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New efficient ruthenium metathesis catalyst containing chromenyl ligand

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ABSTRACT

A synthesis of new Hoveyda–Grubbs-type catalyst with chromenyl ligand was described herein. The new catalyst was tested in model RCM and CM reactions. The catalyst proved to be quite efficient. It showed activity comparable or superior to that of commercially available Grubbs second-generation complexes.

1. Introduction

The development of well-defined ruthenium alkylidene catalysts (**1**–**3**) (Fig. 1) has made olefin metathesis an important and reliable method for construction of carbon–carbon double bonds [1,2]. The phosphine-free second-generation Hoveyda–Grubbs-type catalysts (e.g. **3**) have received considerable attention because of their tolerance to moisture, oxygen, and a large number of organic functional groups. They show an ease of storage and may be recovered from the reaction mixture and reused. The structure of benzylidene moiety exerts a strong influence on reactivity pattern of the ruthenium carbene complexes. It has been found that these catalysts can be significantly improved by steric or electronic factors. The experience from vitamin E chemistry prompted us to introduce a ligand containing 2*H*-chromenyl fragment. However, some bicyclic ligands bearing oxygen atom (benzofuran and chroman) have been already investigated, *e.g.* in the catalyst **7** (Fig. 1) [3,4]. These structures, structurally related to vitamin E, reveal some specific stereoelectronic effects. The 2p-lone pair electrons of the oxygen atom in heterocyclic ring adopts an orientation approximately perpendicular to the plane of the aromatic ring and interact with the aromatic π-electron system [5,6].

We have recently synthesized ruthenium complexes with chromanylmethylidene ligands (**4**–**6**) [7] (Fig. 1) which promote ring-closing metathesis very slowly, and might potentially serve as a latent olefin metathesis catalyst (*e.g.* in polymerization). The above-mentioned feature of the chromanyl moiety prompted us to design a new Hoveyda–Grubbs-type catalyst, in which the complexing *O*-isopropoxy fragment is replaced by the etheral oxygen of 2*H*-chromenyl ring. In the catalyst a ruthenium center would coordinate to the heterocyclic oxygen, and the benzylidene fragment would stiffen this side of complex. The chelating part functions as a mesomeric donor for a through-bond π-conjugation with the carbene moiety. The reactivity of the ruthenafuran ring can be affected to some extent by aromatic stabilization. According to the recently formulated hypothesis [8] the metallacycle in Hoveyda–Grubbs-type catalysts shows some aromatic character, which inhibits catalytic activity. For such aromaticity the complexing oxygen atom should assume the planar hybridization (i.e. sp^2) and be conjugated with the aromatic ring [8]. However, if the oxygen atom is a part of an adjacent non-aromatic ring, it has less freedom and may not fulfill this prerequisite. For this reason a synthesis of catalysts containing chelating ligands with chroman, benzofuran or benzodioxol moiety was attempted.

2. Results and discussion

In continuation of our project concerning the synthesis of new Hoveyda–Grubbs-type catalysts we decided to substitute the *ortho*-isopropoxybenzylidene ligand with a chromanyl or benzofuranyl moiety. In the previously described catalysts **4**–**6** the chelating oxygen atom derived from an isopropoxyl substituent [7], while in the present approach a new complex was designed with reversed chromenyl ligand (e.g. **8**). In the complex the central ruthenium atom is chelated by the ring oxygen atom. Due to specific orientation of 2p-lone pair electrons such complex may reveal some new attributes (Fig. 2).

