Synthetic Methods

Chelating Ruthenium Phenolate Complexes: Synthesis, General Catalytic Activity, and Applications in Olefin Metathesis Polymerization

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Abstract: Cyclic Ru-phenolates were synthesized, and these compounds were used as olefin metathesis catalysts. Investigation of their catalytic activity pointed out that, after activation with chemical agents, these catalysts promote ring-closing metathesis (RCM), enyne and cross-metathesis (CM) reac-

tions, including butenolysis, with good results. Importantly, these latent catalysts are soluble in neat dicyclopentadiene (DCPD) and show good applicability in ring-opening meta-thesis polymeriyation (ROMP) of this monomer.

Introduction

Catalytic olefin metathesis has become a powerful tool for the formation of carbon–carbon bonds in organic and polymer chemistry.^[1] The success of olefin metathesis has spurred intense investigation for new catalysts for this transformation.^[2] Most of the efforts in designing new catalysts concentrated on finding more efficient ones, such as Grubbs II-generation catalyst (1).^[1,2] However, very reactive catalysts do not always give good results in ring-opening metathesis polymerization (ROMP) of some monomers, like dicyclopentadiene (DCPD), especially when an industrial scale is considered.^[3,4]

To solve this problem, a number of latent Ru-catalysts have been developed in recent years.^[5] The use of such catalysts in ROMP allows for the catalyst to be mixed with the monomer with no polymerization at RT, in order to give enough time to handle the formulation. Once required, the catalyst can be acti-

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vated by chemical or physical methods. In addition, such latent catalysts shall exhibit high solubility in a monomer (no co-solvent needed) and high thermal stability.^[5] The few Ru catalysts that amply fulfill these prerequisites, and have been successfully used in ROMP of DCPD, are complexes bearing bidentate Schiff base ligands (e.g., **2** and **3** in Figure 1).^[6]



Figure 1. Grubbs (1) and two selected Schiff-base-bearing catalysts (2 and 3). Mes = 2,4,6-trimethylphenyl, Cy = cyclohexyl.

Recently, we reported the synthesis of chelating ruthenium sulfonamides (**4**, Figure 2),^[7a] a new family in the kingdom of ruthenium-based metathesis catalysts bearing altered anionic ligands.^[8] These complexes exhibit nearly no activity in metathesis reactions; however, they can be easily "turned on" by the addition of some Brønsted acids.



Figure 2. Ru-amide (4) and planned Ru-phenolate (5 a) complexes and Hoveyda–Grubbs catalyst (6). py = pyridine

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Results and Discussion

For the next step, we were interested in analogous NHC-containing Ru-phenolate salts, such as compound **5a** (see Figure 2)^[7b] These—at the time—conjectural complexes can be considered analogues of **6**, the so-called Grubbs–Hoveyda IIgeneration catalyst, which contains in its structure a phenolether fragment that coordinates to a metal center (Figure 2).^[2,9–11] Hoveyda-type complexes became a very successful and popular class of olefin metathesis catalysts, the activity of which could be fine-tuned by altering the strength of the Ru···O_(ether) chelate.^[2] Recently, Pietraszuk et al. have published independently on similar structures containing a cyclic Ru-phenolate fragment.^[7c]

Here, we present a full account of the preparation, characterization, and catalytic activity of three representative II-generation complexes (5a-c) that bear the cyclic Ru-phenolate fragment. The syntheses presented in Scheme 1 were performed



Scheme 1. Preparation of complexes 5 a-c. SIMes and IMes are N-heterocyclic carbene ligands.

using corresponding propenyl phenols (**7 a**, **b**) in dichloromethane at reflux, with **1a** and **1b**^[12] as a ruthenium source. As noted previously,^[7a] addition of tricyclohexylphosphine (PCy₃) (3 equiv relative to the Ru complex) leads to higher yields of the products. Catalysts **5 a**–**c** were isolated by column chromatography as air-stable solids and characterized spectroscopically.^[13]

Single crystals of compounds **5a** and **5b** (see Figures 3 and 4) suitable for X-ray diffraction analysis were grown at RT from *n*-heptane solutions (for crystallographic details see Supporting Information).

This allowed us to confirm the molecular assignment of new Hoveyda-type catalysts. The coordination geometry of the ruthenium center in both complexes is a distorted square pyramid, the apex of which is formed by the carbene atom C(22) with a Ru–C bond of 1.844(5) and 1.832(2) Å for **5a** and **5b**, respectively. The fact that the phenol anion coordinates with the



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Figure 3. Molecular structure of 5 a (thermal ellipsoids at 50% probability level; hydrogen atoms and co-crystallized *n*-heptane omitted for clarity).



