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Ruthenium–arene complexes bearing imidazol(in)ium-2-dithiocarboxylate ligands: Evaluation of their catalytic activity in the synthesis of enol esters

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ABSTRACT

The catalytic activity of four ruthenium imidazol(in)ium-2-dithiocarboxylates was evaluated for the synthesis of vinyl esters through addition of 4-acetoxybenzoic acid to 1-hexyne, and compared to those of the parent ruthenium–*N*-heterocyclic carbene complexes and [$RuCl_2$(*p*-cymene)(PPh_3)] (a standard catalyst). It turned out that ruthenium imidazol(in)ium-2-dithiocarboxylates were poorly active and selective. Quantitative yields, indeed, were obtained only after extended reaction times. However, the catalytic activity could be improved significantly under microwave heating or conventional heating in a sealed tube at 160 °C, driving the reaction to completion in less than 4 h of reaction.

1. Introduction

Metal complexes bearing imidazol(in)ium-2-dithiocarboxylate ligands constitute a new class of compounds in coordination chemistry. Preliminary experiments in this field were conducted by Borer et al. who showed that 1,3-dimethylimidazolium-2-dithiocarboxylate (Scheme 1) formed stable complexes with a range of transition metal halides or nitrates [1]. The products obtained were characterized by IR and UV–Vis spectroscopies only. Measurements of electrical conductivity, magnetic susceptibility, or cyclic voltammetry complemented the analyses in some cases, but no NMR or XRD analyses were reported. As part of our research program directed toward *N*-heterocyclic carbenes (NHCs) and related chemistry [2], we recently reported the synthesis of ruthenium–arene complexes bearing imidazol(in)ium-2-dithiocarboxylate ligands (**1**–**4**), which are stable, 18-electron cationic species (Scheme 2) [3]. These compounds were fully characterized by various analytical techniques and the molecular structure of complex **1** was determined by X-ray diffraction analysis.

The catalytic activity of these complexes has never been reported. However, preliminary experiments have shown that catalyst systems generated in situ from the ruthenium dimer [$RuCl_2$(*p*-cymene)]$_2$ (*p*-cymene = 4-isopropyltoluene) and imidazol(in)ium-2-dithiocarboxylates were poorly active in olefin metathesis and atom transfer radical polymerization (ATRP) [3]. Furthermore, related in situ-generated palladium-based catalyst systems were moderately active for the Suzuki–Miyaura cross-coupling of aryl halides with *trans*-2-phenylvinylboronic acid [4]. With well-defined ruthenium imidazol(in)ium-2-dithiocarboxylates **1**–**4** in hand (Scheme 2), we became interested in investigating their catalytic activity. To this aim, we selected the synthesis of enol esters from carboxylic acids and alkynes as the first test-reaction, as it is well established that this process can be catalyzed by a variety of ruthenium complexes with good to excellent yields and selectivities [5]. In this paper, we report the results of this investigation.

2. Experimental

2.1. Materials

All reactions were carried out under an inert atmosphere, using reagents (Aldrich) and solvents (Aldrich, Labotec) dried and purified by standard techniques [6]. Ruthenium imidazol(in)ium-2-dithiocarboxylates **1**–**4** [3], [$RuCl_2$(*p*-cymene)(PPh_3)] **8** [7], and [$RuCl_2$(*p*-cymene)(NHC)] **12**–**14** [8] were synthesized according to the literature, and their NMR data were in accord with literature values. Microwave-assisted syntheses were performed using a single-mode Discover reactor from CEM Corp. (Matthews, NC) where the temperature was monitored with an IR sensor. Thermogravimetric analyses were performed under nitrogen using a TA Q500 instrument and a HI-Res dynamic heating rate.

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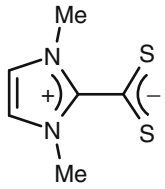
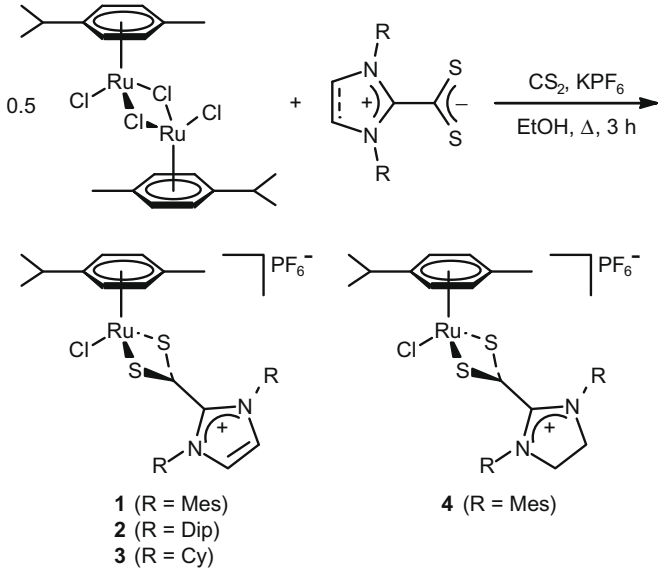


Scheme 1. Structure of 1,3-dimethylimidazolium-2-dithiocarboxylate.



