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Isocyanate- and Isothiocyanate-Derived Ru^{IV}-Based Alkylidenes: Synthesis, Structure, and Activity

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Abstract: The synthesis and characterization of a series of isocyanate- and isothiocyanate-derived second generation Grubbs–Hoveyda-type ruthenium–alkylidene complexes, that is, $[Ru(N{=}C{=}O)_2(IMesH_2)(=CH\text{-}2\text{-}(2\text{-}PrO)\text{-}C_6H_4)]$ (**1**), $[Ru(N{=}C{=}O)_2(1,3\text{-}dimesityl\text{-}3,4,5,6\text{-}tetrahydropyrimidin\text{-}2\text{-}ylidene)(=CH\text{-}2\text{-}(2\text{-}PrO)\text{-}C_6H_4)]$ (**2**), $[Ru(N{=}C{=}S)_2(IMesH_2)(=CH\text{-}2\text{-}(2\text{-}PrO)\text{-}C_6H_4)]$ (**3**), and $[Ru(N{=}C{=}S)_2(1,3\text{-}dimesityl\text{-}3,4,5,6\text{-}tetrahydropyrimidin\text{-}2\text{-}ylidene)(=CH\text{-}2\text{-}(2\text{-}PrO)\text{-}C_6H_4)]$ (**4**), and their activity in various metathesis reactions are described. Compounds **1**–**4** were prepared by reaction of the parent complexes $[RuCl_2(IMesH_2)(=CH\text{-}2\text{-}(2\text{-}PrO)C_6H_4)]$ (**5**) ($IMesH_2$ = 1,3-bis-(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene) and $[RuCl_2(1,3\text{-}dimesityl\text{-}3,4,5,6\text{-}tetrahydropyrimidin\text{-}2\text{-}ylidene)(=CH\text{-}2\text{-}(2\text{-}PrO)\text{-}C_6H_4)]$ (**6**) with silver cyanate and thiocyanate, respectively. The X-ray structure of **1** was determined, confirming the isocyanate-type bonding of the ligand. The isothiocyanate-type bonding in **3** and **4** was unambiguously confirmed by IR and ^{13}C NMR spectroscopy. The isocyanate-derived complexes **1** and **2** were found to be excellent catalysts for the ring-opening metathesis polymerization (ROMP) of *cis*-cycloocta-1,5-diene (COD). Both **1** and **2** yielded poly(COD) with a *trans*-content of about 80%. First-order kinetics with unprecedentedly high rate constants of polymerization (k_p = 0.068 and 0.26 s^{-1}, respectively) were observed. Compounds **3** and **4** were also active initiators for the ROMP of COD, however, they generated poly(COD) with a *cis*-content of 80 and 67%, respectively. Complexes **1** and **2** also showed good catalytic activity in cross-metathesis (CM) reactions. Finally, **1**–**4** were also found to be excellent catalysts for the regioselective cyclopolymerization of diethyl 2,2-dipropargylmalonate (DEDPM), resulting in poly(DEDPM) almost entirely based on five-membered repeat units, that is, cyclopent-1-ene-1,2-vinylenes.

Keywords: alkenes · homogeneous catalysis · metathesis · polymerization · ruthenium

Introduction

The development of well-defined transition metal alkylidenes paved the road for metathesis into numerous applications in organic and polymer chemistry as well as materials science.[1] Both Schrock-[1–5] and Grubbs-type[1,6,7] catalysts and initiators have been subject to numerous modifications, which significantly broadened the range of applications. In Ru-based Grubbs-type catalysts, variations in the N-heterocyclic carbene[8–23] (NHC) as well as in the alkylidene (benzylidene) ligand[24–44] have been reported. Furthermore, the replacement of the chloride ligands by triflate, various carboxylates, and phenoxides has been described,[45–55] a concept that has also been used for catalyst immobilization purposes.[56] So far, the bis(perfluorocarboxylate)-derivatives of the second generation Grubbs- and Grubbs–Hoveyda catalysts are the only Ru–alkylidenes that allow for the cyclopolymerization of 1,6-heptadiynes,[46,48,49] a task that may otherwise only be accomplished in a controlled or even living manner by particularly designed Schrock catalysts.[57–65]

There are only few reports on Ru-isocyanates and isothiocyanates. Nagao et al. synthesized a series of polypyridine ruthenium (II) isocyanates and isothiocyanates.[66] Werner

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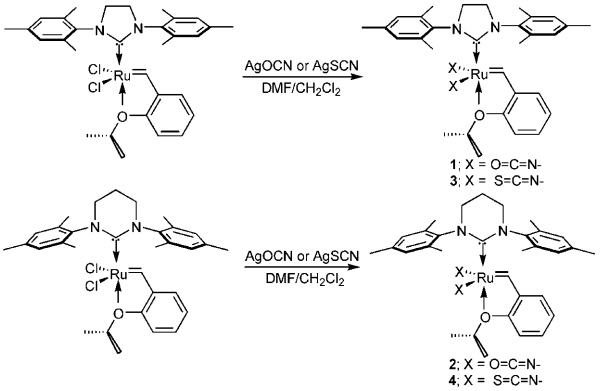
et al. reported a number of Ru^{IV} mono- and di(isocyanato) allenylidenes and alkylidenes of the general formula $RuXX'(PR_3)_2(CHR)$ and $RuXX'(PR_3)_2(C{=}CHR)$ (X = Cl, N=C=O; X′ = C=C=O). However, no attempts to use these compounds in any metathesis-based reactions have been undertaken so far.[67] Herein, we report the extension of the concept of pseudo-halide derivatives of Grubbs' catalyst and describe the synthesis and metathetical activity of well-defined isocyanate-, and isothiocyanate-derived second generation Grubbs–Hoveyda catalysts.

Abstract in German: Wir berichten über die Synthese und Charakterisierung von Isocyanat- und Isothiocyanat basierten Grubbs–Hoveyda-Typ Rutheniumalkylidenkomplexen der 2. Generation, d. h. über [Ru(N=C=O)$_2$(IMesH$_2$)(=CH-2-(2-PrO)-C$_6$H$_4$)] (**1**), [Ru(N=C=O)$_2$(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-yliden)(=CH-2-(2-PrO)-C$_6$H$_4$)] (**2**), [Ru(N=C=S)$_2$(IMesH$_2$)(=CH-2-(2-PrO)-C$_6$H$_4$)] (**3**) und [Ru(N=C=S)$_2$(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-yliden)(=CH-2-(2-PrO)-C$_6$H$_4$)] (**4**) und deren Aktivität in verschiedenen Metathesereaktionen. Die Verbindungen **1**–**4** wurden mittels Reaktion der Startkomplexe [RuCl$_2$(IMesH$_2$)(=CH-2-(2-PrO)C$_6$H$_4$)] (**5**) (IMesH$_2$ = 1,3-Bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-yliden) und [RuCl$_2$(1,3-Dimesityl-3,4,5,6-tetrahydropyrimidin-2-yliden)-(=CH-2-(2-PrO)-C$_6$H$_4$)] (**6**) mit Silbercyanat bzw. Silberthiocyanat hergestellt. Die Struktur von Komplex **1** wurde mittels Einkristallröntgenstrukturanalyse ermittelt und bestätigte die Isocyanat-Bindungsstruktur des Liganden. Die Isothiocyanat Bindungsstruktur in **3** und **4** wurde zweifelsfrei mittels IR und ^{13}C NMR Spektroskopie bestimmt. Die Isocyanat-basierten Komplexe **1** und **2** erwiesen sich als exzellente Katalysatoren für die Ring öffnende Metathesepolymerisation (ROMP) von *cis*-Cycloocta-1,5-dien (COD). Sowohl Komplex **1** als auch Komplex **2** erlaubten die Synthese von poly(COD) mit einem hohen *trans*-Anteil von ca. 80%. Eine Polymerisationskinetik erster Ordnung mit unerwartet hohen Reaktionsraten (k_p = 0.068 bzw. 0.26 s^{-1}) wurden beobachtet. Die Komplexe **3** und **4** waren ebenfalls aktive Initiatoren für ROMP von COD, allerdings resultierte daraus poly(COD) mit einem hohen *cis*-Anteil von 80 bzw. 67%. Die Komplexe **1** und **2** zeigten auch eine gute katalytische Aktivität in der Kreuzmetathese (CM). Schließlich erwiesen sich die Komplexe **1**–**4** auch als exzellente Katalysatoren für die regioselektive Cyclopolymerisation von Diethyl-2,2-dipropargylmalonat (DEDPM). In allen Fällen wurde Poly(DEDPM) erhalten, welches ausschließlich aus 5-gliedrigen Repetiereinheiten, d.h. Cyclopent-1-ene-1,2-vinylenen besteht.

