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Journal of Organometallic Chemistry 575 (1999) 187–192

Journal of Organometallic Chemistry

2-Imidazoline– and 1,4,5,6-tetrahydropyrimidine–ruthenium(II) complexes and catalytic synthesis of furan

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Received 31 December 1996

Abstract

The complexes $RuCl_2(L^1)$(arene) (**3–4**) ($L1 = HC{=}NCH_2CH_2NR$, R = Et, arene = *p*-$MeC_6H_4CHMe_2$ or C_6Me_6) and $RuCl_2(L^2)$(arene) (**5–6**) ($L^2 = HC{=}NCH_2CH_2CH_2NR$, R = Me, Ph, CH_2Ph, *p*-MeC_6H_4) have been synthesized by reaction of $[RuCl_2(arene)]_2$ with 1-alkyl-2-imidazoline (**1**) or 1-alkyl-1,4,5,6-tetrahydropyrimidine (**2**). In each of these complexes (**3–6**) the ligand is bound via the imine (N=C) nitrogen atom. The new complexes are capable of catalyzing the activation of (*Z*)-3-methylpent-2-en-4-yn-1-ol into 2,3-dimethylfuran in very good yield, via intramolecular cyclization, and the 1,4,5,6-tetrahydropyrimidine complexes **5** and **6** appeared to be the best catalyst precursors. Cyclic voltammetry shows that the nature of the arene ligand, rather than that of the nitrogen containing ligand, controls the electron-richness of the complexes.

Keywords: Ruthenium; 2-Imidazoline; 1,4,5,6-Tetrahydropyrimidine; Catalytic synthesis of furan

1. Introduction

The use of simple ruthenium(II) complexes has recently allowed the discovery of new organic reactions especially for the selective transformations of alkynes such as their regioselective coupling with alkenes [1,2], the synthesis of γ,δ-unsaturated ketones [3] and aldehydes [4], or the skeleton rearrangement of enynes [5]. Ruthenium–vinylidene intermediates have offered the access to alkenylcarbamates [6] or α,β-unsaturated ketones [7]. Regioselective addition reactions to terminal alkynes are also promoted by ruthenium complexes in the synthesis of 1- or 2-alkenyl esters [8,9] or the access to furans by intramolecular transformations of *Z*-enynols [10]. Most of the involved ruthenium(II) catalyst precursors contain simple phosphines and hydrocarbon ligands and their catalytic activity and selectivity is largely dependent on slight modifications of the ligands [11]. The design of new hydrocarbon–ruthenium(II) catalysts but containing simple nitrogen-bound ligand for their evaluation in catalysis is thus motivated.

The metal chemistry of heteroaromatic compounds such as imidazole and pseudo-imidazole derivatives [12–14] have received widespread attention over the last decade. By contrast, only limited studies with imidazolines [15,16] and 2-phenylimidazoline [17] have been performed. Lappert and co-workers have studied molybdenum and rhodium chemistry of 2-imidazoline [18,19] and the 1-ethyl-2-imidazoline platinum(II) complex has just been structurally characterized [19]. Moreover selective antimicrobial activities of *N*-benzyl-2-imidazoline complexes of rhodium(I) have recently been described [20].

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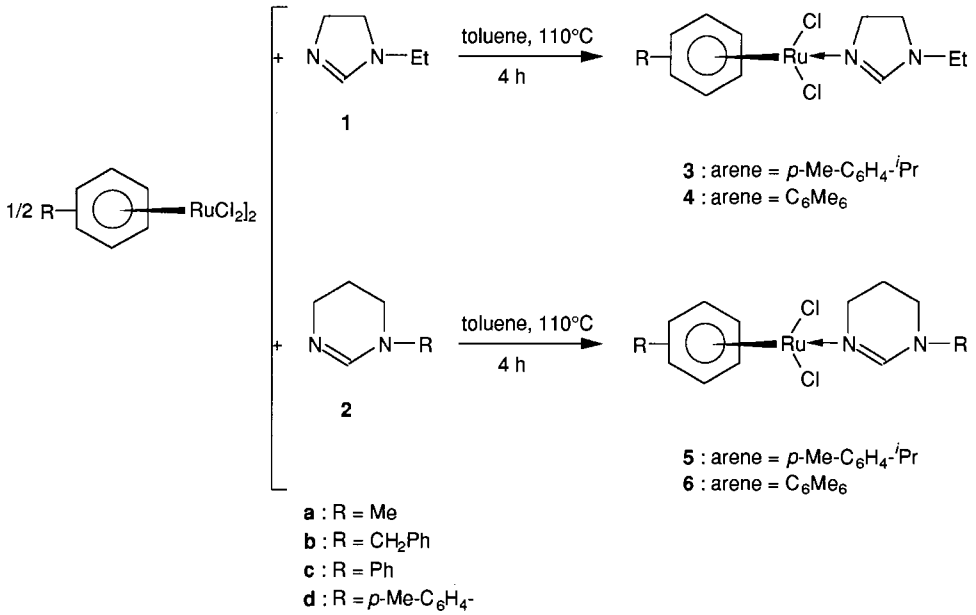
0022-328X/99/$ - see front matter
PII: S0022-328X(98)00992-9