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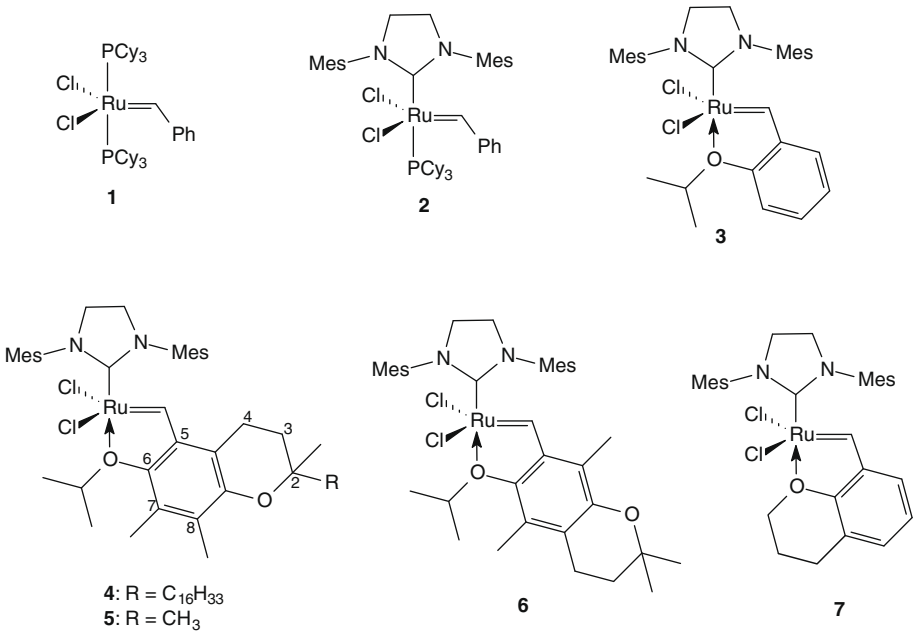


Fig. 1. Selected ruthenium metathesis catalysts. Mes – 2,4,6-trimethylphenyl.

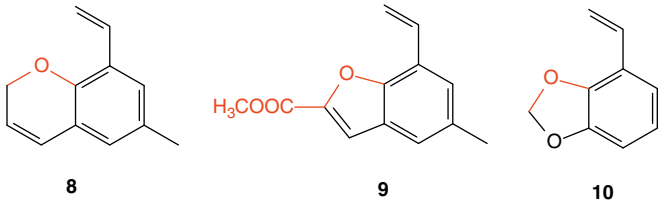


Fig. 2. Ligands for new Hoveyda–Grubbs-type catalysts.

The synthesis of two other ligands: methyl 5-methyl-7-vinylbenzofuran-2-carboxylate (**9**) and 4-vinyl-1,3-benzodioxol (**10**) was also carried out. In these structures the five-membered oxygen-containing heterocyclic ring is less puckered and more rigid, compared to the chroman system [5].

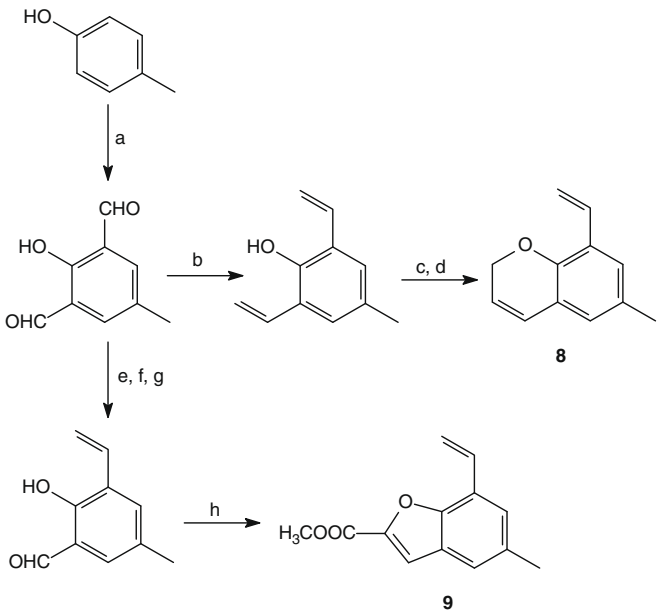
2.1. Synthesis of ligands and catalysts

The ligand **8** (6-methyl-8-vinyl-2*H*-chrom-3-ene) was synthesized in four steps (Scheme 1). *p*-Cresol (chosen in order to avoid substitution in *p*-position) was doubly formylated using Duff method [9], followed by Wittig methylenation afforded 4-methyl-2,6-divinylphenol. Etherification with allyl bromide, followed by ring-closing metathesis with Grubbs first-generation complex (**1**) yielded chromene **8** (overall yield 58%).

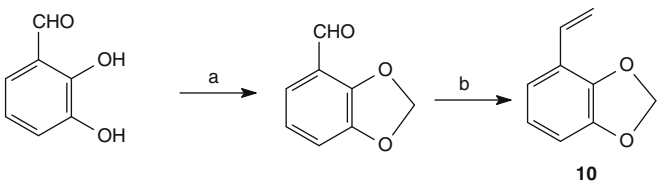
The ligand **9** (methyl 5-methyl-7-vinylbenzofuran-2-carboxylate) was obtained from 2-hydroxy-5-methyl-1,3-benzenedicarboxaldehyde in four steps. Monoprotection of the dialdehyde as dimethylacetal, followed by Wittig methylenation, and finally condensation with methyl chloroacetate [10] afforded benzofuran **9** (Scheme 1).

