and **9**, coordination of the 1,3,4-oxadiazole moiety to the metal center *via* its electron-enricher nitrogen atom was confirmed by two single-crystal X-ray diffraction studies realized on complexes **5** (see Electronic Supplementary Material) and **9** (Figure 3).

The complex **9** crystallizes in the triclinic asymmetric space group *P*-1 with two distinct ruthenium complexes (**9A** and **9B** complexes in which the ruthenium atoms are labeled Ru(1) and Ru(2), respectively) and four molecules of chloroform (Figure 3 and Table 1). The ruthenium atoms adopt typical piano-stool geometries with the *p*-cymene acting as the seats of the stools (Ru-centroid of *p*-cymene = 1.654 and 1.673 Å in **9A** and **9B**, respectively). The bond lengths of Ru-Cl and Ru-N were found to be 2.4362(8), 2.4481(8) and 2.1165(18) Å in **9A**, respectively and 2.4184(8), 2.4253(9) and 2.1174(18) Å in **9B**, respectively, values close to those reported for similar ruthenium complexes.^[25-26] The oxadiazole rings are almost perpendicular to the *p*-cymene (dihedral angles of 87.10 and 88.28° **9A** and **9B**, respectively) and planar with the phenyl substituents (dihedral angles of 6.68 and 4.74° in **9A** and **9B**, respectively). The six aromatic rings are two by two nearly parallel with dihedral angle of 6.82° (*p*-cymene), 8.80° (oxadiazole) and 8.43° (phenyl). Interestingly, as previously observe on similar ruthenium complexes,^[25] intramolecular hydrogen bonds involving chlorine atoms and a hydrogen atom of the NH₂ moieties can be observed (length NH...Cl 2.454 and 2.922 Å in complex **9A** and 2.467 and 3.033 Å in complex **9B**). In addition, two intermolecular hydrogen bonds (NH3B...C11 2.543 and NH6B...Cl3 2.340 Å) linked the two complexes **9A** and **9B**.

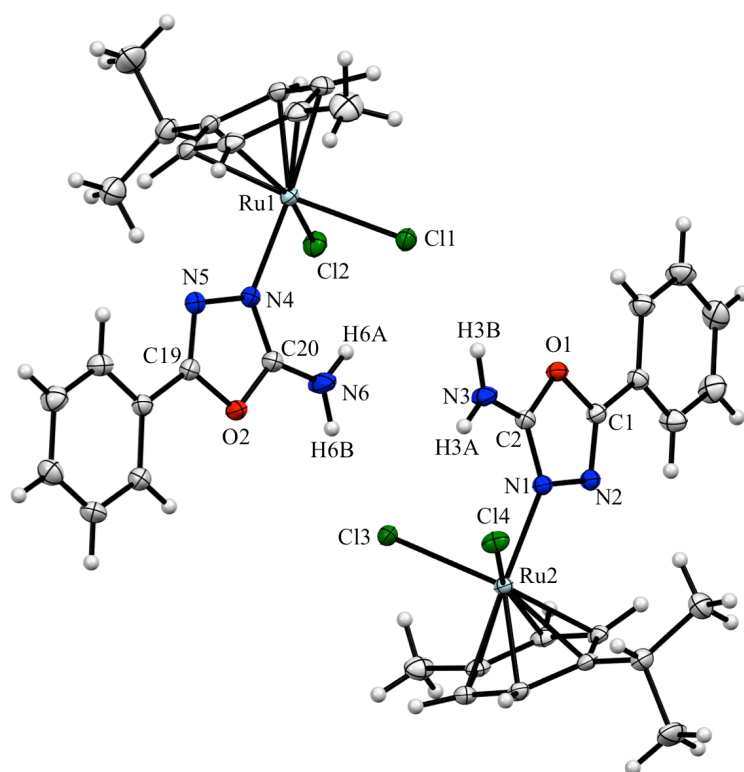


Figure 3. ORTEP drawing of complexes **9A** and **9B** showing 50% probability thermal ellipsoids. For clarity, the four molecules of chloroform are not shown. Important bond lengths (Å) and angles (°): Ru(1)-Cl(1) 2.4481(8), Ru(1)-Cl(2) 2.4362(8), Ru(1)-N(4) 2.1165(18), N(4)-N(5) 1.411(2), N(5)-C(19) 1.287(3), C(19)-O(2) 1.379(3), O(2)-C(20) 1.355(3), C(20)-N(4) 1.312(3), Ru(2)-Cl(3) 2.4184(8), Ru(2)-Cl(4) 2.4253(9), Ru(2)-N(1) 2.1174(18), N(1)-N(2) 1.409(2), N(2)-C(1) 1.286(3), C(1)-O(1) 1.380(2), O(1)-C(2) 1.355(2), C(2)-N(1) 1.318(3), Cl(1)-Ru(1)-Cl(2) 86.91(2), Cl(1)-Ru(1)-N(4) 86.52(5), N(4)-Ru(1)-Cl(2) 88.96(5), N(4)-N(5)-C(19) 105.80(17), N(5)-C(19)-O(2) 112.78(18), C(19)-O(2)-C(20) 102.96(16), O(2)-C(20)-N(4) 111.70(19), C(20)-N(4)-N(5) 106.76(17), Cl(3)-Ru(2)-Cl(4) 87.93(6), Cl(4)-Ru(2)-N(1) 87.78(5), N(1)-Ru(2)-Cl(3) 93.88(7), N(1)-N(2)-C(1) 105.92(16), N(2)-C(1)-O(1) 112.83(17), C(1)-O(1)-C(2) 103.04(15), O(1)-C(2)-N(1) 111.46(17), C(2)-N(1)-N(2) 106.74(16).

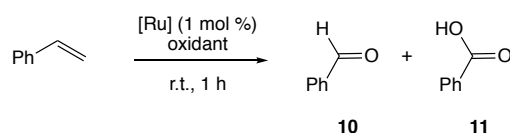
Table 1. Crystal data and structure refinement parameters for **9**.

CCDC depository	2112331
color / shape	brown / prism
chemical formula	C ₂₀ H ₂₃ Cl ₈ N ₃ ORu
formula weight	706.08
temperature	120(2) K
wavelength	0.71073 Å
crystal system	triclinic
space group	<i>P</i> -1 (number 2)

unit cell parameters	a, b, c	9.980(3), 14.364(4), 20.894(6) Å
	α, β, γ	98.026(7), 93.729(7), 109.693(7)°
volume		2772.1(14) Å ³
Z		4
D		1.692 g cm ⁻³
μ		1.356 mm ⁻¹
absorption correction		multi-scan
T_{\min}, T_{\max}		0.6953, 0.7456
$F(000)$		1408
crystal size		0.200 x 0.150 x 0.120 mm
diffractometer		Bruker PHOTON-III CPAD
index ranges		$-12 \leq h \leq 13, -18 \leq k \leq 18, -27 \leq l \leq 27$
θ range for data collection		$1.960 \leq \theta \leq 27.947^\circ$
reflections collected		74432
independent/observed		13271, 11777
R_{int}		0.0309
refinement method		full-matrix least-squares on F^2
data/restraints/parameters		13271 / 13 / 631
goodness-of-fit on F^2		1.043
final R indices ($I > 2.0 \sigma(I)$)		$R_1 = 0.0275, wR_2 = 0.0614$
R indices (all data)		$R_1 = 0.0335, wR_2 = 0.0651$
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$		1.151, -0.732 eÅ ⁻³

Oxidative cleavage of olefins

With the aim to explore the best reaction conditions for the ruthenium-catalyzed Lemieux-Johnson-type oxidation of olefins or alkynes, styrene was chosen as benchmark substrate (Scheme 4).