Results and Discussion

Synthesis and Structure of Complexes 1–4

Complexes **1** and **3** were prepared by chloride metathesis from the second generation Grubbs–Hoveyda catalyst RuCl$_2$(IMesH$_2$)(=CH-2-(2-PrO)-C$_6$H$_4$) (**5**).[68] Thus, reaction of **5** with silver cyanate and thiocyanate, respectively, allowed for the synthesis of **1** and **3** as dark green and dark yellow-green solids in 84 and 78% yield (Scheme 1). Complexes **2** and **4** were prepared in an analogous way from RuCl$_2$(1,3-dimesityltetrahydropyrimidin-2-ylidene)(CH-2-(2-PrO)-C$_6$H$_3$) (**6**), [13] and were isolated as light green and dark yellow-green amorphous powders in 83 and 75% yield, respectively. In the ^{1}H NMR spectrum, complexes **1**–**4** were characterized by an upfield shift of the alkylidene proton signal (16.37 ppm (**1**) and 16.40 (ppm) (**3**) as well as 16.08 ppm (**2**) and 16.02 ppm (**4**)), as compared to the alkylidene signal of parent **5** (16.56 ppm)[68] and **6** (16.48 ppm).[13] In the ^{13}C NMR, the signals for the isocyanate carbon of **1** and **2** were found at δ = 134.6 and 133.7 ppm, the signals for the isothiocyanate carbon of **3** and **4** were found at δ = 132.5 and 133.4 ppm, respectively. No additional signals around 110 ppm, which would be indicative for cyanate or thiocyanate formation, were observed. To further distinguish between iso(thio)cyanate and (thio)cyanate coordination, we first recorded the IR-spectra of **1**–**4**. These were in accordance with those of other Ru-isocyanate and isothiocyanate complexes.[66] Thus, the values for the ν_{CN} band for **1**–**4** were 2216, 2225, 2083, and 2088 cm^{-1} (Figures S5–S8 in the Supporting Information). However, in order to provide unambiguous proof for the mode of coordination of the SCN$^-$ and OCN$^-$ ligands, we additionally confirmed the structure of **1** by X-ray analysis (Figure 1). Crystals of **1,** suitable for X-ray analysis, were obtained via the layering of *n*-hexane over a concentrated dichloromethane solution of **1**, producing dark green needle-type crystals. Compound **1** crystallizes in the monoclinic space group *C*2/*c*, *a* = 2302.05(3), *b* = 3442.93(8), *c* = 930.01(8) pm, $\alpha = \gamma = 90°$, $\beta = 109.952(2)°$, *Z* = 8.



Scheme 1. Synthesis of catalysts **1**–**4**.

The distance Ru(1)–C(16), that is, the bond length of the Ru-alkylidene, is 180.8(4) pm, and thus differs only slightly from that observed in the related Ru^{IV}-alkylidene pseudoha-

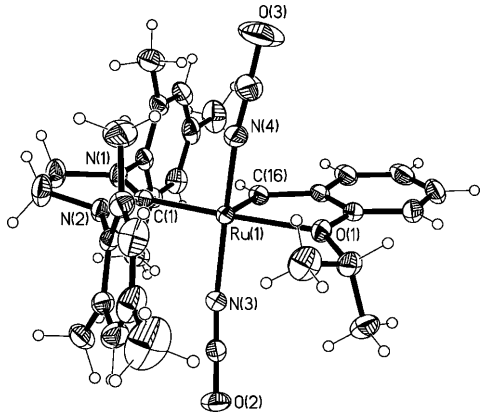


Figure 1. X-ray structure of **1.** Selected bond lengths (pm): Ru(1)–C(16), 180.8(4); Ru(1)–C(1) 196.7(3); Ru(1)–N(3) 202.2(4); Ru(1)–N(4) 200.8(4); Ru(1)–O(1) 225.6(2). Selected bond angles (°): C(16)-Ru(1)-N(4) 96.55(16); C(16)-Ru(1)-N(3) 100.47(16); C(16)-Ru(1)-C(1), 101.75(16); C(1)-Ru(1)-N(4), 91.84(14); C(1)-Ru(1)-N(3), 93.56(13), N(4)-Ru(1)-N(3), 160.68(14); C(16)-Ru(1)-O(1), 79.38(14); C(1)-Ru(1)-O(1), 177.30(12); N(4)-Ru(1)-O(1), 85.59(11); N(3)-Ru(1)-O(1), 88.62(11).

lide complex $Ru(CF_3COO)_2(IMesH_2)(CH\text{-}2\text{-}(2\text{-}PrO)\text{-}C_6H_4)$ (**7**, Ru(1)-C(16) = 182.6(2) pm).[48] The same is true for the distances Ru(1)-C(1) (196.7(3) pm) and Ru(1)-O(1) (225.6(2) pm), which are 197.9(2) and 224.58(15) pm, respectively, in **7**.[48] However, very similar values are also found in the parent complex **5**.[68] These data clearly illustrate that any attempt to predict the catalytic reactivity of a catalyst solely from its structural data may not always be successful.

Ring-Opening Metathesis Polymerization (ROMP) of *cis*-1,5-Cyclooctadiene (COD) by the Action of 1–4

In order to benchmark the existing systems according to a set of experiments and reaction conditions that has been suggested for the characterization of new metathesis catalysts,[69] we first checked for the catalytic activities of complexes **1–4** in ROMP using *cis*-1,5-cyclooctadiene (COD) as a monomer. The isocyanate-derived complexes **1** and **2** showed excellent reactivity in the ROMP of this monomer (Figure 2a). Thus, at room temperature the reaction was completed within 30 seconds by the action of 0.1 mol% of **1** and **2** with respect to COD. Applying first-order kinetics (Figure 2b), the rate constants of polymerization (k_p) are 0.068 and 0.26 s^{-1}, respectively. The catalytic activities of complexes **1** and **2** are thus comparable to those of the recently reported catalyst $RuCl_2$(1,3-dimesityl-4,5,6,7-tetrahydro-1,3-diazepin-2-ylidene)(=CH-2-(2-PrO)C_6H_4), which is based on a 7-membered NHC.[70] As compared to the theoretical value derived from the COD/initiator ratio ($M_{n\,(theor)}$ = 22000 g mol^{-1}), the number average molecular weights (M_n) for poly(COD) prepared by the action of **1** and **2** were 20300 and 51900 g mol^{-1} with polydispersity indices (PDIs) of 2.05 and 1.90, respectively. The poly(COD) that formed by the action of both **1** and **2** displayed a *cis/trans* ratio of 1:4 (Figures S1 and S2 in the Supporting Information). In contrast, the isothiocyanate complexes **3** and **4**