The benzodioxol **10** was synthesized in two steps from commercially available 2,3-dihydroxybenzaldehyde by methylenation of *ortho*-dihydroxyl groups, followed by Wittig reaction (Scheme 2).

The new catalyst **11** was synthesized by an exchange with the Grubbs second-generation complex (**2**) [11,12] (Fig. 3). The styrene **8** was heated with the catalyst **2** in dichloromethane in the presence of CuCl to give the catalyst **11** in 57% yield as a green sub-



Scheme 1. Synthesis of ligands **8** and **9**. *Reagents and conditions*: (a) hexamethylenetetramine, TFA, reflux 24 h, 70%; (b) $Ph_3CH_3P^+Br^-$, BuLi, THF, 90%; (c) allyl bromide, K_2CO_3, 18-C-6, acetone, 1 h, 98%; (d) 1 mol% **1**, CH_2Cl_2, reflux, 3 h, 95%; (e) 2,2-dimethoxypropane, PTSA, MeOH, reflux, 1 h, 52%; (f) $Ph_3CH_3P^+Br^-$, BuLi, THF, 90%; (g) NH_4Cl, MeOH, 50 °C, 1 h, 100%; (h) $ClCH_2COOCH_3$, K_2CO_3, TBAB, 36%.



Scheme 2. Synthesis of ligand **10**. *Reagents and conditions*: (a) CH_2Cl_2, NaH, HMPA, 10 h, 45%; (b) $Ph_3CH_3P^+Br^-$, BuLi, THF, 80%.

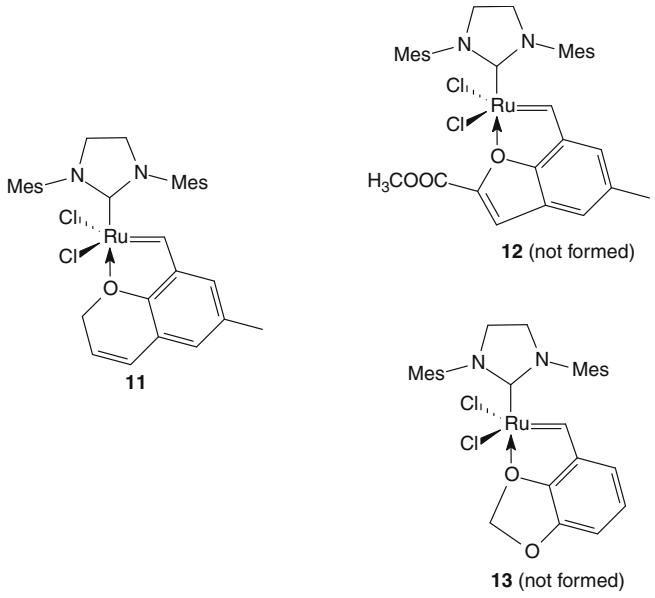


Fig. 3. New catalysts.

stance, which proved to be air-stable and could be easily purified by a standard silica-gel column chromatography. The ^{1}H NMR spectrum for **11** showed the alkylidene proton signal (H-8b) at 16.44 ppm. This value seems to be characteristic for the active Hoveyda-type catalysts as reported by Barbasiewicz et al. [8].

Unfortunately, the synthesis of catalysts **12** and **13** proved unsuccessful. The exchange of ligands **9** and **10** with the catalyst **2** failed. The expected structures were not formed due to weak coordination to the oxygen ligand. The styrene moiety exchange in these systems was probably hampered due to the improper distance between chelating oxygen atom and the ruthenium center. The similar observation was made by Barbasiewicz et al. for benzofuranyl system [4].

2.2. Testing of the new catalyst *11*

The catalyst **11** was tested in standard RCM (Table 1) and CM (Table 2) reactions [10]. For investigation of the relative activity of different catalysts in RCM, the model reactions of diethyl diallylmalonate (**14**), diethyl 2-allyl-2-methallylmalonate (**15**), and diethyl dimethallylmalonate (**16**) were chosen. The reactions led to the cyclic products: **17**, **18**, and **19**, bearing di-, tri- and tetrasubstituted double bonds, respectively (Table 1).

Table 1
Results of ring-closing metathesis reactions promoted by **2**, **3** or **11**[a].

