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Impact of Electronic Modification of the Chelating Benzylidene Ligand in *cis*-Dichloro-Configured Second-Generation Olefin Metathesis Catalysts on Their Activity

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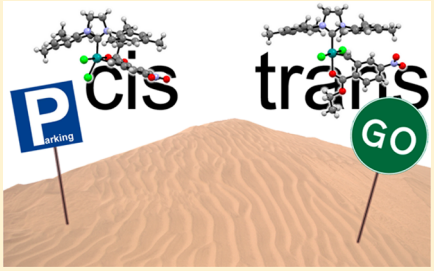
Supporting Information

ABSTRACT: A series of electronically modified second-generation *cis*-dichloro ruthenium ester chelating benzylidene complexes was prepared, characterized, and benchmarked in a typical ring-opening metathesis polymerization (ROMP) experiment. The electronic tuning of the parent chelating benzylidene ligand (2-ethyl ester benzylidene) was achieved by substitution at the 4- and 5-positions with electron-withdrawing nitro or electron-donating methoxy groups. The effect of the electronic tuning on the cis−trans isomerization process was studied experimentally and theoretically. Density functional theory calculations clearly revealed the influence of electronic modification on the relative stability between the cis and trans isomers, which is decisive for the activity of the studied compounds as initiators in ROMP.



INTRODUCTION

Olefin metathesis is a unique carbon−carbon double bond forming reaction catalyzed by transition-metal complexes.[1] In particular, ruthenium-based complexes have attracted considerable interest because they tolerate a wide array of functional groups as well as water and (with some restrictions) oxygen.[2] Typical well-defined ruthenium olefin metathesis catalysts are made up by a carbene and two neutral (phosphines, N-heterocyclic carbene) and two anionic ligands (in most cases chlorides). Already in one of the very early papers on well-defined ruthenium-based catalysts the coexistence of *trans*- and *cis*-dichloro isomers was disclosed.[3] Nevertheless, *cis*-dichloro isomers led a miserable existence after that, although some isolated reports are available.[4] In 2004 the first N-heterocyclic carbene bearing ruthenium carbene complexes with a *cis*-dichloro stereochemistry were disclosed,[5] and since then considerable attention has been paid to the investigation of the scope and the limitation of catalysts bearing this particular stereochemistry. *cis*-Dichloro ruthenium benzylidenes bearing N-heterocyclic carbenes as coligands are characterized by a slower initiation in comparison to their *trans*-dichloro counterparts[6] and exist with O-,[5a,b,7] C═C-,[8] S-,[9] Se-,[10] N-,[5c,11] Br-, I-[12] or P-based[10,13] neutral coligands. Expressed in a generalized manner, the higher thermodynamic stability of the cis isomer is assumed to appear if the second neutral ligand, in addition to the N-heterocyclic carbene, is neither a strongly σ nor a strongly π donating ligand.[10] The slow initiation and pronounced thermal stability are perhaps the most important reasons for the interest in such catalysts today. Such features are beneficial when the metathesis reaction has to be performed at elevated temperatures[7c,d,13d,e] or when a thermally triggered (ring-opening metathesis) polymerization is intended.[5b,c,11b] In many cases, first the trans isomer is obtained, which subsequently isomerizes, releasing the thermodynamically preferred *cis*-configured complex. The underlying isomerization process was studied by experiment[9,13e] and by means of density functional theory based investigations.[10,13e,14] As the essence of these studies, the mechanism of the isomerization can be described by either a dissociative (i.e., the neutral donor ligand dissociates before isomerization) or a concerted pathway (the neutral donor stays in bonding distance to the ruthenium center during the rearrangement of the halides). Furthermore, it was shown that, for energetic reasons, *cis*-dichloro species (at

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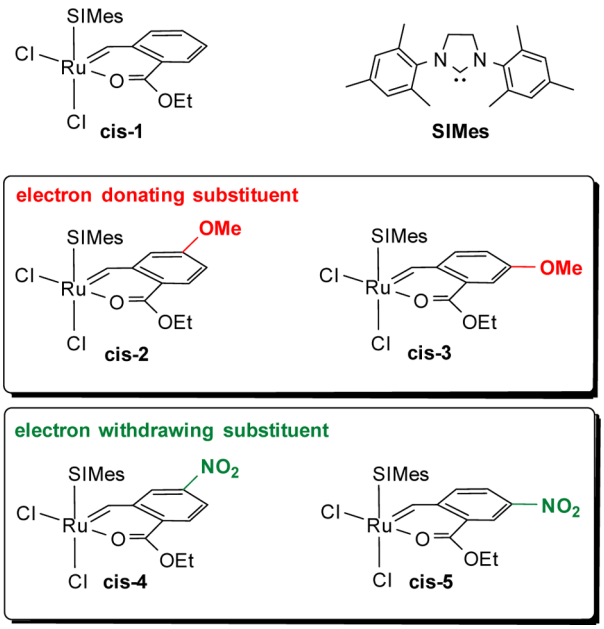
least those bearing N-heterocyclic carbenes as coligands) are considerably worse in catalyzing olefin metathesis reactions in comparison to their isomerization products and it is postulated that isomerization to the trans species has to take place in order to gain catalytic activity.[14c,d]

In this work we report on our studies on the impact of electronic modification of the chelating carbene ligand on the ratio of cis and trans isomers, on the isomerization process, and further on the resulting catalytic properties of the different complexes. As the starting point we used a *cis*-dichloro ruthenium complex bearing a chelating ester substituted benzylidene ligand (**cis-1**)[5b] and prepared analogues in which the benzylidene ligand is further modified with electron-donating (−OMe) or electron-withdrawing groups ($-NO_2$) (see Chart 1). The impact of a similar electronic tuning on the

