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Cationic ruthenium allenylidene complexes as a new class of performing catalysts for ring closing metathesis

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Published on 01 January 1998 on http://pubs.rsc.org | doi:10.1039/A803286F

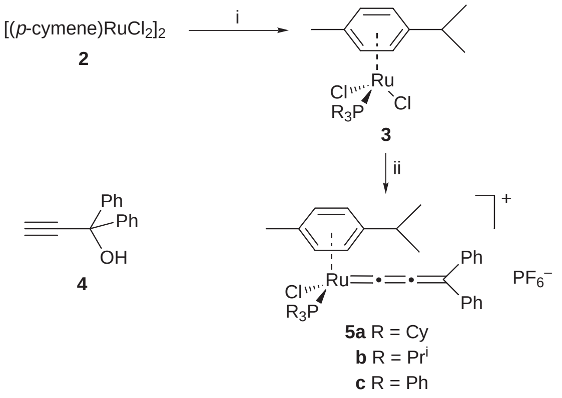
Cationic allenylidene ruthenium complexes [Ru=C=C=CR$_2$(L)(Cl)(arene)]PF$_6$ (L = PCy$_3$, PPr$^i{}_3$), easily prepared from RuCl$_2$(L)(*p*-cymene), prop-2-yn-1-ol and NaPF$_6$, are found to be excellent catalyst precursors for ring closing olefin metathesis.

The recent development of a new generation of well-defined catalysts precursors for olefin metathesis has had a tremendous impact on progress in this field.[1,2] Most popular among them are the *neutral 16-electron* ruthenium carbene complexes Cl$_2$(PCy$_3$)$_2$Ru=CHR (**1a**: R = Ph, **1b** R = —CH=CPh$_2$) described by Grubbs[3] which are distinguished by excellent activity as well as good compatibility with various functional groups in the substrates. Since these catalysts are fairly stable against oxygen and moisture, they represent a simple yet efficient tool for advanced organic synthesis and polymer chemistry. A major drawback, however, resides in the use of either diazoalkanes or diphenylcyclopropene for the preparation of these complexes, *i.e.* reagents which are hazardous or rather difficult to make, respectively. However, an improvement of the synthesis of complexes **1** synthesis has just been achieved starting from Ru(H)(H$_2$)Cl(PCy$_3$)$_2$.[4]

We now describe a new class of efficient single-component catalyst for ring closing olefin metathesis: the *cationic 18-electron* allenylidene ruthenium complexes [Ru=C=C=CR$_2$(PR$_3$)(Cl)(arene)]PF$_6$ **5**, easily available in three steps from RuCl$_3$.*x*H$_2$O, which also provide an unprecedented example of the involvement of metal allenylidene complexes in catalysis.[5]

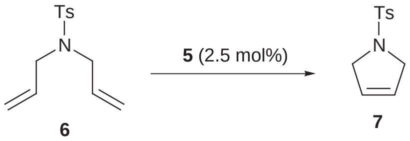
The 18-electron complexes of the general formula (η^6-arene)RuCl$_2$(PR$_3$) such as **3**, which are readily obtained from commercially available [(η^6-arene)RuCl$_2$]$_2$ **2** upon addition of a phosphine,[6] are very active in catalytic transformations of alkynes,[7] but exhibit only very low catalytic activity for ring opening metathesis polymerization (ROMP) of strained cycloalkenes and ring closing metathesis (RCM). However, they can be activated either upon addition of diazoalkanes[8] or by *in situ* irradiation with UV light.[9] A route has been designed in order to straightforwardly introduce around a Ru(+2) site only *one* bulky phosphine, *one* cumulenylidene ligand attached to the metal *via* a Ru=C bond, and *one* easy to displace *p*-cymene group, three likely conditions to produce an active olefin metathesis catalyst precursor. As the activation of prop-2-yn-1-ols with selected ruthenium precursors has been shown to give the Ru=C=C=CR$_2$ moiety,[10] complexes **3** were reacted with a prop-2-ynyl alcohol such as **4** in the presence of NaPF$_6$ in MeOH at ambient temperature and cleanly led to the formation of the cationic allenylidene complexes **5a-c**, isolated in high yields as violet powders (Scheme 1). It is noteworthy that the corresponding salts with less bulky R$_3$P groups existed only as transient allenylidene intermediates *in situ* adding methanol to give methoxycarbene [Ru=C(OMe)CH=CR$_2$] complexes[11] which are inactive as olefin metathesis catalysts.

A preliminary assessment of the performance of these complexes in ring closing metathesis revealed a strong correlation with the nature of the chosen phosphine. In line with



Scheme 1

Table 1 Screening of the catalytic activity of the allenylidene complexes **5**[a]



6 **7**

Entry	Catalyst	Solvent	Additive	*T*/°C	*t*/h	Yield (%)[b]
1	**5c**	toluene	—	80	3	2
2	**5b**	toluene	—	80	3	66
3	**5b**	CH$_2$Cl$_2$	—	40	26	95 (76)
4	**5a**	toluene	—	80	3	79
5	**5a**	toluene	—	80	4	100 (83)
6	**5a**	toluene	PCy$_3$ (5%)[c]	80	3	31

[a] General conditions: diene (1 mmol), catalyst (0.025 mmol), solvent (5 ml). [b] GC yield (isolated yield). [c] Based on the diene.

