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Synthesis and Properties of Bimetallic Hoveyda–Grubbs Metathesis Catalysts

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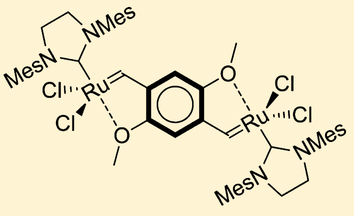
Supporting Information

ABSTRACT: The catalytic activity of ruthenium Hoveyda–Grubbs complexes in olefin metathesis is a function of complex steric and electronic effects acting on initiation and propagation steps. In order to study the π-electron factors influencing the initiation process, we attempted syntheses of bimetallic complexes with common organic ligands bearing two chelate rings. While most of the studied ligand exchange reactions of the isomeric bis-chelating benzene derivatives gave mixtures of unstable complexes, a homodinuclear derivative of 1,4-dimethoxy-2,5-divinylbenzene was sparingly soluble and precipitated from the reaction mixture in a pure form. The complex was studied with spectroscopic and X-ray methods, which confirmed the symmetrical bimetallic structure. However, in model metathesis reactions the catalyst displayed activity very comparable to the related monometallic complexes. This suggests that in the bimetallic system two consecutive initiation processes of the metathesis catalyst (first, bimetallic complex + olefin → monometallic complex + propagating species; second, monometallic complex + olefin → styrene + propagating species) proceed at similar rates and, thus, no cooperativity between the two steps is displayed. Properties of the family of bimetallic complexes were probed with NMR studies, and π-electronic effects operating in the systems were discussed.

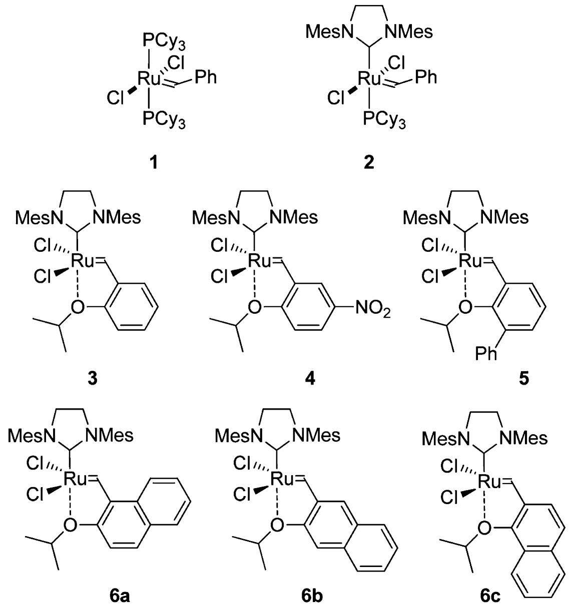


chelates initiate independently

INTRODUCTION

In recent years olefin metathesis has left a prominent mark in the field of synthetic organic chemistry as a tool for manipulation of carbon–carbon multiple bonds.[1] The methodology is represented in the literature by numerous examples, including ring-closing metathesis (RCM), cross metathesis (CM), enyne metathesis (ENYNE), ring-opening metathesis polymerization (ROMP), etc. At the same time progress in the development of novel catalytic systems based on molybdenum and ruthenium is ongoing[2] and concerns improvements of activity and stability,[3−9] approached by detailed mechanistic studies, as well as "trial and error" attempts. Homogeneous olefin metathesis (pre)catalysts based on ruthenium have been intensively explored, and their mechanism of action has been investigated in detail.[10] To enter the metathesis reaction, the complexes usually require a rate-determining initiation step, which corresponds to phosphine dissociation (for complexes **1** and **2**; Chart 1) or chelate opening, as postulated for dissociative and interchange mechanisms of initiation of the Hoveyda-type complexes (**3** and **4**).[10,11] The rate of initiation of the chelate complexes can be varied by electronic and steric effects acting on the Ru···O coordination, and numerous improvements in the area were achieved by Grela (**4**),[4] Blechert (**5**),[5] and others.[2b,c] Recently we demonstrated another electronic effect in naphthalene-based analogues of the parent Hoveyda–Grubbs catalyst (**6a**–**c**).[9]

Chart 1. Selected Metathesis Catalysts[a]



[a]Complexes **6a**–**c** display conjugated tricyclic structures similar to those of phenanthrene and anthracene.

Complexes **6** investigated in our study[9a] displayed surprising differences in catalytic activity. Complex **6b**, in which the chelate ring assembled on the naphthalene ligand formed a linear tricyclic structure, was only slightly suppressed in comparison with **3**.[9c] In contrast, the two isomeric complexes **6a**,**c** were completely inactive in model metathesis reactions of *N*,*N*-diallyltosylamine at room temperature. At first the origin of the differences was unclear, but we suspected that it cannot arise from simple

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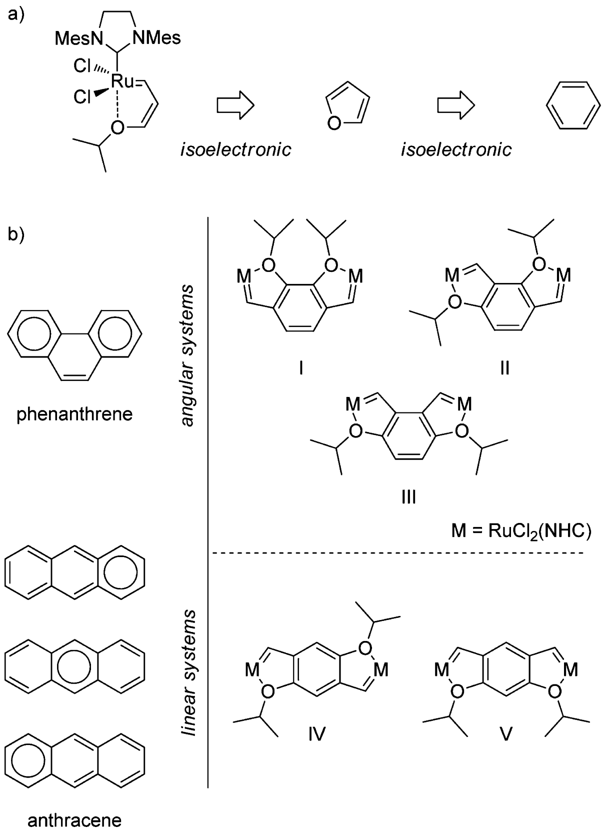
inductive and steric effects described in the literature.[12] However, even more amazing was the *magnitude* of the effect—the latent complexes **6a,c** required very harsh conditions to initiate. In the model RCM reaction, when it was tested in refluxing toluene (111 °C), the complexes initiated at a rate similar to that displayed by complex **6b** at 0 °C.[9a] Unexpectedly, the explanation of the riddle came out of the Clar rule, which describes the properties of polycyclic aromatic hydrocarbons (PAHs). When we considered the chelate ring assembled from *i*PrO and Ru=CH– substituents as a benzene ring (Chart 2a), the π-electron structure of the complexes extended into tricyclic systems similar to those of phenanthrene and anthracene. According to the Clar rule, the PAHs tend to maximize the number of completed aromatic sextets, and the location of the sextets corresponds to rings of increased aromatic character. Thus, phenanthrene possesses two sextets localized on external rings, while in anthracene only one sextet delocalized over all rings is present (Chart 2b, left). By this analogy, the external chelate ring in angular complexes **6a,c** is stabilized, while in **6b** the stabilization is only moderate and is similar to that displayed by **3**. As the hydrocarbons differ with distribution of the π-electron density, the same applies to the ruthenium complexes, in which the chelate rings differ with the strength of electron delocalization.[13] It is worth stressing that, although all of the complexes **6** possess conjugated chelate rings, considerable electron delocalization appears only in **6a,c**. In fact, the chelate rings of the synthesized complexes **6a,c** meet general criteria of aromaticity:[9a] (a) energetic properties,[14] attributed to their stability and correlation with low catalytic activity,[15] (b) magnetic properties, where ^{1}H NMR resonances of benzylidene protons are shifted downfield ($\Delta\delta$ = +1.6 ppm) by an induced diamagnetic ring current of the aromatic chelate in comparison with **6b**, and (c) structural properties, demonstrated by the bond alternation of naphthalene ligand, which resembles that observed in phenanthrene, with an increased bond alternation of the middle ring.