Entry	Substrate	Product	Catalyst	Time	Yield[b] (%)
1	EtOOC COOEt	EtOOC COOEt	**2**	75 min	>99
2			**3**	60 min	>99
3			**11**	45 min	>99
	14	**17**			
4	EtOOC COOEt	EtOOC COOEt	**2**	90 min	63
5			**3**	90 min	80
6			**11**	90 min	68
	15	**18**			
7	EtOOC COOEt	EtOOC COOEt	**2**	16 h	38
8			**3**	16 h	15
9			**11**	16 h	18
	16	**19**			

[a] Reaction conditions for substrates **14** and **15**: 20 °C, 0.1 M, CH_2Cl_2, 0.5 mol% catalyst; for substrate **16**: 80 °C, 0.06 M, toluene, 5 mol% catalyst.
[b] Determined by ^{1}H NMR.

The catalyst **11** was compared with catalyst **2** and Hoveyda–Grubbs second-generation catalyst (**3**). The results showed that **11** is the most effective in RCM for diallylmalonate **14** (entry 3; 100% conversion after 45 min), whereas the catalyst **3** yielded complete conversion after 60 min (entry 2) and catalyst **2** after 75 min (entry 1). It should be mentioned, that our results are similar to those, obtained for commercially available catalysts: **2** and **3**, reported by Ritter et al. [13]. It should be emphasized that the results collected in Table 1 show that the catalyst **11** reveals activity comparable to that of commercial catalysts: **2** and **3**. The catalyst **11** proved to be active in RCM reactions leading to tetrasubstituted alkenes (entry 9, Table 1), but it is less efficient than catalyst **2** (entry 7).

The easily available and not too volatile olefinic substrates for cross-metathesis reactions were chosen: **20**, **21**, **22** and **23**. Three CM reactions of allyl-decyl ether (**21**) were tested: with allyl-cyclohexyl ether (**22**), but-3-enyl benzoate (**23**) and ethyl acrylate (**20**). The products (**24**, **25**, **26**, respectively) were isolated by flash chromatography, and analyzed by ^{1}H NMR. The *E*/*Z* ratio was determined by ^{1}H NMR (Table 2). The catalyst **11** appeared to be very active in these cross-metathesis reactions, in some cases even superior to the commercially available catalysts. As it could be expected, the catalyst **11** promotes reaction between deactivated **20** and activated **21** olefins to afford exclusively the product **26** of *E* configuration (entry 3, Table 2). In addition to the CM products **24**, **25** and **26** the homometathesis product deriving from **21** was also formed in all reactions in varying amounts. The homometathesis products of **22** (entries 1–4, Table 2) and **23** (entries 5–8) were also obtained in minor amounts.

3. Conclusions

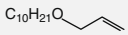
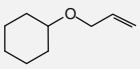
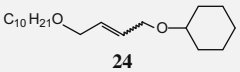
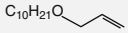
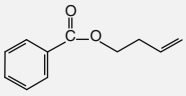
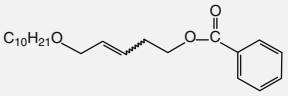
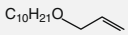
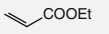
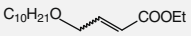
In summary, syntheses of ligands: **8**, **9** and **10** for construction of the new Hoveyda–Grubbs-type catalysts have been described. The oxygen atom coordinating to the metallic center was incorporated into 5- or 6-membered heterocyclic ring (benzofuran, benzodioxol and 2*H*-chromene). The corresponding styrenes were subjected to ligand exchange reaction with catalyst **2**. However, only chromenyl ligand **8** was successfully converted to the new Hoveyda–Grubbs-type catalyst **11**. The new catalyst **11** was tested in model RCM and CM reactions. The catalyst proved to be quite efficient. It showed activity comparable or superior to that of commercially available Grubbs second-generation (**2**) and Hoveyda–Grubbs second-generation (**3**) complexes.

4. Experimental

4.1. General remarks

All manipulations of organometallic compounds were performed using standard Schlenk techniques under an atmosphere of dry argon. CH_2Cl_2 was dried by distillation over CaH_2, trifluoroacetic acid over P_2O_5, THF over Na/benzophenone. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker spectrometer (400 and 100 MHz, respectively). Spectra are referenced relative to the chemical shift (δ) of TMS. Mass spectra were obtained at 70 eV with AMD-604 spectrometer. IR spectra were recorded on a Nicolet series II Magna-IR 550 FT-IR spectrometer. Flash chromatography (FC) was performed on Merck silica gel 230–400 mesh.