Scheme 2. Synthesis and structure of the ruthenium imidazol(in)ium-2-dithiocarboxylate complexes **1**–**4** used in this work.

2.2. General procedures for the addition of 4-acetoxybenzoic acid to 1-hexyne

2.2.1. Conventional reactions at 60 °C

A 50-mL dry round-bottom Pyrex vessel containing a stirring bar and fitted with a three-way stopcock was charged with the catalyst (0.02 mmol), sodium carbonate (0.04 mmol, 4.2 mg), and 4-acetoxybenzoic acid (2.5 mmol, 450 mg), and then purged of air (three vacuum–nitrogen cycles). 13 mL of a stock solution containing 1-hexyne (3.75 mmol), dodecane (internal standard) in water-saturated toluene were then added under nitrogen. The resulting mixture was placed in an oil bath and allowed to react at 60 °C. The reaction was monitored by withdrawing samples at regular time intervals from the reaction mixture and analyzing them by gas chromatography (GC).

2.2.2. Conventional heating in sealed tubes at 160 °C

A 10-mL glass tube equipped with a stirring bar was charged with the catalyst (0.004 mmol), sodium carbonate (25 w-% in Celite, 0.008 mmol, 0.85 mg), and 4-acetoxybenzoic acid (0.5 mmol, 90 mg), and then purged of air (three vacuum–nitrogen cycles) before a stock solution (2.6 mL) containing 1-hexyne (0.75 mmol) and dodecane (internal standard) in water-saturated toluene was added. The tube was sealed under vacuum and immersed in an oil bath heated at 160 °C. After a given reaction time, the ampoule was drawn out of the bath and cooled down to room temperature.

2.2.3. Microwave-assisted reactions at 160 °C

A 10-mL glass vial containing a Teflon-coated stir bar was charged with the catalyst (0.004 mmol), sodium carbonate (25 w-% in Celite, 0.008 mmol, 0.85 mg), and 4-acetoxybenzoic acid (0.5 mmol, 90 mg) and then purged of air (three vacuum–nitrogen cycles) before a stock solution (2.6 mL) containing 1-hexyne (0.75 mmol) and dodecane (internal standard) in water-saturated toluene was added. The vial was capped under nitrogen, heated to 160 °C (monitored by IR sensor) using a dynamic heating rate, and then held at that temperature in a CEM Discover instrument with 150-W microwave power, programmed so as $t = 0$ when the desired temperature is attained. No simultaneous cooling was applied. After rapid air-cooling by the unit, the reaction mixture was analyzed by GC.

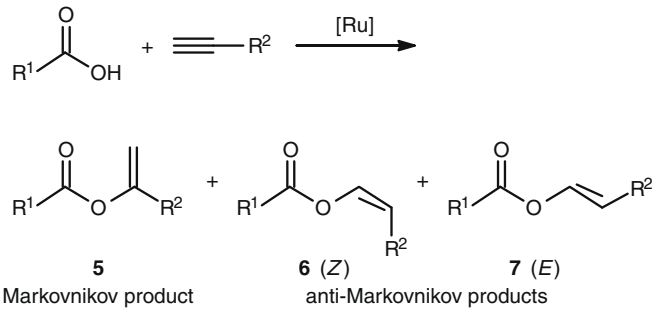
2.3. Analysis of the reaction mixtures and characterization of the products

GC analyses were performed on a Varian Star 3400 CX gas chromatograph equipped with a RSLM-150 capillary column (25 m × 0.25 mm; film thickness, 0.25 μm) and a flame ionization detector. The enol esters were purified by distillation under high vacuum and characterized by ^{1}H and ^{13}C NMR spectroscopy, according to the literature [5]. ^{1}H NMR and ^{13}C NMR spectra were recorded at 298 K with a Bruker DRX 400 spectrometer operating at 400.13 and 100.62 MHz, respectively.