Scheme 1.

We now report (i) the preparation of new arene–ruthenium(II) complexes containing the non-aromatic heterocycles, the *N*-ethyl-2-imidazoline (**1**) and 1,4,5,6-tetrahydropyrimidines (**2**) ligands coordinated through the nitrogen atom, and (ii) their use as catalyst for the selective cyclization of (*Z*)-3-methylpent-2-en-lyn-1-ol into 2,3-dimethylfuran.

2. Results and discussion

2.1. Synthesis of ruthenium(II) complexes 3–6

The reaction of the 1-ethyl-2-imidazoline **1** with the binuclear (arene)ruthenium(II) halide complexes $[RuCl_2(p\text{-}MeC_6H_4CHMe_2)]_2$ and $[RuCl_2(C_6Me_6)]_2$ proceeds smoothly, in refluxing toluene, to give the orange complexes **3** (73%) and **4** (81%) (Scheme 1). Analogously, the reaction of 1-alkyl- or 1-aryl-1,4,5,6-tetrahydropyrimidines **2a–d** with the same ruthenium precursors $[RuCl_2(arene)]_2$ in refluxing toluene for 4 h afforded the orange complexes **5a** (78%), **5b** (85%), **5c** (66%) and **5d** (89%) containing the η^6-*p*-cymene ligand and **6a** (86%), **6b** (89%) and **6d** (87%) containing the hexamethylbenzene ligand (Scheme 1).

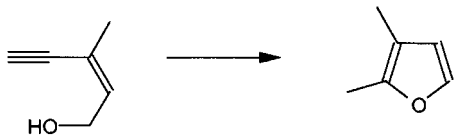
The complexes **3–6**, which are very stable in the solid state, have been characterized by analytical and spectroscopic data (Tables 1–3). The IR data for complexes **3–6** clearly indicate the presence of the –C=N– group (Table 2), with a ν(C=N) vibration at 1610–1647 cm^{-1}. The absence of both the N–H stretching frequency at ca. 3200 cm^{-1} and N–H bending frequency in the region 1400–1450 cm^{-1} shows the absence of imino hydrogen in the reaction products. Moreover, the C_2 and C_2–H nuclei of the ligands are effective probes for the NMR studies: in ^{1}H-NMR the =C_2–H proton is observed as a sharp singlet at δ 7.0–8.0 ppm (Table 2). The $^{13}C\{^1H\}$-NMR spectra exhibit a singlet in the range δ 150–160 ppm for the N=C_2H carbon (Table 3). The proposed ring structures in compounds **4**, **5d** and **6d** were confirmed by ^{1}H coupled ^{13}C-NMR: the spectrum of **4** showed the C_2 carbon as a doublet at δ 159.8 ppm (^1J(CH) = 196.5 Hz) and the –NCH_2– carbon as two triplets at δ 47.8 and 53.4 (^1J(CH) = 125 Hz). Similarly, the resonance for the C_2 carbons of **5d** and **6d** gives a doublet at δ 152.8 (^1J(CH) = 200 Hz) and δ 153.0 (^1J(CH) = 196 Hz), respectively. These observations clearly exclude tautomerization within the ligand and carbene (or ylide) ligand formation [21].