Chart 2. (a) Coniugated Chelate Rings of the Ruthenium Complexes Considered as Isoelectronic with Other Six-π-Electron Rings, such as Furan and Benzene,[9a,c] and (b) Bis-Chelate Complexes Assembled on a Benzene Core with Structures Related to the Tricyclic Aromatic Hydrocarbons Phenanthrene (I–III) and Anthracene (IV and V)[a]

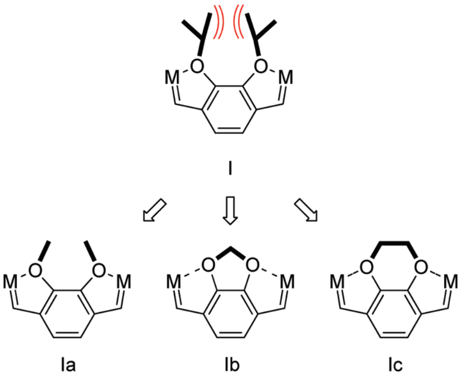


[a] NHC = 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene.

With the aromaticity-controlled activity concept[9a,c] in mind, we considered bimetallic systems (Chart 2b, right), in which tricyclic structures related to phenanthrene (variants **I–III**) and anthracene (variants **IV** and **V**) are composed from benzene rings decorated with two chelates. Numerous bimetallic metathesis catalysts have been described in the literature, and their structures range from derivatives of 1,4-divinylbenzene in a bimetallic variant of complex **2**,[16] homo-[17] and hetero-dinuclear halogeno-bridged complexes,[18] derivatives of titano-[19] and ferrocene,[20] up to W–Sn[21] and Ru–Sn[22] systems featured by a direct metal–metal bond. Although bimetallic Hoveyda-type complexes are less common, they are represented by examples in which one metal atom modifies the properties of the ruthenium catalytic center[22,23] and those with two[24,25] or more[26] catalytic centers present in one molecule. Although some of the complexes display unique features, it was not until a report by Lemcoff,[24] in which homodinuclear ruthenium metathesis catalysts designed for selective dimer ring-closing metathesis were described. The catalytic activity of complexes fitted with a dimeric N-heterocyclic carbene (NHC) ligand, in which two saturated 1,3-dimesityl-2-imidazolin-2-ylidene (SiMes) structures were linked by para positions of the aryl substituents, was tested on 1,12-tridecadiene as a substrate. The preferred formation of a 22-membered-ring product was observed. The unusual selectivity toward the dimeric product was attributed to *cooperativity* of the catalytic centers,[27] which simultaneously bind both olefinic end groups of the substrate and combine them with end groups of second molecule of the substrate in two concerted metathesis acts.

Our designed bimetallic complexes **I–V** were expected to display other interesting properties. When they are subjected to the metathesis reaction conditions, the bimetallic catalysts can possibly initiate twice: first when the bimetallic complex reacts with olefin and releases a monometallic complex and 14-electron propagating species (one of the two metal centers is released) and second when the so-formed monometallic complex combines again with the olefin, giving a free styrene ligand and a second propagating species. The initiation behavior poses an open question about the relative rates of the two processes—the first initiation may actually be faster or slower or proceed at a rate similar to that of the second one. We hypothesized that the bimetallic structures, particularly those from the first group (**I–III**), can be stabilized with the same π-electronic effect, which operates in angular complexes **6a,c**. Thus, the bimetallic catalysts should initiate slowly as a result of an increased electron delocalization in the chelate rings. However, when the first propagating species is released, the resulting monometallic catalyst should initiate relatively quickly (with a rate comparable to that displayed by **3**), lacking any further stabilization. Thus, from the five isomers the chelate rings of complexes **I–III** were expected to be latent, with the first initiation rate being much smaller than the latter rate. In turn, linear systems represented by variants **IV** and **V** should display a different behavior, where the consecutive initiations proceed at similar rates, by analogy with the properties of complexes **3** and **6b**.

Preliminary analysis suggested that some of the bimetallic complexes (Chart 2b) may suffer from severe steric hindrance between ligands coordinated to adjacent metal centers (for a discussion of calculated structures of the bimetallic complexes see the Supporting Information). Thus, we abandoned the synthesis of isomers **II**[28] and **III**, in which the aromatic arms of NHC ligands may collide, and focused on structure **I**. In this structure repulsion between coordinating *i*PrO groups was expected; thus, we decided to replace them with methoxyl groups (MeO, **Ia**) and alternatively form five- and six-membered rings of dioxolane (**Ib**) and dioxane (**Ic**), respectively.