Scheme 4. Ruthenium-catalyzed oxidative cleavage of styrene.

First, in a series of runs, five oxidants (three equivalents per substrate), namely *meta*-chloroperoxybenzoic acid (*m*-CPBA), *tert*-butyl hydroperoxide (*t*BuOOH), potassium persulfate (KHSO₅), hydrogen peroxide (H₂O₂) and sodium periodate (NaIO₄), were compared using precatalyst **1** in a mixture of H₂O/MeCN/EtOAc (2/4/4 mL) at room temperature for 1 hour. Except when using NaIO₄, which led to a conversion into benzaldehyde (**10**) of 64 %, low conversions were measured (Table 2, entries 1-5). Note that, in such catalytic conditions, the over-oxidation leading to the formation of benzoic acid (**11**) was only detected in the case of *m*-CPBA. By changing the solvent mixture, the conversion into product **10** increased in the order H₂O/CH₂Cl₂, H₂O/MeOH, H₂O/MeCN to reach 85 % with H₂O/EtOAc (Table 2, entries 6-9). Surprisingly, performing the reaction in pure water (2 mL) led to a 91 % conversion onto benzaldehyde (Table 2, entry 10). In the latter run, small amount of over-oxidation by-product **11** was detected (3 %). Addition of a phase-transfer catalyst, tetra-*n*-butylammonium iodide, did not improve the conversion into **10** (Table 2, entry 11). Control experiments performed in the absence of ruthenium complex failed to form benzaldehyde from styrene and revealed that over-oxidation by-product **11** could be obtained from benzaldehyde in such reaction conditions (Table 2, entries 12 and 13).

Table 2. Ruthenium-catalyzed oxidative cleavage of styrene; the search for optimal catalytic conditions: effect of oxidant and solvent.^[a]

Entry	Solvent (mL)	Oxidant agent	Products distribution	
			10 (%)	By-product 11 (%)
1	H ₂ O/MeCN/EtOAc (2/4/4)	<i>m</i> -CPBA	17	17
2	H ₂ O/MeCN/EtOAc (2/4/4)	<i>t</i> BuOOH	12	/
3	H ₂ O/MeCN/EtOAc (2/4/4)	KHSO ₅	8	/
4	H ₂ O/MeCN/EtOAc (2/4/4)	H ₂ O ₂	2	/
5	H ₂ O/MeCN/EtOAc (2/4/4)	NaIO ₄	64	/
6	H ₂ O/MeOH (2/8)	NaIO ₄	16	/
7	H ₂ O/EtOAc (2/8)	NaIO ₄	85	6
8	H ₂ O/MeCN (2/8)	NaIO ₄	41	traces
9	H ₂ O/CH ₂ Cl ₂ (2/8)	NaIO ₄	10	/
10	H ₂ O (2)	NaIO ₄	91	3
11 ^[b]	H ₂ O (2)	NaIO ₄	16	/
12 ^[c]	H ₂ O (2)	NaIO ₄	/	/
13 ^[c, d]	H ₂ O (2)	NaIO ₄	91	9

Conditions: [a] ruthenium complex **1** (0.0033 g, 0.5×10^{-3} mmol, 1 mol %), styrene (0.052 g, 0.5 mmol), oxidant (1.5 mmol), decane (0.025 mL), r.t., 1 h. The conversions were determined by GC, the calibration being based on decane; [b] with tetra-*n*-butylammonium iodide (10 mol %); [c] without ruthenium complex; [d] using benzaldehyde instead of styrene.

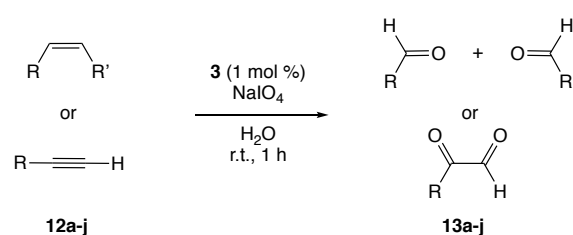
To continue the optimization of the catalytic conditions, three ruthenium complexes **1-3** were evaluated with a metal loading of 1 mol %. As interfered from Table 3, the higher conversion into **10** (97 %) was observed when the precatalyst **3** bearing the more electron donor *iso*-propyloxy moiety was employed (Table 3, entries 1-3). Changing the amount NaIO₄ from two to four equivalents per styrene showed that the best result (97 % conversion) was obtained when three equivalents of the oxidizing agent was employed (Table 3, entries 3-7).

Table 3. Ruthenium-catalyzed oxidative cleavage of styrene; the search for optimal catalytic conditions: effect of ruthenium complex and amount of NaIO₄.^[a]

Entry	Ruthenium complex	NaIO ₄ (equiv./styrene)	Products distribution	
			10 (%)	By-product 11 (%)
1	1	3	91	3
2	2	3	85	2
3	3	3	97	2
4	3	2	56	1
5	3	2.5	62	1
6	3	3.5	93	5
7	3	4	78	2

Conditions: [a] ruthenium complex (1 mol %), styrene (0.052 g, 0.5 mmol), NaIO₄, H₂O (2 mL), decane (0.025 mL), r.t., 1 h. The conversions were determined by GC, the calibration being based on decane.

Under optimized catalytic conditions, complex **3** and NaIO₄ (3 equiv./Ru) in water at room temperature for 1 h, we probed the scope of the reaction with a variety of structurally diverse substrates **12a-j** (Scheme 5 and Table 4).


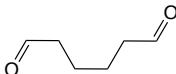
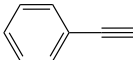
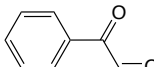


Scheme 5. Ruthenium-catalyzed oxidative cleavage of olefins and alkynes.