2.2. Electrochemical studies of complexes 3–6

The complexes **3–6** containing both the η^6-arene and *N*-bonded cyclic ligands have been studied in cyclic voltammetry in order to evaluate the electron-richness of the complexes. The measurements were performed in dichloromethane solution containing 40 mmol of complex and Bu_4NPF_6 as an electrolyte. All complexes gave a reversible oxidation at 100 mV s^{-1} scan rates. The potential values $E_{1/2}$ (V vs. SCE) are given in Table 4.

The results show that, as observed before with $RuCl_2$(PR3)(arene) complexes, the C_6Me_6–ruthenium(II) derivatives oxidize at lower potential than their *p*-cymene–ruthenium(II) analogues, due to the electron-donating capability of the C_6Me_6 group [22].

2.3. Catalytic synthesis of 2,3-dimethylfuran



(1)

In order to evaluate the catalytic potential of the nitrogen to ruthenium(II) bounded complexes **3–6** their activity toward the activation and intramolecular cyclization of (*Z*)-3-methyl-2-en-4-yn-1-ol into 2,3-dimethylfuran has been studied (Eq. 1). This reaction had been previously shown to occur via catalysis with $RuCl_2(PPh_3)$(*p*-cymene) [10]. The reaction is performed in neat (*Z*)-3-methyl-2-en-4-yn-1-ol (10 mmol) with 0.1 mmol of the ruthenium catalysts **3–6**. The reaction requires a temperature of 80°C for 1–12 h to reach the complete transformation of the enynol. The results are summarized in Table 5.

They show that, for the same nitrogen ligand, the ruthenium complexes associated with the C_6Me_6 ligand lead to more active catalysts than their related *p*-cymene complexes [entries 3 (32 h) vs. 7 (12 h) and entries 8 (12 h) vs. 16 (2 h)]. The nature of the arene ligand appears to bring a strong influence. With the *p*-cymene ligand the redox potentials are in the range 1.23–1.12 V_{SCE} whereas they are in the range 0.92–0.97 with the C_6Me_6 ligand, no matter what nitrogen ligand is employed (Table 4). This noticeable effect of C_6Me_6 suggests that the arene is kept bounded to the ruthenium atom in the catalytic species.

The electron-richness of the ruthenium(II) precursors is an important factor. The discovery of this intramolecular addition of the O–H group to the C≡C bond was previously understood only in terms of electrophilic activation of the alkyne bond. It is likely that the ruthenium(II) moiety provides a catalytic electrophilic activation but only in a short range of redox potentials e.g. not with very electrophilic or electron-rich ruthenium(II) complexes.

The nature of the nitrogen ligand has also a strong influence on the catalytic activity and the 1,4,5,6-tetrahydropyrimidine ligand in complexes **5–6** allows the reaction to be completed at 80°C more rapidly than the 2-imidazoline complexes **3–4**. The best catalysts appear to be related to the ligand **2a** as complex **6a** leads to the best yield after only 2 h (entry 16) with respect to complexes **6b** and **6d** [entries 19 (22 h) and 21 (14 h)].

3. Experimental

3.1. General

Unless otherwise stated, manupilations were performed under an oxygen-free nitrogen atmosphere by using dried solvents and standard Schlenk techniques. Compounds **1** and **2** were prepared as previously described [23,24]. $[RuCl_2(p\text{-}MeC_6H_4CHMe_2)]_2$ and $[RuCl_2(C_6Me_6)]_2$ were prepared according to literature methods [25].

Infrared spectra were recorded as KBr pellets in the range 4000–400 cm^{-1} on a ATI UNICAM systems 2000 Fourier transform spectrometer. ^{1}H-NMR spectra (300 MHz) and ^{13}C-NMR spectra (75.5 MHz) were recorded using a Bruker AM 300 WB FT spectrometer with δ referenced to external $SiMe_4$. Microanalyses were performed by the TUBITAK (Ankara, Turkey) or CNRS Service Central d'Analyse (Vernaison, France).