Figure 4. The molecular structure of **5 b** (thermal ellipsoids at 50% probability level; hydrogen atoms omitted for clarity).

metal center by replacing one of the chlorine atoms alters the geometry around the ruthenium center. The Ru(1)–O(1) bond lengths in **5a** (2.120(3) Å) and **5b** (2.1152(16) Å) are significantly shorter than the analogous Ru(1)–O(1) bond equal to 2.261(3) Å in the Hoveyda catalyst **6**.^[9a] The observed bond lengths of the NHC carbon C(1) are longer: 2.065(5)–2.072(2) Å compared with 1.981(5) Å in **6**.^[9a] To validate if these structural changes influence the chemical activity of **5a** and **b**, we used a standard set of metathesis reactions.

Ring closing metathesis (RCM) of diethyldiallyl malonate **8** promoted by phenolate **5***a* was chosen as the first assay (Scheme 2). Figure 5 shows that although **5***a* is inactive in the model reaction, the addition of trimethylsilyl chloride (TMSCI) or etheral solution of HCl (10 mol% each) causes a dramatic increase in activity. Interestingly, a non acidic additive, C_2Cl_6 (10 mol%) also exhibits a detectable activation potential.^[14]

The comparative screening of catalysts 5a-c and 6 in the RCM of 8, presented in Figure 6, shows some basic structure– activity relationships. Complex 5a, activated by TMSCI, exhibits

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Figure 5. Activity of 5 a in RCM of 8 in the presence of various activating agents. Conditions as in Scheme 2.



Figure 6. Comparative test of catalysts 5 a-c and 6 in RCM of 8. Conditions as in Scheme 2.

activity comparable to that of Hoveyda catalyst **6**. Interestingly, the electron-withdrawing effect of the nitro group placed at the para position, with respect to the phenolate fragment, caused catalyst **5b** to initiate slower than **5a**. However, the overall conversion obtained with this catalyst was the highest in the series. Replacing the SIMes ligand with the Me₂IMes^[12] ligand significantly reduced the activity of the resultant catalyst **5c**.

Next, catalysts 5a-c (1–2 mol%) were screened in a selected set of RCM, enyne, and CM reactions in the presence of TMSCI (Table 1). The first entry is a ring-closing metathesis reaction of diethylallylmethallyl malonate **10**. Due to steric effects, this substrate is more challenging in RCM than **8**; however, good performance of the studied catalysts was observed for 1 mol% loading (Table 1, entry 1). Enyne cycloisomerisation (entry 2) also proceeded well with the new catalysts (**5**c again gave the lowest yield). The CM reaction of allylbenzene **14** and *cis*-1,4-



[a] Conditions: CH_2CI_2 (0.1 M), 40 °C, 2 h, catalyst 1 mol%, 1MSCI 10 mol%. [b] Conversion was determined by GC for entries 1 and 4 using durene as an internal standard. [c] Catalyst 6 was used without TMSCI. [d] E/Z ratio: 9:1 (for cat. 6, 5 a, and 5 b), 5:1 (for 5 c). [e] Conditions: toluene (0.1 M), 80 °C, overnight, cat. 2 mol%, TMSCI 20 mol%. 2-Butene 18 was used as a standard solution (1 M) in CH_2CI_2 . E/Z-ratio was not determined.

diacetoxy-2-butene **15** (2 equiv) was, under chosen conditions, quite challenging, even for the active Hoveyda catalyst **6**. Interestingly, the nitro-substituted **5b** was very effective in this case (entry 3). Butenolysis of methyl oleate (**17**) was chosen next (entry 4); in this case, catalysts **5a** and **5c** gave the lowest conversions of **17**, while **5b** was again the catalyst of choice, providing similar results to **6**. Finally, CM between estrone derivative **21** and 2-methylbut-2-ene **22** (3 equiv) proceeded very well, even with only 1 mol% of the catalysts **5a** and **5c**.