Chart 1. Compounds under Investigation

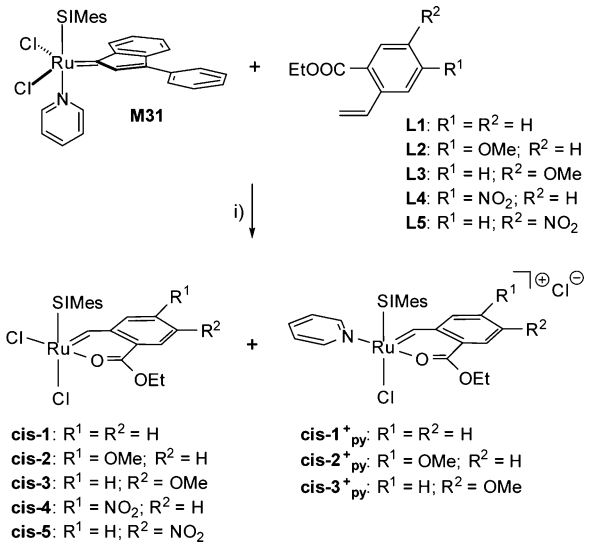


catalytic activity of *trans*-dichloro-configured second-generation Hoveyda-type catalysts has already been described experimentally[15] and theoretically.[16] In simplified terms, the activity increases in this system with the implementation of electron-withdrawing substituents on the benzylidene moiety and is lowered in case of the presence of electron-donating groups. The effect of the electronic tuning on the activity was primarily explained by the variation of the energy of the transition state for the decoordination of the O-donor of the chelating benzylidene ligand.[15,16] Taking these studies as an inspiration, we herein wish to disclose the effect of the electronic tuning of the benzylidene ligand in *cis*-dichloro species.

RESULTS AND DISCUSSION

Synthesis and Characterization. Aiming at the preparation of electronically modified ester-chelating benzylidene complexes, a series of differently substituted 2-vinylbenzoic acid ethyl ester derivatives was prepared. Carbene-precursors **L1**−**L5** featured no additional substituent (**L1**), an electron-donating methoxy group at the position meta (**L2**) or para (**L3**) to the vinyl group, or an electron-withdrawing nitro group at a position meta (**L4**) or para (**L5**) to the vinyl group and were prepared following known protocols (cf. the Supporting Information).[17] Complexes **cis-1**−**cis-5** were obtained from a carbene-exchange reaction of **M31** with 1.2−1.5 equiv of **L1**−**L5**. The reaction was performed in CH_2Cl_2 at 25 °C and is typically complete after 17 h. Extraction of the reaction mixture with 5 vol % hydrochloric acid allowed for the separation of most of the pyridine, and subsequent precipitation of the products with *n*-pentane yielded the desired complexes **cis-1**−**cis-5** in crude form. In particular, complexes **cis-1**−**cis-3** are contaminated with major impurities (6−13%), which were tentatively assigned to the cationic pyridine-containing species **cis-1**$^+_{py}$−**cis3**$^+_{py}$, as shown in Scheme 1.[18] A similar impurity

Scheme 1. Syntheses of cis-1−cis-5[a]



[a]Legend: (i) CH_2Cl_2, 25 °C, 17 h.

was not present in the crude product mixtures of **cis-4** and **cis-5**. Upon subsequent purification by column chromatography analytically pure **cis-1**−**cis-5** were obtained in moderate to good yield. The complexes were characterized by ^{1}H and ^{13}C NMR spectroscopy, elemental analysis, and single-crystal X-ray crystallography. ^{1}H NMR spectroscopy suggested a *cis*-dichloro structure in all cases, as evidenced by a complete loss of symmetry (distinct signals for all four aromatic mesityl protons and all six mesityl methyl groups) and a diastereotopic splitting of the methylene group of the ethyl ester moiety, indicating a chiral ruthenium center. Variation of the electron density of the benzylidene ligand is reflected by the ^{1}H NMR shift of the carbene's proton: electron-rich derivatives **cis-3** and **cis-2** showed the corresponding singlet at 18.57 and 18.92 ppm and the electron-poor systems **cis-4** and **cis-5** exhibited the resonance at lower field, namely at 19.09 and 19.30 ppm, respectively. The unsubstituted complex **cis-1** showed the corresponding signal at 18.96 ppm. Similarly, the ^{13}C resonance of the carbene was shifted according to the electronic modification of the benzylidene ligand. While **cis-1**−**cis-3** exhibited deshielded carbene resonances in the range of 282.9−283.8 ppm, the nitro-group-bearing derivatives gave signals at lower fields (278.0 ppm for **cis-4** and 276.7 ppm for **cis-5**). The same trend could be found for the C═O resonance of the ester group. In this case, however, the trend was less pronounced. Unsubstituted **cis-1** showed the carbonyl C peak at 177.0 ppm. Methoxy derivatives **cis-2** and **cis-3** were characterized by the corresponding resonances at 176.1 and 178.2 ppm, respectively,

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and in the nitro derivatives **cis-4** and **cis-5** the peak was shifted to higher fields (176.1 ppm for **cis-4** and 175.7 ppm for **cis-5**). Comparable carbene proton shifts were obtained for electronically modified Hoveyda-type initiators,[15] indicating that the strongest impact on the carbene proton shifts was evoked by the corresponding para-substituted benzylidene ligands. An EDG functionalization (R^2 = O^{i}Pr) shields the proton, leading to an upfield-shifted carbene proton (as for **cis-3**), while a nitro group exerts the opposite effect (**cis-5**).

