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Synthesis and catalytic properties of 1-alkyl-2-imidazolineruthenium(II) complexes

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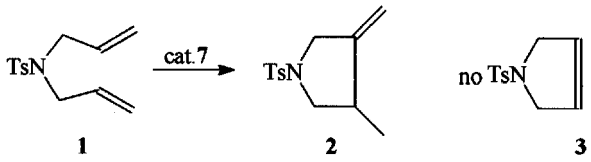
New [$RuCl_2$(imidazoline)(arene)] complexes have been prepared. The complexes were characterized by conventional spectroscopic methods and elemental analyses. Upon reaction with 1,1-diphenylprop-2-ynol they generate catalyst precursors that can perform the cycloisomerization of diallyltosylamide into *N*-tosyl-α-methylenepyrrolidine. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: imidazoline; olefin isomerization; ruthenium complexes; cycloisomerization

INTRODUCTION

Transition-metal complexes with nitrogen-containing ligands have recently shown their potential to perform selective catalytic transformations of molecules with atom economy.[1,2] In particular, a variety of [RuX_2(arene)(L)] complexes has been shown to promote catalytic reactions such as nucleophilic addition to triple bonds to form furans (L = imidazoline, tetrahydropyrimidine,[3] benzimidazole[4]), hydrogen transfer (L = amino acid,[5] amino alcohol[6,7]), cyclopropanation (L = diamine[8]), or Diels–Alder cycloaddition and Claisen rearrangement (L = bisoxazoline[9,10]). 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.[11,12]

Transition-metal-catalysed cycloisomerization reactions from α,ω-dienes are a topic of current interest.[13] The formation of α-methylenecyclopentane derivatives of type **2** (Scheme 1) has already been observed with several metal catalysts, including palladium,[14–16] nickel,[16] rhodium[17,18] and titanium.[19] Other efficient catalytic systems based on ruthenium precursors, such as [Ru(cod)Cl_2]$_n$ or [Cp*Ru(cod)Cl] in protic solvents,[20–22] or generated *in situ* from [$RuCl_2$(*p*-cymene)]$_2$, an imidazolinium salt and a base[23,24] have been reported.



Scheme 1.

We now report (i) the straightforward preparation of new $RuCl_2$(η^6-arene)(L) complexes with an *N*-coordinated imidazoline ligand and (ii) their *in situ* transformation into [RuCl(η^6-arene)(imidazoline)(allenylidene)][OTf] precursors providing efficient catalysts for cycloisomerization of diallyltosylamide into *N*-tosyl-α-methylenepyrrolidine (Scheme 1).

EXPERIMENTAL

Manipulations were prepared with standard Schlenk techniques under an inert atmosphere of nitrogen with previously dried solvents. The complexes [$RuCl_2$(arene)]$_2$ were prepared according to known methods.[25] 1-Substituted imidazolines **5** were prepared according to the literature.[26,27] IR spectra were recorded as KBr pellets in the range 400–4000 cm^{-1} on an ATI UNICAM 2000 spectrometer. ^{1}H NMR (300 MHz) and ^{13}C NMR (75.5 MHz) were recorded on a Bruker AM 300 WB FT spectrometer with chemical shifts referenced to residual solvent $CDCl_3$. Microanalyses were performed by the TÜBITAK analyses centre.

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Preparation of the ruthenium imidazoline complexes 6a–f

A solution of the *N*-substituted imidazoline **5** (1.05 mmol) and $[RuCl_2(p\text{-cymene})]_2$ (**4a**) or $[RuCl_2(\text{hexamethylbenzene})]_2$ (**4b**; 0.5 mmol) in toluene (20 ml) were heated under reflux for 2 h. Upon cooling to room temperature, orange crystals of **6a–f** were obtained. The crystals were filtered, washed with diethyl ether (3 × 15 ml) and dried under vacuum.