3.2. Synthesis of *3* and *4*

A solution of **1** (0.23 g, 2.34 mmol) in toluene (20 ml) and $[RuCl_2(p\text{-}Me_2CHC_6H_4Me)]_2$ (0.71 g, 1.17 mmol) were heated for 4 h under reflux. *n*-Hexane (5 ml) was added to the solution while warm. Upon cooling to room temperature (r.t.), orange crystals of **3** formed. The product **3** was filtered, washed with *n*-hexane (2 × 20 ml), dried under vacuum and a 73% yield was obtained. Using a similar procedure to that leading to **3**, from $[RuCl_2(C_6Me_6)]_2$ (1.0 g, 1.5 mmol) and **1** (0.32

Table 1
Physical measurement of new 2-imidazoline and 1,4,5,6-tetrahydropyrimidine ruthenium(II) complexes **3–6**

Compound	M.p. (°C)	Yield (%)	Micro analysis—found (calculated) (%)		
			C	H	N
3	168–169	73	44.23 (44.56)	5.90 (5.98)	7.68 (6.93)
4	220–221	81	46.98 (47.28)	6.49 (6.53)	6.65 (6.48)
5a	146–147	78	44.73 (44.56)	6.11 (5.98)	7.21 (6.93)
5b	176–177	85	52.41 (52.50)	6.01 (5.87)	5.85 (5.83)
5c	175–176	66	51.79 (51.50)	5.53 (5.62)	6.28 (6.01)
5d	170–171	89	52.78 (52.50)	5.96 (5.87)	6.02 (5.83)
6a	286–287	86	47.21 (47.22)	6.55 (6.53)	6.72 (6.48)
6b	260–261	89	54.45 (54.33)	6.39 (6.34)	5.66 (5.51)
6d	230–231	87	54.41 (54.33)	6.50 (6 34)	5.63 (5.51)

Table 2
IR and ^{1}H-NMR spectroscopic data for compounds **3–6**[a]