Single-crystal X-ray diffraction analysis confirmed the structural suggestion from the evaluation of ^{1}H NMR data (*cf.* Figure 1). All compounds under investigation exhibited a

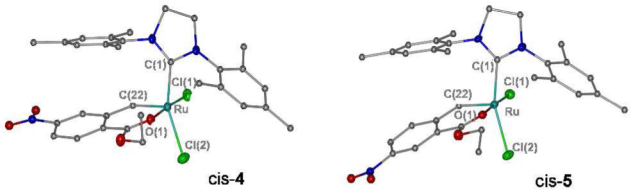

Figure 1. Crystal structures of **cis-4** and **cis-5**. All non-carbon atoms are shown as 30% ellipsoids. Hydrogen atoms are removed for clarity.

distorted-square-pyramidal coordination mode of the ruthenium atom bearing a *cis*-dichloro arrangement. The apex of the pyramid was in all cases formed by the carbene carbon (C(22)). Important bond lengths and angles are presented in Table 1. The electronic tuning of the benzylidene ligand hardly influenced the Ru−Cl(1) (2.352(1)−2.374(3) Å) and Ru−Cl(2) bond lengths (2.344(2)−2.367(2) Å). The same accounted for the Ru−C(22) and Ru−C(1) distances. Minor deviations did not systematically follow the anticipated effect of the substitution. Only the Ru−O(1) distance somehow reassembled the expected tendency of shorter Ru−O bonds for methoxy-substituted complexes and longer Ru−O bonds for the nitro derivatives. However, the effects were not very pronounced, as can be seen in Table 1. All in all, all solid-state structures were very similar, except for one feature worth mentioning: the ethyl ester residue in **cis-4** was out of plane, pointing toward the NHC ligand, while in all other complexes it was in a coplanar arrangement with the benzylidene ligand. Although this phenomenon might be best explained by packing effects, it nevertheless played a role in the theoretical study described below.

Considerations of the Isomerization. As discussed in the Introduction, it is generally believed that second-generation *cis*-dichloro ruthenium benzylidene complexes have to isomerize to their trans counterparts before they become active in olefin metathesis transformations. Herein we aim at studying the energetic isomerization profiles for the series of electronically modified compounds under investigation. Three plausible cis−trans isomerization mechanisms were examined by DFT calculations. Crystal structures were taken as models to obtain optimized geometries of **cis-1**−**cis-5**. The three pathways that were considered can be characterized as a chloride dissociative pathway through transition state **TS1**, a concerted pathway, through transition state **TS2**, and an oxygen dissociative pathway, through transition state **TS3**, as schematically shown for **cis-2** in Figure 2. Results for all complexes are given in Table 2. The first pathway, corresponding to chloride dissociation, was considered because **cis-2** exhibits a pronounced lability of the chloride in a position trans to the NHC ligand.[7f,19] DFT calculations confirmed that dissociation of either Cl1 or Cl2 leads to the same product **cis-Cl**$^+$ bearing the newly formed vacant coordination site trans to the NHC ligand. This step is distinctly higher in energy ($\Delta E_{\text{cis-Cl+-cis}}$ = 33.4−38.3 kcal/mol) than the highest transition states observed for the other two pathways. Furthermore, after chloride dissociation another energy barrier of about 15 kcal/mol has to be overcome to finally arrive at the desired trans product. Overall the upper barrier window for this first dissociative pathway ranges from 49.7 to 53.9 kcal/mol. These data suggest that this isomerization pathway is strongly disfavored.[20] However, calculations reveal a distinctly higher energy demand for chloride dissociation in the nitro-substituted derivatives ($\Delta E_{\text{cis-Cl+-cis}}$ = 38.3 and 38.1 kcal/mol for **cis-4** and **cis-5**), in comparison to the unsubstituted or methoxy-substituted congeners (33.4−35.6 kcal/mol). These findings are the key for understanding why the cationic pyridine complexes **cis-4**$^+_{\text{py}}$ and **cis-5**$^+_{\text{py}}$ were not observed as byproducts in the synthesis of the nitro complexes. The second and third pathways, i.e. the concerted (**TS2**) and the dissociative mechanisms (**TS3**$_{\text{cis}}$), show similar upper barriers in the range of 27.4−31.3 kcal/mol. Complexes **cis-2** and **cis-5** might isomerize rather through a concerted transition state[14b] to form the trans counterpart. On the other hand, complexes **cis-1**, **cis-3**, and **cis-4** may pursue an oxygen dissociative pathway, first overcoming **TS3**$_{\text{cis}}$[21] and then reaching the generally accepted olefin metathesis active trans 14e complex by overcoming **TS3**$_{\text{trans}}$, which is about 10 kcal/mol lower in energy than **TS3**$_{\text{cis}}$. However, there is no clear trend to conclude that one of the two pathways is clearly favored, since the transition states **TS2** and **TS3**$_{\text{cis}}$ differ in energy by less than 1.5 kcal/mol. Further, in some cases **TS2** is

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for Complexes cis-1−cis-5

	cis-1[5b]	cis-2[7f]	cis-3	cis-4	cis-5
Ru−C(22)	1.821(2)	1.824(3)	1.833(9)	1.813(3)	1.805(5)
Ru−C(1)	2.024(2)	2.010(2)	2.008(8)	2.022(3)	2.033(5)
Ru−O(1)	2.088(1)	2.076(1)	2.072(6)	2.093(2)	2.083(3)
Ru−Cl(1)	2.368(1)	2.363(2)	2.374(3)	2.352(1)	2.356(1)
Ru−Cl(2)	2.356(2)	2.344(2)	2.354(3)	2.367(2)	2.351(1)
C(1)−Ru−C(22)	98.68(7)	98.7(1)	97.7(4)	97.5(1)	99.0(2)
O(1)−Ru−Cl(2)	85.81(4)	85.53(6)	84.6(2)	85.63(6)	86.1(1)
C(22)−Ru−O(1)	89.86(7)	89.9(1)	89.4(3)	90.2(1)	90.1(2)
C(22)−Ru−Cl(1)	91.88(6)	89.6(1)	92.4(3)	90.6(1)	92.4(2)
C(22)−Ru−Cl(2)	106.15(6)	111.3(1)	107.9(3)	107.8(1)	102.8(2)
Cl(1)−Ru−Cl(2)	90.49(2)	91.21(3)	92.08(9)	91.69(3)	91.92(5)