$RuCl_2$(p-cymene)(N-(2-methoxyethyl)imidazoline) ***6a***

Yield 0.28 g (65%). ^{1}H NMR ($CDCl_3$): δ 7.15 (s, 1H, NC*H*N), 3.39 (m, 4H, NCH_2CH_2N), 3.53 (t, *J* 9.83, 2H, CH_2CH$_2$OCH$_3$), 4.05 (t, *J* 9.75 2H, CH$_2$CH_2OCH$_3$), 3.27 (s, 3H, CH$_2$CH$_2$OCH_3), 5.21 (d, *J* 5.08) and 5.36 (d, *J* 5.07, 4H, $(CH_3)_2CHC_6H_4CH_3$-*p*), 2.21 (s, 3H, $(CH_3)_2CHC_6H_4CH_3$-*p*), 2.93 (sept, *J* 6.79, 1H, $(CH_3)_2CHC_6H_4CH_3$-*p*), 1.23 (d, *J* 6.76, 6H, $(CH_3)_2CHC_6H_4CH_3$-*p*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 161.2 (NCHN), 47.2, 49.1 (NCH$_2$CH$_2$N), 57.3 (CH$_2$CH$_2$OCH$_3$), 70.4 (CH$_2$CH$_2$OCH$_3$), 58.8 (CH$_2$CH$_2$OCH$_3$), 80.5, 81.2, 96.5, 101.9 ($(CH_3)_2CHC_6H_4CH_3$-*p*), 18.7 ($(CH_3)_2CHC_6H_4CH_3$-*p*), 0.6 ($(CH_3)_2CHC_6H_4CH_3$-*p*), 22.2 ($(CH_3)_2CHC_6H_4CH_3$-*p*). Anal. Found: C, 44.42; H, 6.09; N, 6.70. Calc. for $C_{16}H_{26}Cl_2N_2O$ Ru: C, 44.24, H, 6.03, N, 6.45%.

$RuCl_2$(p-cymene)(N-(phenyl)imidazoline) ***6b***

Yield 0.43 g (96%). ^{1}H NMR($CDCl_3$): δ 7.92 (s, 1H, NC*H*N), 3.89 and 4.27 (t, *J* 10.25 and 10.27, 4H, NCH_2CH_2N), 7.16 (m, 5H, C_6H_5), 2.17 (s, 3H, $(CH_3)_2CHC_6H_4CH_3$-*p*), 5.24 and 5.39 (d, *J* 5.91 and 5.90, 4H, $(CH_3)_2CHC_6H_4CH_3$-*p*), 2.95 (sept, *J* 6.87, 1H, $(CH_3)_2CHC_6H_4CH_3$-*p*), 1.23 (d, *J* 6.94, 6H, $(CH_3)_2CHC_6H_4CH_3$-*p*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 155.5 (NCHN), 47.32, 57.35 (NCH$_2$CH$_2$N), 115.2, 123.3, 129.6, 138.3 (C_6H_5), 18.8 ($(CH_3)_2CHC_6H_4CH_3$-*p*), 81.4, 81.8, 96.9, 102.6 ($(CH_3)_2CHC_6H_4CH_3$-*p*), 30.8 ($(CH_3)_2CHC_6H_4CH_3$-*p*), 22.3 ($(CH_3)_2CHC_6H_4CH_3$-*p*). Anal. Found: C, 50.30; H, 5.26; N, 6.29. Calc. for $C_{19}H_{24}Cl_2N_2Ru$: C, 50.44; H, 5.35; N, 6.19%.