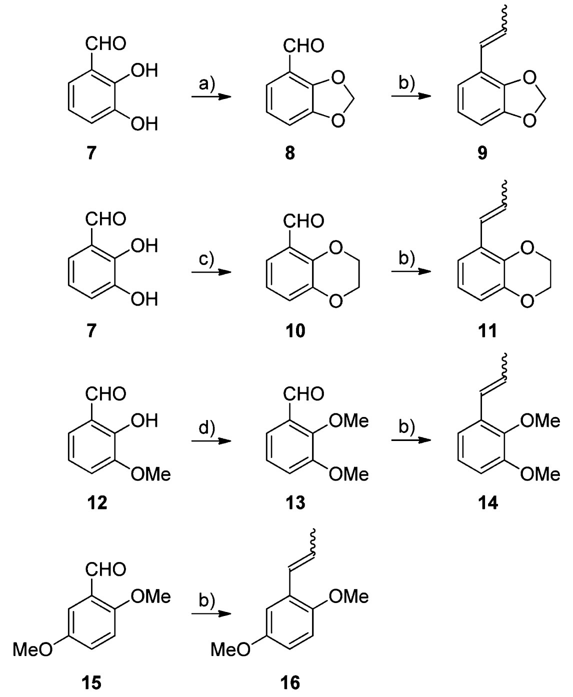
In turn, complexes related to variants **IV** and **V** (Chart 2b) seemed to be attainable, and we planned their synthesis from the corresponding dimethoxydivinylbenzenes.[29]

To study the initiation behavior of the designed bimetallic complexes, we needed to measure the activity of two types of catalysts: bimetallic and monometallic. The latter catalysts, which are expectedly released after the first initiation step from the bimetallic structures, can be synthesized from the same substrates as the bimetallic catalysts, provided that the substrates react in an equimolar ratio to favor monocomplexation of the bis-chelating ligands (dimethoxydivinylbenzenes). Although monocoordinated complexes bearing free vinyl substituents have been described in the literature,[25] we worried about their stability and possible separation problems, when mixtures of the mono- and dimetalated species are formed. To avoid these difficulties, we decided to synthesize related monometallic complexes not from the bis-chelate ligands but from benzene derivatives bearing *one* olefinic and two alkoxyl substituents. The catalytic activity of the catalysts should be very similar to that of monometalated species bearing free vinyl substituents (derived from monometalation of the bis-olefinic ligands bearing two olefinic and two alkoxyl substituents) and should take advantage of the improved stability by suppressing possible equilibrations (monometallic + monometallic ⇆ bimetallic + bis-olefinic ligand). In this report we present attempts to synthesize the mono- and bimetallic complexes and discuss the results supported by ^{1}H NMR studies and considerations of π-electron effects operating in the chelate rings.

■ RESULTS AND DISCUSSION

Synthesis of Ligands. The synthesis started at the preparation of ligands bearing one propenyl substituent.[30] The ligands were synthesized in short sequences starting from inexpensive, commercially available substrates: 2,3-dihydroxybenzaldehyde (**7**), *o*-vanillin (**12**), and 2,5-dimethoxybenzaldehyde (**15**), by alkylations and Wittig reactions. The products **9**, **11**, **14**, and **16** were produced as *E*/*Z* mixtures of isomers (Scheme 1).

Scheme 1. Synthesis of Ligands 9, 11, 14, and 16[a]

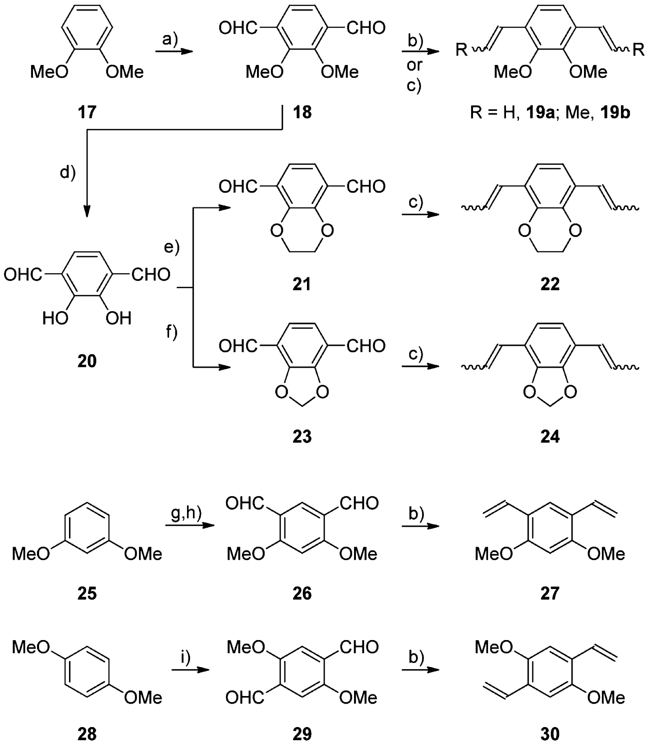


[a]Legend: (a) CH_2I_2; K_2CO_3, DMF, 70 °C, 16 h, 73% **8**;[31] (b) $Ph_3PC_2H_5Br$, *t*-PeOK/toluene, THF, 92% **9**, 94% **11**, 94% **14**, 95% **16**;[31] (c) $BrCH_2CH_2Br$; K_2CO_3, DMF, 70 °C, 16 h, 91% **10**;[31] (d) CH_3I; K_2CO_3, DMF, 45 °C, 42 h, 99% **13**. DMF = dimethylformamide.

Next we synthesized the bis-chelating ligands with two olefinic and two alkoxy substituents. The syntheses started with the dimetalation of dimethoxybenzenes (1,2, **17**; 1,3, **25**; 1,4, **28**). The procedures were not efficient and suffered from moderate yields and selectivity; however, they offered an unique diversity toward a palette of isomers and an easy access to the needed structures from inexpensive substrates. 1,4-Diformyl-2,3-dimethoxybenzene (**18**) was prepared from **17** according to the literature method,[32] which required purification of the product by column chromatography followed by crystallization. In contrast to the metalation of veratrole (**17**), attempts to metalate benzodioxane and benzodioxolane failed to give diformyl derivatives.[33] Thus, the required aldehydes **21** and **23** were obtained by demethylation of **18**, followed by alkylation and Wittig reactions. In similar sequences aldehydes **26** and **29** were prepared from dimethoxybenzenes **25** and **28**, as shown in Scheme 2.[34,35]

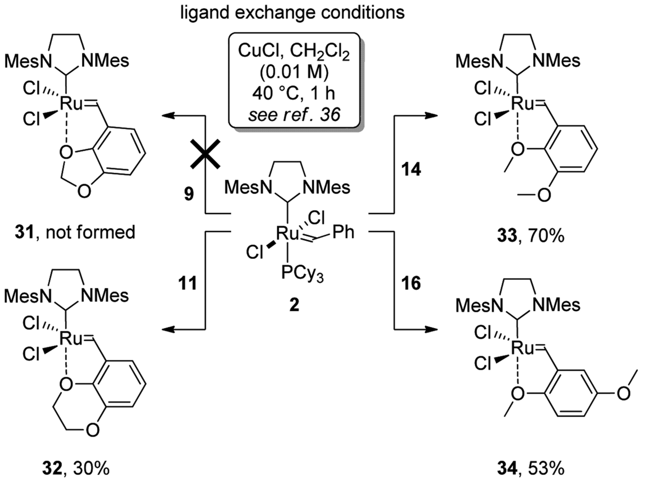
Synthesis and Properties of Ruthenium Complexes. Synthesis of the ruthenium complexes started with the reactions of ligands **9**, **11**, **14**, and **16** with the Grubbs catalyst **2** under the ligand exchange conditions described by Blechert.[36] In preparative experiments the styrenes were combined with complex **2** and CuCl as a phosphine scavenger and refluxed in dichloromethane for 1 h. The reaction mixtures with ligands **11**, **14**, and **16** became green, which suggested the formation of the desired chelate complexes. Moreover, TLC analyses of the mixtures confirmed the disappearance of the magenta complex **2**.