Table 2
Results of cross-metathesis reactions promoted by **1**, **2**, **3** or **11**[a].

Entry	Substrates		Product	Catalyst	*E*/*Z*[b]	(%)[c]
1				**1**	3:1	36
2				**2**	6:1	21
3	**21**	**22**	**24**	**3**	8:1	18
4				**11**	8:1	35
5				**1**	2:1	19
6				**2**	6:1	25
7	**21**			**3**	5:1	19
8		**23**	**25**	**11**	4:1	23
9				**1**	Only *E*	5
10				**2**	Only *E*	22
11	**21**	**20**	**26**	**3**	Only *E*	67
12				**11**	Only *E*	61

[a] Reaction conditions for entries 1–8: 40 °C, 0.1 M, CH_2Cl_2, 1 mol% catalyst, 3 h; for entries 9–12: 40 °C, 0.4 M, CH_2Cl_2, 2.5 mol% catalyst, 3 h.
[b] Determined by ^1H NMR.
[c] Isolated by column chromatography.

4.2. Synthesis of ligand **8**

4.2.1. 2-Hydroxy-5-methyl-1,3-benzenedicarboxaldehyde

To a solution of *p*-cresol (200 mg, 1.85 mmol) in anhydrous trifluoroacetic acid (10 mL) hexamethylenetetramine (519 mg, 3.7 mmol) was added. The mixture was stirred and refluxed overnight. The reaction mixture was treated with 1 M HCl for 10 min and extracted with CH_2Cl_2. The combined extracts were washed with brine and water, and dried over $MgSO_4$. After concentration *in vacuo* the crude product was purified by FC (hexane–ethyl acetate v/v 20:1) to afford 2-hydroxy-5-methyl-1,3-benzenedicarboxaldehyde (212 mg; 70%) as a pale yellow crystalline material. Mp 124–126 °C, IR ($CHCl_3$) ν 1683, 1604, 1217, 962, 749, 626 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 11.44 (s, 1H, –OH), 10.19 (s, 2H, –CHO), 7.80 (s, 2H, H-3 and 5), 2.37 (s, 3H, H-4a) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.1, 161.6, 137.9, 129.5, 122.8, 20.0 ppm.

4.2.2. 4-Methyl-2,6-divinylphenol

Methyltriphenylphosphonium bromide (928 mg, 2.6 mmol) and butyllithium (2.5 M solution in hexane; 1.56 ml, 3.9 mmol) were stirred in dry THF (5 mL) for 3 h under argon atmosphere. A solution of 2-hydroxy-5-methyl-1,3-benzenedicarboxyaldehyde (106 mg, 0.65 mmol) in THF (5 mL) was then added dropwise during 1 h and the reaction mixture was refluxed for 5 h. The solvent was evaporated to dryness, and the residue was dissolved in CH_2Cl_2 (10 mL), washed with water, dried over Mg_2SO_4 and concentrated *in vacuo*. The crude product was purified by FC (hexane–ethyl acetate v/v 50:1) and 4-methyl-2,6-divinylphenol (93 mg; 90%) was isolated as a yellow oil. IR ($CHCl_3$) ν 3597, 2925, 1460, 1265, 914 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.11 (s, 2H, H-3 and 5), 6.92 (m, 2H, =CH), 5.77 (dd, 2H, J = 17.7 and 1.3 Hz, $=CH_2$), 5.43 (dd, 2H, J = 11.2 and 1.3 Hz, $=CH_2$), 2.30 (s, 3H, H-4a) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.0, 131.8, 129.6, 127.3, 125.0, 116.4, 20.5 ppm.