Oxidative cleavage of substituted styrene including electro-donating groups such as *tert*-butyl (**12a**) and methoxy (**12b**) led to the formation of aldehydes **13a** and **13b** in good conversions, of 53 and 73 %, respectively (Table 4, entries 1 and 2). Conversely, the presence of electron-withdrawing groups such as chloride (**12c**) and fluoride (**12d**) efficiently promotes the reaction and the products **13c** and **13d** were obtained with excellent conversions of 81 and 100 %, respectively (Table 4, entries 3 and 4), which indicate that no significant electronic effects were observed for the styrene substituents on the catalytic system. Unsurprisingly, sterically hindered α -methylstyrene (**12e**) afforded the corresponding ketone **13e** with a moderate conversion of 43 % (Table 4, entry 5). Linear α -olefins **12f-h** could also be efficiently converted into the corresponding aldehydes, however, the solubility of these olefins in water seems to be limiting to obtain total conversions (Table 4, entries 6-8). The catalytic system is also able to carry out the oxidative cleavage of cyclic olefins like cyclohexene (**12i**), in this case dialdehyde **13i** was obtained with a full conversion (Table 4, entry 9). However, in the case of alkynes, the catalytic system led to oxidation products with modest conversions. In fact, phenylacetylene (**12j**) was converted into phenylglyoxal (**13j**) in only 28 % (Table 4, entry 10).

Table 4. Ruthenium-catalyzed oxidative cleavage of various olefins and alkynes.^[a]

Entry	Substrate	Product	Conversion (%)
1			53
2			72
3			81
4			100
5			43
6			66
7			96
8			49

9		12i		13i	100
10		12j		13j	28

Conditions: [a] complex **3** (0.0034 g, 1 mol %), olefin or alkyne (0.5 mmol), NaIO₄ (0.321 g, 1.5 mmol) H₂O (2 mL), r.t., 1 h. The conversions were determined by ¹H NMR after extraction with Et₂O.

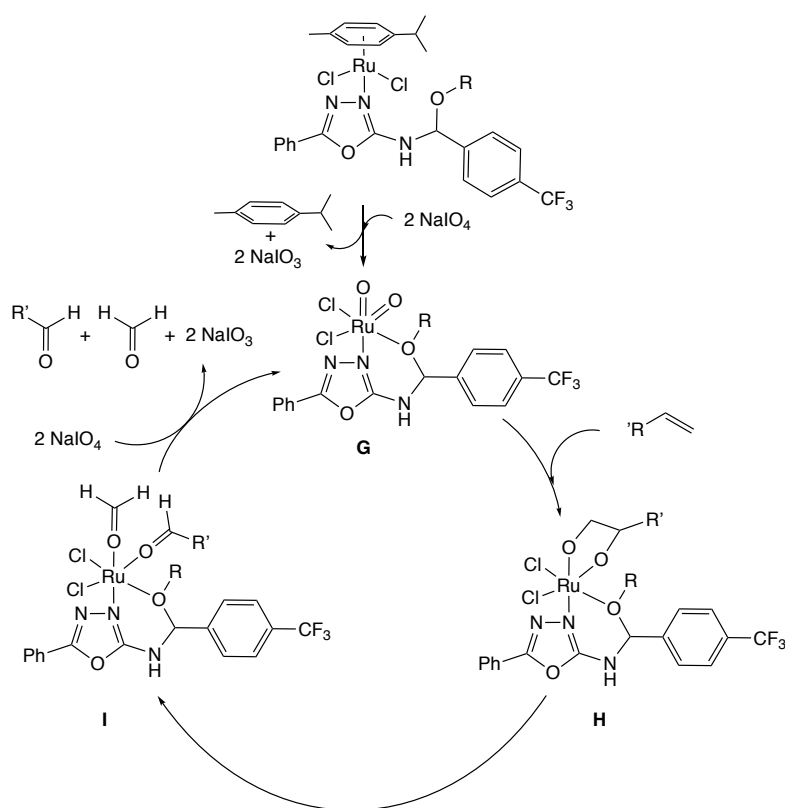
In order to get more information about the activation of precatalyst **3** and the nature of the active species and thus the mechanism of the reaction, comparisons with complexes **1**, **5**, **8** and **9** were performed (Table 5). Under optimized catalytic conditions, the comparison between complexes **1** and **3** (different alkyloxy moieties, OMe and O^{*i*}Pr, respectively) showed that the precatalyst with the most electron donating substituent (O^{*i*}Pr) is most efficient for the formation of product **10** (Table 5, entries 1 and 2). Substitution of the η⁶-*p*-cymene of complex **1** by η⁶-benzene (complex **5**), known to be easier release from the metal, increases the amount of formed benzaldehyde (Table 5, entries 1 and 3). Reaction between complex **3** and an excess of NaIO₄ in CH₂Cl₂ led rapidly to a new instable species characterized by UV-visible spectroscopy with a peak at 406 nm (see Electronic Supplementary Material), which could be attributed to a Ru(IV)-oxo intermediate.^[27] These findings clearly indicate that the activation step of the precatalyst **3** consists in the dissociation of the η⁶-*p*-cymene ligand and stabilization of the intermediate by coordination with the oxygen atom of the *iso*-propyloxy moiety to form a 6-membered ring (*N,O*)-chelate.^[28] This is confirmed by the use of alkyloxy-free precatalysts **8** and **5**, which led to lower catalytic activities (Table 5, entries 4 and 5). The hemilabile ruthenium (II) intermediate was then oxidized with NaIO₄ to form the well documented *cis*-Ru(VI)-dioxo active specie **G**.^[15, 16c, 17b, 20] Concerted [3 + 2] cycloaddition with olefin formed the ruthenium(IV) specie **H**, which after C-C bond cleavage, led to intermediate **I**, that releases the aldehydes and regenerates the active species **G** (Scheme 6).

Table 5. Ruthenium-catalyzed oxidative cleavage of styrene; control experiments for mechanistic study.^[a]

Entry	Ruthenium complex	Products distribution	
		10 (%)	By-product 11 (%)
1	1	91	3
2	3	97	2
3	5	96	2

4	8	67	2
5	9	87	3

Conditions: [a] ruthenium complex (1 mol %), styrene (0.052 g, 0.5 mmol), NaIO₄, H₂O (2 mL), decane (0.025 mL), r.t., 1 h. The conversions were determined by GC, the calibration being based on decane.



Scheme 6. Proposed mechanism for the ruthenium-catalyzed oxidative cleavage of olefins.

Conclusion

In conclusion, reaction between an 1,3,4-oxadiazole-derived imine and [RuCl₂(η⁶-p-cymene)]₂ in an alcoholic solution of dichloromethane readily form arene-ruthenium(II) complexes in which the 1,3,4-oxadiazole moieties are coordinated to the ruthenium center *via* their electronically enriched nitrogen atom at position 3 in the aromatic ring. The presence in the coordination sphere of the metal of a hemilabile alkyloxy substituent was put in use to stabilize the active species in the Lemieux-Johnson-type oxidation of olefins and alkynes *via* the formation of a (N,O)-chelate. Performing the catalytic reactions in water at room temperature with NaIO₄ as oxidant led to excellent conversions of olefins into the

corresponding aldehydes, but a lower reactivity was observed in the case of alkynes. These results constitute a clear illustration of the potential of polydentate 1,3,4-oxadiazole-derived ligands in homogeneous catalysis.