3. Results and discussion

To evaluate the catalytic activity of ruthenium complexes **1**–**4** in the synthesis of enol esters, we investigated the reaction between 4-acetoxybenzoic acid and 1-hexyne at 60 °C, using a protocol that has already proven to be successful [9]. Noteworthily, water-saturated toluene was used as the solvent, and sodium carbonate as an activator [5j]. As illustrated in Scheme 3 (R^1 = 4-$AcOC_6H_4$, R^2 = n-C_4H_9), three adducts were expected from the reaction: the Markovnikov product (**5**) as well as the *anti*-Markovnikov isomers **6** (*Z*) and **7** (*E*).

The results shown in Table 1 and Fig. 1 demonstrate that ruthenium imidazol(in)ium-2-dithiocarboxylates **1**–**4** are exceedingly sluggish catalysts. Indeed, at 60 °C, the reactions proceeded to 10–30% overall yield in 50 h and, after 200 h of reaction, no more than 66% yield was obtained. Consequently, several hundreds of hours or so were required for the reactions to reach completion (Fig. 1 and Fig. Sd1 (see Appendix A. Supplementary data)). In marked contrast, when [$RuCl_2$(*p*-cymene)(PPh_3)] (**8**, Scheme 4) a typical catalyst for the synthesis of enol esters [9a] was used, 100% yield was obtained after 16 h only! We hypothesized that the exceedingly low catalytic activity of **1**–**4** was due to an enhanced stability of the complexes. In order to rationalize the large discrepancy observed between complexes **1**–**4** and **8** in terms of



Scheme 3. Synthesis of enol esters from carboxylic acids and terminal alkynes.

Table 1
Influence of the catalyst on the addition of 4-acetoxybenzoic acid to 1-hexyne catalyzed by complexes **1**–**4**, **8**, and **12**–**14**.[a]

Complex	Reaction time (h)	Yield (%)[b]	Selectivities (%)[c]		
			5	**6**	**7**
1	50	14	36	35	29
	200	51	39	30	31
2	50	29	33	36	31
	200	66	39	32	29
3	50	11	24	42	34
	200	46	28	35	37
4	50	26	25	40	35
	200	64	27	35	38
8	8	62	95.5	3.5	1
	15	99	95.5	3.5	1
12	50	61	80.5	17	2.5
	200	98	81	17	2
13	50	56	71.5	21	7.5
	200	98	72	20.5	7.5
14	25	83	82.5	14.5	3
	50	99	83	14	3

[a] Reaction conditions: 4-acetoxybenzoic acid, 1.15 mmol; 1-hexyne, 1.725 mmol; catalyst, 9.2×10^{-3} mmol; Na_2CO_3, 18.4×10^{-3} mmol; water-saturated toluene, 6 mL; temperature, 60 °C under nitrogen.
[b] Determined by GC using dodecane as internal standard.
[c] Determined by GC.

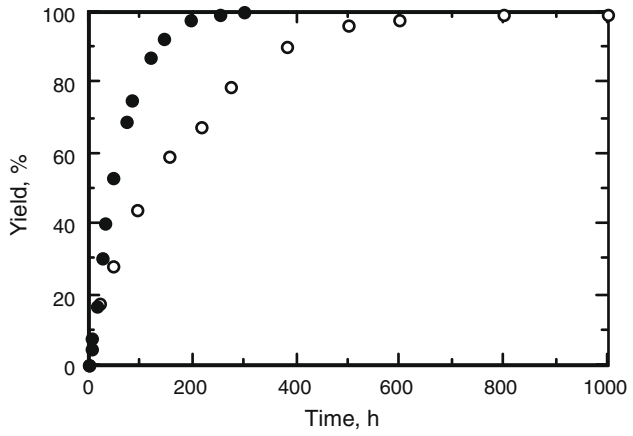
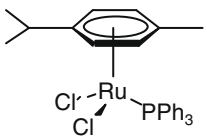


Fig. 1. Influence of the catalyst on the enol ester yield for reactions between 4-acetoxybenzoic acid and 1-hexyne catalyzed by complexes **2** (○) and **13** (●). Reaction conditions: 4-acetoxybenzoic acid, 1.15 mmol; 1-hexyne, 1.725 mmol; catalyst, 9.2×10^{-3} mmol; Na_2CO_3, 18.4×10^{-3} mmol; water-saturated toluene, 6 mL; temperature, 60 °C under nitrogen.



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Scheme 4. Structure of $[RuCl_2(p\text{-cymene})(PPh_3)]$ (**8**).

catalytic activity, we probed their thermal stabilities in the solid phase by thermogravimetric analysis (TGA). The decomposition profiles shown in Fig. 3 and Fig. Sd4, albeit quite different, reveal that the first sign of degradation appeared around 180 °C, corresponding to the loss of the *p*-cymene ligand.