4.2.3. 1-Allyloxy-4-methyl-2,6-divinylbenzene

The mixture of 4-methyl-2,6-divinylphenol (93 mg, 0.58 mmol) in dry acetone (3 mL), potassium carbonate (160 mg, 1.16 mmol), allyl bromide (75 μL, 0.87 mmol) and 18-C-6 (5 mg) was refluxed for 1 h. The mixture was filtered through a pad of Celite and concentrated *in vacuo*. The residue was purified by FC (hexane–ethyl acetate v/v 200:1) and 114 mg of 1-allyloxy-4-methyl-2,6-divinylbenzene as a colourless oil was obtained (98% yield). IR ($CHCl_3$) ν 2925, 1288, 1711, 1450, 916 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.25 (s, 2H, H-3 and 5), 6.99 (m, 2H, =CH), 6.05 (m, 1H, H-2′); 5.74 (dd, 2H, J = 17.8 and 1.1 Hz, $=CH_2$), 5.42 (dd, 1H, J = 17.1 and 1.4 Hz, H-3′), 5.25 (dd, 2H, J = 11.0 and 1.0 Hz, $=CH_2$), 5.25 (dd, 1H, J = 10.2 and 1.1 Hz, H-3′), 4.27 (d, 2H, J = 5.5 Hz, H-1′), 2.32 (s, 3H, H-4a) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.8, 133.6, 133.3, 131.5, 130.9, 126.2, 117.1, 114.7, 74.8, 20.8 ppm; ESI-MS: 201.1 (M^++H, 100%).

4.2.4. 6-Methyl-8-vinyl-2H-chrom-3-ene (**8**)

To a solution of 1-allyloxy-4-methyl-2,6-divinylbenzene (114 mg, 0.57 mmol) in dry CH_2Cl_2 (2 mL) in a Schlenk flask, a solution of catalyst **1** (5 mg, 1 mol%) in CH_2Cl_2 (1 mL) was added. The reaction mixture was stirred at 40 °C for 5 h and concentrated *in vacuo*. The residue was purified by FC (hexane–ethyl acetate v/v 200:1) and product **8** (93 mg; 95%) was obtained as a colorless oil. IR ($CHCl_3$) ν 2923, 1628, 1467, 1154, 913 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.13 (s, 1H, H-7), 7.01 (m, 1H, =CH), 6.71 (s, 1H, H-5), 6.40 (dt, 1H, J = 9.8 and 1.8 Hz, H-4), 5.80 (dt, 1H, J = 9.8 and 3.6 Hz, H-3), 5.73 (dd, 1H, J = 17.8 and 1.5 Hz, $=CH_2$), 5.25 (dd, 1H, J = 11.2 and 1.5 Hz, $=CH_2$), 4.82 (dd, 2H, J = 3.6 and 1.8 Hz, H-2), 2.26 (s, 3H, H-4a) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.1, 131.0, 130.0, 126.7, 126.0, 124.9, 124.8, 122.4, 122.0, 114.2, 65.5, 20.5 ppm; *m/z* (EI) 172 (84), 171 (100), 157 (57), 129 (27), 128 (43), 127 (13).

4.3. Synthesis of ligand **9**

4.3.1. 2-Hydroxy-3-dimethoxymethyl-5-methylbenzaldehyde

To a solution 2-hydroxy-5-methyl-1,3-benzenedicarboxaldehyde (106 mg, 0.65 mmol) in MeOH (5 mL) 2,2-dimethoxypropane (80 μL, 0.65 mmol) and *p*-toluenesulphonic acid (5 mg) was added and the mixture was refluxed. The reaction progress was monitored by TLC. After 1 h the reaction was quenched with a few drops of Et_3N and the mixture was concentrated *in vacuo*. The residue was purified by FC (hexane–ethyl acetate v/v 30:1) and 71 mg of 2-hydroxy-3-dimethoxymethyl-5-methylbenzaldehyde as a pale yellow solid was obtained (52% yield). Mp 60–61 °C; IR ($CHCl_3$) ν 2861, 1683, 1461, 1110, 1047, 747, 685 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 11.10 (s, 1H, –OH), 9.89 (s, 1H, –CHO); 7.62 and 7.35 (2s, 2H, H-3 and 5), 5.69 (s, 1H, H-1′), 3.42 (s, 6H, H-2a′, 2b′), 2.36 (s, 3H, H-4a) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.3, 157.1, 135.7, 133.7, 128.8, 126.1, 120.4, 98.6, 53.9, 20.3 ppm.