The results presented in Table 1 show that the newly obtained phenolate catalysts, when activated, can be used in typical olefin metathesis transformations, usually leading to good results, even with a loading of 1–2 mol%. As expected, the observed levels of activity were not higher than those exhibited by the known and successful catalyst **6**; however, the new catalysts have special properties, such as chemo-switchability and solubility in a wide spectrum of solvents. Importantly, the new complexes **5a**–**c** are characterized by their high solubility both in polar and non polar solvents, including pentane. This property can be utilized, for example, to polymerize some non polar monomers, such as dicyclopentadiene (DCPD), without using any additional co-solvent.^[15]

To gain more information about the specific behavior of phenolate-type catalysts (**5a**-**c**) in ROMP, we studied their performance in polymerization of *endo,exo*-bicyclo[2.2.1]hept-5-

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Scheme 3. ROMP benchmark reaction.

ene-2,3-dicarboxylic acid dimethyl ester (**24** Scheme 3), before focusing on DCPD. This reaction has been used in previous reports for benchmarking novel initiator systems,^[16] because polymers of **24** are rarely prone to degradation by secondary metathesis (back-biting) reactions.^[17] Accordingly, the number-average molecular weight (M_n) of the polymers produced read-ily permits the assessment of the initiation efficiency of the novel catalysts, because it is indirectly proportional to the ratio of initiation rate to propagation rate constants (k_i/k_p).

For a first estimation, only the initiator **5a** was used in a benchmark reaction with **24** and the results were compared with data obtained for well-established olefin metathesis initiators **M31**,^[18] **1**, and **6**. Catalyst **M31** is characterized by a fast initiation and is well-suited for performing controlled/living polymerization, producing polymers with short chain lengths and a polydispersity index (PDI) of <1.1. In contrast, a relatively high M_n and PDI (\approx 300 kg mol⁻¹ and > 2, respectively) can be attributed to a slow, non concurrent initiation, as with **1**. Hoveyda catalyst **6** is a compromise, showing a M_n value of 89 kg mol⁻¹ and a PDI of 1.3. Results are summarized in Table 2.

Table 2. ROMP benchmark reaction of 24. ^[a]								
Entry	Reference	Initiator	Solvent	T [°C]	<i>t</i> [h]	$M_{\rm n} [{\rm kg}{ m mol}^{-1}]^{[{ m b}]}$	PDI ^[b]	
1	[16e]	M31	CH ₂ Cl ₂	RT	0.1	62	1.05	
2	[16e]	1	CH_2CI_2	RT	6	292	2.3	
3	[16e]	6	CH_2CI_2	RT	0.5	89	1.3	
4	[16g]	M31	toluene	80	0.5	54	1.1	
5		5 a	toluene	RT	24	n.d. (58% conv.)		
6		5a+HCI	toluene	RT	0.5	153	1.8	
7		5 a	toluene	80	24	n.d. (73% conv.)		
8		5 a + HCl	toluene	80	0.5	213	1.8	
[a] Conditions: $[mon] = 0.1 \text{ M}$, $[mon]/[Ru] = 300$ [b] Determined by GPC in THF on the basis of polystyrene calibration. n.d. = not determined.								

The reactions were carried out under inert conditions, using the Schlenk technique. We investigated the activity of pure and HCl-activated **5a** at RT and elevated temperature (80 °C). In both cases, toluene was selected as a solvent, because the presence of a chloride source might influence the reactivity of the complex. The monomer was added in an excess of 300 equiv with respect to the initiator. After completion of the polymerization (monitored by TLC), the reaction was quenched by the addition of an excess of ethyl vinyl ether. Subsequently, the polymers were precipitated in cold methanol, dried, and analysed by gel permeation chromatography in THF against a polystyrene standard. Two activation modes were investigated: 1) activation by temperature, and 2) chemo-activation by the addition of HCl. As seen in Table 2 (entries 5 and 7), the reactivity of **5a** can be enhanced by temperature. The conversion was improved from 58% at RT to 73% at 80°C. However, no completion was reached, because the catalyst decomposes within 24 h under both reaction conditions. With the addition of HCl (10 equiv) in diethyl ether, the reaction at RT leads to full conversion in less than 1 h. The obtained polymers (entry 6) were found to have a higher molecular weight and slightly broader weight distribution (153 kg mol⁻¹, 1.8) than those produced with Hoveyda catalyst **6** (89 kg mol⁻¹, 1.3). These results were not improved when HCl was added at 80°C, as revealed by gel permeation chromatography (GPC) data (entry 8).