Scheme 2. Synthesis of Ligands 19a,b, 22, 24, 27, and 30[a]



[a]Legend: (a) *n*-BuLi, TMEDA, Et_2O, then DMF, 30% **18**;[32] (b) Ph_3PCH_3Br, *t*-PeOK/toluene, THF, 90% **19a**, 85% **27**, 97% **30**; (c) $Ph_3PC_2H_5Br$, *t*-PeOK/toluene, THF; for 56% **19b**, 97% **22**, 96% for **24**; (d) BBr_3, CH_2Cl_2, hexane, 0 °C to room temperature, 3.5 h, 88% **20**; (e) $BrCH_2CH_2Br$; K_2CO_3, DMF, 70 °C, 16 h, 77% **21**;[31] (f) CH_2I_2, K_2CO_3, DMF, 70 °C, 21 h, 68% **23**[31]; (g) Br_2, CH_3COOH; (h) *n*-BuLi, Et_2O, then DMF, 39% **26** from two steps;[34] (i) *n*-BuLi, Et_2O, TMEDA, then DMF, 55% **29**.[35] TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, DMF = dimethylformamide.

Scheme 3. Attempts To Synthesize Complexes 31−34



In contrast, the reaction mixture with ligand **9** became dark brown and only a polar tarlike spot was detected in TLC. The latter result was consistent with previous findings by us[29a] and Hryniewicka et al.[37] for the five-membered chelating ether functions. The derivatives suffer from destabilization, where the coordinating oxygen atom inserted into the five-membered ring is tilted away from the ruthenium center, which makes the complex unstable.

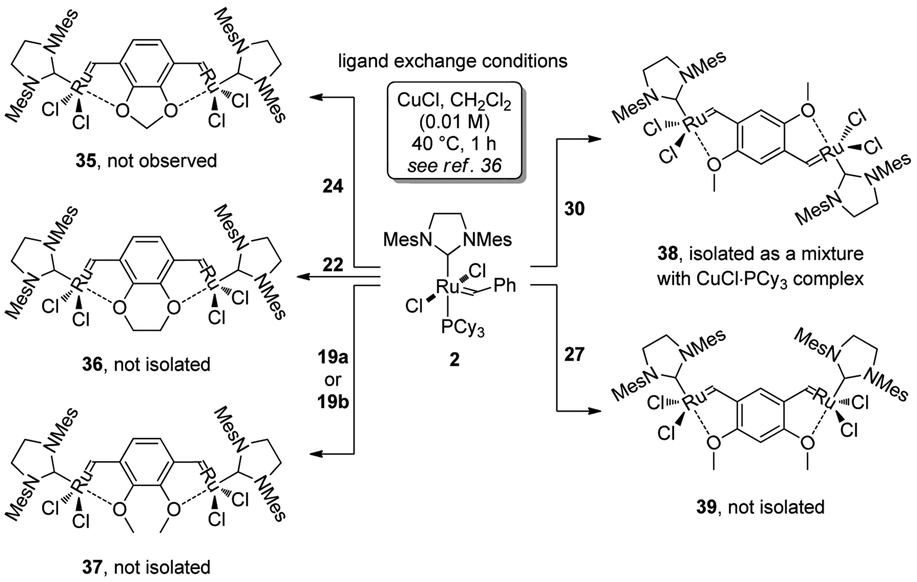
Reactions of the Grubbs complex **2** with ligands **11**, **14**, and **16** gave after workup and column chromatography complexes **32**−**34** in good to moderate yields ranging from 30 to 70% (Scheme 3).[38]

The successful synthesis of complexes **32**−**34** encouraged us to attempt reactions with the bis-chelating ligands **19**,[39] **22**, **24**, **27**, and **30** under similar reaction conditions. We used a 2-fold molar excess of complex **2** to favor the formation of bimetallic species, other reaction conditions remaining intact. Similarly to the previous experiments, during the reaction courses with styrenes **19**, **22**, **27**, and **30** the mixtures turned deep green, characteristic of the progress of the ligand exchange reaction. After 1 h of reflux, the heating bath was removed and the mixture was concentrated in vacuo. Addition of ethyl acetate caused dissolution of a green residue and gave a white-gray suspension of the insoluble $CuCl·PCy_3$ complex. The suspension was filtered, and the filtrate was concentrated and subjected to column chromatography. The green band of the product was collected and analyzed with NMR methods. Surprisingly, the products from the reactions of ligands **19b** and **22** appeared as mixtures, which displayed multiple benzylidene signals and complicated patterns in the aliphatic and aromatic regions of their ^1H NMR spectra. Numerous attempts to further purify the products by chromatography and crystallization were unsuccessful and always resulted in poor mass recovery in the range 10−30%. Although the different behaviors of the mono- and bimetallic complexes (or more precisely complexes formed under the reaction conditions) were unclear, we initially assumed that the complexes derived from ligands **19** and **22** decompose more easily, because of their structure (Scheme 4).

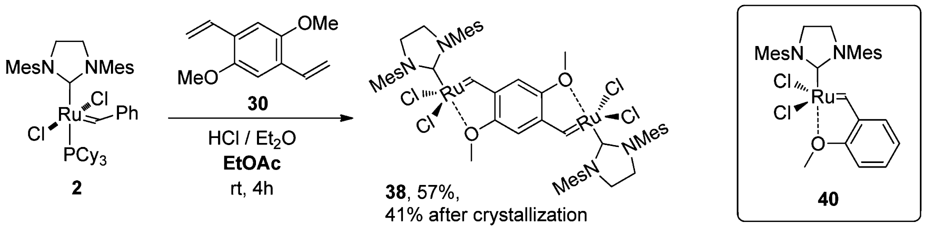
Similar attempts were made for ligands **27** and **30**, corresponding to variants **IV** and **V** (Chart 2b). Although the reaction with ligand **27** gave a result similar to previous reactions, the reaction with **30** distinctly differed. When the reaction mixture was evaporated and a small amount of ethyl acetate was added to separate the CuCl−phosphine complex, we observed the formation of large amounts of a green solid, which was only sparingly soluble in ethyl acetate. The solid contained the CuCl−phosphine complex, but the substance was accompanied by an unidentified green product. The green solid was collected, dried in vacuo, and analyzed with ^1H NMR spectroscopy. Surprisingly, only *one* benzylidene signal was observed at 16.11 ppm, and the relatively simple aromatic region of the spectrum was accompanied by large aliphatic peaks in agreement with the structure of $CuCl·PCy_3$. Obviously the bimetallic complex was formed, but the observed selectivity resulted from its low solubility, rather than the selectivity of the reaction itself. With this point in mind, we attempted the synthesis with a different phosphine scavenger—a solution of HCl in ethyl ether—to avoid contamination of the product with the insoluble copper complex. Under these conditions, where the reaction mixture was concentrated in vacuo and the residue was suspended in ethyl acetate and filtered, the crude complex **38** was isolated as a green powder in 35% yield. Finally, the procedure was further improved when we applied ethyl acetate as a *solvent* for the ligand exchange reaction with the homogeneous phosphine scavenger (Scheme 5). By taking advantage of the precipitation of the product during the reaction course and crystallization of the collected solid, we isolated analytically pure **38** in 41% yield.