It should also be noted that, although 1-hexyne was used in excess (1.5 equiv. relative to the carboxylic acid), the reaction generated only a trace amount of dimers **9**–**11** (Scheme 5). Also

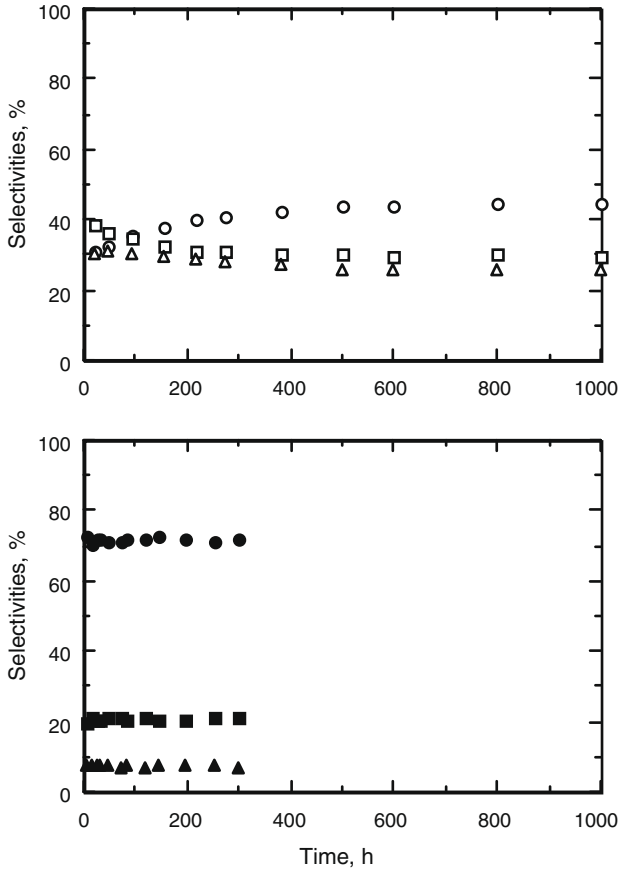


Fig. 2. Influence of the catalyst on the enol ester selectivities for reactions between 4-acetoxybenzoic acid and 1-hexyne catalyzed by complexes **2** (○, □, △) and **13** (●, ■, ▲). Enol esters: **5** (○, ●), **6** (□, ■), and **7** (△, ▲). Reaction conditions: 4-acetoxybenzoic acid, 1.15 mmol; 1-hexyne, 1.725 mmol; catalyst, 9.2×10^{-3} mmol; Na_2CO_3, 18.4×10^{-3} mmol; water-saturated toluene, 6 mL; temperature, 60 °C under nitrogen.

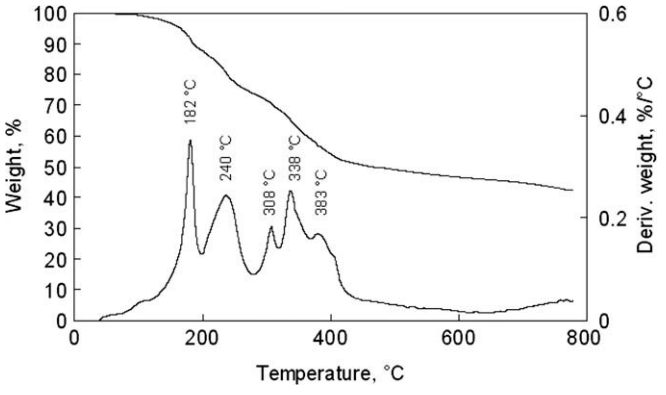
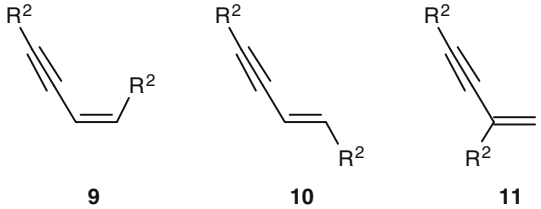


Fig. 3. TGA curves for complex **1**.



9 **10** **11**

Scheme 5. Dimerization products of 1-hexyne ($R^2 = n\text{-}C_4H_9$).

noteworthy was the observation that the formation of enol esters was not selective and that the selectivities changed over reaction time when complexes **1**–**4** were employed as catalyst precursors (Fig. 2 and Fig. Sd1). Thus, in all cases, the amount of the Markovnikov adduct (**5**) slightly increased over reaction time, concomitantly with the decrease of the (*Z*)-*anti*-Markovnikov isomer (**6**). The changes in the thermodynamically more stable (*E*)-*anti*-Markovnikov isomer (**7**) are, however, more difficult to rationalize. These observations strongly contrast with those made when [$RuCl_2$(*p*-cymene)(PPh_3)] (**8**) was used as the catalyst precursor. With the latter system, indeed, the reaction showed a high and constant selectivity for the Markovnikov product (up to 96%) throughout the run (Fig. Sd1).

