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New tunable catalysts for olefin metathesis: Controlling the initiation through electronic factors

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Abstract

Synthesis and screening of catalytic activity of two novel ruthenium carbene complexes **9** and **10** bearing substituents in 2-isopropoxybenzylidene ligand is described. These precatalysts constitute excellent tools for RCM and enyne metathesis by combining high stability with a possibility of their on-demand activation by heat and Brønsted (**9**) or Lewis acids (**10**).

Keywords: Ruthenium; Metathesis; Catalysis; Catalyst activation; Carbene complex

1. Introduction

Finding of a subtle balance between the stability of the catalyst (and its insensitivity to impurities), and its high activity has been called one of the "Holy Grails" of catalysis. This is especially visible in the field olefin metathesis: a fairly old reaction that has long remained as laboratory curiosity without significance for advanced organic chemistry [1]. New organometallic catalysts which combine high catalytic activity with fairly good stability, however, have revolutionized the field [2,3]. The tremendous success of this transformation is largely due to discovery of active, well-defined first-generation ($(PCy_3)_2Cl_2Ru$=CHPh, **1**), second-generation (**2**) and third-generation (**3**) ruthenium carbene complexes [4–6].

The chromatography-stable phosphane-free complex **4**, described by Hoveyda et al. [7] initiates more slowly than the highly active Grubbs' benzylidenes **2** and **3**. We have described a similarly stable and reusable catalysts **5**, prepared from an inexpensive α-asarone [8]. Despite lower initiation activities, the use of catalysts **4** and **5** was proved to be advantageous in many cases, particularly in reactions of electron-deficient olefins [7,8]. Wakamatsu and Blechert have shown that the sterically altered complex **6**, substituted *ortho*- to the chelating isopropoxy ligand initiates dramatically faster than the parent catalyst **4**, while retaining acceptable thermal stability [9,10]. Our group has recently introduced the stable 5- and 4-nitro-substituted analogues **7**, **8** which were shown to exhibit impressive activity in ring-closing (RCM), cross (CM) and enyne-metathesis [11–13]. As a result, the more easily available catalyst **7** [14] has found a successful application in target-oriented syntheses [15–17] and in the pharmaceutical industry [18,19].

In this article, we provide details of the syntheses and catalytic activities of two new Hoveyda-type complexes **9** and **10**, initiation efficiency of which can be easily controlled.

2. Experimental

2.1. Materials

Styrene **10b** was prepared according to previously published procedures [20,21]. Solvents were dried with appropriate drying agents (THF: K; Et_2O: $NaAlH_4$; CH_2Cl_2 and DMF: CaH_2) and distilled prior to use. Ruthenium carbene **2**, aldehydes **9a** and **9b** and other reagents were from Aldrich or Fluka. Cesium carbonate was from Chemetall GmbH.

2.2. Preparation of catalysts (*9*) and (*10*)

2.2.1. 4-(Diethylamino)-2-isopropoxybenzaldehyde (*9b*)

K_2CO_3 (1.2 g, 9.0 mmol) and Cs_2CO_3 (410 mg, 1.3 mmol) were placed in a round bottom flask. A solution of 4-(diethylamino)-2-hydroxybenzaldehyde **9a** (1.1 g, 6 mmol) in dry DMF (15 ml) was added. After stirring for 10 min at