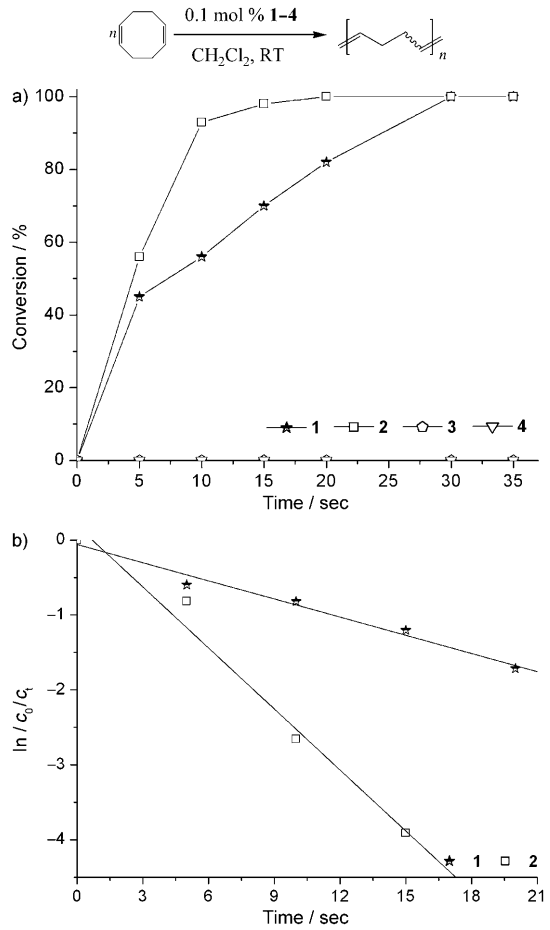


Figure 2. a) Kinetics of ROMP of COD by the action of **1–4**. b) First-order plots for **1** and **2** in the ROMP of COD. [initiator] = 1.8 mM, [COD] = 1.8 M.

showed a comparable moderate reactivity in the ROMP of COD. Applying the same conditions, complete conversion of the monomer (200 equivalents with respect to **3** or **4**) was observed within **7** h. The number average molecular weights (M_n) were 45500 and 59200 g mol^{-1} with PDIs of 2.17 and 1.89, respectively. Interestingly, poly(COD) that formed by the action of **3** or **4** displayed a *cis/trans* ratio of 4:1 and 2:1, respectively (Figures S3 and S4 in the Supporting Information). We are unable to explain these differences in the *cis/trans* ratio at the current time.

Ring-Closing Metathesis (RCM) by the Action of 1–4

The catalytic activity of complexes **1–4** in various RCM reactions using diethyl 2,2-diallylmalonate (DEDAM), diethyl 2-allyl-2-methallylmalonate, and diethyl 2,2-dimethallylmalonate was investigated. Monomer conversion was monitored by GC-MS. Surprisingly, complexes **1** and **2** (both used at a 0.1 mol% level), which were found to be highly active in ROMP (see above), were totally inactive in the RCM of the above-mentioned dienes. In contrast to that, we found very moderate activity in the RCM of the above-mentioned sub-

strates with **3** and **4** (both used at a 1 mol% level). Conversion of DEDAM reached only 30 and 1%, respectively, by the action of **3** and **4** within 90 min. Complexes **1**, **2**, and **4** did not show any significant reactivity in the RCM of diethyl 2-allyl-2-methallylmalonate. With **3**, a conversion of only 12% was achieved in the RCM of diethyl 2-allyl-2-methallylmalonate within 2 h. Consequently, no significant activity at all was observed in the RCM of diethyl bis(methallyl) malonate. A summary of the results in RCM is given in Table 1.

Cross-Metathesis (CM) Reactions by the Action of 1–4

Complexes **1** and **2** were found to be good catalysts for the CM of allylbenzene with *cis*-1,4-diacetoxy-2-butene (Figure 3). Substrate conversion to the desired product was 72% within 20 min by the action of **1** and 68% within the same time by the action of **2** (both at a 2.5 mol% level). In the CM of methyl acrylate with 5-hexenyl acetate, however, 96 and 65% conversion to methyl-4-acetoxyhex-2-enoate was achieved with **1** and **2** within two hours (Figure 4). In contrast to **1** and **2**, the isothiocyanate-derived complexes **3** and **4** showed only 1% yield in the CM between allylbenzene and *cis*-1,4-diacetoxy-2-butene within 60 min (Figure 3), 30% and 1% conversion, respectively, were observed in the CM of methyl acrylate with 5-hexenyl acetate (Figure 4).

Cyclopolymerization of DEDPM by the Action of 1–4

Finally, we studied the catalytic activity of complexes **1–4** for the cyclopolymerization of diethyl dipropargyl malonate (DEDPM) (Scheme 2). Both the isocyanate- and the isothiocyanate-derived initiators **1–4** showed good reactivity in the cyclopolymerization of DEDPM. The isolated yields were 80, 97, 98, and 78%, respectively, for poly(DEDPM) synthesized by the action of **1–4** (Table 1).

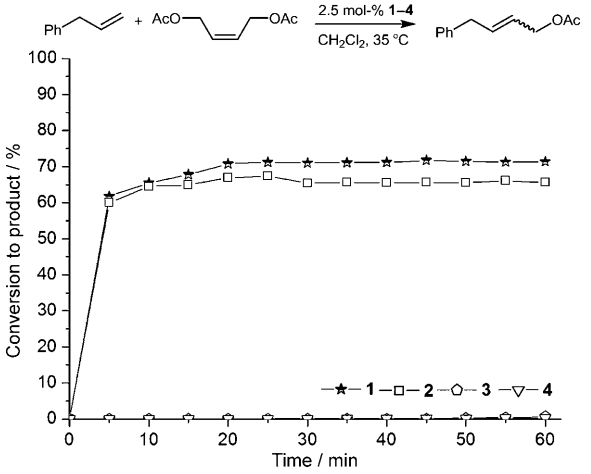


Figure 3. CM of allylbenzene with *cis*-1,4-diacetoxy-2-butene by the action of **1–4**. [initiator] = 0.5 mM, [allylbenzene] = 0.2 M, [*cis*-1,4-diacetoxy-2-butene] = 0.4 M.