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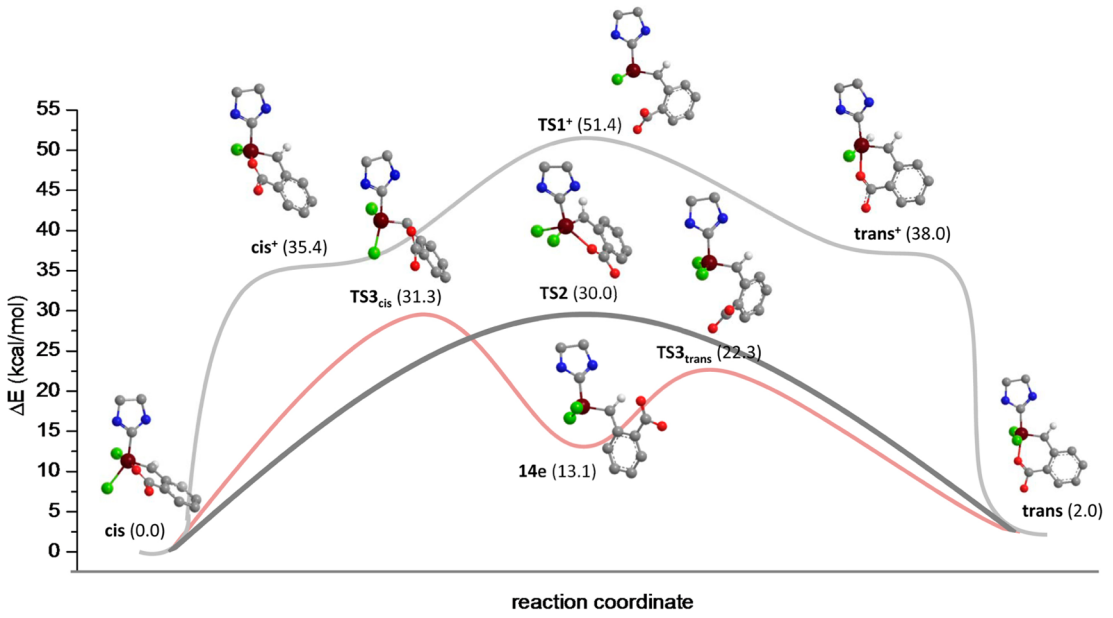

Figure 2. Potential pathways for cis−trans isomerization (for **cis-2**): halide dissociative (**TS1**$^+$), concerted (**TS2**), and oxygen dissociative mechanisms (**TS3**) (solvation model PCM; solvent CH_2Cl_2).

Table 2. Energies (kcal/mol) of cis-1−cis-5 according to the Activation Mechanism[a]

initiator	cis	cis-Cl$^+$	TS1$^+$	trans-Cl$^+$	TS2	TS3$_{cis}$	14e	TS3$_{trans}$	trans	trans$_{exp}$
1	0	35.6	51.1	38.0	29.4	**29.1**	13.9	20.2	1.6	1.6 ± 0.4
2	0	35.4	51.4	37.5	**30.0**	31.3	13.1	22.3	2.0	2.3 ± 0.6
3	0	33.4	49.7	36.9	28.8	**27.4**	13.7	20.2	0.9	1.3 ± 0.3
4	0	38.3	53.9	39.6	30.1	**29.7**	14.4	18.7	0.4	0.4 ± 0.2
5	0	38.1	52.9	40.4	**28.7**	29.0	12.2	18.8	0.6	1.0 ± 0.3

[a]Values in boldface type highlight the more likely pathway (solvent CH_2Cl_2, solvation model PCM).

slightly lower in energy and in the other **TS3$_{cis}$** is lower in energy (see Table 2).

Having established a mechanistic understanding of the isomerization pathway, we now discuss the position of the cis−trans equilibrium. A solution of pure **cis-1−cis-5** (c = 6.3 μM) in $CDCl_3$ was prepared and the isomerization progress at room temperature was monitored via ^{1}H NMR spectroscopy. After 3 days the equilibrium was balanced for **cis-1−cis-3** and **cis-5** (**trans-1**, 6%; **trans-2**, 2%; **trans-3**, 10%; **trans-5**, 16%), whereas for **cis-4** balancing was finished in 15 days (**trans-4**, 33%). From this data set, the free energies ($\Delta G_{trans-cis}$) were calculated to be between 0.4 ± 0.2 and 2.3 ± 0.6 kcal/mol in favor of the cis isomer and were found to be in good agreement with the corresponding values determined by DFT calculations ($\Delta E_{trans-cis}$) in CH_2Cl_2 (cf. Table 2). Experimental isomerization studies in solvents other than $CDCl_3$ were not conducted because more apolar solvents (such as benzene and toluene) provide insufficient solubility of the cis compounds at room temperature and more polar solvents (such as pyridine and protic solvents) favor the formation of cationic species (cf. Scheme 1). As an alternative, DFT calculations simulating solutions in benzene, toluene, THF, $CHCl_3$, and CCl_4 were carried out, revealing increased populations of the trans species in solvents with dielectric constants lower than that of CH_2Cl_2 (cf. the Supporting Information). Similar results were obtained in preceding studies and are discussed in detail there.[9g,f]

Additionally, the isomerization rate could be roughly correlated to the energy of the highest transition state for isomerization,[22] by determining the trans content after 1 h (at room temperature in $CDCl_3$). Complex **cis-3** (TS = 27.4 kcal/mol) reached almost the equilibrium after that time, resulting in 9 ± 0.5% **trans-3** (which is 90 ± 5% of the theoretical amount of **trans-3**). Complex **cis-1** gave 3 ± 0.5% of **trans-1** (50 ± 8% of the theoretical amount, TS = 29.1 kcal/mol), and **cis-5** gave 4 ± 0.5% of **trans-5** (25 ± 3%, TS = 28.7 kcal/mol) in 1 h at room temperature. In contrast, no trans product could be observed in the cases of **cis-4** (TS = 29.7 kcal/mol) and **cis-2** (TS = 30.0 kcal/mol) after 1 h isomerization time.