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room temperature 2-iodopropane (0.9 ml, 9 mmol) was added. The reaction was carried out for the next 24 h at room temperature. After pouring onto a saturated aqueous solution of K_2CO_3 the reaction mixture was extracted with MTBE. The combined organic layers were washed with 1 M solution of NaOH and then with brine, dried ($MgSO_4$) and the solvent was removed under reduced pressure. Crude 4-(diethylamino)-2-isopropoxybenzaldehyde **9b** was obtained as a dark red oil (1.3 g, 5.4 mmol; 91%). IR (KBr) *ν*: 2976, 2930, 2867, 2836, 2758, 1658, 1587, 1547, 1521, 1471, 146, 1406, 1391, 1356, 1299, 129, 1238, 1210, 1106, 1076, 1015, 979, 930 cm^{-1}. ^1H NMR (200 MHz, C_6D_6) *δ*: 10.72 (s, 1H, C*H*O), 8.1 (d, *J* = 9.2 Hz, 1H, Ar*H*), 6.03 (dd, *J* = 9.2, 2.1 Hz, 1H, Ar*H*), 5.93 (d, *J* = 2.1 Hz, 1H, Ar*H*), 4.3 (sept., *J* = 6 Hz, 1H, C*H*(CH_3)$_2$), 2.87 (q, *J* = 7.1 Hz, 4H, C$H_2$$CH_3$), 1.09 (d, *J* = 6 Hz, 6H, CH(CH_3)$_2$), 0.82 (t, *J* = 7.1 Hz, 6H, CH_2CH_3). ^{13}C NMR (100 MHz, C_6D_6) *δ*: 186.4, 163.0, 153.6, 130.5, 116.6, 105.06, 95.7, 70.7, 44.6, 22.0, 12.6. MS (70 eV) *m/e* (int [%]): 235 (32) $M^{+\bullet}$, 220 (31); 192 (7); 178 (100); 162 (9); 150 (14.5); 148 (8); 136 (2); 122 (4); 106 (2); 94 (4); 77 (5); 65 (9); 41 (9). HRMS calcd. for $C_{14}H_{22}NO_2$: 236.1572 [$M + H^+$]; found: 236.1653 [22].

2.2.2. 4-(Diethylamino)-2-isopropoxystyrene (*9c*)

To a suspension of $Ph_3P{=}CH_2$ (1.01 g, 2.04 mmol, Aldrich) in dry THF (25 ml) a solution of 4-(diethylamino)-2-isopropoxybenzaldehyde **9b** (344 mg, 1.46 mmol) in THF (5 ml) was added at −78 °C. After 60 min the reaction mixture was warmed to room temperature and was stirred overnight at this temperature. After pouring onto a saturated aqueous solution of $NaHCO_3$ the reaction mixture was extracted with MTBE. The combined organic layers were dried ($MgSO_4$) and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (*c*-hexane/ethyl acetate/triethyl amine 95:5:0.15, v/v/v) to afford **9c** as a yellow oil (210 mg, 61%). ^1H NMR (500 MHz, $CDCl_3$) *δ*: 7.34 (d, *J* = 8.6 Hz, 1H, C*H*=), 6.93 (q, *J* = 17.8, 11.1 Hz, 1H, Ar*H*), 6.29 (dd, *J* = 8.6, 2.5 Hz, 1H, Ar*H*), 6.18 (d, *J* = 2.5 Hz, 1H, C*H*=), 5.52 (dd, *J* = 17.8, 1.7 Hz, 1H, C*H*=), 4.98 (dd, *J* = 11.1, 1.7 Hz, 1H, C*H*=), 4.48 (sept., *J* = 6.06 Hz, 1H, C*H*(CH_3)$_2$), 3.34 (q, *J* = 7.1 Hz, 4H, CH_2CH_3), 1.35 (d, *J* = 6.06 Hz, 6H, CH(CH_3)$_2$), 1.16 (t, *J* = 7.1 Hz, 6H, C$H_2$$CH_3$). ^{13}C NMR (125 MHz, $CDCl_3$) *δ*: 156.4, 148.6, 131.7, 127.2, 116.0, 108.9, 105.0, 98.6, 71.0, 44.5, 22.3, 12.7. MS (70 eV) *m/e*: 233 (53) $M^{+\bullet}$, 219 (12), 191 (6), 190 (5.5), 177 (12.5), 176 (100), 148 (11.5), 118 (3.5), 91 (4.5), 41 (2). HRMS calcd. for C_{15} $H_{23}N_3O_3$: 233.1780 $[M]^{+\bullet}$; found: 233.1782 [22].