Complex **38** was characterized by ^1H and ^{13}C NMR, ESI MS, and IR techniques. The ^1H and ^{13}C spectra both displayed only

Scheme 4. Attempts To Synthesize Complexes 35−39



Scheme 5. Improved Procedure of Synthesis of Complex 38[a]



[a]The reaction was carried out in ethyl acetate with an ethereal solution of HCl as a phosphine scavenger. The bimetallic complex precipitated from the reaction mixture and was crystallized to afford **38** of analytical purity. Inset: complex **40** with one chelate ring, described in the literature.[29a]

a small number of resonances, consistent with the symmetrical bimetallic structure. The structure was further confirmed by X-ray structural studies. Complex **38** crystallized in the monoclinic $P2_1/c$ space group and displayed a geometry typical for this class of ruthenium metathesis catalysts (Figure 1). An analysis of the key structural parameters of the chelate showed only minor differences in comparison to the related Grubbs−Hoveyda complex bearing a MeO coordinating group (**40**; Table 1).[29a] It is worth noting that the single Ru−O and =C−C_{Ar} bonds in the complex **38** were actually shorter and the benzylidene Ru=C double bond was longer than in **40**. The reduced alternation of the bond lengths suggested a stronger π-electron delocalization of the chelate rings in the extended tricyclic complex **38**.

Although we expected that in complexes related to variants **IV** (**38**) and **V** (**39**) (Chart 2b) unique stabilizing π-electron effects are absent, the bimetallic complex **38** was tested in benchmark RCM reactions. In the activity studies as a model of the monometallic intermediate catalyst, we tested complex **34**, lacking a free olefinic substituent. Activity profiles of RCM reactions of diethyl diallylmalonate and diethyl allylmethallylmalonate catalyzed with **34** and **38** are presented in Figure 2.

An honest evaluation of activity of complex **38** requires consideration of the initiation process, in which two propagating species are released in two consecutive initiation steps, with the intermediate monometallic complex bearing a free vinyl group (Scheme 6).

At the beginning of the metathesis reaction, when the bimetallic complex **38** is subjected to an olefinic substrate, it initiates,[41a] and the rate of the initiation depends on its concentration roughly in the same way as for **34**. However, when the reaction proceeds further, the intermediate monometallic complex released from **38** also initiates.[41b] From that perspective, in order to compare activities of the catalysts **38** and **34**, the concentration of monometallic complex should be doubled to compensate for the final concentration of the propagating species. In our activity studies the catalytic activity was tested at 0.5 mol % of **38** and compared with the activity of the complex **34** at concentrations of 0.5 and 1.0 mol %. The results demonstrated that the activities of **38** and **34** are very similar to each other, and **38** shows activity intermediate between those exhibited by **34** at the two concentrations 0.5 and 1.0 mol %. This is consistent with our expectations that the chelate rings of the bimetallic system **38**, derived from anthracene (variant **IV**, Chart 2b), possess properties similar to those of **34**. Thus, the rates of initiation of the mono- and bimetallic complexes are roughly similar to each other, and the same apply to the rates of the consecutive initiation processes of the bimetallic catalyst **38**.

NMR Studies of Synthesis of Complexes 36−39. The unsuccessful attempts to synthesize the bimetallic complexes **35**−**37** and **39** seemed puzzling, considering that the related monometallic derivatives **32**−**34** were easily isolated. We thought that a closer examination of the reactions with NMR methods might help to understand the results and attribute the observed

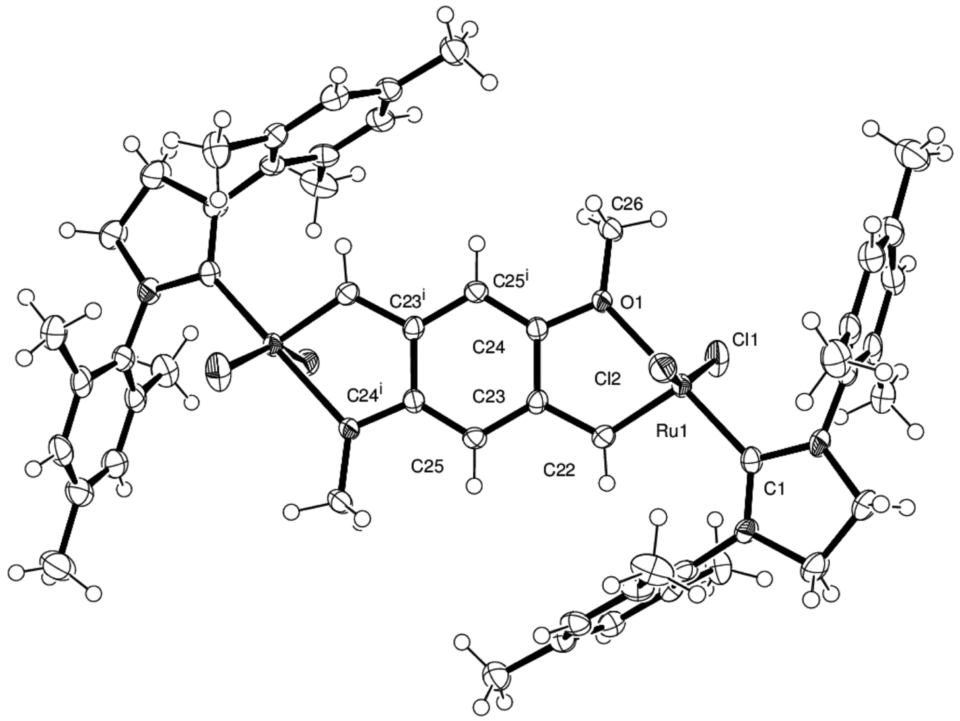


Figure 1. ORTEP[40] drawing of the molecule of complex **38** represented by thermal ellipsoids drawn at the 50% probability level. The content of the asymmetric unit was extended by applying a center of symmetry operator to obtain the whole moiety. Selected bond lengths (Å) are presented in Table 1.