$RuCl_2$(p-cymene)(N-(2,4,6-trimethylbenzyl) imidazoline) ***6c***

Yield 0.48 g (94%). ^{1}H NMR ($CDCl_3$): δ 7.17 (s, 1H, NC*H*N), 3.27 and 3.99 (t, *J* 10.17 and 10.02, 4H, NCH_2CH_2N), 6.78 (s, 2H, 2,4,6-$(CH_3)_3C_6H_2CH_2$), 4.23 (s, 2H, 2,4,6-$(CH_3)_3C_6H_2CH_2$), 2.18, 2.19 (s, 9H, 2,4,6-$(CH_3)_3C_6H_2CH_2$), 2.13 (s, 3H, $(CH_3)_2CHC_6H_4CH_3$-*p*), 5.13 (d, *J* 5.95) and 5.30 (d, *J* 5.55, 4H, $(CH_3)_2CHC_6H_4CH_3$-*p*), 2.89 (sept, *J* 6.90, 1H, $(CH_3)_2CHC_6H_4CH_3$-*p*), 1.19 (d, *J* 6.93, 6H, $(CH_3)_2CHC_6H_4CH_3$-*p*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 160.9 (NCHN), 45.3, 48.0 (NCH$_2$CH$_2$N), 127.9, 129.5, 137.4, 138.0 (2,4,6-$(CH_3)_3C_6H_2CH_2$), 57.2 (2,4,6-$(CH_3)_3C_6H_2CH_2$), 19.9, 20.9 (2,4,6-$(CH_3)_3C_6H_2CH_2$), 80.8, 81.9, 96.8, 101.8 ($(CH_3)_2CHC_6H_4CH_3$-*p*), 18.7 ($(CH_3)_2CHC_6H_4CH_3$-*p*), 30.7 ($(CH_3)_2CHC_6H_4CH_3$-*p*), 22.2 ($(CH_3)_2CHC_6H_4CH_3$-*p*). Anal. Found: C, 54.46; H, 6.12; N, 5.71. Calc. for $C_{23}H_{32}Cl_2N_2Ru$: C, 54.33; H, 6.34; N, 5.51%.

$RuCl_2$(hexamethylbenzene)(N-(2-methoxyethyl) imidazoline) ***6d***

Yield 0.41 g (89%). ^{1}H NMR ($CDCl_3$): δ 8.24 (s, 1H, NC*H*N), 3.39 (m, 4H, NCH_2CH_2N), 3.42 (m, 2H, CH_2CH$_2$OCH$_3$), 3.48 (m, 2H, CH$_2$CH_2OCH$_3$), 3.31 (s, 3H, CH$_2$CH$_2$OCH_3), 2.03 (s, 18H, $C_6(CH_3)_6$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 162.1 (NCHN), 46.6, 47.7 (NCH$_2$CH$_2$N), 54.2 (CH$_2$CH$_2$OCH$_3$), 70.3 (CH$_2$CH$_2$OCH$_3$), 58.6 (CH$_2$CH$_2$OCH$_3$), 92.5 ($C_6(CH_3)_6$), 13.5 ($C_6(CH_3)_6$). Anal. Found: C, 46.39; H, 6.34; N, 6.27. Calc. for $C_{18}H_{30}Cl_2N_2ORu$: C, 46.75; H, 6.54; N, 6.06.

$RuCl_2$(hexamethylbenzene)(N-(phenyl) imidazoline) ***6e***

Yield 0.42 g (88%). ^{1}H NMR ($CDCl_3$): δ 7.81 (s, 1H, NC*H*N), 3.79 and 4.07 (t, *J* 10.17 and 10.19, 4H, NCH_2CH_2N), 7.21 (m, 5H, C_6H_5), 2.03 (s, 18H, $C_6(CH_3)_6$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 154.6 (NCHN), 47.0, 53.6 (NCH$_2$CH$_2$N), 114.9, 123.1, 129.7, 138.5 (C_6H_5), 90.8 ($C_6(CH_3)_6$), 15.9 ($C_6(CH_3)_6$). Anal. Found: C, 52.41; H, 5.89; N, 5.90. Calc. for $C_{21}H_{28}Cl_2N_2Ru$: C, 52.50; H, 5.87; N, 5.83%.

