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# Ruthenium Olefin Metathesis Catalysts with N-Heterocyclic Carbene Ligands Bearing *N*-Naphthyl Side Chains

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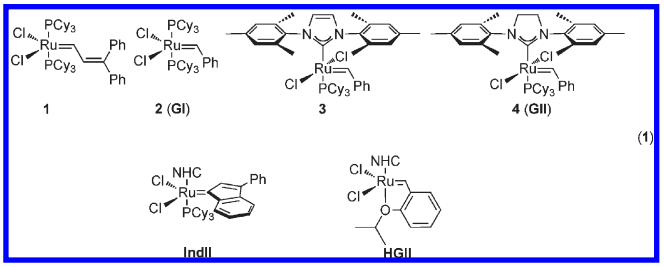
A series of second-generation ruthenium-based olefin metathesis catalysts bearing *N*-naphthyl-substituted N-heterocyclic carbene (NHC) ligands have been prepared and fully characterized. By reaction with the appropriate NHC, these complexes are readily accessible in one synthesis step from the commercially available first-generation precursors [$RuCl_2$(=CHPh)($PCy_3$)$_2$] (Grubbs I, **GI**) or [$RuCl_2$(=CH-*o*-*i*PrO-Ph)($PCy_3$)] (Hoveyda−Grubbs I, **HGI**) by simple exchange of one phosphine ligand with the free NHCs. Time-dependent conversions in the ring-closing metathesis (RCM) of standard substrates leading to di- as well as trisubstituted olefins have been measured for these catalysts. When benchmarked against the parent SIMes-containing the Grubbs II precatalyst (**GII**), most of these new NHC structures show enhanced reactivity in RCM. From these comparative studies, valuable information was gathered which shows that the alkyl substitution on the naphthyl side chains can enhance or lower the catalytic performance, depending on the bulk and the position of these alkyl groups. The behavior of the best performing precatalysts has been investigated in the RCM of a series of representative substrates, in enyne metathesis reactions as well as in cross-metathesis (CM).

## 1. Introduction

Olefin metathesis represents one of the most useful and versatile tools in organic synthesis for the formation of carbon−carbon double bonds. Numerous types of metathesis reactions such as ring-closing metathesis (RCM), enyne metathesis, ring-opening metathesis polymerization, and cross-metathesis (CM) have been developed.[1] Most prominent in synthetic organic chemistry is the RCM reaction, which gives access to an impressive range of unsaturated carbo- and heterocyclic ring systems.[2] The discovery of the well-defined ruthenium carbene catalyst **1** by Grubbs in 1992 generalized their use,[3] the properties of the Grubbs catalyst leading to higher compatibility with functional groups as well as an increased ease of handling compared to the Schrock family of catalysts.[4] Subsequently, the Grubbs first-generation catalyst **2** (**GI**)[5] and second-generation catalysts **3** and **4** (**GII**),[6,7] containing N-heterocyclic carbene (NHC) ligands,[8] were reported between 1995 and 1999 (eq 1).




Successful variations of the original second-generation catalysts **3** and **4** have since then appeared and have led,

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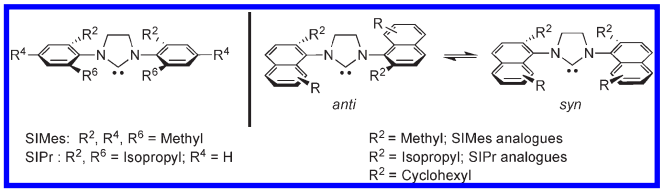
**Chart 1. Imidazolin-2-ylidenes with Phenyl (Left) and Naphthyl (Right) Side Chains**