Table 1. Selected Bond Lengths (Å) of Complexes 38 and 40[29a]

bond type	38	40[29a]
Ru−O	2.2507(19)	2.265(5)
Ru═C	1.826(3)	1.798(9)
═C−C_{Ar}	1.448(4)	1.465(13)
iPrO−C_{Ar}	1.364(3)	1.355(10)

problems to synthesis-related issues, where the expected bimetallic products are formed in only small amounts, or to structural effects, related to the stability of the complexes themselves. To reach this goal, we repeated the reactions on a small scale in NMR tubes and followed them with ^{1}H NMR spectroscopy (Figure 3).

The results revealed severe selectivity problems, in accord with the results of our synthetic attempts. Reactions with ligands **22** and **19a** displayed the gradual disappearance of the substrate complex **2** and the development of one sharp resonance (**19a**), or a set of overlapping resonances around 16.5 ppm (**22**). In turn, reactions with ligands **30** and **27**, corresponding to the tricyclic

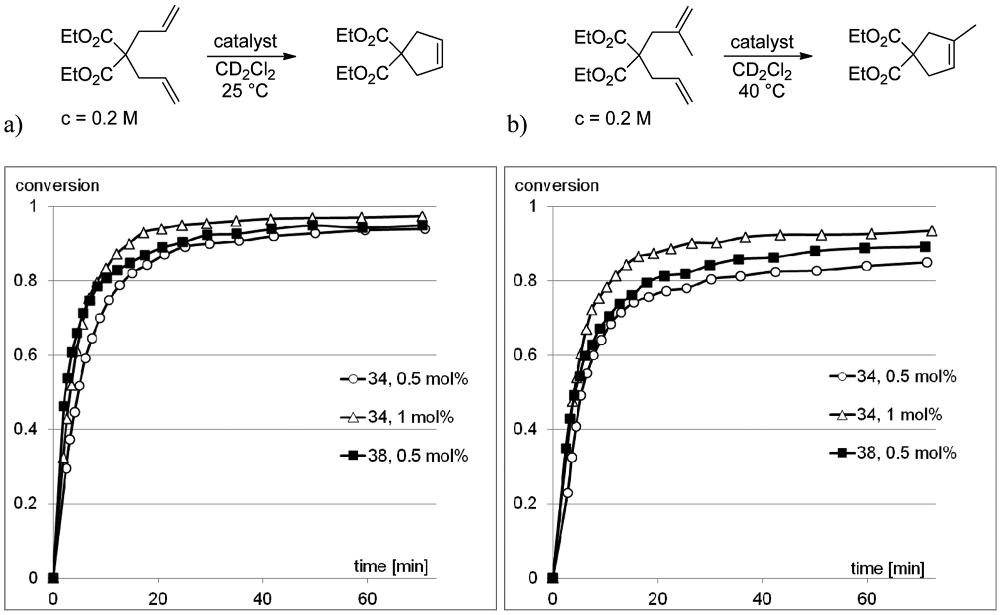
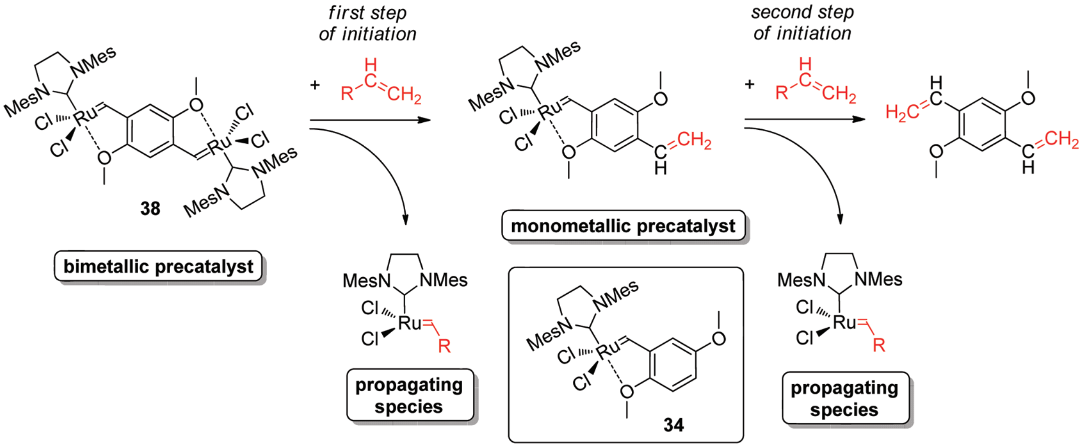


Figure 2. Reaction profiles of the ring-closing metathesis determined by ^{1}H NMR: (a) diethyl diallylmalonate (25 °C, CD_2Cl_2, 0.2 M concentration of substrate); (b) diethyl allylmethallylmalonate (40 °C, CD_2Cl_2, 0.2 M concentration of substrate).

Scheme 6. Initiation Behavior of the Bimetallic Complex 38 Consisting of Two Steps, When the First and Second Propagating Species Are Released[a]



[a]The monometallic complex **34** serves as a model of an intermediate monometallic complex released after the first initiation step.