Due to the industrial importance of poly(DCPD) as a valuable material,^[15] there is a strong need to develop well-defined catalysts for effective ROMP reactions of DCPD. To get a first impression about the switchability of initiator 5a in DCPD, simultaneous thermal analysis (STA) was conducted with and without the addition of HCl. For this purpose, initiator (100 ppm) was added to DCPD (1 mL). The formulation was then homogenized, cooled with liquid N₂ and placed in DSC pans. The measurements were commenced at 20°C with a heating rate of 3°Cmin⁻¹. The polymerization exotherm was read out as a function of temperature. Switching temperatures for the initiators were equalized to the onset temperature of the exothermic heat flow. Without HCl, an onset temperature of 72 °C was found for initiator 5a. Moreover, a mass loss of 38% was observed, which was due to a retro-Diels-Alder reaction occurring to its volatile educt, cyclopentadiene at 69°C (Scheme 4).^[15d]



Scheme 4. Competing thermal degradation and ROMP of DCPD (25).

In contrast, HCI-activated polymerization already occurs below 50 $^{\circ}$ C (an exact value could not be determined as STA has a domain of uncertainty in the low-temperature area). However, the marginal mass loss of less than 6%, is assigned to toluene, which was added in exactly this amount to DCPD. This result is the final proof that full polymerization occurred.

Next, complexes **5a** and **5b** were tested in bulk polymerization in neat DCPD. The commercially available catalyst **1** was utilized as reference material, because it is known to show sufficient mechanical properties of industrially produced poly-(DCPD).^[15d] Because of the good solubility of catalysts **5a** and **5b** in DCPD, we performed the polymerization in the neat monomer, without any co-solvent. Again, the influence of temper-



Table 3. ROMP of DCPD.							
Entry	Catalyst (monomer/ catalyst ratio)	Additive ^[a]	7 [°C]	t [min]	Yield of poly(DCPD) [%] ^[b]	Form of poly(DCPD)	
1	1 (16 000)	none	28	30	> 99	solid, hard	
2	1 (50 000)	none	80	24 h	>99	solid, hard	
3	5a (16000)	none	28	180	n.d.	liquid	
4	5a (16000)	none	28	960	90	solid, soft	
5	5 a (31 000)	HCI	80	10	>99	solid, hard	
6	5 a (40 000)	HCI	80	30	>99	solid, hard	
7	5 a (62 500)	HCI	80	120	97	solid, soft	
8	5 a (125000)	HCI	80	120	75	solid, soft	
9	5 b (31 000)	HCI	80	10	>99	solid, hard	
10	5 b (31 000)	p-TsOH	80	60	85	solid, soft	
11 ^[c]	5 b (16000)	HCI	28–	24 h	>99	solid, hard	
			60	+10			
				min			
[a] For entries 4–11, 4 equiv (rel. to catalyst) of the additive was used. [b] The yield was calculated based on the weight of obtained solid mate- rial. n.d.=not determined, [c] The reaction was carried out at 28 °C for							

ature and additives on the performance of phenolate catalysts in polymerization and on the nature of the resultant poly-

24 h, HCl was added, and the reaction continued at 60 $^\circ\text{C}$ for 10 min.

(DCPD)^[19] was studied. The first reactions (Table 3, entries 1, 3, and 4) were conducted at 28 °C without any additives. No co-solvent was required to dissolve **5a** in the monomer, whereas a stock solution of **1** in DCM had to be used because this catalyst is insoluble in neat DCPD. Importantly, although **1** initiated the reaction almost immediately after addition, no visual signs of polymerization were observed even after 3 h when **5a** was used, which proves that the initiation can be nicely controlled in this case. After a prolonged time, the progress of the reaction with a phenolate catalyst can be observed, because after 16 h a gelatinous polymer was isolated with a 90% yield.