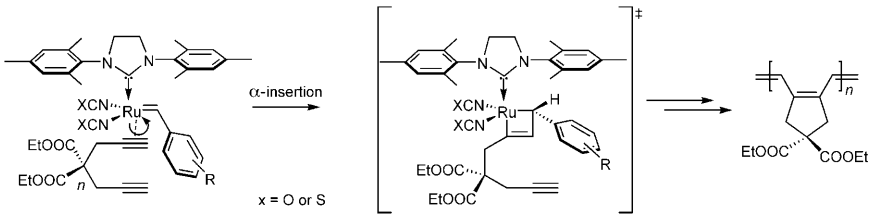
The reactivity of **1–4** in the cyclopolymerization reaction is comparable to that of other bis(trifluoroacetate)-modified second generation Grubbs–Hoveyda-type ruthenium initiators. In terms of polymer structure, all cyclopolymerizations proceeded selectively by α-insertion[71,72] and the resulting poly(DEDPM) was based on greater than 98% five-membered repeat units, that is, on cyclopent-1-ene-1,2-vinylenes (Figure 5). The results obtained with **1–4** thus fit the recently proposed mechanism for the Ru^{IV}-alkylidene triggered cyclopolymerization of 1,6-heptadiynes, which suggests a *trans*-orientation of the intermediary ruthenacyclobutenes, preventing the formation of six-membered repeat units.[50]

A more detailed investigation of the reaction kinetics revealed that the activity in cyclopolymerization decreased in the order **3**~**2**>**1**>**4** (Figure 6a) This is in sharp contrast to the order of reactivity found in the ROMP of COD, which is **2**>**1**>**4**>**3**, or in CM, where the order was **1**>**2**>**3**>**4**. Plots of $\ln(c_0/c_t)$ versus time (Figure 6b) revealed that the polymerization of DEDPM by either **1** or **4** followed roughly first-order kinetics while the one initiated by **2** or **3** did not. However, the plots for initiators **1** and **4** also displayed some sigmoidal shape. The higher control in cyclopolymerization achieved by **1** and **4**

Table 1. Summary of the results for ROMP, RCM, CM, and cyclopolymerization by the action of **1–4**.

substrate	catalyst [mol%]	yield [%]	TON
COD	**1** (0.1)	99[a]	990
COD	**2** (0.1)	99[a]	990
COD	**3** (0.1)	95[a]	950
COD	**4** (0.1)	98[a]	980
DEDAM	**1** (1)	0[b]	0
DEDAM	**2** (1)	0[b]	0
DEDAM	**3** (1)	30[b]	30
DEDAM	**4** (1)	1[b]	1
diethyl 2-allyl-2-methallylmalonate	**1** (1)	0[b]	0
diethyl 2-allyl-2-methallylmalonate	**2** (1)	0[b]	0
diethyl 2-allyl-2-methallylmalonate	**3** (1)	12[b]	12
diethyl 2-allyl-2-methallylmalonate	**4** (1)	0[b]	0
allyl benzene/1,4-diacetoxy-*cis*-2-butene	**1** (2.5)	72[b]	29
allyl benzene/1,4-diacetoxy-*cis*-2-butene	**2** (2.5)	68[b]	27
allyl benzene/1,4-diacetoxy-*cis*-2-butene	**3** (2.5)	1[b]	0.4
allyl benzene/1,4-diacetoxy-*cis*-2-butene	**4** (2.5)	1[b]	0.4
methyl acrylate/5-hexenyl acetate	**1** (2.5)	99[b]	39
methyl acrylate/5-hexenyl acetate	**2** (2.5)	65[b]	26
methyl acrylate/5-hexenyl acetate	**3** (2.5)	30[b]	12
methyl acrylate/5-hexenyl acetate	**4** (2.5)	1[b]	0.4
DEDPM	**1** (1)	80[a]	80
DEDPM	**2** (1)	97[a]	97
DEDPM	**3** (1)	98[a]	98
DEDPM	**4** (1)	78[a]	78

[a] yield of isolated product, [b] by GC-MS.



Scheme 2. Regioselective cyclopolymerization of DEDPM by the action of **1–4**. [initiator] = 1.8 mM, [DEDPM] = 0.18 M.

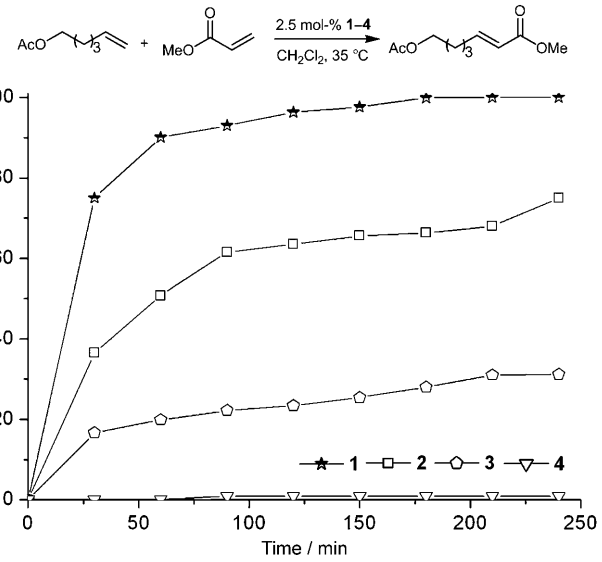


Figure 4. CM of methyl acrylate with 5-hexenyl acetate by the action of **1–4**. [initiator] = 4.3 mM, [5-hexenyl acetate] = [methyl acrylate] = 0.18 M.

was also reflected by the values for M_n and the PDI. Using a ratio of DEDPM/**1–4** of 1:200, polymers with M_n = 75800 g mol^{-1}, 40500 g mol^{-1}, 13500 g mol^{-1}, and 12400 g mol^{-1} with PDIs of 1.33, 2.45, 2.66, and 2.09 were obtained. Particularly, poly(DEDPM) prepared by the action of **3** or **4** displayed much lower molecular weights than anticipated (using a DEDPM/initiator ratio of 200:1, the theoretical value for $M_{n(\text{theor.})}$ is 47400 g mol^{-1}). In combination with the high PDIs, the low molecular weights of poly(DEDPM) prepared by the action of **2–4** are indicative of substantial back-biting and/or chain transfer during the polymerization.

Conclusions

A series of isocyanate- and isothiocyanate-derived ruthenium (IV) NHC alkylidene complexes have been successfully synthesized and their catalytic activity has been determined for selected metathesis reactions. The new compounds showed excellent reactivity in the ROMP of COD and good reactivity in various CM reactions, however, their activity in RCM was comparatively poor. All four novel catalysts and initiators performed differently depending on the type of metathesis reaction. While the novel systems certainly add to the existing armor of Ru^{IV}-alkylidenes with particular strengths for selected applications, particular attention must be devoted to the questions about the origin of high or low activity of certain Ru-based metathesis catalysts/initiator in a particular metathesis reaction. Similarly, the specific differences in the *cis/trans* ratio in ROMP-derived polymers need to be addressed.

Experimental Section

General: All manipulations were performed under a N_2 atmosphere in a glove box (LabMaster 130, MBraun, Garching, Germany) or by standard Schlenk techniques unless specified otherwise. Propargyl bromide