Over the past decade, microwave heating has proven to be a useful tool for rapid compound synthesis [10] and has found application in catalysis [11]. Pursuing our research program [9], we carried out the synthesis of vinyl esters in a sealed vessel heated at 160 °C in a CEM Discover monomode microwave reactor. We found that as expected microwave-assisted syntheses catalyzed by **1**–**4** were much faster than related experiments performed under conventional heating at 60 °C. The reaction times, indeed, could be reduced from several hundreds of hours at 60 °C to around 4 h under microwave heating at 160 °C (Fig. 4 and Fig. Sd3). Because of the ongoing debate over non-thermal microwave effects [12], we decided to perform similar reactions in sealed tubes immersed in a thermostatically controlled silicon oil heating bath kept at 160 °C. Contrary to our previous observations [9a], we observed that the reactions were twice as fast under conventional heating than under microwave heating (Fig. 4 and Table 2). It is also noteworthy that at 160 °C the reaction rates were found not to be significantly influenced by the substituents of the imidazol(in)ium fragment, contrary to the selectivities, which again changed over reaction time (Fig. 5 and Table 2).

We have previously shown that although imidazol(in)ium-2-dithiocarboxylates are stable compounds, they slowly decompose in the solid state upon thermal activation, more likely releasing carbene ligands [3]. As a consequence, we believe that the changes in the selectivities might be due to the involvement of a new catalytic species produced during the decomposition of the coordinated imidazol(in)ium-2-dithiocarboxylate ligands in complexes **1**–**4** when heated to 60 °C for an extended time, or to 160 °C for a few hours. To substantiate this hypothesis, we investigated the catalytic activity of three [$RuCl_2$(*p*-cymene)(NHC)] complexes, **12**–**14** (Scheme 6), for the synthesis of enol esters.

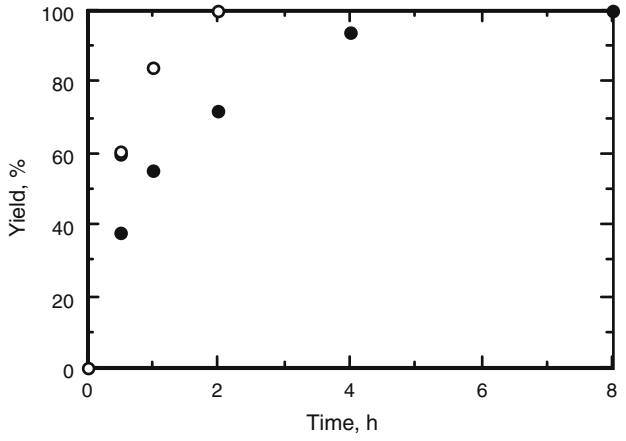


Fig. 4. Influence of the heating mode on the enol ester yield for reactions between 4-acetoxybenzoic acid and 1-hexyne catalyzed by complex **1** at 160 °C. Conventional heating in an oil bath (○); microwave heating (●). Reaction conditions: 4-acetoxybenzoic acid, 0.5 mmol; 1-hexyne, 0.75 mmol; catalyst, 4×10^{-3} mmol; Na_2CO_3, 8×10^{-3} mmol; water-saturated toluene, 2.6 mL; temperature, 160 °C under nitrogen.

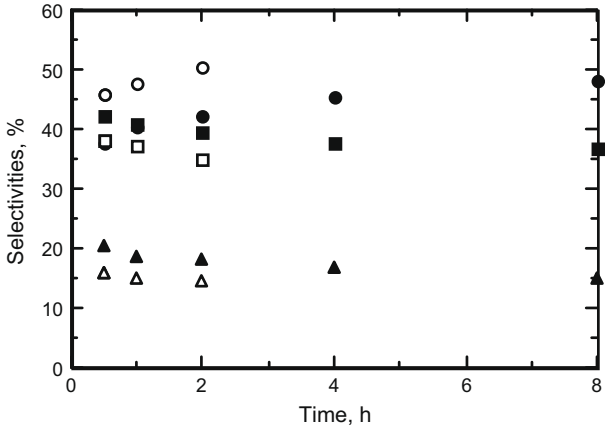
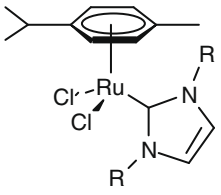


Fig. 5. Influence of the heating mode on the enol ester selectivities for reactions between 4-acetoxybenzoic acid and 1-hexyne catalyzed by complex **1** at 160 °C. Conventional heating in an oil bath (○,□,△); microwave heating (●,■,▲). Enol esters: **5** (○,●), **6** (□,■), and **7** (△,▲). Reaction conditions: 4-acetoxybenzoic acid, 0.5 mmol; 1-hexyne, 0.75 mmol; catalyst, 4×10^{-3} mmol; Na_2CO_3, 8×10^{-3} mmol; water-saturated toluene, 2.6 mL; temperature, 160 °C under nitrogen.