2.2.3. Ruthenium catalyst (*9*)

Carbene complex **2** (89.1 mg, 0.105 mmol), CuCl (10.4 mg, 0.105 mmol) and CH_2Cl_2 (5 ml) were placed in a Schlenk tube equipped with a condenser. A solution of styrene **9c** (27.0 mg, 0.116 mmol) in CH_2Cl_2 (3 ml) was added and the resulting solution was stirred under argon at 40 °C for 1 h. The reaction mixture was concentrated in vacuo and the resulting material was purified by column chromatography on silica. Elution with *c*-hexane/ethyl acetate/triethyl amine (4:1:0.1) removed **9** as a brown band. Removal of the solvent, washing of the minimal amount of cold *n*-pentane and drying under vacuum afforded **7** as a dark brown microcrystalline solid (32 mg, 44%). IR (KBr) *ν*: 3437, 2972, 2919, 1600, 1544, 1512, 1480, 1446, 1398, 1355, 1305, 1266, 1253, 1205, 1145, 1120, 1075, 976 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) *δ*: 15.65 (s, 1H, Ru=C*H*), 7.04 (s, 4H, Mes*H*), 6.68 (d, *J* = 8.8 Hz, 1H, Ar*H*), 6.12 (dd, *J* = 8.8, 2.2 Hz, 1H, Ar*H*), 6.00 (d, *J* = 1.6 Hz, 1H, Ar*H*), 4.86 (sept., *J* = 6.1 Hz, 1H, C*H*(CH_3)$_2$), 4.15 (s, 4H, CH_2), 3.31 (t, *J* = 7.1 Hz, 4H, C$H_2$$CH_3$), 2.49 (s, 12H, Mes-*o*-CH_3), 2.38 (s, 6H, Mes-*p*-CH_3), 1.42 (d, *J* = 6.1 Hz, 6H, CH(CH_3)$_2$), 1.14 (t, *J* = 7.1 Hz, 6H, CH_2CH_3). ^{13}C NMR (125 MHz, $CDCl_3$) *δ*: 298, 216.2, 155.8, 150.8, 138.8, 138.3, 138.3, 130.5, 129.7, 125.6, 115, 104.3, 96.3, 74.4, 55.0, 45.5, 25.8, 21.5, 20, 12.8. MS (70 eV) *m/e* (int [%]): 696 (6) $M^{+\bullet}$, 582 (5), 556 (5), 554 (9), 438 (9), 372 (5), 307 (7), 305 (40), 304 (100), 303 (85), 301 (7), 290 (8.5), 289 (19), 274 (7), 259 (4), 235 (6), 233 (17), 221 (52), 220 (17), 218 (26), 207 (13), 206 (70), 198 (11.5), 178 25), 176 (36), 165 (11), 164 (93), 158 (15), 148 (10), 145 (9), 136 (18), 134 (11), 117 (19), 107 (7), 91 (11), 77 (13), 55 (11), 44 (18), 43 (11), 41 (14). HRMS calcd. for $C_{35}H_{47}N_3O^{35}Cl_2{}^{102}Ru$: 697.2139 [$M + H]^+$; found: 697.2129 [22].

2.2.4. (4-Isopropoxy-3-vinylphenyl)(diphenyl)-methanol (*10c*)