Polymerization. Separation and isolation of initiators **cis-1−cis-5** rendered a comparative activity study possible, and ring-opening metathesis polymerization (ROMP) of dimethyl bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate (**8**) was used as the benchmark reaction. First, monomer **8** was polymerized at room temperature with **cis-1−cis-5** as the (pre)initiators and the reaction was monitored by means of arrayed ^{1}H NMR spectroscopy. The obtained data are depicted in Figure 3 in a time/conversion plot. The most active compound is **cis-5** ($t_{1/2}$ = 98 min), followed by **cis-4** ($t_{1/2}$ = 122 min), **cis-3** ($t_{1/2}$ = 161 min), and **cis-1** ($t_{1/2}$ = 372 min); **cis-2** ($t_{1/2}$ = 440 min) is the least active initiator of all. The descending order of activity should in theory depend on the activation energy for the isomerization (at least if it is assumed that no transition state during propagation is higher than the activation energy for the isomerization). This holds true for the activity increase from **cis-2** to **cis-1** and to **cis-3**, but the two most active initiators, the nitro derivatives **cis-4** and **cis-5**, show higher barriers for the cis−trans isomerization process than **cis-3**. Nevertheless the

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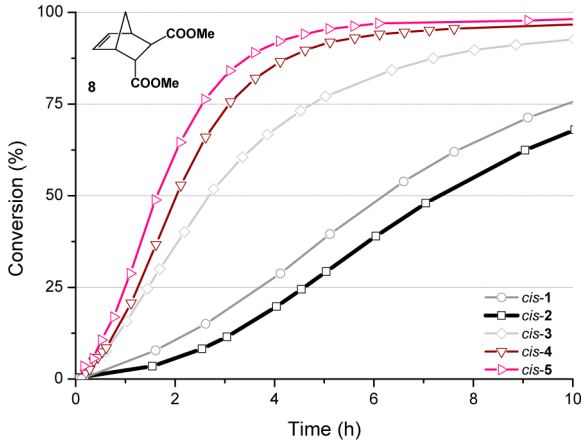

Figure 3. Time/conversion plot for the polymerization of **8** with initiators **cis-1**−**cis-5** relying on ^{1}H NMR data. Reaction conditions: [**8**]:[initiator] = 70:1; [**8**] = 0.13 mol L^{-1}; reaction temperature 25 °C; solvent $CDCl_3$; inert atmosphere of N_2.

trans species is less disfavored in these two cases, which might explain their higher activity in comparison to **cis-1**−**cis-3**.

However, this assumption also bears an inconsistency, because the stated difference between the thermodynamic stabilities of the cis and the trans species in **cis-4** are smaller than those in **cis-5**. Accordingly **cis-5** should be more active than **cis-4**, which is not the case. Here the thermodynamic stability of the actual initiator, the 14e species, seems to be decisive, because most active **cis-5** bears the thermodynamically most favored 14e species (12.2 kcal/mol) and slightly less active **cis-4** leads to a less stable 14e species (14.4 kcal/mol). Accordingly it is proposed that the stationary concentration of the 14e species is an important factor for the activity of the initiators at room temperature. To shed more light on the structure−activity relationship discussed so far, another series of polymerizations of monomer **8**, now at elevated temperature of 80 °C, was carried out. The aim here was to provide the system enough energy to overcome the barrier for cis−-trans isomerization and to assess the initiation efficacy of **cis-1**−**cis-5** under these conditions. Therefore, a monomer to initiator ratio of 300:1 was chosen and the polymerization reaction was carried out until complete conversion of **8** was assured. Thereupon the polymers were isolated and their number-average molecular weights (M_n) were examined by size exclusion chromatography (SEC). This approach allows for an indirect relative assessment of the initiation efficacy, because M_n is proportional to the ratio of the propagation rate (k_p) and the initiation rate constant (k_i), provided that no secondary metathesis occurs. Because k_p is the same in all cases (in all cases the same propagating species occurs), M_n is only dependent on k_i. As a benchmark initiator **M31** was included in the study. **M31** is known for providing fast and complete initiation ($k_i \gg k_p$) and **poly8** prepared with **M31** at room temperature is characterized by a M_n value of 62 kg/mol and a PDI of <1.1 (relative to poly(styrene) standards; [**8**]:[**M31**] = 300:1).

At 80 °C and with **M31** as the initiator, **poly8** with an M_n value similar to that at room temperature was obtained. The polymerization was finished after about 10 min. *cis*-Dichloro initiators under investigation gave **poly8** with higher M_n values, decreasing from 281 (**cis-2**) to 116 (**cis-4**) (cf. Table 3), meaning that the initiation efficacy is in the best case

Table 3. Characterization of poly8 Prepared with cis-1−cis-5 at Elevated Temperature[a]

initiator	time (min)[b]	M_n[c]	PDI[c]
M31	10 ± 2	54	1.1
cis-1	30 ± 4	242	1.7
cis-2	35 ± 4	281	1.9
cis-3	15 ± 3	176	1.6
cis-4	12 ± 2	116	1.5
cis-5	12 ± 2	144	1.5

[a]Reaction conditions: [**8**]:[initiator] = 300:1; [**8**] = 0.1 mol L^{-1}; reaction temperature 80 °C; solvent toluene; inert atmosphere of N_2. [b]Time until conversion is complete (checked by thin-layer chromatography). [c]Determined by SEC relative to poly(styrene) standards in THF.

approximately 2 times lower than in case of the fast and fully initiating compound **M31**. These observations, i.e. low activity at room temperature and moderate initiation efficacy at higher temperature, are typical for *cis*-dichloro initiators in general. Electronic modification either decreases (**cis-2**) or increases the initiation efficacy (**cis-3**−**cis-5**). Analyzing these data, a linear correlation between the measured M_n values and the difference between the calculated thermodynamic stabilities of the *trans*-configured and the *cis*-configured isomers ($\Delta E_{trans-cis}$) can be found (see Figure 4). The meaning of this correlation is that