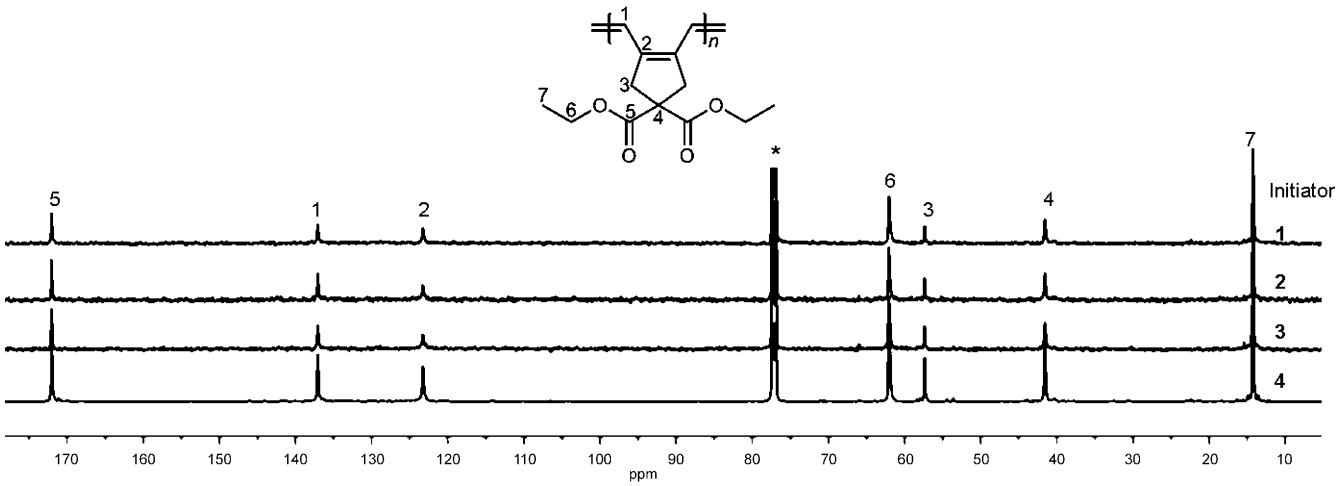


Figure 5. ^{13}C NMR spectra of poly(DEDPM) in $CDCl_3$; (* denotes $CDCl_3$).

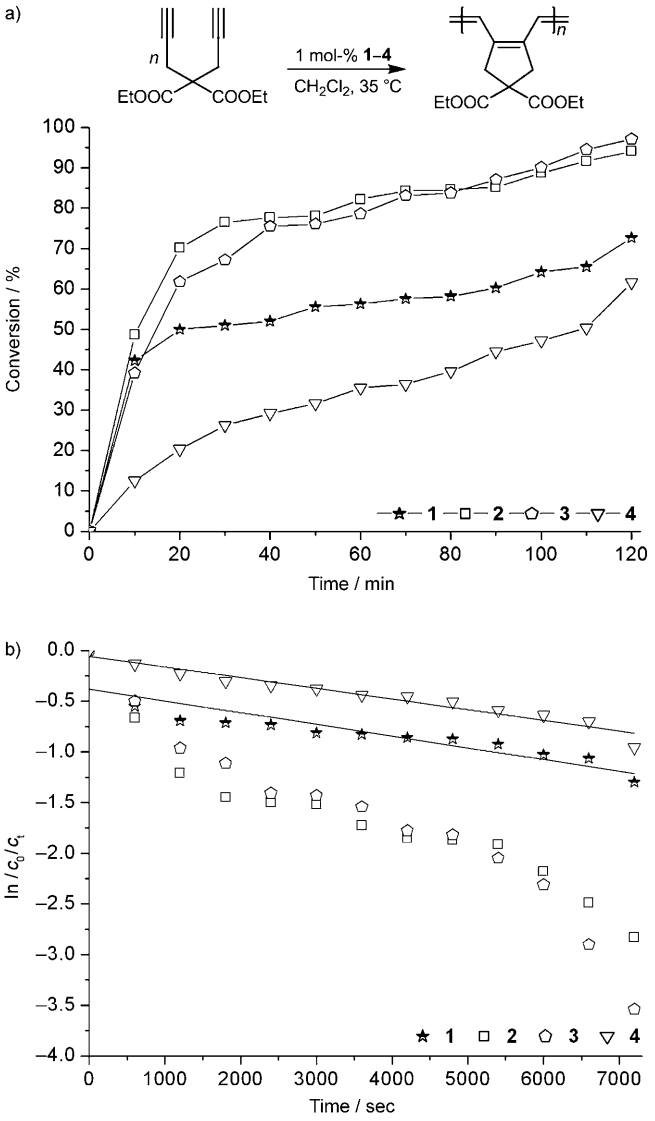


Figure 6. Kinetics of the cyclopolymerization of DEDPM by the action of **1–4**. a) conversion versus time, b) First order plot. [initiator] = 4.2 mM, [DEDPM] = 0.42 M.

(80 wt.% solution in toluene), chloroform, acetonitrile, *cis*-1,5-cyclooctadiene (COD), $CDCl_3$, and CD_2Cl_2 were distilled from CaH_2 under argon and stored over molecular sieves (4 Å). Allylbenzene and *cis*-1,4-diacetoxy-2-butene were distilled from anhydrous K_2CO_3 and stored over molecular sieves (4 Å). 5-Hexenyl acetate was distilled and stored under dinitrogen. *n*-Hexane was distilled from sodium-benzophenone under N_2. Reagent grade DMF was dried over CaH_2 and stored over molecular sieves (4 Å). Diethyl ether, CH_2Cl_2, THF, toluene, and pentane were dried by an SPS solvent purification system (MBraun, Garching, Germany). Purchased starting materials and other chemicals or reagents were used without further purification.

NMR spectra were recorded on a Bruker Avance^{II+} 600 and Bruker Spectrospin 250 spectrometer, respectively, in the indicated solvent at 25 °C and are listed in parts per million downfield from tetramethylsilane as an internal standard for proton and carbon. FT-IR spectra were recorded on a Bruker Vector22 spectrometer using ATR technology. UV/Vis spectra were recorded on a UV-21IPC spectrometer. GC-MS investigations were carried out on a Shimadzu GCMS-QP5050 equipped with an AOC-20i Autosampler, using an SPB fused silica (Rxi-5MS) column (30 m × 0.25 mm × 0.25 μm film thickness) and on a Shimadzu GCMS-QP2010S equipped with an AOC-20i Autosampler using an SPB fused silica (Rxi-5MS) column (30 m × 0.25 mm × 0.25 μm film thickness), respectively. The injection temperature was 150 °C, the initial column temperature was 70 °C. It was then increased to 121 °C within 7 min. Diethyl 2,2-dipropargylmalonate (DEDPM),[73] diethyl 2-allyl-2 methallylmalonate[74] diethyl 2,2-dimethallylmalonate[74] as well as [$RuCl_2$(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene)(=CH-2-(2-PrO)-C_6H_4)][13] were prepared according to published procedures and checked for purity by HRMS-, NMR-, and IR-spectroscopy. GPC measurements were performed on an LC10 AD liquid chromatograph equipped with an SIL-10 ADVP auto injector, a CTO-10AC column oven, an SCL-10AVP system controller and an RID-10A refractive index detector (all from Shimadzu). A precolumn and three consecutive Plgel 5 μm MiniMIX-c columns (7.5 × 300 mm, Polymer Laboratories, Varian) were operated in $CHCl_3$ applying a flow rate of 0.3 mL min^{-1}. Molecular weights were determined by calibration with poly(styrene).