To a stirred solution of *t*-BuLi (1.2 ml, 1.98 mmol, 1.20 equiv. 1.7 M in pentane) at −78 °C was added a solution of **10b** (217 mg, 0.90 mmol) in dry Et_2O (8 ml). After stirring for 15 min to the resulted clear yellow solution a solution of Ph_2CO (197 mg, 1.08 mmol) in THF (2 ml) was added at −78 °C. The reaction mixture was stirred at −78 °C for 1 h, and was then gently warmed to rt. Pure **10c** was isolated by column chromatography on silica gel (eluent: ethyl acetate/*c*-hexane 2:8, v/v) as a colorless oil (194 mg, 64%). MS (70 eV) *m/e* (int [%]): 344 (30) $M^{+\bullet}$, 285 (7), 267 (20), 239 (5), 225 (83), 197 (10), 165 (8), 147 (20), 105 (100), 77 (83), 51 (20). ^1H NMR (400 MHz, $CDCl_3$) *δ*: 7.43 (d, *J* = 2.5 Hz, 1H, Ar*H*), 7.25–7.34 (10H, m, Ph*H*), 7.28 (dd, *J* = 2.5, 8.6 Hz, 1H, Ar*H*), 7.05 (dd, *J* = 17.9, 11.2 Hz, 1H, Ar*H*), 6.75 (d, *J* = 8.6 Hz, 1H, C*H*=), 5.59 (dd, *J* = 1.6, 17.8 Hz, 1H, C*H*=), 5.17 (dd, *J* = 1.6, 11.3 Hz, 1H, =C*H*), 4.53 (sept., *J* = 6.0 Hz, 1H, C*H*(CH_3)$_2$), 2.80 (br.s, 1H, O*H*), 1.35 (d, *J* = 6.0 Hz, 6H, CH(CH_3)$_2$). ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 154.3, 147.0, 138.8, 131.9, 128.5, 127.9, 127.1, 126.9, 126.3, 114.3, 113.0, 81.8, 70.7, 22.2 [23].

2.2.5. Ruthenium catalyst (*10*)

Carbene complex **2** (65 mg, 0.075 mmol), CuCl (8.9 mg, 0.09 mmol) and CH_2Cl_2 (4 ml) were placed in a Schlenk tube equipped with a condenser. A solution of styrene **10c** (31 mg, 0.09 mmol) in CH_2Cl_2 (2 ml) was added and the resulting solution was stirred under argon at 40 °C for 1 h. The reaction mixture was concentrated in vacuo and the resulting material was purified by column chromatography on silica. Elution with *c*-hexane/ethyl acetate (3:1) removed **10** as a green band. Removal of the solvent, washing of the minimal amount of cold *n*-pentane and drying under vacuum afforded **10** as a bright green microcrystalline solid (60 mg, 99%). IR (KBr) *ν*: 3437, 2924, 2850, 1590, 1485, 1447, 1260, 1132, 1103, 1033, 936,

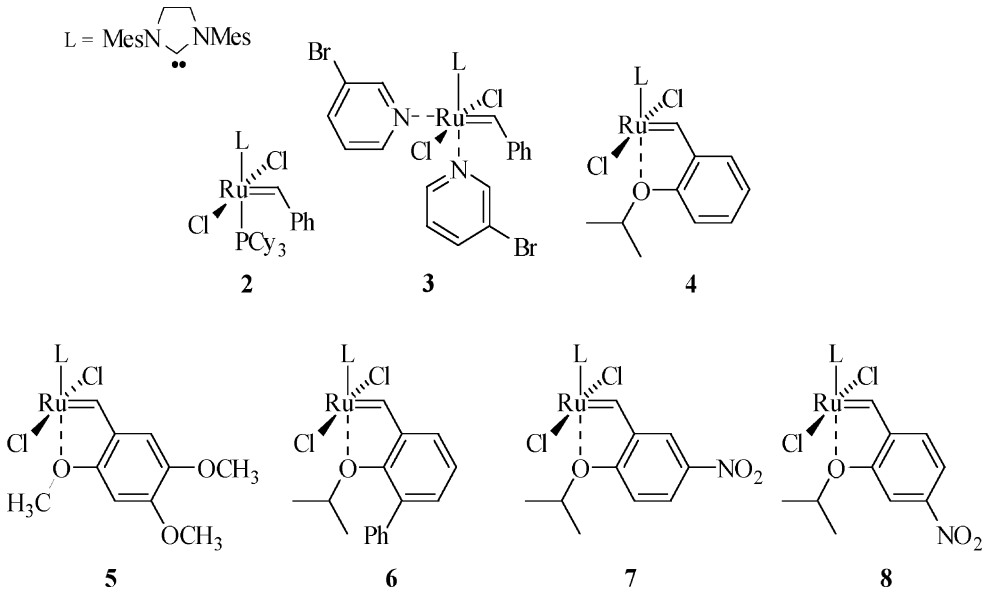


Fig. 1. Modern catalysts for olefin metathesis. Cy = cyclohexyl, Mes = 2,4,6-trimethylphenyl.