$RuCl_2$(hexamethylbenzene)(N-(2,4,6-trimethylbenzyl) imidazoline) ***6f***

Yield 0.37 g (69%). ^{1}H NMR ($CDCl_3$): δ 7.09 (s, 1H, NC*H*N), 3.18 and 3.21 (t, *J* 10.11, 4H, NCH_2CH_2N), 6.79 (s, 2H, 2,4,6-$(CH_3)_3C_6H_2CH_2$), 4.21 (s, 2H, 2,4,6-$(CH_3)_3C_6H_2CH_2$), 2.18, 2.21 (s, 9H, 2,4,6-$(CH_3)_3C_6H_2CH_2$), 1.94 (s, 18H, $C_6(CH_3)_6$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 159.8 (NCHN), 45.4, 48.0 (NCH$_2$CH$_2$N), 128.2, 129.0, 129.5,

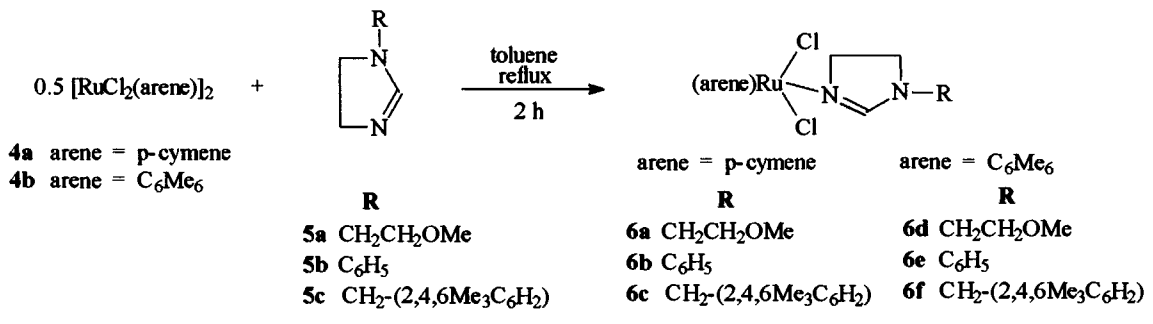
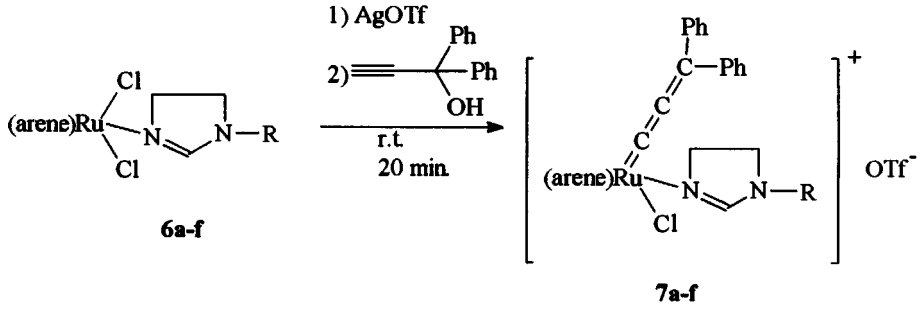


Figure 1. Synthesis of ruthenium (II)–imidazoline complexes.

Table 1. Selected analytical data for the new imidazoline ruthenium complexes (**6a–f**)

Complex	Isolated yield (%)	M.p. (°C)	$V_{(C=N)}$ (cm^{-1})	^{13}C NMR, C(2) δ(ppm)[1]	^{13}C NMR, C(2) $J_{C-H}(H_3)$	^{1}H NMR, H(2)δ(ppm)
6a	65	142–143	1608	161.2	195.4	7.15
6b	96	199–200	1591	155.5	197.4	7.92
6c	94	209–210	1614	160.9	198.2	7.17
6d	89	149–150	1608	162.1	196.3	8.24
6e	88	296–297	1614	154.6	200.3	7.81
6f	69	182–183	1620	159.8	198.9	7.09



Scheme 2.

137.2 (2,4,6-$(CH_3)_3C_6H_2CH_2$), 53.3 (2,4,6-$(CH_3)_3C_6H_2CH_2$), 19.9, 21.0 (2,4,6-$(CH_3)_3C_6H_2CH_2$), 90.5 ($C_6(CH_3)_6$), 15.7 ($C_6(CH_3)_6$). Anal. Found: C, 56.04; H, 6.83; N, 5.18. Calc. for $C_{25}H_{36}Cl_2N_2Ru$: C, 55.96; H, 6.76; N, 5.22%.