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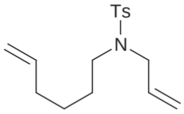
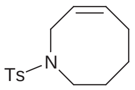
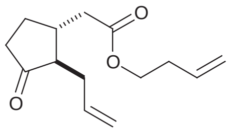
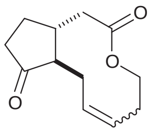
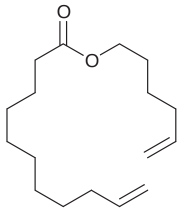
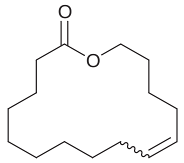
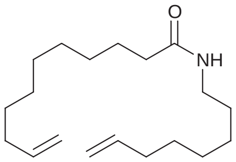
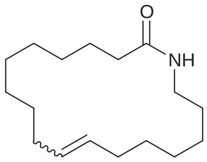
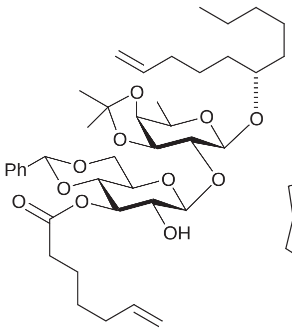
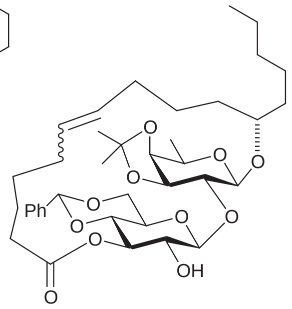
Table 2 Ring closing metathesis employing Ru-allenylidene catalyst **5a**[a]

Substrate	Product	Yield (%)
 **8**	 **9**	75
 **10**	 **11**	40
 **12**	 **13**	90
 **14**	 **15**	73
 **16**	 **17**	85

[a] All reactions using **5a** were carried out in toluene at 80 °C using a catalyst loading of 5 mol%.

previous observations with ruthenium-based initiators,[3,8,9] their catalytic activity decreases in the order $PCy_3 > PPr^i_3 \gg PPh_3$ (Table 1). With **5a** (2.5 mol%) as the catalyst, diene **6** is quantitatively cyclized to dihydropyrrole **7** after 4 h in toluene at 80 °C (entry 5). Dichloromethane can also be used, although the turnover frequency of **5** is slightly lower in this particular reaction medium at 40 °C (*cf.* entries 2 and 3).

Having established the optimum reaction conditions, we applied catalyst **5a** to RCM of a set of representative diene substrates. As can be seen from the results compiled in Table 2, this catalyst nicely applies to the formation of essentially all ring sizes ⩾ 5, including macrocyclic and medium sized products. The isolated yields obtained were found to be good to excellent and are comparable to those previously obtained using the Grubbs carbenes **1** [**9**: 75% *vs.* (68%);[12] **13**: 90% *vs.* (79%);[2c] **15**: 73% *vs.* 83%;[2a] **17**: 85% *vs.* 77%[2d]]. Only in the case of the 10-membered ring of jasmine ketolactone **11**, did the allenylidene complex **5a** turn out to be somewhat less efficient [**11**: 40% *vs.* (86%)[13]].

Particularly noteworthy are the smooth cyclizations of the conformationally flexible dienes **12** and **14** to 16- and 18-membered cycloalkenes **13** and **15**, respectively. The hydrogenation of compound **13** under standard conditions leads to the macrocyclic musk exaltolide,[14] which is used as a valuable perfume ingredient. Disaccharide **17** is an advanced intermediate *en route* to tricolorin A, a carcinostatic resin glycoside isolated from *Ipomoea tricolor*.[2d] The examples summarized in Table 2 clearly highlight the excellent compatibility of the allenylidene catalyst **5a** with various functional groups, including even unprotected secondary hydroxy groups.

Although the mode of action of these new metathesis catalysts and the nature of the actual intermediates involved in the catalytic cycle require further indepth studies, we have shown that the addition of an excess of PCy_3 strongly retards the metathetic conversion.

Current work in our laboratories is aiming at investigating the mechanism as well as to further explore the preparative scope of these readily accessible and highly promising metathesis catalysts, since they allow substantial possible variations of their basic structural motive.

The authors are grateful to Deutscher Akademischer Austauschdienst (DAAD) for a stipend to M. P., covering his stay in Mülheim for a three month period. We also thank K. Langemann and T. Müller, Mülheim, for providing various starting materials.

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Received in Cambridge, UK, 1st May 1998; 8/03286F