850, 758, 702 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ: 16.40 (s, 1H, Ru=C*H*), 7.51 (dd, $J = 8.7$, 2.2 Hz, 1H, Ar*H*), 7.28–7.37 (10H, m, Ph*H*), 7.00 (s, 4H, Mes*H*), 6.85 (d, $J = 2.2$ Hz, 1H, Ar*H*), 6.75 (d, $J = 8.7$ Hz, 1H, Ar*H*), 4.91 (sept., $J = 6.1$ Hz, 1H, C*H*(CH_3)$_2$), 4.18 (s, 4H, CH_2), 2.65 (s, 1H, O*H*), 2.48 (s, 12H, Mes-*o*-CH_3), 2.26 (s, 6H, Mes-*p*-CH_3), 1.31 (d, $J = 6.1$ Hz, 6H, CH(CH_3)$_2$). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 296.9, 211.8 151.6, 146.6, 144.6, 141.2, 138.9, 129.7, 129.3, 127.9, 127.8, 127.2, 122.5, 112.5, 81.2, 77.2, 75.3, 51.5, 26.9, 21.1. 21.0. MS (FAB) *m/e* (int [%]): 808 (10) M^+. The molecular formula was confirmed by comparing the theoretical and experimental isotope patterns for the $[M]^+$ ion ($C_{44}H_{48}Cl_2N_2O_2Ru$) found to be identical within the experimental error limits [23].

2.3. General procedure for in situ activation of (*9*) and (*10*)

To a solution of catalysts **9** and **10** (0.05–0.025 mmol, 5.0–2.5 mol%) in CH_2Cl_2 (40 ml) in a Schlenk tube a solution of the additive (0.05–0.025 mmol, 5.0–2.5 mol%) was added in CH_2Cl_2 (5 ml) under argon at root temperature. Next, a solution of diene **11** or **12** (1.0 mmol) was introduced in CH_2Cl_2 (5 ml) and the reaction mixture was stirred for 1–16 h at room temperature. Progress of the reaction was followed by TLC and GC. Conversions were calculated by GC, using *n*-nonane as an internal standard.

3. Results and discussion

In the case of Hoveyda–Grubbs complexes, initiation requires dissociation of the aryl ether ligand as well as a metathesis step [7]. The slower rate of initiation of **4**, **5** is likely due to the less facile dissociation of the bidentate ligand from the metal center. The higher activity of **7** and **8** may be the result of faster initiation of the catalytic cycle due to a more facile release of the electron deficient substituted benzylidene ligand. We proposed that the nitro group in the benzylidene fragment of **7** and **8** would weaken O → Ru chelation and facilitates faster initiation of the catalytic cycle [12]. In addition, the suppression of oxygen reassociation to the Ru center caused by a electron-withdrawing group (EWG) and the increased electron deficiency at the initiating carbene species should make these complexes more active in olefin metathesis [12] (Figs. 1 and 2 and Scheme 1).

In accordance with this assumption we observed that the very stable (several months at +4 °C in air) complex **9** [22] (Scheme 2), bearing the electron-donating (EDG) diethylamino group [24] shows practically no activity in olefin metathesis with model substrate **11** (Scheme 2). We envisaged that addition of 1 equiv. of acid can activate **9** via protonation of diethylamino group (electron donating to electron withdrawing activity switch, Fig. 4) and accelerate ring-closure of **11**. In line with this expectation, the in situ formed salts obtained by treatment of **9**