Table 2
Microwave heating vs. conventional heating for reactions between 4-acetoxybenzoic acid and 1-hexyne catalyzed by complexes **1**–**4**, **8**, and **12**–**14** at 160 °C[a].

Complex	Microwave heating				Conventional heating			
	Yield (%)[e]	Selectivities (%)[f]			Yield (%)[e]	Selectivities (%)[f]		
		5	**6**	**7**		**5**	**6**	**7**
1[b]	38	38	42	20	60	46	38	16
2[b]	43	23	46	31	70	31	43	26
3[b]	46	16	56	28	80	28	46	26
4[b]	43	18	56	26	64	25	42	33
8[c]	100	87	10	3	–	–	–	–
12[d]	74	74	21	5	58	73	23	4
13[d]	72	66	29	5	61	64	31	5
14[d]	74	69	23	8	62	67	25	8

[a] Reaction conditions: 4-acetoxybenzoic acid, 0.5 mmol; 1-hexyne, 0.75 mmol; catalyst, 4×10^{-3} mmol; Na_2CO_3, 8×10^{-3} mmol; water-saturated toluene, 2.6 mL; temperature, 160 °C under nitrogen.
[b] Reaction time, 30 min.
[c] Reaction time, 5 min.
[d] Reaction time, 10 min.
[e] Determined by GC using dodecane as internal standard.
[f] Determined by GC.



12 (R = Mes)
13 (R = Dip)
14 (R = Cy)

Scheme 6. Structure of the [$RuCl_2$(*p*-cymene)(NHC)] complexes **12**–**14** used in this work.

During the past decade or so, Ru–NHC complexes have emerged as effective catalysts for a variety of reactions [13], including olefin metathesis [14]. To the best of our knowledge, however, only a few studies have been reported on the use of Ru–NHC catalysts for the synthesis of enol esters [15]. Not surprisingly, in these reactions both the yields and the selectivities strongly depended on the catalyst's structure (Scheme 7). In particular, ruthenium complexes bearing the 1,3,4-triphenyl-4,5-dihydro-1*H*-1,2,4-triazol-5-ylidene ligand (**15**–**18**) generally favored the *anti*-Markovnikov isomers [15a,d,e], whereas ruthenium–vinylidene complexes (**20** and **21**) produced selectively the Markovnikov adduct [15b,c]. Furthermore, with Ru–NHC complexes bearing Schiff base ligands (**22**), enyne formation took precedence of enol ester synthesis [15f].

Having in hand [$RuCl_2$(*p*-cymene)(NHC)] complexes **12**–**14** [8], the test-reaction between 4-acetoxybenzoic acid and 1-hexyne was first investigated at 60 °C, using the experimental conditions described above. It turned out that Ru–NHC complexes **12**–**14** displayed a higher activity than ruthenium imidazol(in)ium-2-dithiocarboxylates **1**–**4** (Fig. 1 and Table 1). Thus, with catalysts **12** and **13** bearing, respectively, a mesityl and a 2,6-diisopropylphenyl group on the nitrogen atoms, the reactions proceeded to quantitative yields in 200 h, against 50 h with the cyclohexyl-substituted catalyst **14**. The reactions were further accelerated at 160 °C, either

