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Synthesis and catalytic properties of 1-alkylperimidineruthenium (II) complexes

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Abstract

Four new [$RuCl_2$(perimidine)(*p*-cymene)] complexes have been prepared and characterized. Upon reaction with 1,1-diphenylprop-2-yn-1-ol they generate catalyst precursors, which perform the cycloisomerization of diallyltosylamide into *N*-tosyl-α-methylenepyrrolidine.

Keywords: Perimidine; Olefin isomerization; Ruthenium complexes; Cycloisomerization

1. Introduction

The transition metal complexes with nitrogen-containing ligands have recently shown their potential to perform selective catalytic transformations of molecules with atom economy [1]. Especially, a variety of [RuX_2(arene)(L)] complexes are promoting catalytic reactions such as nucleophilic addition to triple bonds to form furans (L = imidazoline, tetrahydropyrimidine [2], benzimidazole [3]), hydrogen transfer (L = amino acid [4], amino alcohol [5]), cyclopropanation (L = diamine [6]), or Diels–Alder cycloaddition and Claisen rearrangement (L = bisoxazoline [7,8]). It is also well established that [$RuCl_2$(arene)(L)] complexes can easily be transformed via activation of propargylic alcohols into cationic ruthenium allenylidene complexes, which have shown catalytic properties in olefin metathesis [9].

Transition metal catalyzed cycloisomerization reactions from α,ω-dienes is a topic of current interest [10]. The formation of α-methylenecyclopentane derivatives of type **2** has already been observed with several metal catalysts including palladium [11,12], nickel [12], rhodium [13] and titanium [14]. Other efficient catalytic systems based on ruthenium precursors such as $[Ru(cod)Cl_2]_n$ in protic solvents [15], or generated in situ from $[RuCl_2(p\text{-cymene})]_2$, an imidazolinium salt and a base [16] have been reported.

We now report: (i) the straightforward preparation of new $RuCl_2$(*p*-cymene)(L) complexes with a *N*-coordinated perimidine ligand; and (ii) their in situ transformation into efficient catalysts for cycloisomerization of diallyltosylamide into *N*-tosyl-α-methylenepyrrolidine (Scheme 1).

2. Results and discussion

The complex $[RuCl_2(p\text{-cymene})]_2$ was prepared according to known methods [17]. 1-Substituted perimidines **5** were prepared according to the literature [18,19]. The reaction of *N*-alkylperimidine (**5a**–**d**) with the binuclear $[RuCl_2(p\text{-cymene})]_2$ (**4**) complex proceeded smoothly in refluxing toluene to give the $RuCl_2$(perimidine)(arene) complexes (**6a**–**d**) as crystalline solids in 83–92% yields (Scheme 2).

Complexes **6a**–**d**, which are very stable in the solid state, have been characterized by analytical and spectroscopic techniques (Table 1). The IR data show the presence of a C=N bond with a υ(C=N) vibration at 1629–1634 cm^{-1}, and the ^1H NMR spectra clearly exhibit a singlet at 8.00–8.45 ppm

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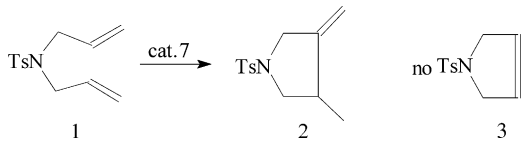
Table 1
Selected analytical data for the new perimidine ruthenium complexes (**6a–d**)

Complex	Isolated yield (%)	mp (°C)	$\nu_{(C=N)}$ (cm^{-1})	^{13}C NMR C(2), δ (ppm) ($^{1}JC–H$)	^{1}H NMR H(2), δ (ppm)
6a	83	202–203	1629	155.3 (206.6 Hz)	8.00
6b	90	228–229	1631	152.2 (208.3 Hz)	8.45
6c	92	177–178	1633	154.9 (204.7 Hz)	8.20
6d	86	195–196	1634	156.5 (207.3 Hz)	8.02



Scheme 1.

typical of the N=C*H*–N fragment. In ^{13}C NMR, the chemical shift of the corresponding C(2) atom is detected in the region 152.2–156.5 ppm with a $^{1}JC–H$ coupling constant close to 210 Hz. These new complexes show typical spectroscopic signatures which are in line with those recently reported for other $RuCl_2$(arene)(imidazoline) or (benzimidazole) complexes with R = CH_2Ph, Et, $(CH_2)_3Si(OEt)_3$ [2,20,21].

The complexes **6a–d** presented no catalytic activity for the transformation of diallyltosylamide **1** {chlorobenzene (2.5 mL), diallyltosylamide (0.5 mmol), **6** (2.5 mol%, 80 °C, 5 h)}. The known catalytic activities of [RuCl(=C=C=CPh_2)(arene)(L)][X] (L = PCy_3 [9], diaminocarbene [22]) to perform the ring closing metathesis of dienes and ring opening of cyclic olefins, provided impetus to prepare the corresponding cationic ruthenium(allenylidene)(1-alkylperimidine) complexes according to the reaction depicted in Scheme 3. Indeed, purple complexes were prepared in dichloromethane but they were not stable enough to be cleanly isolated and characterized. Their proposed structure **7a–d** is based on previous known preparations of stable ruthenium allenylidene complexes from analogous precursors [9]. However, the subsequent formation of indenylidene complexes via cycloisomerization of the allenylidene ligand, cannot be ruled out [23]. In order to circumvent this instability problem, they were generated in situ from complexes **6a–d** just before use, via abstraction of chloride with silver triflate followed by addition of 1,1-diphenylprop-2-yn-1-ol at room temperature in CH_2Cl_2 (Scheme 3).