As expected, addition of HCl or *p*-TsOH and increasing temperature significantly improved the yield of polymerization promoted by **5a** and **5b** (activation properties of TMSCI were estimated by us as being between those of HCl and *p*-TsOH). By using 5 a and HCl, we were able to obtain solid poly(DCPD) with an almost quantitative yield after 30 min in a reaction carried out at 80 °C and with a monomer to catalyst ratio of 40000:1 (entry 6). Further decrease of the catalyst loading resulted in the isolation of the soft form of poly(DCPD), but still in excellent yields (Table 3, entries 7-8). At this point, we decided to take advantage of the lower activity of the nitro-substituted **5b** to prove the possibility of prolonged storage of the catalyst-monomer mixture. We intentionally ran this experiment with relatively high catalyst loading (Table 3, entry 11) to show that even increased amounts of the initiator do not initiate the polymerization. Contrary to benchmark polymerization with monomer 24, which yielded 52% of polymer, we were pleased to see no sign of the reaction even after keeping the DCPD/catalyst mixture at 28 °C for 24 h. After that time, however, addition of HCl and placing the reaction vessel into an oil bath heated to 60°C resulted in fast and quantitative polymerization, leading to a hard polymer (entry 11). Finally, it should be stressed that, after addition of an acidic activator, both 5a and 5b did not initiate immediately, leaving some time to handle the reaction mixture. All these facts can be of some value in terms of possible practical applications of these complexes. To obtain exact values for mechanical properties of the obtained poly(DCPD) samples, tensile strength tests were performed under the conditions presented in entries 2 and 6 of Table 3. In this case a pre-prepared mixture, containing $30 \,\mu\text{L}$ of toluene per 1 mL of monomer, was used to maintain the monomer, liquidized for better handling at RT. Both initiators were dissolved in the appropriate amount of toluene to reach a total concentration of 60 µL of toluene per 1 mL of DCPD. Additionally, HCl (10 equiv) was added to the DCPD/[5a] formulation. The molds were put in the oven for 24 h at 80 °C. Tensile strength measurement revealed that poly-(DCPD) test bars, initiated with the HCl-activated 5a, exhibit a Young's modulus (E) of (1.75 ± 0.10) GPa and maximum strain $(R_{\rm m})$ of (29 ± 2) MPa. Mechanical properties are in accordance with tensile strength values obtained with 1 (1.6-1.9 GPa, 40-50 MPa, elongation at yield or break 4-5%) which are representative for industrially produced and applied poly(DCPD).^[20]

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Conclusion

In summary, we synthesized three cyclic Ru-phenolates (**5a**–**c**) and studied their effectiveness as catalysts in olefin metathesis reactions.^[7b] The investigation of their catalytic activity showed that, after activation with some chemical agents, they promote RCM, enyne, and CM reactions, including butenolysis, with good results. Catalysts **5a** and **5b** also show applicability in ROMP of DCPD. Practical advantages of using these particular complexes are their solubility in neat DCPD and the possibility of delaying the initiation of the polymerization reaction until a specific time.

Experimental Section

For full details on synthetic procedures, characterization, and screening of complexes **5a–c**, and for details of X-ray measurements of **5a** and **5b**, see the Supporting Information. CCDC-1013670 (**5a**) and CCDC-1013671 (**5b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Representative synthesis of a phenolate complex (5 a)

A Schlenk flask equipped with a magnetic stirring bar was charged under argon with Grubbs II-generation complex **1** (200 mg, 0.236 mmol), propenyl phenol derivative **7a** (63 mg, 0.47 mmol), dry DCM (7 mL) and PCy₃ (132 mg, 0.47 mmol). The reaction mixture was stirred for 5 h at 50 °C. After this time, solvent was evaporated by vacuum and crude product was purified by column chromatography (SiO₂, 10% ethyl acetate/*c*-hexane). After removal of solvents, complex **5a** remained as a green solid (152 mg, 78% yield). Analytical data: ¹H NMR (500 MHz, CD₂Cl₂): δ = 15.85 (s, 1 H), 7.07 (s, 1 H), 7.00–6.96 (m, 3 H), 6.66 (d, *J*=8.4 Hz, 1 H), 6.44 (dd, *J*=

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7.7, 1.4 Hz, 1 H), 6.24 (s, 1 H), 6.20 (t, J=7.2 Hz, 1 H), 4.01–3.96 (m, 1 H), 3.83–3.70 (m, 2 H), 3.64–3.59 (m, 1 H), 2.63 (s, 3 H), 2.54 (s, 3 H), 2.50 (s, 3 H), 2.35 (s, 3 H), 2.27 (s, 3 H), 1.66–1.50 (m, 13 H), 1.29 (s, 3 H), 1.11–0.70 ppm (m, 20 H); ¹³C NMR: (126 MHz, CD₂Cl₂): δ = 281.36, 222.21, 221.66, 180.31, 148.30, 139.54, 139.17, 138.78, 137.63, 137.32, 136.98, 134.69, 130.23, 130.05, 129.70, 129.00, 122.38, 116.17, 111.26, 32.52, 32.39, 29.45, 28.92, 28.23, 28.15, 28.12, 28.04, 27.34, 27.03, 21.33, 21.14, 19.40, 18.92, 18.66, 16.76 ppm; ³¹P NMR (202 MHz, CD₂Cl₂): δ = 29.11 ppm; IR (film from DCM): $\tilde{\nu}$ =2925, 2849, 1890, 1583, 1463, 1335, 1266, 1132, 849, 752 cm⁻¹; MS (MALDI TOF) *m/z* (%): 828.34 [*M*⁺].

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