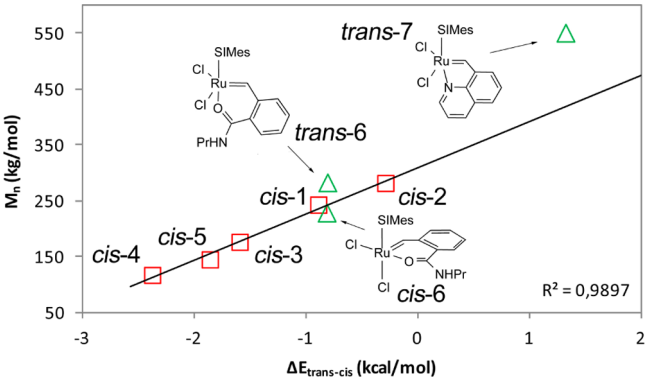

Figure 4. Correlation between the number-average molecular weight of **poly8** prepared with different initiators and theoretically determined thermodynamic cis−trans equilibrium constant (solvation model PCM; solvent toluene).

the initiation efficacy is above all determined by the position of the cis−trans equilibrium, assuming that this equilibrium is reached quickly at 80 °C. Thus, electronic tuning of the benzylidene ligand translates into altered balancing of the cis−trans equilibrium, which is in turn responsible for the observed initiation efficacy of the initiators.

This finding has several important implications: (a) at a reaction temperature which is high enough to provide a fast (relative to initiation) balancing of the cis−trans equilibrium, the initiation efficacy is dependent on the relative thermodynamic stability of the trans isomer in comparison to the cis isomer, (b) this postulate should hold true no matter if a pure cis isomer or a pure trans isomer is initially used, and accordingly, (c) a trans-configured initiator might be deactivated at elevated temperature if a thermodynamically more stable cis isomer is accessible. To further evaluate the general validity of this correlation, the $\Delta E_{trans-cis}$ value for two reported initiators (**6** and **trans-7**)[7a,11b] was calculated (see the

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Supporting Information) and plotted against the corresponding M_n values of **poly8** (obtained with these initiators in the literature). Indeed all three data points[23] fit, indicating a more general applicability of the postulate that the assessment of the thermodynamic equilibrium position of the cis−trans isomerization is suited to predict the initiation efficacy of not only *cis*- but also *trans*-dichloro ruthenium benzylidene initiators at elevated temperature. Another experiment further confirms this fact, as similar M_n values for **poly8** were observed when employing pure **cis-4** (M_n = 116 kg/mol, PDI = 1.5, t = 12 min) or a mixture of **4** (trans:cis = 2:1, M_n = 110, PDI = 1.3, and t = 10 min).

CONCLUSIONS

In summary, we disclosed the effect of electronic tuning of the chelating benzylidene ligand in *cis*-dichloro-configured second-generation olefin metathesis (pre)initiators/catalysts on their catalytic performance. The activation of *cis*-dichloro species in olefin metathesis occurs through isomerization to the trans species. Hence, the mechanism of this process was studied experimentally and theoretically. DFT calculations revealed that isomerization proceeds through either an oxygen dissociative or a concerted pathway. Both pathways display similarly high transition energies; however, no clear trend allows a determination of which is the favored one. Experimentally it was shown that energy barriers to overcome the transition state can already be reached at room temperature. The isomerization rate is dependent on the relative energy stability of the transition state and can be accelerated at elevated temperatures, leading to a specific thermodynamic equilibrium for each system in a given solvent. Experimental results were found to be in good agreement with theoretically calculated thermodynamic equilibrium constants. At elevated temperatures (about 80 °C) and in the presence of a substrate the cis−trans isomerization equilibrium is reached quickly and is the key for explaining the observed activity of the (pre)initiators in ROMP. Hence, the thermodynamic equilibrium constant for the cis−trans isomerization is above all responsible for the initiation efficacy of not only *cis*- but also *trans*-dichloro ruthenium initiators at elevated temperatures.

EXPERIMENTAL SECTION

General Considerations. All reactions were carried out under a nitrogen atmosphere. Solvents were dried by distillation over appropriate drying agents. Ligands **L1**−**L5** were prepared, starting from commercially available compounds, as described in the Supporting Information. *cis*-Dichloro(H_2IMes)(2-ethyl esterbenzylidene-κ^2C,O)Ru (**cis-1**) and *cis*-dichloro(H_2IMes)(2-ethyl ester-5-methoxybenzylidene-κ^2C,O)Ru (**cis-2**) were prepared according to literature procedures.[5b,7f] All other chemicals were purchased from commercial resources (Alfa Aesar, Sigma-Aldrich, Roth) and used as received. NMR spectra were recorded on a Bruker Avance 300 MHz or a Varian INOVA 500 MHz spectrometer. Chemical shifts (δ) are given relative to TMS and coupling constants (J) in Hz. Gel permeation chromatography (GPC) was used to determine molecular weights and the polydispersity index. Measurements were carried out in THF with the following arrangement: a Merck Hitachi L6000 pump, separation columns of Polymer Standards Service (5 μm grade size), and a refractive-index detector from Wyatt Technology. For calibration, polystyrene standards purchased from Polymer Standard Service were used. X-ray measurements were performed on a Bruker AXS Kappa APEX II diffractometer using Mo Kα radiation.