Experimental part

All manipulations were carried out under dry argon. Solvents were dried by conventional methods and were distilled immediately before use. Routine ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{19}\text{F}\{^1\text{H}\}$ spectra were recorded with Bruker FT instruments (AC 300 and 500). ^1H NMR spectra were referenced to residual protonated solvents ($\delta = 7.26$ ppm for CDCl_3). ^{13}C NMR chemical shifts are reported relative to deuterated solvents ($\delta = 77.16$ ppm for CDCl_3). ^{19}F NMR spectroscopic data are given relative to external CCl_3F . Chemical shifts and coupling constants are reported in ppm and Hz, respectively. UV-visible spectra were performed on an Agilent Technologies Cary 60 UV-Vis spectrometer. Infrared spectra were recorded with a Bruker FT-IR Alpha-P spectrometer. Elemental analyses were carried out by the Service de Microanalyse, Institut de Chimie, Université de Strasbourg. (*E*)-1-(4-Trifluoromethylphenyl)-*N*-(5-phenyl-1,3,4-oxadiazol-2-yl)-methanimine (**4**)^[25] and 5-phenyl-1,3,4-oxadiazol-2-amine (**7**)^[29] were prepared by literature procedures.

General procedure for the synthesis of the ruthenium(II) complexes **1-3** and **5**.

Method A. In a Schlenk tube under argon, $[\text{RuCl}_2(\eta^6\text{-arene})]_2$ (0.25 mmol) and (*E*)-1-(4-trifluoromethylphenyl)-*N*-(5-phenyl-1,3,4-oxadiazol-2-yl)-methanimine (**4**) (0.140 g, 0.50 mmol) were introduced. CH_2Cl_2 (11.5 mL) and MeOH (36.5 mL) were then added successively. The reaction mixture was heated at 50°C for 1 hour. After completion of the reaction, the resulting solution was concentrated to *ca.* 1 mL, upon which *n*-hexane (20 mL) was added. The precipitate was separated by filtration, washed with *n*-hexane and dried under a vacuum.

Method B. In a Schlenk tube under argon, $[\text{RuCl}_2(\eta^6\text{-}p\text{-cymene})]_2$ (0.153 g, 0.25 mmol) and (*E*)-1-(4-trifluoromethylphenyl)-*N*-(5-phenyl-1,3,4-oxadiazol-2-yl)-methanimine (**4**) (0.140 g, 0.50 mmol) were introduced. CH_2Cl_2 (20 mL) and ethanol or *iso*-propanol (2 mL) were then added successively. The reaction mixture was heated at 50°C for 16 hour. After completion of the reaction, the resulting solution was concentrated to *ca.* 1 mL, upon which *n*-hexane (30

mL) was added. The orange/red precipitate was separated by filtration, washed with *n*-hexane and dried under a vacuum.

Dichloro-[methoxy(5-phenyl-1,3,4-oxadiazol-2-ylamino)(4-trifluoromethylphenyl)

methyl](η^6 -*p*-cymene) ruthenium(II) (1). Method A, orange/red solid, yield 95 %. $^1\text{H NMR}$ (300 MHz, CDCl_3): δ = 8.43 (d, 1H, NH, $^3J_{\text{HH}}$ = 8.3 Hz), 7.79 (dd, 2H, arom. CH of C_6H_5 , $^3J_{\text{HH}}$ = 7.5 Hz, $^4J_{\text{HH}}$ = 1.5 Hz), 7.70 (d, 2H, arom. CH of $\text{C}_6\text{H}_4\text{CF}_3$, $^3J_{\text{HH}}$ = 8.4 Hz), 7.62 (d, 2H, arom. CH of $\text{C}_6\text{H}_4\text{CF}_3$, $^3J_{\text{HH}}$ = 8.4 Hz), 7.54-7.45 (m, 3H, arom. CH of C_6H_5), 5.79 (d, 1H, CHOCH_3 , $^3J_{\text{HH}}$ = 8.1 Hz), 5.66 and 5.41 (AA'BB' spin system, 2H, arom. CH of *p*-cymene, $^3J_{\text{HH}}$ = 6.3 Hz), 5.65 and 5.41 (AA'BB' spin system, 2H, arom. CH of *p*-cymene, $^3J_{\text{HH}}$ = 6.3 Hz), 3.40 (s, 3H, OCH_3), 3.16 (hept, 1H, $\text{CH}(\text{CH}_3)_2$, $^3J_{\text{HH}}$ = 6.9 Hz), 2.33 (s, 3H, CH_3 of *p*-cymene), 1.32 (d, 6H, $\text{CH}(\text{CH}_3)_2$, $^3J_{\text{HH}}$ = 6.9 Hz) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3): δ = 162.07 (s, arom. Cquat para of CF_3), 157.05 (s, arom. Cquat $\text{C}(\text{Ph})=\text{N}$), 140.99 (s, arom. Cquat $\text{C}(\text{NH})=\text{N}$), 131.74 (s, arom. CH), 130.92 (q, arom. Cquat CCF_3 , $^2J_{\text{CF}}$ = 32.4 Hz), 129.26 (s, arom. CH), 127.29 (s, arom. CH), 125.99 (s, arom. CH), 125.68 (s, arom. CH), 125.65 (s, arom. CH), 124.08 (q, CF_3 , $^1J_{\text{CF}}$ = 272.9 Hz), 123.07 (s, arom. Cquat of C_6H_5), 103.42 (s, arom. Cquat of *p*-cymene), 98.81 (s, arom. Cquat of *p*-cymene), 84.98 (s, CHOCH_3), 83.54 (s, arom. CH of *p*-cymene), 83.52 (s, arom. CH of *p*-cymene), 81.71 (s, arom. CH of *p*-cymene), 81.65 (s, arom. CH of *p*-cymene), 54.81 (s, OCH_3), 30.73 (s, $\text{CH}(\text{CH}_3)_2$), 22.44 (s, $\text{CH}(\text{CH}_3)_2$), 22.37 (s, $\text{CH}(\text{CH}_3)_2$), 18.94 (s, CH_3 of *p*-cymene) ppm; $^{19}\text{F}\{^1\text{H}\}$ NMR (282 MHz, CDCl_3): δ = -62.69 (s, CF_3) ppm. IR: ν = 1649 cm^{-1} (C=N). MS (ESI-TOF): m/z = 620.09 $[\text{M} - \text{Cl}]^+$, 678.04 $[\text{M} + \text{Na}]^+$ (expected isotopic profiles). Elemental analysis calcd. (%) for $\text{C}_{27}\text{H}_{28}\text{O}_2\text{N}_3\text{F}_3\text{Cl}_2\text{Ru}$ (655.50): C 49.47, H 4.31, N 6.41; found C 49.15, H 4.26, N 6.34.