	$\nu(CN_2)$ (cm^{-1})	C2–*H*	4,5 (or 4,6) CH_2	Others
3	1610	7.2 (s)	3.5 and 4.1 (t, *J* 10 Hz)	3.1(q, *J* 7Hz) CH_2CH_3; 1.1 (t, *J* 7 Hz) CH$_2$CH_3; 5.2 and 5.3 (d, *J* 6 Hz) [(CH$_3$)$_2$CHC$_6$H$_4$(CH$_3$)-*p*]; 1.1 (d, *J* 7 Hz) [(CH_3)$_2$CHC$_6$H$_4$(CH$_3$)-*p*]; 2.2 (s) [(CH$_3$)$_2$CHC$_6$H$_4$(CH_3)-*p*]; 3.0 (sept, *J* 7) [(CH$_3$)$_2$C*H*C$_6$H$_4$(CH$_3$)-*p*]
4	1614	7.1 (s)	3.4 and 4.0 (t, *J* 10 Hz)	3.0 (q, *J* 7 Hz) CH_2CH$_3$; 1.0 (t, *J* 7 Hz) CH$_2$CH_3; 2.0 (s) C$_6$(CH_3)$_6$
5a	1647	7.2 (s)	3.1 and 3.6 (t, *J* 6 Hz)	1.9 (qu, *J* 6 Hz) NCH$_2$CH_2CH$_2$N; 2.8 (s) CH_3; 5.1 and 5.3 (d, *J* 6 Hz) [(CH$_3$)$_2$CHC$_6$H$_4$(CH$_3$)-*p*]; 1.2 (d, *J* 7 Hz) [(CH_3)$_2$CHC$_6$H$_4$(CH$_3$)-*p*]; 2.2 (s) [(CH$_3$)$_2$CHC$_6$H$_4$(CH_3)-*p*]; 2.9 (sept, *J* 7) [(CH$_3$)$_2$C*H*C$_6$H$_4$(CH$_3$)-*p*]
5b	1639	8.2 (s)	3.0 and 3.6 (t, *J* 6 Hz)	1.8 (qu, *J* 6 Hz) NCH$_2$CH_2CH$_2$N; 4.2 (s) CH_2C$_6$H$_5$; 7.1–7.3 (m) CH$_2$C$_6$*H*$_5$; 5.2 and 5.3 (d, *J* 6 Hz) [(CH$_3$)$_2$CHC$_6$H$_4$(CH$_3$)-*p*]; 1.2 (d, *J* 7 Hz) [(CH_3)$_2$CHC$_6$H$_4$(CH$_3$)-*p*]; 2.2 (s) [(CH$_3$)$_2$CHC$_6$H$_4$(CH_3)-*p*]; 2.9 (sept, *J* 7) [(CH$_3$)$_2$C*H*C$_6$H$_4$(CH$_3$)-*p*]
5c	1637	8.0 (s)	3.7 and 3.8 (t, *J* 6 Hz)	1.8 (qu, *J* 6 Hz) NCH$_2$CH_2CH$_2$N; 7.0–7.3 (m) C$_6$H$_5$; 5.2 and 5.4 (d, *J* 6 Hz) [(CH$_3$)$_2$CHC$_6$H$_4$(CH$_3$)-*p*]; 1.3 (d, *J* 7 Hz) [(CH_3)$_2$CHC$_6$H$_4$(CH$_3$)-*p*]; 2.2 (s) [(CH$_3$)$_2$CHC$_6$H$_4$(CH_3)-*p*]; 3.0 (sept, *J* 7) [(CH$_3$)$_2$C*H*C$_6$H$_4$(CH$_3$)-*p*]
5d	1639	7.9 (s)	3.6 and 3.8 (t, *J* 6 Hz)	2.0 (qu, *J* 6 Hz) NCH$_2$CH_2CH$_2$N; 2.3 (s) C$_6$H$_4$CH_3-*p*; 6.9–7.3 (m) C$_6$H$_4$CH_3-*p;* 5.2 and 5.3 (d, *J* 6 Hz) [(CH$_3$)$_2$CHC$_6$*H*$_4$(CH$_3$)-*p*]; 1.3 (d, *J* 7 Hz) [(CH_3)$_2$CHC$_6$H$_4$(CH$_3$)-*p*]; 2.2 (s) [(CH$_3$)$_2$CHC$_6$H$_4$(CH_3)-*p*]; 3.0 (sept, *J* 7) [(CH$_3$)$_2$C*H*C$_6$H$_4$(CH$_3$)-*p*]
6a	1645	7.0 (s)	3.1 and 3.3 (t, *J* 6 Hz)	1.9 (qu, *J* 6 Hz) NCH$_2$CH_2CH$_2$N; 2.8 (s) CH_3; 2.0 (s) C$_6$(CH_3)$_6$
6b	1637	7.3 (s)	3.0 and 3.3 (t, *J* 6 Hz)	1.8 (qu, *J* 6 Hz) NCH$_2$CH_2CH$_2$N; 4.2 (s) CH_2C$_6$H$_5$; 7.1–7.3 (m) CH$_2$C$_6$*H*$_5$; 2.0 (s) C$_6$(CH_3)$_6$
6d	1635	7.7 (s)	3.5 and 3.6 (t, *J* 6 Hz)	1.8 (qu, *J* 6 Hz) NCH$_2$CH_2CH$_2$N; 2.3 (s) C$_6$H$_4$CH_3-*p*; 6.9–7.2 (m) C$_6$*H*$_4$CH$_3$-*p*; 2.0 (s) C$_6$(CH_3)$_6$

[a] s, singlet; d, doublet; t, triplet; q, quartet; qu, quintet; sept, septet; chemical shifts in ppm from SiMe$_4$; solvent CDCl$_3$.

g, 3.2 mmol), complex **4** was obtained in 81% yield (Tables 1–3).

3.3. Synthesis of **5** and **6**

A solution of 1-methyl-1,4,5,6-tetrahydropyrimidine **2a** (0.26 g, 2.7 mmol) in toluene (30 ml) was added to [RuCl$_2$(*p*-Me$_2$CHC$_6$H$_4$Me)]$_2$ (0.70 g, 1.2 mmol) and the mixture was heated for 4 h under reflux. The resulting solution, on addition of *n*-hexane (20 ml) and cooling to r.t., gave an orange solid. The product **5a** was filtered, washed with *n*-hexane (2 × 20 ml), dried under vacuum and a 78% yield was obtained (Tables 1–3).