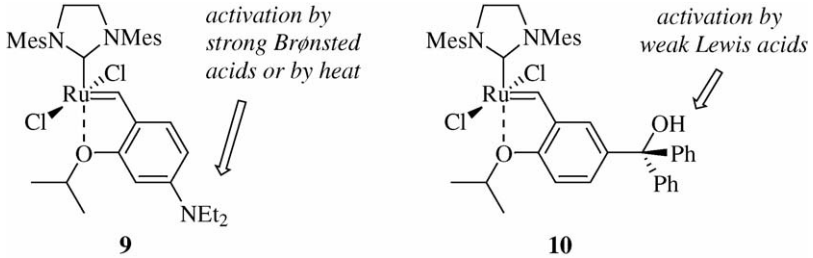
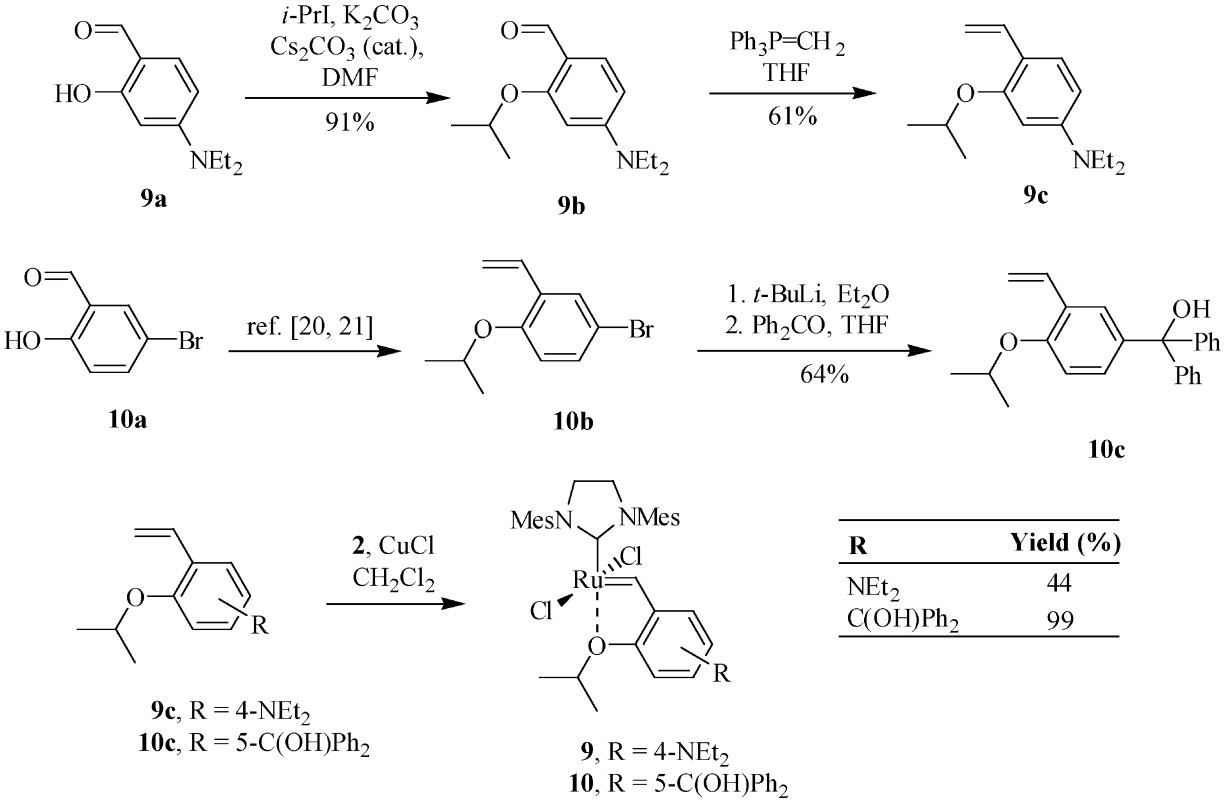


Fig. 2. New ruthenium initiators.



R	Yield (%)
NEt_2	44
$C(OH)Ph_2$	99

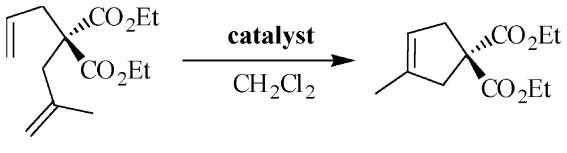
Scheme 1. Preparation of complexes **9** and **10**.

with organic acids are of high activity (Fig. 3), in one case surpassing even the parent Hoveyda–Grubbs complex **4** in terms of initiation speed [25]. Interestingly, different acids lead to complexes of different activity, and hydrochloric acid (used as a 2 M solution in ethyl ether) produces catalyst of the lowest activity.