[Ru(N=C=O)$_2$(IMesH$_2$)(=CH-2-(2-PrO)-C$_6$H$_4$)] (1): [$RuCl_2$(IMesH$_2$)(=CH-2-(2-PrO)-C_6H_4)] (600 mg, 0.95 mmol) was dissolved in CH_2Cl_2 (5 mL). A slightly turbid solution of AgOCN (2 equiv, 288 mg, 1.95 mmol) in DMF (2 mL) was added slowly. Stirring was continued for 60 min and the formation of a precipitate was observed. The AgCl was filtered off and the solution was evaporated to dryness. The residue was redissolved in CH_2Cl_2, the solution was flashed over a pad of silica gel (2 cm) and then evaporated to dryness, yielding **1** as a dark green solid. Pure product was obtained by crystallization from *n*-hexane, affording dark green needles in 84% yield (520 mg, 0.82 mmol), which were also found suitable for X-ray analysis. ^{1}H NMR (600.25 MHz, $CDCl_3$, 25 °C): δ = 16.37 (s, 1H; Ru=C*H*Ar), 7.50 (t, ^3J (H,H) = 7.80 Hz, 1H; aromatic CH), 7.11 (s, 4H; mesityl aromatic CH), 6.92 (t, ^3J (H,H) = 7.20 Hz, 1H; aromatic CH), 6.83 (d, ^3J (H,H) = 7.20 Hz, 1H; aromatic CH), 6.79 (d, ^3J (H,H) = 8.40 Hz, 1H; aromatic CH), 4.84 (sept, ^3J (H,H) = 6.60 Hz, 1H; $(CH_3)_2CH$OAr), 4.16 (s, 4H; $N(CH_2)_2N$), 2.42 (s, 18H; mesityl *o*- and *p*-CH_3), 1.09 ppm (d, ^3J (H,H) = 6.10 Hz, 6H; $(CH_3)_2$CHOAr); ^{13}C NMR (150.95 MHz, $CDCl_3$, 25 °C): δ = 299.7, 210.2, 152.5, 144.1, 139.4, 138.9, 134.6, 130.1, 129.7, 122.8, 122.6, 112.6, 74.6, 51.5, 21.2, 20.6, 18.4 ppm; IR (ATR mode): $\tilde{\nu}$ = 3550 (w), 2918 (m), 2361 (m), 2216 (vs), 1589 (m), 1574 (s), 1484 (m), 1453 (w), 1401 (w), 1376 (w), 1335 (w), 1264 (vs), 1215 (m), 1155 (m), 1112 (m), 1035 (m), 937 (m), 852 (m), 806 (m), 778 cm^{-1} (m); HRMS (ESI): calcd. for $C_{33}H_{38}N_4O_3Ru$: 640.1987, found: 640.2306 [M^+] (28.7%).

[Ru(N=C=O)$_2$(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene)(=CH-2-(2-PrO)-C$_6$H$_4$)] (2): This compound was prepared from [$RuCl_2$(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene)(=CH-2-(2-PrO)-C_6H_4)][13] (325 mg, 0.51 mmol) and AgOCN (165 mg, 1.1 mmol) following the procedure described for **1**. The product was isolated as a light green powder in 83% yield (280 mg, 0.42 mmol). ^{1}H NMR (600.25 MHz, $CDCl_3$, 25 °C): δ = 16.08 (s, 1H; Ru=C*H*Ar), 7.49 (t, ^3J (H,H) = 7.80 Hz, 1H; aromatic CH), 7.11 (s, 4H; mesityl aromatic CH), 6.88 (t, ^3J (H,H) = 7.20 Hz, 1H; aromatic CH), 6.80 (d, ^3J (H,H) = 7.20 Hz, 1H; aromatic CH), 6.71 (d, ^3J (H,H) = 8.40 Hz, 1H; aromatic CH), 4.68 (sept, ^3J (H,H) = 6.00 Hz, 1H; $(CH_3)_2CH$OAr), 3.55, 3.60 (t, ^3J (H,H) = 6.01 Hz, 4H; $N(CH_2$-CH_2-$CH_2)N$), 2.35, 2.49, 2.55 (3 × s, 12H; mesityl *o*-CH_3), 2.32 (brs, 2H; $N(CH_2$-CH_2-$CH_2)N$), 2.25 (s, 6H; mesityl *p*-CH_3), 0.91 ppm (d, ^3J (H,H) = 6.10 Hz, 6H; $(CH_3)_2$CHOAr); ^{13}C NMR (150.95 MHz, $CDCl_3$, 25 °C): δ = 303.9, 201.9, 151.8, 145.1, 144.2, 141.6, 140.2, 138.5, 136.8, 135.5, 133.7, 130.2, 130.1, 129.8, 122.8, 122.7, 112.5, 74.1, 49.8, 49.5, 21.6, 21.2, 21.1, 20.7, 19.6, 17.8 ppm; IR (ATR mode): $\tilde{\nu}$ = 3546 (w), 2980 (w), 2922 (w), 2361 (m), 2342 (m), 2225 (vs), 2054 (w), 1947 (w), 1669 (w), 1608 (w), 1591 (m), 1576 (m), 1493 (s), 1453 (m), 1379 (m), 1312 (m), 1290 (s), 1262 (w), 1240 (w), 1208 (s), 1159 (w), 1115 (s), 1037 (m), 940 (m), 918 (w), 882 (w), 854 (w), 808 (w), 751 (vs), 671 cm^{-1} (w); HRMS (ESI) calcd. for $C_{34}H_{40}N_4O_3Ru$: 654.2144, found: 654.2472 [M^+] (36.6%).

[Ru(N=C=S)$_2$(IMesH$_2$)(=CH-2-(2-PrO)-C$_6$H$_4$)] (3): [$RuCl_2$(IMesH$_2$)(=CH-2-(2-PrO)-C_6H_4)] (150 mg, 0.24 mmol) was dissolved in CH_2Cl_2 (5 mL). A slightly turbid solution of AgSCN (2 equiv, 81 mg, 0.48 mmol) in DMF (2 mL) was slowly added. Stirring was continued for 60 min and

the formation of a precipitate was observed. The AgCl was filtered off and the solution was evaporated to dryness. The residue was redissolved in CH_2Cl_2, the solution was flashed over a pad of silica gel (2 cm) and then evaporated to dryness, yielding **3** as a light yellow green solid. The product was obtained by washing the material with dry pentane, which afforded a yellow-green powder in 78% yield (125 mg, 0.18 mmol). ^{1}H NMR (600.25 MHz, $CDCl_3$, 25°C): δ = 16.40 (s, 1H; Ru=C*H*Ar), 7.60 (t, ^3J (H,H) = 7.80 Hz, 1H; aromatic CH), 7.14 (s, 4H; mesityl aromatic CH), 6.96 (t, ^3J (H,H) = 7.20 Hz, 1H; aromatic CH), 6.84 (d, ^3J (H,H) = 8.40 Hz, 1H; aromatic CH), 6.80 (d, ^3J (H,H) = 7.20 Hz, 1H; aromatic CH), 4.90 (sept, ^3J (H,H) = 6.00 Hz, 1H, $(CH_3)_2CHOAr$), 4.20 (s, 4H; N-$(CH_2)_2$N), 2.43 (s, 18H; mesityl *o*- and *p*-CH_3), 1.08 ppm (d, ^3J (H,H) = 6.00 Hz, 6H; $(CH_3)_2$CHOAr); ^{13}C NMR (150.95 MHz, $CDCl_3$, 25°C): δ = 311.8, 206.5, 153.4, 146.9, 144.2, 139.9, 138.6, 132.5, 129.9, 123.5, 123.1, 112.9, 75.5, 51.6, 21.2, 20.5, 18.4 ppm; IR (ATR mode): $\tilde{\nu}$ = 2976 (w), 2918 (m), 2359 (m), 2341 (m), 2142 (m), 2083 (vs), 1607 (m), 1589 (m), 1485 (s), 1453 (m), 1407 (w), 1377 (w), 1316 (w), 1289 (s), 1267 (m), 1231 (w), 1157 (w), 1135 (w), 1113 (w), 1097 (w), 1034 (w), 935 (m), 912 (m), 851 (w), 817 (w), 749 cm^{-1} (w); HRMS (ESI) calcd. for $C_{32}H_{38}N_4OS_2Ru$: 672.1531, found: 614.1784 $[M-NCS]^+$ (50%).