Table 3
^{13}C-NMR spectroscopic data for compounds **3–6**[a]

	*C*2	Ring 4,5 (or 4,5)–CH_2	Others
3	160.9	48.1, 57.3	42.3 CH_2CH$_3$; 13.6 CH$_2$CH_3; 81.1, 81.5, 96.6, 102.1 [(CH$_3$)$_2$CH*C*$_6$H$_4$(CH$_3$)-*p*]; 22.2 [(*C*H$_3$)$_2$CHC$_6$H$_4$(CH$_3$)-*p*]; 18.7 [(CH$_3$)$_2$CHC$_6$H$_4$(*C*H$_3$)-*p*]; 30.7 [(CH$_3$)$_2$*C*HC$_6$H$_4$(CH$_3$)-*p*]
4	159.8	47.8, 53.4	42.2 CH_2CH$_3$; 13.6 CH$_2$CH_3; 90.5 *C*$_6$(CH$_3$)$_6$; 15.7 C$_6$(*C*H$_3$)$_6$
5a	154.8	48.1, 49.5	18.5 NCH$_2$*C*H$_2$CH$_2$N; 40.8 *C*H$_3$; 81.4, 81.6, 96.0, 102.1 [(CH$_3$)$_2$CH*C*$_6$H$_4$(CH$_3$)-*p*]; 22.2 [(*C*H$_3$)$_2$CHC$_6$H$_4$(CH$_3$)-*p*]; 18.5 [(CH$_3$)$_2$CHC$_6$H$_4$(*C*H$_3$)-*p*]; 30.6 [(CH$_3$)$_2$*C*HC$_6$H$_4$(CH$_3$)-*p*]
5b	155.1	42.6, 49.9	22.6 NCH$_2$*C*H$_2$CH$_2$N; 57.7 *C*H$_2$C$_6$H$_5$; 127.7, 128.0, 128.9, 135.7 CH$_2$*C*$_6$H$_5$; 81.4, 81.8, 96.1, 102.7 [(CH$_3$)$_2$CH*C*$_6$H$_4$(CH$_3$)-*p*]; 22.3 [(*C*H$_3$)$_2$CHC$_6$H$_4$ (CH$_3$)-*p*]; 18.6 [(CH$_3$)$_2$CHC$_6$H$_4$(*C*H$_3$)-*p*]; 30.7 [(CH$_3$)$_2$*C*HC$_6$H$_4$(CH$_3$)-*p*]
5c	152.7	44.2, 50.1	22.6 NCH$_2$*C*H$_2$CH$_2$N; 118.9, 124.8, 129.6, 143.7 *C*$_6$H$_5$; 81.2, 81.9, 96.5, 102.6 [(CH$_3$)$_2$CH*C*$_6$H$_4$(CH$_3$)-*p*]; 22.3 [(*C*H$_3$)$_2$CHC$_6$H$_4$(CH$_3$)-*p*]; 18.6 [(CH$_3$)$_2$CHC$_6$H$_4$(*C*H$_3$)-*p*]; 30.7 [(CH$_3$)$_2$*C*HC$_6$H$_4$ (CH$_3$)-*p*]
5d	152.8	44.4, 50.1	20.1 NCH$_2$*C*H$_2$CH$_2$N; 119.2, 130.1, 134.7, 141.4 *C*$_6$H$_4$CH$_3$-*p*; 20.9 C$_6$H$_4$C*H*$_3$-*p*; 81.4, 81.7, 96.1, 102.6 [(CH$_3$)$_2$CH*C*$_6$H$_4$(CH$_3$)-*p*]; 22.3 [(*C*H$_3$)$_2$CHC$_6$H$_4$(CH$_3$)-*p*]; 18.6 [(CH$_3$)$_2$CHC$_6$H$_4$(*C*H$_3$)-*p*]; 30.7 [(CH$_3$)$_2$*C*HC$_6$H$_4$(CH$_3$)-*p*]
6a	154.9	45.0, 46.9	22.3 NCH$_2$*C*H$_2$CH$_2$N; 40.9 *C*H$_3$; 90.2 *C*$_6$(CH$_3$)$_6$; 15.6 C$_6$(*C*H$_3$)$_6$
6b	155.0	42.9, 47.0	22.4 NCH$_2$*C*H$_2$CH$_2$N; 57.4 *C*H$_2$C$_6$H$_5$; 127.7, 128.1, 128.9, 135.9 CH$_2$*C*$_6$H$_5$; 90.3 *C*$_6$(CH$_3$)$_6$; 15.7 C$_6$(*C*H$_3$)$_6$
6d	153.0	44.6, 47.4	22.6 NCH$_2$*C*H$_2$CH$_2$N; 119.5, 128.2, 129.0, 130.1, 134.7, 141.6 C$_6$H$_4$CH$_3$-*p*; 20.8 C$_6$H$_4$*C*H$_3$; 90.6 *C*$_6$(CH$_3$)$_6$-*p*; 15.7 C$_6$(*C*H$_3$)$_6$

[a] Chemical shifts in ppm from SiMe$_4$; solvent CDCl$_3$.