Dichloro-[ethyloxy(5-phenyl-1,3,4-oxadiazol-2-ylamino)(4-trifluoromethylphenyl)

methyl](η^6 -*p*-cymene) ruthenium(II) (2). Method B, orange/red solid, yield 93 %. $^1\text{H NMR}$ (300 MHz, CDCl_3): δ = 8.39 (d, 1H, NH, $^3J_{\text{HH}}$ = 8.4 Hz), 7.78 (dd, 2H, arom. CH of C_6H_5 , $^3J_{\text{HH}}$ = 8.1 Hz, $^4J_{\text{HH}}$ = 2.1 Hz), 7.71 (d, 2H, arom. CH of $\text{C}_6\text{H}_4\text{CF}_3$, $^3J_{\text{HH}}$ = 8.4 Hz), 7.61 (d, 2H, arom. CH of $\text{C}_6\text{H}_4\text{CF}_3$, $^3J_{\text{HH}}$ = 8.4 Hz), 7.53-7.45 (m, 3H, arom. CH of C_6H_5), 5.83 (d, 1H, CHOCH_3 , $^3J_{\text{HH}}$ = 7.8 Hz), 5.65 and 5.41 (AA'BB' spin system, 2H, arom. CH of *p*-cymene, $^3J_{\text{HH}}$ = 6.3 Hz), 5.65 and 5.41 (AA'BB' spin system, 2H, arom. CH of *p*-cymene, $^3J_{\text{HH}}$ = 6.3 Hz), 3.80-3.70 (m, 1H, OCH_2CH_3), 3.61-3.51 (m, 1H, OCH_2CH_3), 3.15 (hept, 1H, $\text{CH}(\text{CH}_3)_2$, $^3J_{\text{HH}}$ = 6.9 Hz), 2.33 (s, 3H, CH_3 of *p*-cymene), 1.32 (d, 6H, $\text{CH}(\text{CH}_3)_2$, $^3J_{\text{HH}}$ = 6.9 Hz), 1.21 (t, 3H, OCH_2CH_3 , $^3J_{\text{HH}}$ = 6.9 Hz) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3): δ =

162.08 (s, arom. Cquat para of CF₃), 156.93 (s, arom. Cquat C(Ph)=N), 141.64 (s, arom. Cquat C(NH)=N), 131.74 (s, arom. CH), 130.81 (q, arom. Cquat CCF₃, ²J_{CF} = 27.2 Hz), 129.28 (s, arom. CH), 127.26 (s, arom. CH), 126.02 (s, arom. CH), 125.96 (s, arom. CH), 123.44 (q, CF₃, ¹J_{CF} = 277.7 Hz), 123.14 (s, arom. Cquat of C₆H₅), 103.42 (s, arom. Cquat of *p*-cymene), 98.81 (s, arom. Cquat of *p*-cymene), 83.97 (s, CHOCH₃), 83.52 (s, arom. CH of *p*-cymene), 81.71 (s, arom. CH of *p*-cymene), 81.67 (s, arom. CH of *p*-cymene), 63.16 (s, OCH₂CH₃), 30.74 (s, CH(CH₃)₂), 22.44 (s, CH(CH₃)₂), 22.40 (s, CH(CH₃)₂), 18.95 (s, CH₃ of *p*-cymene), 15.03 (s, OCH₂CH₃) ppm; ¹⁹F{¹H} NMR (282 MHz, CDCl₃): δ = -62.68 (s, CF₃) ppm. IR: ν = 1646 cm⁻¹ (C=N). MS (ESI-TOF): m/z = 634.10 [M - Cl]⁺, 692.06 [M + Na]⁺ (expected isotopic profiles). Elemental analysis calcd. (%) for C₂₈H₃₀O₂N₃F₃Cl₂Ru (669.53): C 50.23, H 4.52, N 6.28; found C 50.18, H 4.48, N 6.19.

Dichloro-[isopropoxy(5-phenyl-1,3,4-oxadiazol-2-ylamino)(4-trifluoromethylphenyl)methyl](η⁶-*p*-cymene) ruthenium(II) (3). Method B, orange/red solid, yield 97 %. ¹H NMR (500 MHz, CDCl₃): δ = 8.32 (d, 1H, NH, ³J_{HH} = 7.5 Hz), 7.74 (dd, 2H, arom. CH of C₆H₅, ³J_{HH} = 7.5 Hz, ⁴J_{HH} = 1.5 Hz), 7.68 (d, 2H, arom. CH of C₆H₄CF₃, ³J_{HH} = 8.5 Hz), 7.59 (d, 2H, arom. CH of C₆H₄CF₃, ³J_{HH} = 8.5 Hz), 7.53-7.46 (m, 3H, arom. CH of C₆H₅), 5.80 (d, 1H, CHOCH(CH₃)₂, ³J_{HH} = 7.5 Hz), 5.64 and 5.40 (AA'BB' spin system, 2H, arom. CH of *p*-cymene, ³J_{HH} = 6.5 Hz), 5.63 and 5.40 (AA'BB' spin system, 2H, arom. CH of *p*-cymene, ³J_{HH} = 6.5 Hz), 4.01 (hept, 1H, OCH(CH₃)₂, ³J_{HH} = 6.0 Hz), 3.14 (hept, 1H, CH(CH₃)₂ of *p*-cymene, ³J_{HH} = 7.0 Hz), 2.32 (s, 3H, CH₃ of *p*-cymene), 1.31 (d, 6H, CH(CH₃)₂ of *p*-cymene, ³J_{HH} = 7.0 Hz), 1.22 (d, 3H, OCH(CH₃)₂, ³J_{HH} = 6.0 Hz), 1.18 (d, 3H, OCH(CH₃)₂, ³J_{HH} = 6.0 Hz) ppm; ¹³C{¹H} NMR (126 MHz, CDCl₃): δ = 161.94 (s, arom. Cquat para of CF₃), 156.80 (s, arom. Cquat C(Ph)=N), 142.51 (s, arom. Cquat C(NH)=N), 131.63 (s, arom. CH), 130.72 (q, arom. Cquat CCF₃, ²J_{CF} = 32.5 Hz), 129.26 (s, arom. CH), 127.22 (s, arom. CH), 125.85 (s, arom. CH), 125.56 (s, arom. CH), 125.53 (s, arom. CH), 124.12 (q, CF₃, ¹J_{CF} = 272.7 Hz), 123.14 (s, arom. Cquat of C₆H₅), 103.32 (s, arom. Cquat of *p*-cymene), 98.80 (s, arom. Cquat of *p*-cymene), 83.61 (s, arom. CH of *p*-cymene), 83.49 (s, arom. CH of *p*-cymene), 82.52 (s, arom. CH of *p*-cymene), 81.61 (s, arom. CH of *p*-cymene), 81.60 (s, CHOCH(CH₃)₂), 69.50 (s, OCH(CH₃)₂), 30.72 (s, CH(CH₃)₂), 23.13 (s, OCH(CH₃)₂), 22.44 (s, CH(CH₃)₂ of *p*-cymene), 22.33 (s, CH(CH₃)₂ of *p*-cymene), 21.31 (s, OCH(CH₃)₂), 18.92 (s, CH₃ of *p*-cymene) ppm; ¹⁹F{¹H} NMR (282 MHz, CDCl₃): δ = -62.64 (s, CF₃) ppm. IR: ν = 1634 cm⁻¹ (C=N). MS (ESI-TOF): m/z = 648.12 [M - Cl]⁺, 706.08 [M + Na]⁺ (expected

isotopic profiles). Elemental analysis calcd. (%) for $C_{29}H_{32}O_2N_3F_3Cl_2Ru$ (683.55): C 50.96, H 4.72, N 6.15; found C 50.91, H 4.68, N 6.09.