[Ru(N=C=S)$_2$(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene)(=CH-2-(2-PrO)-C$_6$H$_4$)] (4): Complex **4** was prepared from [$RuCl_2$(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene)(=CH-2-(2-PrO)-C_6H_4)][13] (311 mg, 0.48 mmol) and AgSCN (164 mg, 0.98 mmol) following the same procedure as described for **3**. The product was obtained as a dark yellow-green powder in 75% yield (252 mg, 0.36 mmol). ^{1}H NMR (600.25 MHz, $CDCl_3$, 25°C): δ = 16.02 (s, 1H; Ru=C*H*Ar), 7.59 (t, ^3J (H,H) = 7.20 Hz, 1H; aromatic CH), 7.18 (s, 2H; mesityl aromatic CH), 7.12 (s, 2H; mesityl aromatic CH), 6.92 (t, ^3J (H,H) = 7.80 Hz, 1H; aromatic CH), 6.77 (d, ^3J (H,H) = 8.40 Hz, 2H; aromatic CH), 4.75 (sept, ^3J (H,H) = 6.60 Hz, 1H; $(CH_3)_2CHOAr$), 3.55, 3.61 (t, ^3J (H,H) = 5.40 Hz, 4H; N(CH_2-CH_2-CH_2)N), 2.37, 2.50, 2.59 (3×s, 12H; mesityl *o*-CH_3), 2.31 (brs, 2H; N(CH_2-CH_2-CH_2)N), 2.26 (s, 6H; mesityl *p*-CH_3), 0.90 ppm (d, ^3J (H,H) = 6.00 Hz, 6H; $(CH_3)_2$CHOAr); ^{13}C NMR (150.95 MHz, $CDCl_3$, 25°C): δ = 316.1, 197.9, 153.1, 145.2, 144.8, 143.6, 142.1, 141.1, 138.8, 136.7, 133.4, 132.9, 130.2, 129.7, 123.7, 122.9, 112.6, 75.1, 49.8, 49.5, 21.4, 21.3, 21.2, 20.6, 19.6, 17.7 ppm; IR (ATR mode): $\tilde{\nu}$ = 2975 (w), 2921 (w), 2858 (w), 2359 (m), 2341 (m), 2088 (vs), 1966 (w), 1667 (w), 1606 (m), 1589 (s), 1574 (m), 1499 (m), 1474 (s), 1452 (m), 1377 (m), 1351 (m), 1293 (w), 1258 (s), 1243 (w), 1207 (m), 1157 (m), 1113 (m), 1096 (m), 1034 (w), 936 (m), 914 (w), 882 (w), 850 (w), 817 (m), 750 (m), 732 (s), 668 cm^{-1} (w); HRMS (ESI) calcd. for $C_{34}H_{40}N_4ORuS_2$: 686.1687, found: 709.1588 $[M+Na]^+$ (100%).

ROMP of *cis*-1,5-cyclooctadiene (COD) by the action of 1–4: Complex **1** (1.18 mg, 1.84×10^{-6} mol, 0.1 mol%), **2** (1.20 mg, 1.84×10^{-6} mol, 0.1 mol%), **3** (1.24 mg, 1.84×10^{-6} mol, 0.1 mol%), or **4** (1.26 mg, 1.84×10^{-6} mol, 0.1 mol%), dissolved in CH_2Cl_2 (0.5 mL), was added to COD (200 mg, 1.84×10^{-3} mol, 0.22 mL) dissolved in 0.5 mL of CH_2Cl_2. *tert*-Butyl benzene (70 μL) was used as an internal standard. The reaction was carried out at room temperature. Conversion of the monomer was monitored by GC-MS.

Poly(COD) [*cis*/*trans* ~ 1:4], prepared by the action of **1**: ^{1}H NMR (600.25 MHz, $CDCl_3$, 25°C): δ = 5.41 (s, 2H; $H_{olefin,}$ *trans*-poly-COD), 5.37 (brs, 2H; $H_{olefin,}$ *cis*-poly-COD), 2.08 (brs, 4H; *cis*-poly-COD), 2.03 ppm (s, 4H; *trans*-poly-COD); ^{13}C NMR (150.95 MHz, $CDCl_3$, 25°C): δ = 130.1 ($C_{olefin,}$ *trans*-poly-COD), 129.5 ($C_{olefin,}$ *cis*-poly-COD), 32.8 ((CH_2)$_2$, *trans*-poly-COD), 27.5 ppm ((CH_2)$_2$, *cis*-poly-COD); IR (ATR mode): $\tilde{\nu}$ = 30003 (w), 2915 (m), 2841 (m), 2359 (w), 2341 (w), 1446 (m), 1352 (w), 1311 (w), 1236 (w), 1054 (w), 963 (vs), 659 cm^{-1} (m). Isolated yield: 99%, M_n = 20300 g mol^{-1}, PDI = 2.05.

Poly(COD) [*cis*/*trans* ~ 1:4], prepared by the action of **2**: ^{1}H, ^{13}C NMR and IR spectra were identical to poly(COD) prepared by the action of **1**. Isolated yield: 99%, M_n = 51900 g mol^{-1}, PDI = 1.90.

Poly(COD) [*cis*/*trans* ~ 4:1], prepared by the action of **3**: ^{1}H NMR (600.25 MHz, $CDCl_3$, 25°C): δ = 5.43 (brs, 2H; $H_{olefin,}$ *trans*-poly-COD), 5.39 (s, 2H; $H_{olefin,}$ *cis*-poly-COD), 2.09 (s, 4H; *cis*-poly-COD), 2.04 ppm (brs, 4H; *trans*-poly-COD); The ^{13}C NMR and IR spectra were identical to poly(COD) prepared by the action of **1**. Isolated yield: 95%, M_n = 45500 g mol^{-1}, PDI = 2.17.

Poly(COD) [*cis*/*trans* ~ 2:1], prepared by the action of **4**: ^{1}H, ^{13}C NMR and IR spectra were identical to poly(COD) prepared by the action of **3**. Isolated yield: 98%, M_n = 59200 g mol^{-1}, PDI = 1.89.

RCM of diethyl 2,2-diallylmalonate by the action of 1–4. Complex **1** (2.72 mg, 4.16×10^{-6} mol, 1.0 mol%), **2** (2.72 mg, 4.16×10^{-6} mol, 1.0 mol%), **3** (2.79 mg, 4.16×10^{-6} mol, 1.0 mol%) or **4** (2.85 mg, 4.16×10^{-6} mol, 1.0 mol%), dissolved in 0.5 mL of CH_2Cl_2, was added to DEDAM (100 mg, 4.16×10^{-4} mol, 0.11 mL), dissolved in the same amount of the same solvent. *tert*-Butyl benzene (65 μL) was used an internal standard. The reaction was carried out at 35°C under an Ar atmosphere. Conversion of the monomer was monitored by GC-MS.

Ring-closing metathesis (RCM) of diethyl 2-allyl-2-methallylmalonate by the action of 1–4. Complex **1** (2.51 mg, 3.93×10^{-6} mol, 1.0 mol%), **2** (2.57 mg, 3.93×10^{-6} mol, 1.0 mol%), **3** (2.64 mg, 3.93×10^{-6} mol, 1.0 mol%), or **4** (2.71 mg, 3.93×10^{-6} mol, 1.0 mol%), dissolved in 0.5 mL of CH_2Cl_2, was added to substrate (100 mg, 3.9×10^{-4} mol), dissolved in the same amount of the same solvent. *tert*-Butyl benzene (65 μL) was used an internal standard. The reaction was carried out at 35°C under an Ar atmosphere. Conversion of the monomer was monitored by GC-MS.