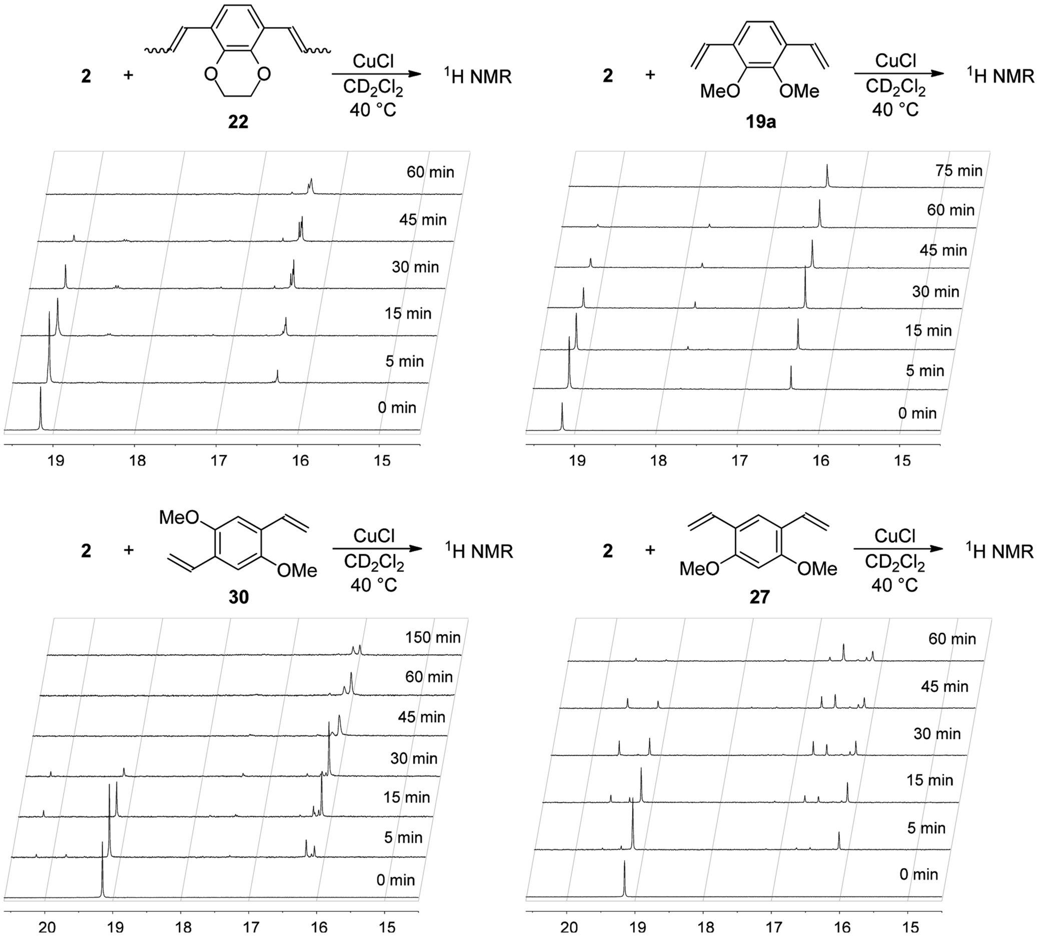
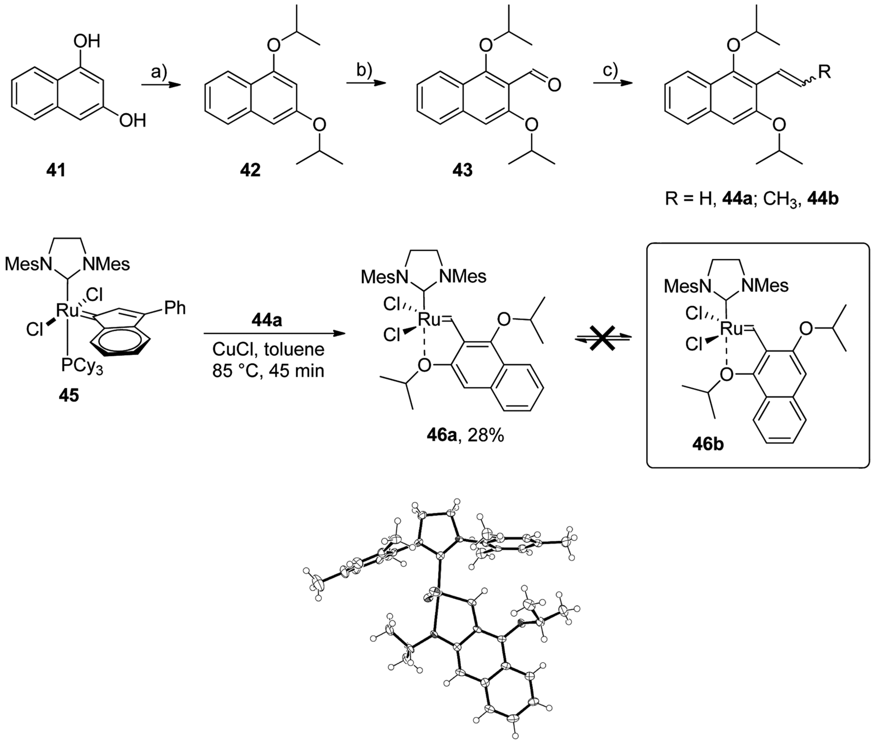


Figure 3. Attempts to synthesize complexes **36**−**39**, followed by ^{1}H NMR. Only the regions related to benzylidene Ru=CH proton resonances are shown. The peak at 19.15 ppm corresponds to the substrate complex **2**.

complexes **38** and **39**, were even less selective and resulted in numerous peaks, which collapsed finally into two broadened peaks (**30**) or remained as eight (!) individual peaks of different intensities in the case of ligand **27**. Although conclusive remarks require further studies, we supposed that syntheses of the complexes **36**, **38**, and **39** suffer from numerous equilibria, which operate when the Grubbs complex **2** is subjected to the ligand exchange. The lack of selectivity was attributed, among other things, to the number of introduced ruthenium atoms (mono- vs bimetallic complexes), the geometry of the complexes (*trans*- and *cis*-Cl_2 isomers[29a]), and possible metatheses, which may dimerize the ligands.[30] In turn, the exchange reaction

Scheme 7. Synthesis of Ligands **44a**,**b** and Ligand Exchange Procedure with Complex **45**[a]



[a]Legend: (a) *i*-PrBr, K_2CO_3, DMF, 60 °C, 92% **42**; (b) *n*-BuLi, TMEDA, Et_2O, then DMF, 80% **43**; (c) R = H, Ph_3PCH_3Br, *t*-PeOK/toluene, THF 96% **44a**, R = CH_3, $Ph_3PC_2H_5Br$, *t*-PeOK/toluene, THF, 99% **44b**. TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, DMF = dimethylformamide.

with ligand **19a** seemed to be selective, in disagreement with the results of the preparative experiment, in which the product isolated by chromatography displayed a complicated ^{1}H NMR spectrum. Although the intrinsic stability of the complexes **36**, **37**, and **39** remains unknown, we assumed that they decompose mainly during attempts to isolate them, while the species observed by NMR are synthetic intermediates or byproducts, rather than products of decomposition. This assumption was supported by complex **38**, which displayed a clear NMR spectrum with one benzylidene peak and was stable in solution in pure form. In general, the outcome of the syntheses of the bimetallic complexes differed substantially from preparations of the monometallic species, where only single complexes are produced. Besides, in preparative experiments attempts of separation of the reaction mixtures with chromatography and crystallization failed, and poor mass recovery of the products was experienced.

Synthesis of Ruthenium Complex with Two Coordinating Sites. Taking into consideration the properties of phenanthrene and the observed properties of the angular complexes **6a**,**c**,[9a] we expected that angular bimetallic complexes **36** and **37**, related to variant **III** (Chart 2b), should be stabilized by electron delocalization of the chelate rings. However, we found that the complexes were actually *less* stable than the related monometallic derivatives, at least in the course of isolation. From that perspective the presence of increased stabilization is unlikely, and a quite different picture emerged. In the Hoveyda–Grubbs complexes presence of the chelate ring triggers a bidirectional effect—the organic ligand is influenced by chelate formation and the chelate ring is influenced by the organic ligand. Thus, in the systems with extended *π*-electron conjugation a competition between local aromaticities (stabilizations arising from electron delocalization) of the individual rings is expected. When tricyclic PAHs are considered, individual rings adapt their electronic structure to minimize the total energy of the system. Thus, in phenanthrene, the internal (middle) ring decreases in aromaticity, while the two external rings gain stabilization, in accordance with the Clar rule. However, this situation is possible because the three carbon rings have similar properties, and thus the loss of aromaticity of the internal ring is justified. The same picture is still probably valid for the naphthalene-based angular complexes **6a**,**c**, in which two carbon rings and one chelate ring are present. However, for the bimetallic systems (**36** and **37**), in which stabilization of both external rings is relatively small, the aromaticity of the benzene ring is mostly preserved and thus only a small stabilization of the chelates is observed.[42] Therefore, the fact that the investigated bimetallic complexes are less stable than their monometallic relatives supports the hypothesis that electron stabilization of the chelate rings is only slight and is much smaller than in the angular naphthalene-based complexes **6a**,**c**. To support this reasoning, we considered one other system related to complexes **6b**,**c** described earlier.[9a] The designed naphthalene ligand **44** bearing *two* coordinating *i*PrO groups was synthesized in a three-step synthetic sequence (Scheme 7). We expected that the ligand might support two different coordination modes for isomeric complexes **46a**,**b**, corresponding to complexes **6b**,**c**, respectively, and allow us to follow their equilibria controlled by the relative stability of the isomers.[15]