4.3.2. 2-Hydroxy-5-methyl-3-vinylbenzaldehyde

The procedure for the synthesis of 4-methyl-2,6-divinylphenol was followed using methyltriphenylphosphonium bromide (292 mg, 0.82 mmol), butyllithium (0.49 mL, 1.23 mmol) and 2-hydroxy-3-dimethoxymethyl-5-methylbenzaldehyde (71 mg,

0.34 mmol) in dry THF (5 mL). After extraction, the organic layer was washed 1 M HCl until the protective group was removed (TLC control, hexane:ethyl acetate 5:1). FC (hexane–ethyl acetate v/v 40:1) gave 50 mg of 2-hydroxy-5-methyl-3-vinylbenzaldehyde as a pale yellow oil (90% yield). IR ($CHCl_3$) ν 3027, 2850, 1655, 1456, 1263, 971 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 11.29 (s, 1H, –OH), 9.85 (s, 1H, –CHO), 7.53 and 7.26 (s, 1H, H-3 and 5), 7.02 (m, 1H, =CH), 5.85 (dd, 1H, J = 17.8 and 0.8 Hz, $=CH_2$), 5.39 (dd, 1H, J = 11.2 and 0.8 Hz, $=CH_2$), 2.35 (s, 3H, H-4a) ppm; ^{13}C NMR (100 MHz $CDCl_3$) δ 196.7, 156.9, 134.7, 133.1, 129.9, 128.8, 126.3, 120.5, 115.8, 20.3 ppm; ESI-MS: 163.1 (M^++H, 100%).

4.3.3. Methyl 5-methyl-7-vinylbenzofuran-2-carboxylate (**9**)

The mixture of 2-hydroxy-5-methyl-3-vinylbenzaldehyde (50 mg, 0.31 mmol), methyl chloroacetate (58 μL, 0.64 mmol), K_2CO_3 (88 mg, 0.64 mmol), TBAB (10 mol%, 10 mg) was stirred mechanically and heated at 110 °C. After 10 min the temperature of the oil bath was increased to 150 °C and heating was continued for next 30 min. After cooling, water was added, and the reaction mixture was extracted with CH_2Cl_2. The combined extracts were washed successively with brine and water, and dried over $MgSO_4$. After concentration *in vacuo* the crude product was purified by FC (hexane–ethyl acetate v/v 20:1) and compound **9** was obtained (24 mg; 36%) as a colorless oil. IR ($CHCl_3$) ν 2955, 1727, 1578, 1438, 1300 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 (s, 1H, H-3), 7.36 and 7.29 (2s, 2H, H-4 and 6), 7.0 (m, 1H, =CH), 6.28 (dd, 1H, J = 17.8 and 0.9 Hz, $=CH_2$), 5.53 (dd, 1H, J = 11.3 and 0.9 Hz, $=CH_2$), 3.98 (s, 3H, $-OCH_3$), 2.46 (s, 3H, H-5a) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 154.2, 151.9, 145.6, 145.4, 133.4, 130.9, 127.3, 121.5, 118.1, 113.7, 52.2, 21.5 ppm; ESI-MS: 239.1 (M^++Na, 55%), 455.1 ($2M^+$+Na, 100%).

4.4. Synthesis of ligand **10**

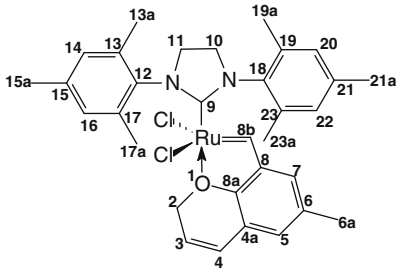
4.4.1. 4-Formyl-1,3-benzodioxol

To a suspension of sodium hydride (139 mg 50% suspension in oil, 2.9 mmol) in HMPA (10 mL) a solution of 2,3-dihydroxybenzaldehyde (200 mg, 1.45 mmol) in HMPA (2 mL) was added with stirring within 10 min. After evolution of gas stopped, dibromomethane (0.15 mL, 2.2 mmol) was added and the solution was stirred for additional 20 min. Then cold water was added and the mixture was extracted with CH_2Cl_2. The combined extracts were washed successively with brine and water, dried over $MgSO_4$ and evaporated *in vacuo*. The oily residue was purified by FC (hexane–ethyl acetate v/v 20:1) affording 98 mg (45%) of 4-formyl-1,3-benzodioxol as a colorless oil. IR ($CHCl_3$) ν 1690, 1464, 1235, 1059 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 10.1 (s, 1H, –CHO), 7.27–6.88 (m, 3H, H-5, 6 and 7), 6.11 (s, 2H, H-2) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.9, 149.2, 148.8, 121.7, 121.0, 119.3, 113.3, 102.4 ppm.