Dichloro-[methoxy(5-phenyl-1,3,4-oxadiazol-2-ylamino)(4-trifluoromethylphenyl)methyl](η^6 -benzene) ruthenium(II) (5). Method B, brown solid, yield 83 %. 1H NMR (300 MHz, $CDCl_3$): δ = 8.21 (d, 1H, NH, $^3J_{HH}$ = 8.1 Hz), 7.77 (dd, 2H, arom. CH of C_6H_5 , $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.2 Hz), 7.68 (d, 2H, arom. CH of $C_6H_4CF_3$, $^3J_{HH}$ = 8.7 Hz), 7.62 (d, 2H, arom. CH of $C_6H_4CF_3$, $^3J_{HH}$ = 8.7 Hz), 7.54-7.45 (m, 3H, arom. CH of C_6H_5), 5.85 (s, 6H, arom. CH of C_6H_6), 5.76 (d, 1H, $CHOCH_3$, $^3J_{HH}$ = 7.8 Hz), 3.42 (s, 3H, OCH_3) ppm; $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ = 161.73 (s, arom. Cquat para of CF_3), 157.03 (s, arom. Cquat $C(Ph)=N$), 140.96 (s, arom. Cquat $C(NH)=N$), 131.91 (s, arom. CH), 131.02 (q, arom. Cquat CCF_3 , $^2J_{CF}$ = 32.5 Hz), 129.28 (s, arom. CH), 127.17 (s, arom. CH), 126.09 (s, arom. CH), 125.71 (s, arom. CH), 125.68 (s, arom. CH), 124.05 (q, CF_3 , $^1J_{CF}$ = 272.5 Hz), 122.80 (s, arom. Cquat of C_6H_5), 85.11 (s, $CHOCH_3$), 84.86 (s, arom. CH of $6H_6$), 55.13 (s, OCH_3) ppm; $^{19}F\{^1H\}$ NMR (282 MHz, $CDCl_3$): δ = -62.70 (s, CF_3) ppm. IR: ν = 1647 cm^{-1} ($C=N$). MS (ESI-TOF): m/z = 432.04 $[M - Cl]^+$, 564.02 $[M + Na]^+$ (expected isotopic profiles). Elemental analysis calcd. (%) for $C_{23}H_{20}O_2N_3F_3Cl_2Ru$ (599.39): C 46.09, H 3.36, N 7.01; found C 45.94, H 3.42, N 6.97.

Preparation of *N*-[butyl(4-trifluoromethyl-phenyl)methyl]-5-phenyl-1,3,4-oxadiazol-2-amine (6): In a Schlenk tube under argon, $nBuLi$ (1.6 M, 0.98 mmol, 0.61 mL) was added dropwise to a solution of (*E*)-1-(4-trifluoromethylphenyl)-*N*-(5-phenyl-1,3,4-oxadiazol-2-yl)-methanimine (0.250 g, 0.89 mmol) in THF (20 mL) at $-78^\circ C$. The reaction was stirred for 30 minutes at $-78^\circ C$ before been allowed to reach room temperature. The solution was washed with brine (2 x 15 mL) and the organic layer was separated, dried over $MgSO_4$, filtered and concentrated in vacuum. The crude product was purified by silica gel column chromatography (petroleum ether/EtOAc 50:50, v/v); yield 92 %. 1H NMR (300 MHz, $CDCl_3$): δ = 7.81 (dd, 2H, arom. CH of C_6H_5 , $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 2.1 Hz), 7.61 (d, 2H, arom. CH of $C_6H_4CF_3$, $^3J_{HH}$ = 8.1 Hz), 7.54 (d, 2H, arom. CH of $C_6H_4CF_3$, $^3J_{HH}$ = 8.1 Hz), 7.45-7.40 (m, 3H, arom. CH of C_6H_5), 6.87 (brs, 1H, NH), 4.78 (t, 1H, $CHCH_2$, $^3J_{HH}$ = 6.4 Hz), 2.10-1.98 (m, 1H, $CHCH_2$), 1.96-1.84 (m, 1H, $CHCH_2$), 1.48-1.30 (m, 4H, $CH_2CH_2CH_3$), 0.89 (t, 3H, CH_2CH_3 , $^3J_{HH}$ = 6.9 Hz) ppm; $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ = 162.71 (s, arom. Cquat para of CF_3), 159.02 (s, arom. Cquat $C(Ph)=N$), 146.49 (s, arom. Cquat $C(NH)=N$), 130.84 (s, arom. CH), 130.00 (q, arom. Cquat CCF_3 , $^2J_{CF}$ = 32.6 Hz), 129.00 (s, arom. CH), 127.05 (s, arom. CH), 125.91 (s, arom. CH), 125.85 (s, arom. CH), 125.82 (s, arom. CH), 124.18 (q, CF_3 , $^1J_{CF}$

= 272.3 Hz), 124.10 (s, arom. Cquat of C₆H₅), 58.33 (s, CHCH₂), 36.89 (s, CHCH₂), 28.40 (s, CH₂CH₂CH₃), 22.47 (s, CH₂CH₂CH₃), 14.01 (s, CH₂CH₂CH₃) ppm; ¹⁹F{¹H} NMR (471 MHz, CDCl₃): δ = -62.52 (s, CF₃) ppm. IR: ν = 1619 cm⁻¹ (C=N). Elemental analysis calcd. (%) for C₂₀H₂₀ON₃F₃ (375.39): C 63.99, H 5.37, N 11;19; found C 64.06, H 5.43, N 11.14.

General procedure for the synthesis of the ruthenium(II) complexes **8** and **9**.

In a Schlenk tube under argon, [RuCl₂(η⁶-*p*-cymene)]₂ (0.061 g, 0.10 mmol) and oxadiazole derivative **6** or **7** (0.20 mmol) were introduced. CH₂Cl₂ (10 mL) was then added and the reaction mixture was stirred at room temperature for 2 hours. After completion of the reaction, the resulting solution was concentrated to *ca.* 0.5 mL, upon which *n*-hexane (10 mL) was added. The orange/red precipitate was separated by filtration, washed with *n*-hexane and dried under a vacuum.