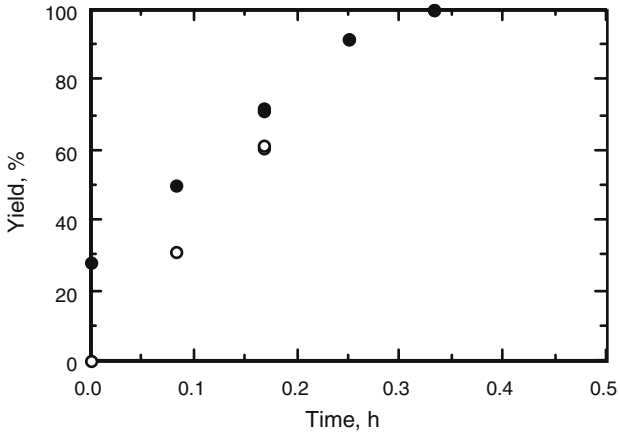
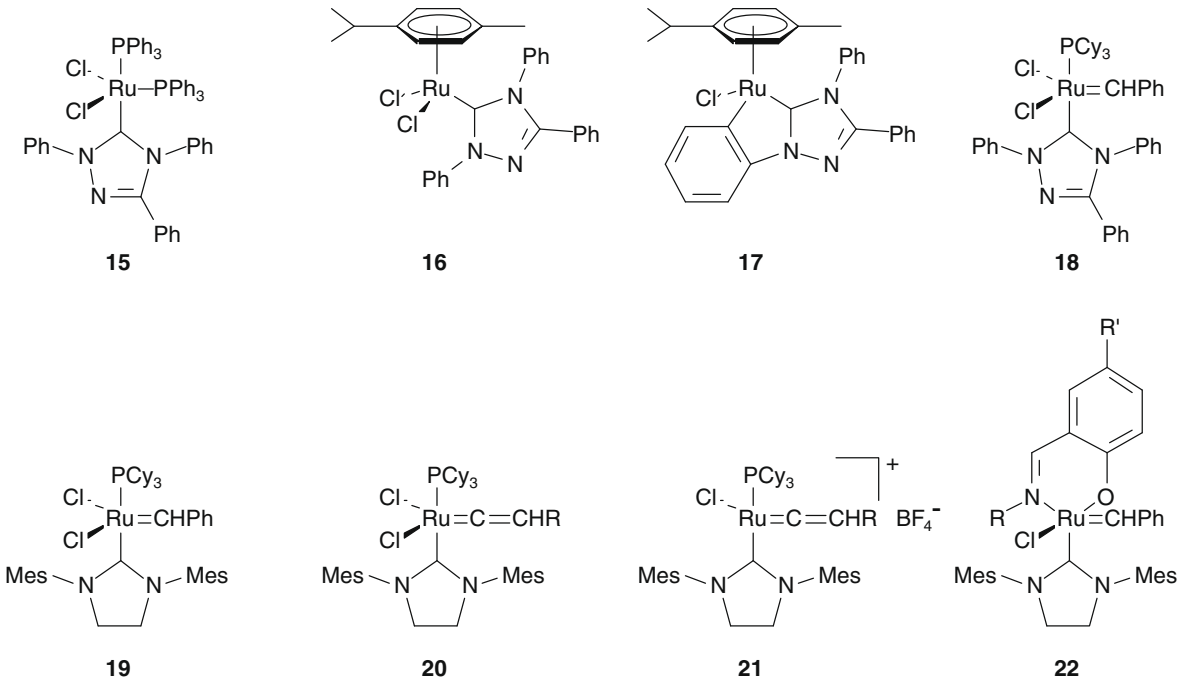


Fig. 6. Influence of the heating mode on the enol ester yield for reactions between 4-acetoxybenzoic acid and 1-hexyne catalyzed by complex **13** at 160 °C. Conventional heating in an oil bath (○); microwave heating (●). Reaction conditions: 4-acetoxybenzoic acid, 0.5 mmol; 1-hexyne, 0.75 mmol; catalyst, 4×10^{-3} mmol; Na_2CO_3, 8×10^{-3} mmol; water-saturated toluene, 2.6 mL; temperature, 160 °C under nitrogen.

under microwave heating or under conventional heating (Table 2 and Figs. Sd2 and Sd3), with a reaction time of 20 min for the reactions to be complete. It is also notable that at 160 °C complexes **12**–**14** behaved similarly in terms of catalytic activity. Under microwaves, for instance, the additions were 72–74% complete over 10 min, regardless of the substituents on the carbene ligand.

We also investigated in detail microwave-assisted and conventionally heated syntheses of enol esters at 160 °C under otherwise identical conditions (stock solution, concentration, etc.). As illustrated in Fig. 6, both heating modes led to different reactivity profiles that converged to the same point, i.e. 100% yield after 20 min of reaction. In Fig. 6, it is also observed that for the microwave-assisted reactions the origin is not intercepted in the plot of yield against time. Thus, the experiment performed during 0 min revealed already 28% yield of enol esters! For the sake of understand-



Scheme 7. Structure of Ru–NHC catalyst precursors for the synthesis of enol esters.