4.4.2. 4-Vinyl-1,3-benzodioxol (**10**)

The procedure for the synthesis of 4-methyl-2,6-divinylphenol was followed using methyltriphenylphosphonium bromide (278 mg, 0.78 mmol), butyllithium (0.47 mL, 1.17 mmol) and 4-formyl-1,3-benzodioxol (98 mg, 0.65 mmol) in dry THF (5 mL). FC (hexane–ethyl acetate v/v 80:1) gave pure product **10** (77 mg; 80%) as a colorless oil. IR ($CHCl_3$) ν 1731, 1454, 1247, 1051 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.89–6.65 (m, 4H, H-5, 6 and 7; =CH), 6.01 (s, 2H, H-2), 5.92 (d, 1H, J = 17.7 and 1.3 Hz, $=CH_2$), 5.4 (dd, 1H, J = 11.2 and 1.3 Hz, $=CH_2$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.6, 144.9, 131.1, 121.4, 120.4, 120.3, 116.8, 107.6, 100.9 ppm.

4.5. Synthesis of catalyst **11**



To the mixture of catalyst **2** (39.5 mg, 0.047 mmol) and CuCl (5 mg, 0.05 mmol) in dry CH_2Cl_2 (2 mL) a solution of 6-methyl-8-vinyl-2*H*-chrom-3-ene (**8**) (8 mg, 0.047 mmol) in CH_2Cl_2 (1 mL) was added. The solution was stirred at 40 °C for 1 h. The reaction mixture was concentrated *in vacuo*, and the residue was dissolved in a small volume of ethyl acetate. The insoluble material was filtered off, and the filtrate was evaporated to dryness. The crude product was purified by FC (hexane–ethyl acetate v/v 5:1) to give 17 mg (57% yield) of the green catalyst **11**. IR ($CHCl_3$) ν 2993, 2921, 1606, 1480, 1268 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 16.44 (s, 1H, H-8b), 7.09 (s, 4H, H-14, 16, 20 and 22), 6.94, 6.49 (2d, 2H, J = 1.6 Hz; 1.2 Hz, H-5 and 7), 6.3 (dt, 1H, J = 10.1 and 2.0 Hz, H-4), 5.59 (dt, 1H, J = 10.0 and 3.4 Hz, H-3), 4.88 (dd, 2H, J = 3.3 and 2.1 Hz, H-2), 4.14 (s, 4H, H-10 and 11), 2.47 (s, 12H, H-13a, 17a, 19a and 23a), 2.42 (s, 6H, H-15a and 21a), 2.31 (s, 3H, H-6a) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 291.8, 210.2, 146.3, 142.8, 138.8, 138.6, 136.2, 132.9, 129.5, 126.8, 122.7, 122.5, 121.2, 67.5, 51.7, 21.1, 20.2, 19.2 ppm; TOF MS FD+ (4,34 eV; m/z): 636,13; calculated for $C_{32}H_{36}Cl_2N_2O^{102}Ru$: 636.1248, found: 636.1285.

4.6. General RCM procedure for **14** and **15**

To a solution of diene **14** or **15** (1 mmol) in CH_2Cl_2 (8 mL, c 0.1 M) a solution of catalyst **2**, **3** or **11** (0.5 mol%) in CH_2Cl_2 (2 mL) was added. The resulting mixture was stirred at room temp. for 90 min and controlled by TLC. The crude product was analyzed by ^1H NMR.

4.7. General RCM procedure for **16**

To a solution of diene **16** (0.5 mmol) in toluene (6 mL, c 0.06 M) a solution of catalyst **2**, **3** or **11** (5 mol%) in toluene (2 mL) was added. The resulting mixture was stirred at 80 °C for 16 h and controlled by TLC. The crude product was analyzed by ^1H NMR.

4.8. General CM procedure for **24** and **25**

To a mixture of alkenes **21** and **22** or **21** and **23** (1 mmol both) in CH_2Cl_2 (8 mL, c 0.1 M) a solution of catalyst **1**, **2**, **3** or **11** (1 mol%) in CH_2Cl_2 (2 mL) was added. The resulting mixture was stirred at 40 °C for 3 h and controlled by TLC. The crude product was purified by FC and analyzed by ^1H NMR.

4.9. General CM procedure for **26**

To a mixture of alkenes **20** and **21** (1 mmol both) in CH_2Cl_2 (2 mL, c 0.4 M) a solution of catalyst **1**, **2**, **3** or **11** (2.5 mol%) in CH_2Cl_2 (0.5 mL) was added. The resulting mixture was stirred at 40 °C for 3 h and controlled by TLC. The crude product was purified by FC and analyzed by ^1H NMR.

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