It is noteworthy that, when the RCM of diene **13** catalyzed by **9** as a free base was performed at room temperature (Table 1, entry 5) practically no reaction was observed. However increasing of reaction temperature to 45 °C (in refluxing CH_2Cl_2) the formation of the metathesis product **14** was quantitative (entry 6). This renders catalyst **9** and analogues derived thereof potentially interesting thermally switchable catalysts [26]. Again, quantitative transformation of **13** at ambient temperature can be achieved by using the in situ formed salt of **9** with (−)-camphor-10-sulfonic acid (entry 7).

Complex **10**, bearing "neutral"-$C(OH)Ph_2$ substituent, in reaction with **11** exhibits similar activity to that of parent Hoveyda catalyst **4** [12] (>70% of the conversion after 16 h; Fig. 5). It must be noted that this complex, prepared in high yield as a bright green microcrystalline solid shows also excellent stability. A sample of **10** was stored in air (+4 °C) for 3 years and after that time TLC analysis showed only minute decomposition. Simply passing out this sample through a Pasteur pipette with silica gel afforded 80% of the regenerated catalyst in analytically pure form.

We speculated that addition of an equimolar amount of acid can activate this complex to much higher extent via formation (at least in some amount) highly active carbocationic species $\mathbf{10}^+$ (Fig. 4). To test this possibility, the effect of various additives on complex **10** stability and activity was screened. Addition of HBF_4 (0.025 equiv.) to the mixture of **10** (0.025 equiv.) and **11**



Scheme 2. Estimation of relative activity of **9** and **10**.

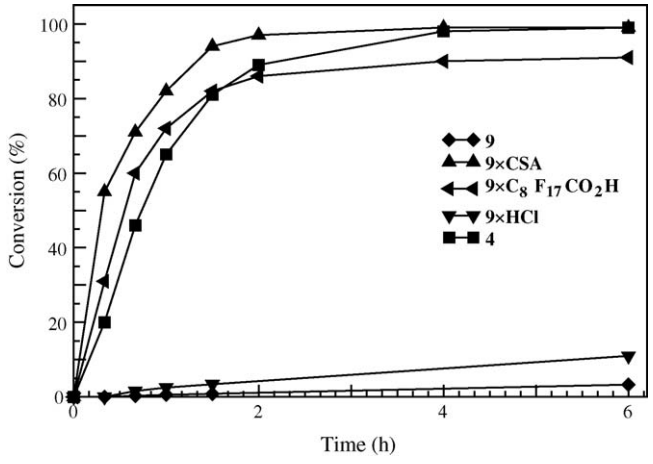
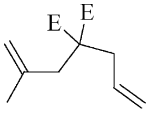
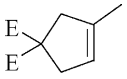
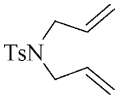
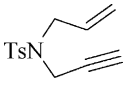
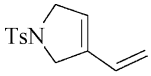
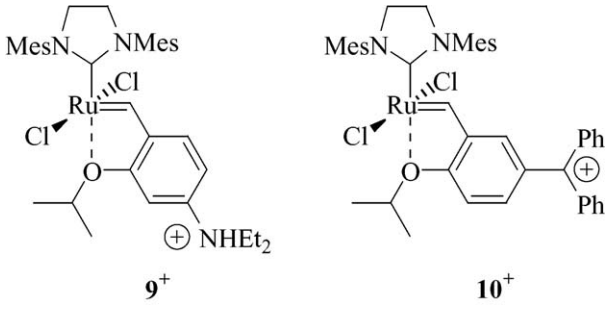


Fig. 3. RCM of **11** using catalysts **4** and **9** and in situ formed salts of **9**. CSA = (−)-camphor-10-sulfonic acid. Conditions: catalyst, 5 mol.%, CH_2Cl_2, 25 °C.