Table 4
Cyclic voltammetric data of ruthenium(II) complexes[a]

Compound	$E_{1/2}$ (V_{SCE})	ΔE_p (mV)
3	1.23	97
4	0.92	92
5b	1.12	63
5c	1.14	100
5d	1.17	89
6a	0.94	150
6b	0.94	120
6d	0.97	86

[a] E in V vs. SCE, Pt working electrode, 100 mV s^{-1}. Recorded in CH_2Cl_2 solution containing n-Bu_4NPF_6 (0.05 M) as supporting electrolyte.

Table 5
Catalytic synthesis of 2,3-dimethylfuran at 80°C[a]

Entry	Catalyst	Time (h)	Yield (%)[b,c]
1	**3**	1	23
2	**3**	23	72
3	**3**	32	85 (73)[c]
4	**4**	1	34
5	**4**	2	72
6	**4**	4	85
7	**4**	12	87 (79)[c]
8	**5a**	12	98 (88)[c]
9	**5c**	1	50
10	**5c**	2	64
11	**5c**	12	86 (79)[c]
12	**5d**	1	68
13	**5d**	2	85
14	**5d**	5	96 (86)[c]
15	**6a**	1	56
16	**6a**	2	98 (88)[c]
17	**6b**	4	62
18	**6b**	17	87
19	**6b**	22	99 (84)[c]
20	**6d**	1	56
21	**6d**	14	86 (75)[c]

[a] Reaction conditions: To 0.1 mmol of the ruthenium catalyst 10 mmol of neat (*Z*)-3-methylpent-2-en-4-yn-1-ol were added. The mixture was stirred in an oil bath at 80°C.
[b] Yields determined by gas chromatography.
[c] Isolated yield after distillation.

Using a similar procedure to that leading to **5a**, from 1-benzyl-1,4,5,6-tetrahydropyrimidine, **3b** (0.60 g, 3.4 mmol) and $[RuCl_2(p\text{-}Me_2CHC_6H_4Me)]_2$ (0.95 g, 1.5 mmol), complex **5b** was obtained in 85% yield.

Using a similar procedure to that leading to **5a**, from 1-phenyl-1,4,5,6-tetrahydropyrimidine, **2c**, (0.35 g, 2.2 mmol) and $[RuCl_2(p\text{-}Me_2CHC_6H_4Me)]_2$ (0.65 g, 1.1 mmol), complex **5c** was obtained in 66% yield.

Using a similar procedure to that leading to **5a**, from 1-*p*-tolyl-1,4,5,6-tetrahydropyrimidine, **2d** (0.40 g, 2.3 mmol) and $[RuCl_2(p\text{-}Me_2CHC_6H_4Me)]_2$ (0.65 g, 1.1 mmol), complex **5d** was obtained in 89% yield.

Compound **6a**, was prepared in the same way as **5a**, from **2a** (0.45 g, 4.6 mmol) and $[RuCl_2(C_6Me_6)]_2$ (1.35 g, 2.0 mmol) to give the orange product **6a** in 86% yield (Tables 1–3).

Using a similar procedure, 1-benzyl-1,4,5,6-tetrahydropyrimidine **2b** (0.40 g, 2.3 mmol) and $[RuCl_2(C_6Me_6)]_2$ (0.73 g, 1.1 mmol), afforded **6b** in 89% yield. 1-*p*-Tolyl-1,4,5,6-tetrahydropyrimidine **2d** (0.55 g, 3.2 mmol) and $[RuCl_2(C_6Me_6)]_2$ (1.00 g, 1.5 mmol), afforded **6d** in 87% yield.

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