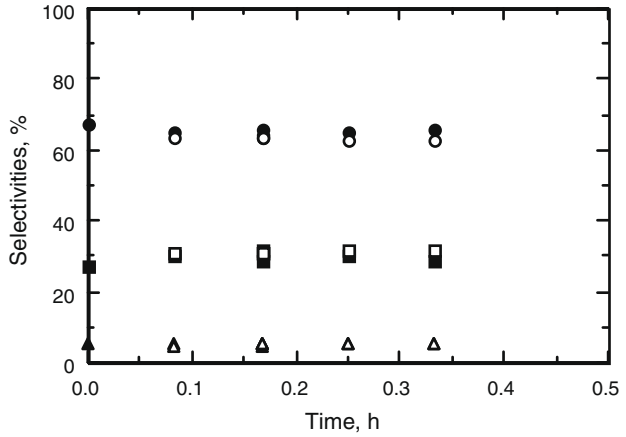


Fig. 7. Influence of the heating mode on the enol ester selectivities for reactions between 4-acetoxybenzoic acid and 1-hexyne catalyzed by complex **13** at 160 °C. Conventional heating in an oil bath (○,□,△); microwave heating (●,■,▲). Enol esters: **5** (○,●), **6** (□,■), and **7** (△,▲). Reaction conditions: 4-acetoxybenzoic acid, 0.5 mmol; 1-hexyne, 0.75 mmol; catalyst, 4×10^{-3} mmol; Na_2CO_3, 8×10^{-3} mmol; water-saturated toluene, 2.6 mL; temperature, 160 °C under nitrogen.

ing, it is worth mentioning that the CEM Discover microwave instrument is programmed so as $t = 0$ when the desired temperature is attained and not as expected when irradiation starts. The yield of 28% mentioned above is therefore related to the time that the microwave reactor takes to reach 160 °C the desired temperature [16]. On the other hand, when the syntheses of enol esters were performed under conventional heating, the reactions started with the immersion of the sealed tube in the oil bath and the yield was obviously zero at time $t = 0$. In light of these results and taking into account the temperature problems inherent to both methods, it is likely that conventionally heated reactions are slightly faster than the microwave-heated protocols, as noted above for catalysts **1**–**4** (Fig. 4). It is also worth mentioning that for conventional heating experiments performed at 160 °C based on the temperature of the oil bath, the actual temperature of the reaction mixture is slightly lower, which might result in an extended lifetime of the catalyst compared to reactions carried out in the microwave reactor where the temperature of 160 °C is that of the solution, as determined by the infrared sensor calibrated at regular time intervals.

We also observed that with catalysts **12**–**14** the selectivities depended, not only on the substituents on the carbene ligand, but also on the temperature. Thus, the selectivities for the Markovnikov isomer (**5**) were always ~10% lower at 160 °C than at 60 °C. Furthermore, the selectivities in enol esters remained constant throughout the run (Figs. 2 and 7, and Fig. Sd1–3), as with [$RuCl_2$(*p*-cymene)(PPh_3)] (**8**) [9a].

Because we suspected that the changes in selectivities observed with complexes **1**–**4** could be caused by a partial decomposition of the imidazol(in)ium-2-dithiocarboxylate ligand, releasing the carbene and carbon disulfide, the efficacy of [$RuCl_2$(*p*-cymene)(NHC)] complexes **12**–**14** was tested in the presence of added CS_2. Interestingly, the reactions were not inhibited by CS_2, and the selectivities slightly decreased (Table Sd1). It was then investigated whether the addition of silver salts with non-coordinating counter-ions to ruthenium imidazol(in)ium-2-dithiocarboxylates **1**–**4** would generate more active cationic catalysts. To this end, silver tetrafluoroborate was elected as chloride scavenger. Addition of 1 to 3 equiv. of $AgBF_4$ (relative to complex **2**) to the reaction mixture significantly affects neither the yield, nor the selectivities (Table Sd1). By contrast, a deleterious effect was evidenced when complex **2** and Na_2CO_3 were first treated with $AgBF_4$ in acetonitrile for 30 min, before addition of the reaction mixture.

4. Conclusions

In comparison with [$RuCl_2$(*p*-cymene)(NHC)] and, in particular, [$RuCl_2$(*p*-cymene)(PPh_3)] (a standard catalyst in this field), ruthenium imidazol(in)ium-2-dithiocarboxylates **1**–**4** are poor catalyst precursors for the synthesis of enol esters from carboxylic acids and terminal alkynes. The results are in line with those reported previously in ring-opening metathesis and atom transfer radical polymerizations using catalyst systems generated in situ from the ruthenium dimer [$RuCl_2$(*p*-cymene)]$_2$ and imidazol(in)ium-2-dithiocarboxylates. However, the catalytic activity could be improved significantly at 160 °C under microwave heating or under conventional heating in sealed tubes, as indicated by the reduction of the reaction times from hundreds of hours at 60 °C to 4 h or less at 160 °C. Furthermore, the selectivities in enol esters are not satisfactory and, in addition, they change over reaction time, indicating that the primary catalytic species are presumably transformed into other ones during the reactions. Applications of these complexes to other metal-catalyzed reactions are currently under investigation in our group.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.08.028.

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