Table 1
Comparison of the reactivity of differently activated complexes **9** and **10** in RCM and enyne cycloisomerization reactions

Entry	Substrate	Product	Catalyst (mol%)	Conditions	Conversion (%)[a]
1	 **11**	 **12**	**9** (5)	25 °C, 24 h	8
2			**9** × CSA (5)	25 °C, 6 h	99
3			**9** × $C_6F_{13}CO_2H$ (5)	25 °C, 6 h	91
4			**9** × HCl (5)	25 °C, 6 h	11
5	 **13**	 **14**	**9** (5)	21 °C, 16 h	<1
6			**9** (5)	45 °C, 16 h[b]	99
7			**9** × CSA (5)	21 °C, 16 h	99
8	 **15**	 **16**	**10** + Ph_2SnCl_2 (2.5)	24 °C, 30 min	99
9	**13**	**14**	**10** + Ph_2SnCl_2 (2.5)	24 °C, 30 min	99

E = CO_2Et.
[a] Conversion calculated by GC.
[b] Under reflux in CH_2Cl_2.



9^+ 10^+

Fig. 4. Activation of precatalysts 9 and 10.

(1 equiv.) in CH_2Cl_2 caused instant color change of the solution from bright green to deep purple, however no RCM reaction was observed. This suggests that very fast decomposition of **10** occurred after addition of such strong Brønsted acid. In contrast, more weak acids, such as $ZnCl_2 \times HCl$ or Ph_2SnCl_2 exhibit activating effect on **10** and, at the same time, do not destroy propagating Ru species (Fig. 5).

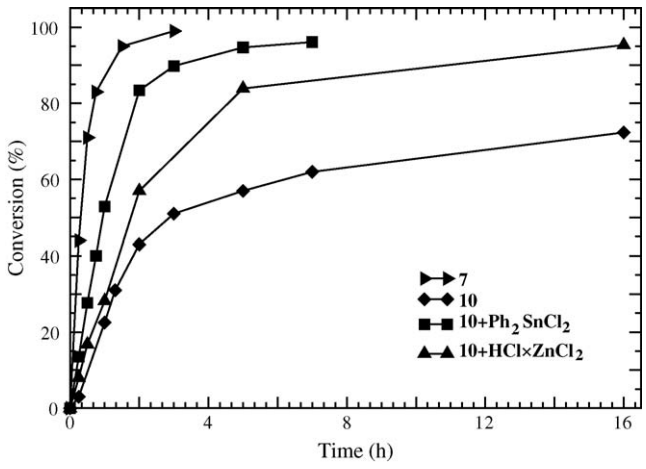


Fig. 5. RCM of **11** using catalysts **10** (2.5 mol%) and **7** (1 mol%). Conditions: CH_2Cl_2, 28 °C.

The "binary" catalyst formed from **10** and Ph_2SnCl_2 was found to be of highest activity, reacting dramatically faster than parent complex **10** (Fig. 5). An additional illustration of the superior activity of this system is given in Table 1 for the cyclization diene **12** and ene-yne **15** (entries 8 and 9), which proceed smoothly at ambient temperature in the presence of 2.5 mol% of **10** + Bu_2SnCl_2 in less than 30 min.

4. Conclusion

In a summary the newly discovered ruthenium species **9** and **10** bearing substituents in 2-isopropoxybenzylidene ligand constitute excellent tools for RCM and enyne metathesis by combining high stability and a possibility of on-demand activation by acids or heat. This renders catalysts **9** and **10** potentially interesting thermally or chemically switchable catalysts. Perfectly stable and thermally or chemically switchable initiators are of great interest in polymer chemistry and related areas. Further studies corroborating this aspect are underway and will be reported in due course.

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[26] Perfectly stable and thermally or chemically switchable initiators are of great interest in polymer chemistry and related areas. It is desired that monomers and initiator(s) can be mixed and stored without concomitant polymerization. Next, controlled polymerization can be switched on by a certain event, such as irradiation with UV or visible light, treatment with acid, or heat. See, e.g.: C. Slugovc, D. Burtscher, F. Stelzer, K. Mereiter, Organometallics 24 (2005) 2255, and references cited therein.