Preparation of *cis*-Dichloro(H_2IMes)(2-ethyl ester-4-methoxybenzylidene-κ^2C,O)Ru (cis-3). In a Schlenk flask, **M31** (148.8 mg, 0.221 mmol, 1.0 equiv) was dissolved in degassed, dry CH_2Cl_2 (25 mL). 5-Methoxy-2-vinylbenzoic acid ethyl ester (**L3**; 62.9 mg, 0.305 mmol, 1.2 equiv) was added. The reaction mixture was stirred under an argon atmosphere for 20 h, until the color changed from deep red to deep green. Pyridine was removed by extraction with HCl_{aq} (5 vol %). The solvent was reduced in vacuo to 1−2 mL, and the title compound was precipitated with *n*-pentane. The dark green precipitate was filtered and washed with *n*-pentane. For purification column chromatography on silica gel (CH_2Cl_2/MeOH, 20/1 (v/v)) was used. Yield: 95.2 mg (75%) of dark green crystals. TLC: R_f = 0.4 (CH_2Cl_2/MeOH, 20/1 (v/v)). Anal. Calcd for $C_{32}H_{38}Cl_2N_2O_3Ru$ (670.64): C, 57.31; H, 5.71; N, 4.18. Found: C, 57.28; H, 5.91; N, 4.01. ^{1}H NMR (20 °C, $CDCl_3$, 300 MHz): δ 18.57 (s, 1H, Ru=C*H*), 7.54 (d, 1H, $^4J_{HH}$ = 2.5 Hz, ph^3), 7.20 (d, 1H, $^3J_{HH}$ = 8.5 Hz, ph^3), 7.18, 6.94, 6.02 (bs, 4H, mes), 7.08 (dd, 1H, $^3J_{HH}$ = 8.6 Hz, $^4J_{HH}$ = 2.5 Hz, ph^5), 6.74 (d, 1H, $^4J_{HH}$= 2.5 Hz, ph^6), 4.62, 4.41 (m, 2H, CH_2CH$_3$), 4.36−3.59 (m, 4H, H_2Im), 3.90 (s, 3H, OCH_3), 2.69, 2.48, 2.39, 2.12, 1.35 (s, 18H, mes CH_3), 1.47 (t, 3H, $^3J_{HH}$ = 7.1 Hz, CH$_2$CH_3). ^{13}C NMR (20 °C, $CDCl_3$, 125 MHz): δ 282.8 (1C, Ru=CH), 217.4 (1C, C$_q$, CNN), 176.7 (1C, C$_q$, COOEt), 158.8 (1C, C$_q$, ph^4), 139.8, 138.2, 136.3, 134.8, 130.9, 128.5 (6C, C$_q$, mes C), 138.4 (1C, C$_q$, ph^1), 135.5, 132.5 (1C, C$_q$, mes N), 130.2 (1C, ph^5), 129.5 (4 mes H), 122.5 (1C, C$_q$, ph^2), 120.2 (1C, ph^6), 115.2 (1C, ph^3), 64.7 (1C, OCH$_2$CH$_3$), 55.8 (1C, OCH$_3$), 51.0 (2C, H_2Im), 21.2, 20.0, 18.3, 16.4 (6C, mes CH_3), 14.1 (1C, OCH$_2$CH$_3$).

Preparation of *cis*-Dichloro(H_2IMes)(2-ethyl ester-5-nitrobenzylidene-κ^2C,O)Ru (cis-4). In a Schlenk flask, **M31** (64.0 mg, 0.0859 mmol, 1.0 equiv) was dissolved in degassed, dry CH_2Cl_2 (10 mL). The carbene precursor 4-nitro-2-vinylbenzoic acid ethyl ester (**L4**; 22.8 mg, 0.103 mmol, 1.2 equiv) was added, and the reaction mixture was stirred in a Schlenk flask under a nitrogen atmosphere for 17 h. The color changed from deep red to red brown. As described above, the raw product was treated with HCl_{aq} (5 vol %) and subsequently purified by column chromatography with CH_2Cl_2/MeOH 20/1 (v/v), giving a brownish red solid (22.8 mg, 39%). TLC: 0.4 (CH_2Cl_2/MeOH, 20/1 (v/v)). Anal. Calcd for $C_{31}H_{35}Cl_2N_3O_4Ru$ (685.60): C, 54.31; H, 5.15; N, 6.13. Found: C, 54.35; H, 5.17; N, 6.09. ^{1}H NMR (20 °C, $CDCl_3$, 300 MHz): δ 19.09 (s, 1H, Ru=CH), 8.51 (dd, 1H, $^3J_{HH}$ = 8.6 Hz, $^4J_{HH}$ = 1.9 Hz, ph^4), 8.21 (d, 1H, $^3J_{HH}$ = 8.7 Hz, ph^3), 8.11 (d, 1H, $^4J_{HH}$ = 2.1 Hz, ph^6), 7.19, 7.04, 5.96 (s, 4H, mes), 4.71, 4.50 (m, 1H, CH_2CH$_3$), 4.38−3.65 (m, 4H, H_2Im), 2.67, 2.50, 2.41, 1.99, 1.32 (s, 18H, mes CH_3), 1.52 (t, $^3J_{HH}$ = 7.0 Hz, CH$_2$CH_3). ^{13}C NMR (20 °C, $CDCl_3$, 75 MHz): δ 278.0 (1C, Ru=CH), 215.3 (1C, C$_q$, CNN), 176.1 (1C, C$_q$, COOEt), 152.4 (1C, C$_q$, ph^5), n.d. (8C, C$_q$, mes C, mes N), 142.5 (1C, C$_q$, ph^1), 132.5 (1C, C$_q$, ph^3), 131.2, 129.8, 128.2 (4C, mes), 124.0 (1C, C$_q$, ph^2), 122.3 (1C, ph^4), 121.2 (1C, ph^6), 65.9 (1C, OCH$_2$CH$_3$), 51.1 (2C, H_2Im), 18.3 (6C, mes CH_3), 14.1 (1C, OCH$_2$CH$_3$).