The catalytic performances of these in situ generated precursors were evaluated in the transformation of diallyltosylamide (**1**) at 80 °C in chlorobenzene (Scheme 1 and Table 2).

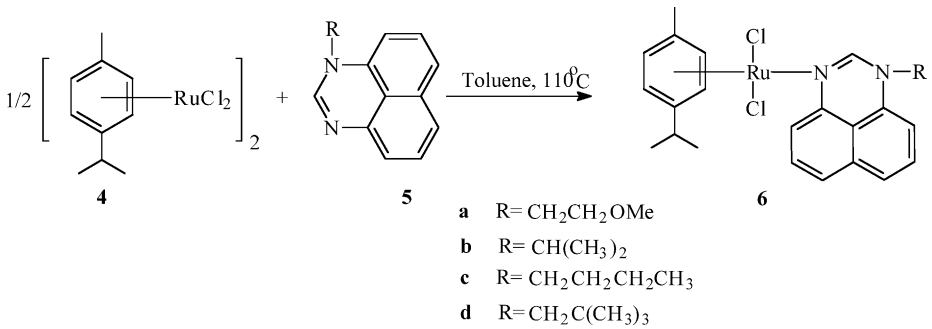
Thus, the catalyst was first generated by successive addition of 0.0125 mmol of silver triflate and 0.0125 mmol of HC≡$CCPh_2OH$ to a solution of 0.0125 mmol (2.5 mol%) of **6a–d** in 2.5 mL of chlorobenzene and stirred at room temperature for 20 min. The diene **1** (0.5 mmol) was then added and the solution was heated at 80 °C for 4–5 h. The in situ prepared complexes **7a–d** led to catalytic activity and to the transformation of the 1,6-diene (**1**) into the cycloisomerization compound **2**. From the results in Table 2, it is evident that the perimidine complex precursor that contains electron donating methoxyethyl substituent (**7a**) is the most effective of the complex examined. The coordinating ability of the alkoxy group may be an important contributor to the increase in reactivity, as has been demonstrated by previous examples [24].

In contrast with the catalyst arising from the allenylidene complex [RuCl(=C=C=CPh_2)(PCy_3)(*p*-cymene)][OTf] [8]

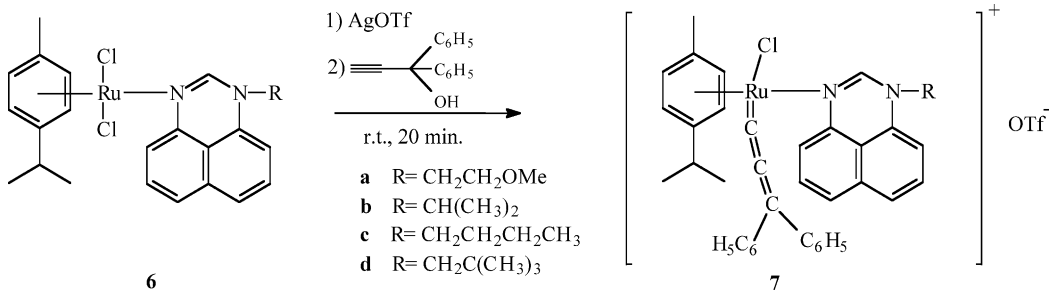
Table 2
Catalytic transformation of diallyltosylamide into *N*-tosyl-α-methylenepyrrolidine[a]

Catalyst precursor	Time (h)	*N*-Tosyl-α-methylenepyrrolidine, **2** (%)[b]
6a	4	98
6b	5	97
6c	5	92
6d	5	96

[a] Conditions: chlorobenzene (2.5 mL), diallyltosylamide (0.5 mmol), 6 (2.5 mol%), AgOTf (2.5 mol%), HC≡$CCPh_2OH$ (2.5 mol%), 80 °C.
[b] Determined by gas chromatography.



Scheme 2. Synthesis of Ru(II)-perimidine complexes.



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Scheme 3.

no trace of **3** was detected, which indicated that no metathesis reaction took place with these precursors **7a–d**.

3. Conclusion

Ruthenium complexes generated in situ from [$RuCl_2$(*p*-cymene)(perimidine)] and 1,1-diphenylprop-2-yn-1-ol are active catalysts to perform the cycloisomerization of 1,6-diallyltosylamide into the *N*-tosylpyrrolidine (**2**) featuring an exocyclic methylene group under neutral and mild conditions. Investigations focusing on the reactivity profile of perimidine and related metal complexes, their efficacy as catalysts in cross-coupling reactions are ongoing in our laboratories.

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