Although ligand exchange reactions of **44a**,**b** with complex **2** were unsuccessful, the experiments were repeated under more harsh conditions with complex **45**.[9b] In the reaction with ligand **44a** we observed the formation of the green product **46a**, which was separated by column chromatography, crystallized, and analyzed by spectral methods. In contrast to our expectations, X-ray structural studies revealed that **46a** is a linear isomer coordinated by the *i*PrO group present in position 3 of the naphthalene core (Scheme 7, inset).[43] Attempts to isomerize complex **46a** in refluxing toluene failed, and also no traces of isomerization and decomposition products were observed in the presence of PCy_3 as a catalyst under reflux (48 h). Although the angular isomer **46b** was expected to be thermodynamically more stable than **46a**, at least when the electronic structure of the conjugated π-electron system is considered,[9a,44] its formation was suppressed probably by steric factors, which destabilize the structure **46b**. In addition, the presence of two *i*PrO substituents crowded around the ruthenium atom might suppress the equilibrium for kinetic reasons, even when **46b** is thermodynamically favored. The presence of a high energy barrier along the isomerization pathway, which requires opening of the chelate ring, was supported by activity studies. In contrast to the related complex **6b**,[9a] the catalyst **46a** was very stable and inactive in the model RCM reaction of diethyl diallylmalonate at 25 °C, while it activated slowly at elevated temperature in toluene (60 °C, Figure 5). Thus, the differences in electronic stabilizations of the isomeric complexes **46a**,**b**, which expectedly should favor formation of the latter complex, were too small to control the product distribution. Although designed naphthalene ligands may control the catalytic activity of complexes **6b**,**c** over a very broad range,[9a] in the case of ligand **44a** the effect appeared too small to overcome other structural factors, which suppressed the formation of **46b**.

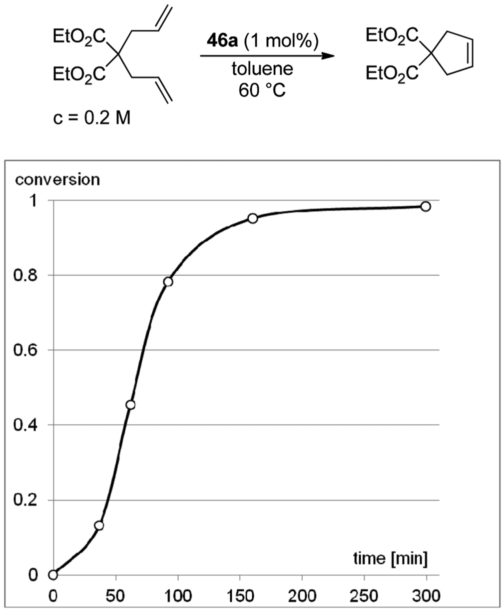


Figure 5. Reaction profile of ring-closing metathesis of diethyl diallylmalonate determined by GC (1.0 mol % of **46a**, 60 °C, toluene, 0.2 M concentration of the substrate).

CONCLUSIONS

In conclusion, we have designed a series of bimetallic Hoveyda–Grubbs type complexes bearing two chelate rings assembled on an organic ligand. The complexes were grouped into angular species, derived from 1,2,3,4-substituted benzenes, and linear ones, in which the chelate rings form a linear tricyclic structure similar to that present in anthracene. Although various structural modifications were tested, synthesis of the bimetallic complexes from the first class failed, and only unstable mixtures of metalated products were isolated in low yields. However, synthesis of complexes related to anthracene encountered similar problems, the symmetrical bimetallic complex **38** was synthesized from 1,4-dimethoxy-2,5-divinylbenzene. Due to the low solubility of the complex, it was isolated by precipitation from the reaction mixture in a ligand exchange reaction with the Grubbs second-generation catalyst **2**. The catalyst **38** was characterized by spectroscopic and X-ray methods, and its activity was tested in model RCM reactions. It displayed activity very similar to that of the related monometallic catalyst **34**. This suggested that no cooperativity of the initiation of **38** is displayed when two propagating species are consecutively released. From the results presented accompanied by ^{1}H NMR studies, we concluded that synthesis of the bimetallic complexes differs substantially from synthesis of the monometallic species. While the latter form selectively,[2b,c,9,29a,36] synthesis of the bimetallic species is disturbed by low selectivity and low stability of the products. The reduced stability of the angular complexes **36** and **37** experienced on attempts of their isolation suggested also that stabilization of the chelate rings, attributed to π-electron delocalization, is relatively small. Although designed naphthalene ligands control the catalytic activity of the similar complexes **6** over a very broad range,[9a] the electronic effects in the bimetallic complexes with two chelate rings are rather suppressed. Probably the presence of two chelate rings assembled on the benzene core cannot overcome its aromatic stabilization and thus the bimetallic complexes **36** and **37**, which were probed by synthesis, do not gain the extra stabilization expected for angular phenanthrene-type structures. Similar conclusions apply to the naphthalene-based monometallic catalyst **46**, featuring two coordinating *i*PrO groups. Although the structural combination enables the formation of two isomeric products with different coordination modes derived from anthracene and phenanthrene, only the linear complex **46a** was isolated. Thus, the expected differences in stabilizations of complexes **46a**,**b**, which should favor formation of the latter for thermodynamic reasons, are too small to control the product distribution.

ASSOCIATED CONTENT

Supporting Information

Text, figures, tables, and CIF files giving spectra for new compounds, analytical and spectral characterization data, experimental procedures, crystallographic data, and molecular coordinates of the calculated complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.

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to vinyl derivatives to avoid possible complications (monometalated complexes of bis-propenyl ligands may display *E*/*Z* isomerism of the free propenyl group). However, in ^{1}H NMR studies of the reactions of complex **2** with ligands **19a**,**b**, no differences were observed.

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(39) Although in a ligand exchange reaction the related monometallic complex **31** was not formed (cf. ref 37), we attempted synthesis of the bimetallic derivative **35**, in which a stabilizing π-electron delocalization was expected.

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