Dichloro-[(5-phenyl-1,3,4-oxadiazol-2-ylamino)(4-trifluoromethylphenyl)pentyl](η⁶-*p*-cymene) ruthenium(II) (8**).** Yield 94 %. ¹H NMR (300 MHz, CDCl₃): δ = 7.87 (d, 1H, NH, ³J_{HH} = 6.0 Hz), 7.66 (dd, 2H, arom. CH of C₆H₅, ³J_{HH} = 7.2 Hz, ⁴J_{HH} = 1.5 Hz), 7.57 (d, 2H, arom. CH of C₆H₄CF₃, ³J_{HH} = 8.7 Hz), 7.53 (d, 2H, arom. CH of C₆H₄CF₃, ³J_{HH} = 8.7 Hz), 7.48-7.41 (m, 3H, arom. CH of C₆H₅), 5.65 and 5.40 (AA'BB' spin system, 2H, arom. CH of *p*-cymene, ³J_{HH} = 5.4 Hz), 5.63 and 5.38 (AA'BB' spin system, 2H, arom. CH of *p*-cymene, ³J_{HH} = 5.4 Hz), 4.50 (q, 1H, CHCH₂, ³J_{HH} = 6.9 Hz), 3.16 (hept, 1H, CH(CH₃)₂ of *p*-cymene, ³J_{HH} = 7.0 Hz), 2.33 (s, 3H, CH₃ of *p*-cymene), 1.91-1.79 (m, 1H, CHCH₂), 1.78-1.67 (m, 1H, CHCH₂), 1.32 (d, 3H, CH(CH₃)₂ of *p*-cymene, ³J_{HH} = 7.0 Hz), 1.30 32 (d, 3H, CH(CH₃)₂ of *p*-cymene, ³J_{HH} = 7.0 Hz), 1.29-1.23 (m, 4H, CH₂CH₂CH₃), 0.84 (t, 3H, OCH₂CH₃)₂, ³J_{HH} = 6.9 Hz) ppm; ¹³C{¹H} NMR (126 MHz, CDCl₃): δ = 162.19 (s, arom. Cquat para of CF₃), 156.27 (s, arom. Cquat C(Ph)=N), 146.46 (s, arom. Cquat C(NH)=N), 131.35 (s, arom. CH), 129.70 (q, arom. Cquat CCF₃, ²J_{CF} = 31.7 Hz), 129.17 (s, arom. CH), 127.09 (s, arom. CH), 125.70 (s, arom. CH), 124.21 (q, CF₃, ¹J_{CF} = 272.4 Hz), 123.16 (s, arom. Cquat of C₆H₅), 103.28 (s, arom. Cquat of *p*-cymene), 98.67 (s, arom. Cquat of *p*-cymene), 83.52 (s, arom. CH of *p*-cymene), 81.47 (s, arom. CH of *p*-cymene), 81.39 (s, arom. CH of *p*-cymene), 58.81 (s, CHCH₂), 37.45 (s, CHCH₂), 30.71 (s, CH(CH₃)₂), 28.02 (s, CH₂CH₂CH₃), 22.48 (s, CH₂CH₂CH₃), 22.41 (s, CH(CH₃)₂ of *p*-cymene), 18.96 (s, CH₃ of *p*-cymene), 13.96 (s, CH₂CH₂CH₃) ppm; ¹⁹F{¹H} NMR (282 MHz, CDCl₃): δ = -62.50 (s, CF₃) ppm. IR: ν = 1655 cm⁻¹ (C=N). MS (ESI-TOF): m/z = 646.14 [M - Cl]⁺, 704.10 [M + Na]⁺ (expected isotopic

profiles). Elemental analysis calcd. (%) for C₃₀H₃₄ON₃F₃Cl₂Ru (681.58): C 52.87, H 5.03, N 6.17; found C 53.03, H 5.16, N 6.12.

Dichloro-(5-phenyl-1,3,4-oxadiazol-2-ylamine)(η^6 -*p*-cymene) ruthenium(II) (9). Yield 96%. ¹H NMR (500 MHz, CDCl₃): δ = 7.86 (dd, 2H, arom. CH of C₆H₅, ³J_{HH} = 8.0 Hz, ⁴J_{HH} = 1.0 Hz), 7.55-7.48 (m, 3H, arom. CH of C₆H₅), 6.18 (s, 2H, NH₂), 5.64 and 5.40 (AA'BB' spin system, 2H, arom. CH of *p*-cymene, ³J_{HH} = 6.5 Hz), 5.65 and 5.41 (AA'BB' spin system, 4H, arom. CH of *p*-cymene, ³J_{HH} = 6.0 Hz), 3.16 (hept, 1H, CH(CH₃)₂ of *p*-cymene, ³J_{HH} = 7.0 Hz), 2.33 (s, 3H, CH₃ of *p*-cymene), 1.31 (d, 6H, CH(CH₃)₂ of *p*-cymene, ³J_{HH} = 7.0 Hz) ppm; ¹³C{¹H} NMR (126 MHz, CDCl₃): δ = 163.32 (s, arom. Cquat C(NH)NH₂), 156.90 (s, arom. Cquat C(Ph)=N), 131.58 (s, arom. CH), 129.15 (s, arom. CH), 125.97 (s, arom. CH), 123.06 (s, arom. Cquat of C₆H₅), 103.24 (s, arom. Cquat of *p*-cymene), 98.51 (s, arom. Cquat of *p*-cymene), 83.42 (s, arom. CH of *p*-cymene), 81.62 (s, arom. CH of *p*-cymene), 30.61 (s, CH(CH₃)₂), 22.25 (s, CH(CH₃)₂ of *p*-cymene), 18.83 (s, CH₃ of *p*-cymene) ppm. IR: ν = 1655 cm⁻¹ (C=N). MS (ESI-TOF): m/z = 432.04 [M - Cl]⁺ (expected isotopic profile). Elemental analysis calcd. (%) for C₁₈H₂₁ON₃Cl₂Ru (467.35): C 42.26, H 4.53, N 8.99; found C 42.31, H 4.62, N 8.95.

General procedure for the ruthenium-catalyzed oxidative cleavage of olefins or alkynes.

In a Schlenk tube in an inert atmosphere a solution of complex **3** (0.0034 g, 1 mol %), NaIO₄ (0.321 g, 1.5 mmol), olefin or alkyne (0.5 mmol) and H₂O (2 mL) were introduced. The reaction mixture was then stirred at room temperature for 1 hour. The organic products were extracted with Et₂O (2 x 5 mL) and the combined organic layers were washed with brine (5 mL), separated, dried over MgSO₄, filtered and concentrated in vacuum. The crude product was analyzed by ¹H NMR spectroscopy.

Acknowledgements

We gratefully acknowledge the Tunisian Ministry of Higher Education and Scientific Research for the financial support (grant for S. H.).

Declaration of competing interest

The authors report no declaration of interest.