Preparation of *cis*-Dichloro(H_2IMes)(2-ethyl ester-4-nitrobenzylidene-κ^2C,O)Ru (cis-5). In a Schlenk flask, **M31** (150.1 mg, 0.200 mmol, 1.0 equiv) was dissolved in degassed, dry CH_2Cl_2 (25 mL). 5-Nitro-2-vinylbenzoic acid ethyl ester (**L5**; 66.8 mg, 0.300 mmol, 1.5 equiv) was added, and the reaction mixture was stirred in a Schlenk flask under an argon atmosphere until the color changed from deep red to olive yellowish black. After 20 h of conversion the product was extracted with HCl_{aq} (5 vol %) to get rid of pyridine. Afterward the complex was precipitated in CH_2Cl_2 (1−2 mL) with *n*-pentane, giving a brown solid, which was filtered and dried in vacuo. The raw product was isolated from side products by column chromatography on silica gel (CH_2Cl_2/MeOH, 20/1, v/v). Yield: 88.9 mg of an ocher solid (65%). TLC: R_f = 0.4 (CH_2Cl_2/MeOH, 20/1 (v/v)). Anal. Calcd for $C_{31}H_{35}Cl_2N_3O_4Ru$ (685.60): C, 54.31; H, 5.15; N, 6.13. Found: C, 54.33; H, 5.20; N, 6.11. ^{1}H NMR (20 °C, $CDCl_3$, 300 MHz): δ 19.37 (s, 1H, Ru=CH), 8.85 (d, 1H, $^4J_{HH}$ = 2.1 Hz, ph^3), 8.45 (dd, 1H, $^3J_{HH}$ = 8.5 Hz, $^4J_{HH}$ = 2.3 Hz, ph^5), 7.47 (d, 1H, $^3J_{HH}$ = 8.5 Hz, ph^6), 7.21, 7.19, 6.96, 5.95 (s, 4H, mes), 4.70, 4.51 (m, 2H, CH_2CH$_3$), 4.41−3.68 (m, 4H, H_2Im), 2.66, 2.52, 2.46, 2.41, 2.09, 1.37 (s, 18H, mes CH_3), 1.54 (t, 3H, $^3J_{HH}$ = 7.1 Hz, CH$_2$CH_3). ^{13}C NMR (20 °C, $CDCl_3$, 125 MHz): δ 276.7 (1C, Ru=CH), 215.2 (1C, C$_q$, CNN), 175.7 (1C, C$_q$, COOEt), 143.8, 143.6 (2C, C$_q$, ph^{1,5}), 140.5, 139.6, 138.8, 138.2, 136.3, 135.6, 131.1, 128.3 (8C, C$_q$, mes C, mes N), 131.7 (1C, ph^4),

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128.8 (1C, ph^6), 130.7, 129.9, 129.85, n.d. (4 mes), 126.8 (1C, ph^3), 120.7 (1C, C_q, ph^2), 65.9 (1C, OCH_2CH_3), 51.1 (2C, H_2Im), 21.3, 20.0, 19.8, 18.2, 16.3 (6C, mes CH_3), 14.1 (1C, OCH_2CH_3).

Polymerization. Experiments were performed in Schlenk flask in degassed solvents under N_2 conditions. The appropriate amount of catalyst **cis-1**−**cis-5** (0.00159 mmol, 1 equiv) was rinsed with toluene (3.8 mL) into a Schlenk flask. The reaction mixture was placed in an oil bath at 80 °C. Then monomer **8** (100 mg, 0.476 mmol, 300 equiv), dissolved in 1 mL of toluene, was added with stirring, giving a concentration of 0.1 M with respect to the monomer. The reaction progress was monitored by TLC on silica gel, using Cy/EtOAc 3/1 (v/v). After reaction completion, an excess of ethyl vinyl ether (200 μL) was added to quench the reaction. Subsequently the polymer was precipitated in methanol and dried under vacuum.

Cis−Trans Isomerization Rate. Stock solutions of the respective complex **cis-1**−**cis-5** (5.5 mM) were prepared in deuterated chloroform (0.7 mL) under inert N_2 conditions and stored in NMR tubes for 1 to 2 weeks, with ^{1}H NMR spectra (300 MHz, 25 °C, $CDCl_3$) being recorded every couple of hours.

Computational Details. DFT geometry optimizations were performed at the GGA level with the Gaussian09 package,[24] using the BP86 functional of Becke and Perdew.[25] No symmetry constraint was used in the geometry optimizations, and the final geometries were confirmed to be either minimum potential energy or transition state structures through frequency calculations. The electronic configuration of the molecular systems was described with the standard split-valence basis set with the polarization function of Ahlrichs and co-workers for H, C, N, O, and Cl (SVP keyword in Gaussian09);[26] for Ru we used the small-core, quasi-relativistic Stuttgart/Dresden effective core potential, with the associated valence basis set (standard SDD keywords in Gaussian09).[27] The reported energies have been obtained through single-point calculations with the M06 functional of Truhlar. In these single-point calculations the electronic configuration of the molecular systems was described by a triple-ζ basis set for main-group atoms (TZVP keyword in Gaussian09),[28] and furthermore, diffuse basis sets have been incorporated for Cl.[29] Solvent effects including contributions of nonelectrostatic terms have been estimated in single-point calculations on the gas-phase optimized structures, on the basis of the polarizable continuum solvation model PCM, using CH_2Cl_2 as the solvent.[30] Solvent effects including contributions of nonelectrostatic terms have been estimated in single-point calculations on the gas-phase optimized structures, on the basis of the polarizable continuum solvation model PCM, using toluene, benzene, THF, CCl_4, $CHCl_3$, and CH_2Cl_2 as the solvents. Finally, bearing in mind that electronic energies follow the same trend as the Gibbs free energies, we used the first value for the sake of better accuracy, comparing the relative stability between cis and trans isomers.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, tables, figures, and CIF and xyz files giving detailed crystallographic data **cis-3**−**cis-5**, procedures and characterization data for the carbene precursors **L1**−**L5**, NMR spectra for complexes **cis-1**−**cis-5**, protocols and detailed results for the polymerization and isomerization experiments, output files of the DFT calculations, and relative energies in gas and solvent phases. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data for **cis-3**−**cis-5** have also been deposited with the CCDC, nos. 977278−977280, and can be obtained free of charge from http://www.ccdc.cam.ac.uk.

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Notes

The authors declare no competing financial interest.

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(20) This situation might change in the presence of donor ligands—work on this particularity is currently ongoing in our laboratories.
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