Ring-closing metathesis (RCM) of diethyl 2,2-dimethallylmalonate by the action of 1–4. Complex **1** (2.38 mg, 3.72×10^{-6} mol, 1.0 mol%), **2** (2.43 mg, 3.72×10^{-6} mol, 1.0 mol%), **3** (2.51 mg, 3.72×10^{-6} mol, 1.0 mol%) or **4** (2.55 mg, 3.72×10^{-6} mol, 1.0 mol%), dissolved in 0.5 mL of CH_2Cl_2, was added to the substrate (100 mg, 3.72×10^{-4} mol), dissolved in the same amount of the same solvent. *tert*-Butyl benzene (65 μL) was used an internal standard. The reaction was carried out at 35°C under an Ar atmosphere. Conversion of the monomer was monitored by GC-MS.

Cross-metathesis (CM) of allylbenzene with *cis*-1,4-diacetoxy-2-butene by the action of 1–4: Complex **1** (6.71 mg, 1.05×10^{-6} mol, 2.5 mol%), **2** (6.91 mg, 1.05×10^{-6} mol, 2.5 mol%), **3** (7.11 mg, 1.05×10^{-6} mol, 2.5 mol%), or **4** (7.25 mg, 1.05×10^{-6} mol, 2.5 mol%), dissolved in 1.0 mL of CH_2Cl_2, was added to a mixture of allylbenzene (50 mg, 4.23×10^{-4} mol, 58 μL) and *cis*-1,4-diacetoxy-2-butene (145 mg, 8.46×10^{-4} mol, 2 equiv, 0.13 mL), dissolved in the same amount of the same solvent. *tert*-Butyl benzene (70 μL) was used as an internal standard. The reaction was carried out at 35°C under an Ar atmosphere. Conversion of the monomer was monitored by GC-MS.

Cross-metathesis (CM) of methyl acrylate with 5-hexenyl acetate by the action of 1–4: Complex **1** (11.1 mg, 1.75×10^{-5} mol, 2.5 mol%), **2** (11.5 mg, 1.75×10^{-5} mol, 2.5 mol%), **3** (11.7 mg, 1.75×10^{-5} mol, 2.5 mol%) or **4** (12.1 mg, 1.75×10^{-5} mol, 2.5 mol%), dissolved in 2.0 mL of CH_2Cl_2, was added to a mixture of methyl acrylate (60 mg, 7.1×10^{-4} mol, 1 equiv, 63 μL) and 5-hexenyl acetate (100 mg, 7.1×10^{-4} mmol, 1 equiv, 0.11 mL), dissolved in the same amount of the same solvent. *tert*-Butyl benzene (70 μL) was used as an internal standard. The reaction was carried out at 35°C under an Ar atmosphere. Conversion of the monomer was monitored by GC-MS.

Cyclopolymerization of diethyl 2,2-dipropargylmalonate (DEDPM) by the action of 1–4: Complex **1** (5.5 mg, 8.46×10^{-6} mol, 1.0 mol%), **2** (5.6 mg, 8.46×10^{-6} mol, 1.0 mol%), **3** (5.6 mg, 8.46×10^{-6} mol, 1.0 mol%) or **4** (5.8 mg, 8.46×10^{-6} mol, 1.0 mol%), dissolved in 1 mL of CH_2Cl_2 was added to DEDPM (200 mg, 8.46×10^{-4} mol) dissolved in the same amount of the same solvent ion. The mixture was stirred for 12 h at 35°C. Ethyl vinyl ether (0.6 mL) was then added and the mixture was stirred for another 30 min. The solvent was removed in vacuo, then 20 mL of dry diethyl ether was added. The product was filtered off and dried in vacuo. The polymer was obtained as a dark-violet powder. Isolated yields were 80, 97, 98 and 78% respectively for poly(DEDPM), synthesized by the action of **1–4**.

For the recording of the reaction kinetics, complexes **1** (1.3 mg, 2.11×10^{-6} mol, 1.0 mol%), **2** (1.4 mg, 2.11×10^{-6} mol, 1.0 mol%), **3** (1.4 mg, 2.11×10^{-6} mol, 1.0 mol%), or **4** (1.5 mg, 2.11×10^{-6} mol, 1.0 mol%) dissolved in 0.6 mL of CH_2Cl_2 was added to DEDPM (50 mg, 2.11×10^{-4} mol) dissolved in the same amount of the same solvent. *tert*-Butyl benzene (60 μL) was used as an internal standard. The reaction was car-

ried out at 35 °C under an Ar atmosphere. Conversion of the monomer was monitored by GC-MS. (**1**; $k_p = 1 \times 10^{-4}\ s^{-1}$, **2**; $k_{p\ (average)} = 3 \times 10^{-4}\ s^{-1}$, **3**; $k_{p\ (average)} = 4 \times 10^{-4}\ s^{-1}$, **4**; $k_p = 1 \times 10^{-4}\ s^{-1}$).

Poly(DEDPM) prepared by the action of **1**: ^{1}H NMR (600.25 MHz, $CDCl_3$, 25 °C): $\delta = 6.68$ (s, 2H; $H_{olefin,}$ =C*H*-C=C-C*H*=), 4.27 (br s, 4H; C_q-CH_2-C=), 3.46 (q, 4H; CH_3CH_2), 1.39 ppm (t, 6H; CH_3CH_2); ^{13}C NMR (150.95 MHz, $CDCl_3$, 25 °C): $\delta = 172.1$ (*C*=O), 137.1 (=*C*H-C=C-*C*H=), 123.2 (=CH-*C*=*C*-CH=), 62.1 (CH_3CH_2), 57.3 (C_q-*C*H_2-C=), 44.1 (C_q-CH_2-C=), 14.2 ppm (*C*H_3CH$_2$); IR (ATR mode): $\tilde{\nu} = 2978$ (w), 2986 (w), 2903 (w), 2361 (w), 1723 (vs), 1444 (w), 1387 (w), 1366 (w), 1246 (s), 1184 (s), 1095 (m), 1010 (m), 947 (w), 897 (w), 860 (m), 736 (m), 702 cm^{-1} (m). Isolated yield: 80 %, $M_n = 75\,800\ g\,mol^{-1}$, PDI = 1.33.

Poly(DEDPM) prepared by the action of **2–4**: ^{1}H-, ^{13}C NMR and FT-IR data were identical to those of poly(DEDPM) prepared by the action of **1. 2**: Isolated yield: 97 %, $M_n = 40\,500\ g\,mol^{-1}$, PDI = 2.45; **3:** Isolated yield: 98 %, $M_n = 13\,500\ g\,mol^{-1}$, PDI = 2.66; **4:** Isolated yield: 78 %, $M_n = 12\,400\ g\,mol^{-1}$, PDI = 2.09.

X-ray analyses for 1. Data were collected on a Nonius KappaCCD diffractometer equipped with graphite-monochromatized $Mo_{K\alpha}$-radiation and a nominal crystal to area detector distance of 36 mm. The structures were solved with direct methods SHELXS86 and refined against F^2 SHELX97.[75] All non-hydrogen atoms were refined with anisotropic displacement parameters and positions of hydrogen atoms were calculated, except for the hydrogen atom at C(16), which was found and refined isotropically with bond restraint (C–H distance of 93 pm). CCDC 729101 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif

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