References

- [1] R. Pappo, D. S. Allen Jr., R. U. Lemieux, W. S. Johnson, *J. Org. Chem.* **1956**, *21*, 478-479.
- [2] a) S. R. Hart, D. C. Whitehead, B. R. Travis, B. Borhan, *Org. Biomol. Chem.* **2011**, *9*, 4741-4744; b) J. M. Gichumbi, B. Omondi, H. B. Friedrich, *J. Organomet. Chem.* **2018**, *856*, 56-62.
- [3] a) L. I. Simándi, T. L. Simándi, *J. Mol. Catal. A: Chem.* **1997**, *117*, 299-309; b) L.-T. Huang, A. Ali, H.-H. Wang, F. Cheng, H.-Y. Liu, *J. Mol. Catal. A: Chem.* **2017**, *426*, 213-222.
- [4] a) T. A. G. Duarte, A. P. Carvalho, L. M. D. R. S. Martins, *Catal. Sci. Technol.* **2018**, *8*, 2285-2288; b) C. C. Wua, B. Liu, X. Geng, Z. Zhang, S. Liu, Q. Hu, *Polyhedron* **2019**, *158*, 334-341.
- [5] a) A. S. Sharma, D. Shah, H. Kaur, *RSC Adv.* **2015**, *5*, 42935-42941; b) B. Liu, P. Wang, A. Lopes, L. Jin, W. Zhong, Y. Pei, S. L. Suib, J. He, *ACS Catal.* **2017**, *7*, 3483-3488.
- [6] a) S. Shibata, K. Kamata, M. Hara, *Catal. Sci. Technol.* **2021**, *11*, 2369-2373; b) J.-J. Ai, B. i.-B. Liu, J. Li, F. Wang, C.-M. Huang, W. Rao, S.-Y. Wang, *Org. Lett.* **2021**, *23*, 4705-4709.
- [7] a) G. Romanowski, J. Kira, M. Wera, *Inorg. Chim. Acta* **2018**, *483*, 156-164; b) L. S. Nogueira, M. M. Antunes, A. C. Gomes, L. Cunha-Silva, M. Pillinger, A. D. Lopes, A. A. Valente, I. S. Gonçalves, *Dalton Trans.* **2019**, *48*, 11508-11519.
- [8] a) A. Choudhary, B. Das, S. Ray, *Inorg. Chim. Acta* **2017**, *462*, 256-265; b) Y.-L. Dong, L. Xu, X.-D. Yang, Z. Su, H.-K. Liu, *Inorg. Chem. Commun.* **2019**, *104*, 14-18.
- [9] A. Wang, H. Jiang, *J. Org. Chem.* **2010**, *75*, 2321-2326.
- [10] a) S. Aini, J. Efendi, H. O. Lintang, S. Chandren, H. Nur, *Catal. Commun.* **2014**, *46*, 150-155; b) S. Ito, Y. Kon, T. Nakashima, D. Hong, H. Konno, D. Ino, K. Sato, *Molecules* **2019**, *24*, article number 2520.
- [11] a) P. Paul, A. Ghosh, S. Chatterjee, A. Bera, S. M. Alam, S. M. Islam, *Inorg. Chim. Acta* **2019**, *492*, 198-212; b) A. Hasnaoui, R. Idouhli, A. Nayad, H. Ouahine, M.-E. Khadiri, M. bouelfida, L. Elfirdoussi, M. A. Ali, *Inorg. Chem. Commun.* **2020**, *119*, article number 108134.
- [12] C. Mi, L. Li, X.-G. Meng, R.-Q. Yang, X.-H. Liao, *Tetrahedron* **2016**, *72*, 6705-6710.
- [13] M. Bonaïdo, F. Borin, M. Bressan, A. Morvillo, *J. Organomet. Chem.* **1989**, *363*, 175-179.
- [14] M. K. Pandey, J. T. Mague, M. S. Balakrishna, *Inorg. Chem.* **2018**, *57*, 7468-7480.
- [15] E. A. Nyawade, H. B. Friedrich, B. Omondi, P. Mpungose, *Organometallics* **2015**, *34*, 4922-4931.
- [16] a) W.-C. Cheng, W.-Y. Yu, K.-K. Cheung, C.-M. Che, *J. Chem. Soc., Chem. Commun.* **1994**, 1063-1064; b) V. Kogan, M. M. Quintal, R. Neumann, *Org. Lett.* **2005**, *7*, 5039-5042; c) Y.-Q. Zhong, H.-Q. Xiao, X.-Y. Yi, *Dalton Trans.* **2016**, *45*, 18113-18119; d) S. Phungsripheng, K. Kozawa, M. Akita, A. Inagaki, *Inorg. Chem.*

- 2016**, *55*, 3750-3758; e) J. M. Gichumbi, H. B. Friedrich, B. Omondi, *J. Coord. Chem.* **2019**, *72*, 135-147; f) S. Pandey, T. Mandal, V. Singh, *ChemistrySelect* **2020**, *5*, 823-828.
- [17] a) T. Mandal, V. Singh, J. Choudhury, *Chem. Asian J.* **2019**, *14*, 4774-4779; b) S. K. Gupta, T. Mandal, T. Gangber, V. Singh, J. Choudhury, *Inorg. Chim. Acta* **2020**, *500*, article number 119195.
- [18] S. Muthumari, R. Ramesh, *ChemistrySelect* **2018**, *3*, 3036-3041.
- [19] M. Poyatos, J. A. Mata, E. Falomir, R. H. Crabtree, E. Peris, *Organometallics* **2003**, *22*, 1110-1114.
- [20] P. Daw, R. Petakamsetty, A. Sarbajna, S. Laha, R. Ramapanicker, J. K. Bera, *J. Am. Chem. Soc.* **2014**, *136*, 13987-13990.
- [21] T. S. Manikandan, R. Ramesh, D. Sémeril, *RSC Adv.* **2016**, *6*, 97107-97115.
- [22] D. De Joarder, S. Gayen, R. Sarkar, R. Bhattacharya, S. Roy, D. K. Maiti, *J. Org. Chem.* **2019**, *84*, 8468-8480.
- [23] M. Dutta, K. K. Bania, S. Pratihar, *ChemCatChem* **2019**, *11*, 2683-2694.
- [24] K. Salzmann, C. Segarra, M. Albrecht, *Angew. Chem. Int. Ed.* **2020**, *59*, 8932-8936.
- [25] S. Hkiri, C. Gourlaouen, S. Touil, A. Samarat, D. Sémeril, *New J. Chem.* **2021**, *45*, 11327-11335.
- [26] a) S. Balaji, M. K. M. Subarkhan, R. Ramesh, H. Wang, D. Sémeril, *Organometallics* **2020**, *39*, 1366-1375; b) S. Saranya, R. Ramesh, D. Sémeril, *Organometallics* **2020**, *39*, 3194-3201.
- [27] A. S. Goldstein, R. S. Drago, *J. Chem. Soc. Chem. Commun.* **1991**, 21-22.
- [28] Note: Attempts to form chelate species from **3** in the presence of AgBF₄ resulted in the formation of a mixture of complexes, probably diastereomers, which we could not be purified by recrystallization. A mass spectroscopic analysis performed on the crude product showed the absence of ruthenium coordinated to two chlorine atoms.
- [29] P. Niu, J. Kang, X. Tian, L. Song, H. Liu, J. Wu, Y. W., J. Chang, *J. Org. Chem.* **2015**, *80*, 1018-1024.