RESULTS AND DISCUSSION

The reaction of *N*-alkylimidazolines and the *N*-aralkylimidazoline **5a–c** with the binuclear $[RuCl_2(p\text{-cymene})]_2$ (**4a**) and $[RuCl_2(\text{hexamethylbenzene})]_2$ (**4b**) complexes proceeded smoothly in refluxing toluene to give the $RuCl_2$(imidazoline)(arene) complexes **6a–f** as crystalline solids in 65–96% yields (Fig. 1).

Complexes **6a–f**, 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 ν(C=N) vibration at 1591–1620 cm^{-1}, and the ^1H NMR spectra clearly exhibit a singlet at 7.09–8.24 ppm typical of the N=C*H*–N fragment. In ^{13}C NMR, the chemical shift of the corresponding C(2) atom was detected in the region 154.6–162.1 ppm with a $^1J_{C-H}$ coupling constant close to 200 Hz. These new complexes show typical spectroscopic signatures that are in line with those recently reported for other $RuCl_2$(arene)(imidazoline) complexes with R = CH_2Ph, Et, $(CH_2)_3Si(OEt)_3$.[3,27–29]

These complexes 6a–f presented no catalytic activity for the transformation of diallyltosylamide (**1**). The known catalytic activities of [RuCl(=C=C=CPh_2)(arene)(L)][X] (L = PCy_3,[11,12] diaminocarbene.[30,31]) to perform the ring-closing metathesis of dienes and ring opening of cyclic olefins, provided impetus to prepare the corresponding cationic ruthenium(allenylidene)(imidazoline) complexes according to the reaction depicted in Scheme 2. Indeed, purple complexes were prepared in dichloromethane but they were not stable enough to be isolated cleanly and characterized. The proposed structures of 7a–f and based on previous known preparations of stable ruthenium allenylidene complexes from analogous precursors.[11,12] However, the subsequent formation of indenylidene complexes via cycloisomerization of the allenylidene ligand, cannot be ruled out.[32] In order to circumvent this instability problem, they were generated *in situ* from complexes 6a–f just before use, via abstraction of chloride with silver triflate followed by addition of 1,1-diphenylprop-2-ynol at room temperature in CH_2Cl_2 (Scheme 2). The catalytic performances of these precursors generated *in situ* were evaluated in the transformation of diallyltosylamide (**1**) at 80 °C in chlorobenzene (Scheme 1, Table 2).

Thus, the catalyst was first generated by successive additions 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–f 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 8–12 h. The 7a–f prepared *in situ* complexes led to catalytic activity and to the transformation of the 1,6-diene 1 into the cycloisomerization compounds **2**.

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

Catalyst	Time (h)	*N*-Tosyl-α-methylene-pyrrolidine (**2**) (%)[b]
7a	10	89
7b	10	83
7c	8	95
7d	12	72
7e	12	66
7f	12	77

[a] Conditions: chlorobenzene (2.5 ml), diallyltosylamide (0.5 mmol), **6** (2.5 mmol%), AgOTf (2.5 mol%), $HC{\equiv}CCPh_2OH$ (2.5 mol%), 80 °C.
[b] Determined by gas chromatography and purity of yield check by NMR.

In contrast to the catalyst arising from the allenylidene complex $[RuCl(=C=C=CPh_2)(PCy_3)(p\text{-cymene})][OTf]$,[10] no trace of **3** was detected, which indicated that no metathesis reaction took place with these precursors **7a**–**f**.

CONCLUSION

From readily available starting materials, such as 1-alkyl-2-imidazoline or 1-alkylbenzimidazole, six new *N*-coordinated ruthenium complexes (6a–f) have been prepared and characterized. The new ruthenium(imidazoline)(allenylidene) complexes generated *in situ* 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.

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