inter alia, to indenylidene precatalysts (**IndII**) and to phosphine-free Hoveyda−Grubbs II type precatalysts (**HGII**).[9] Modification of the NHC ligand (SIMes/IMes; IMes = 1,3-bis-(2,4,6-trimethylphenyl)imidazol-2-ylidene; SIMes = 1,3-bis-(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene) has also been studied. For example, modifying the central five-membered N-heterocycle (four- and six-membered rings),[10] or substituting one or two side chains with alkyl groups,[11] have typically led to decreased activity and/or faster decomposition of the corresponding ruthenium catalysts. On the other hand, introducing the more bulky SIPr ligand did lead to increased activity for simple RCM reactions,[11a,12] but sterically more demanding substrates again led to decreased catalyst stability and lower product yields.[13] Very small modifications of the original SIMes ligand architecture seem more successful, as shown by Grubbs et al., who have recently identified a series of ligands with slightly higher reactivity or better activity for the RCM of hindered substrates.[14,15]

Recent work in our laboratories has led to the synthesis of promising members of a new family of stable, saturated NHC ligands that incorporate bulky naphthyl side chains.[16] The introduction of the naphthyl moieties generates atropisomeric ligands with $C_2$-symmetric (anti) and $C_s$-symmetric (syn) conformations (Chart 1). In a preliminary communication, we reported on the use of these new NHCs as ligands in Grubbs second-generation ruthenium type complexes and showed how some of the new catalyst precursors are superior to SIMes-containing Grubbs II complexes in simple RCM reactions leading to disubstituted olefins.[17]

In the present contribution, we give a full overview of the preparation and characterization as well as on detailed RCM studies involving these new Grubbs II type ruthenium complexes, with both substrates giving disubstituted and trisubstituted olefins. We show that, in contrast to what has been observed with the SIPr-modified Grubbs II type catalyst,[12a,13] correctly substituted naphthyl side chains of the NHC ligand indeed lead to complexes with better overall catalytic behavior in the RCM reaction. These findings were then applied to the synthesis, characterization, and catalytic behavior of some Hoveyda−Grubbs II type ruthenium complexes (type **HGII**, see above) containing the best performing of our naphthyl-substituted NHCs. In addition, we present the synthesis of a ligand incorporating the naphthyl side chain motif with an unsaturated central N-heterocycle and compare the corresponding second-generation ruthenium metathesis catalyst with its saturated congener. To obtain a more complete picture on their activity, we investigated the performance of these catalysts in the RCM of a wider range of substrates as well as in selected enyne and cross-metathesis reactions.

## 2. Results and Discussion

**2.1. Synthesis and Characterization of Grubbs II Type Ruthenium Complexes.** Precatalysts of general formula $[RuCl_2(NHC)(=CHPh)(PCy_3)]$ (Grubbs II type ruthenium complexes, **6a**−**e**) were prepared from $[RuCl_2(=CHPh)(PCy_3)_2]$ (Grubbs I, **GI**) by simple exchange of one phosphine ligand with the corresponding NHCs **5a**−**e** at room temperature in toluene (Scheme 1). The syn:anti ratio of the free NHCs is maintained during synthesis of the complexes, which are therefore present as isomeric mixtures, as shown by $^1H$ and $^{31}P\{^1H\}$ NMR spectroscopy. Completion of the reactions was monitored by $^{31}P\{^1H\}$ NMR spectroscopy (disappearance of the signal corresponding to **GI**). It is of note that **GI** should be completely consumed before workup and the reaction may be driven to completion by adding a slight excess of the corresponding NHC ligand. Analytically pure complexes were best obtained via crystallization/precipitation of the respective compounds by fast diffusion of methanol into a highly concentrated $CH_2Cl_2$ solution containing **6a**−**e**.[18] This synthetic procedure also led to crystalline material for X-ray diffraction studies, and complexes *anti*-**6b**, *syn*-**6c**, *anti*-**6d**, and *anti*-**6e** were unambiguously identified by X-ray structure analysis.

Atomic displacement ellipsoid drawings of the complexes, together with the most relevant bond lengths and angles, are given in Figure 1 and confirm the structural assignment. The compounds exhibit a distorted-square-pyramidal geometry, with the ruthenium−benzylidene bond occupying the apical position and with the two chloride ligands trans to one another. The relative bulk of the alkylated naphthyl side chains of the NHC ligand forces the benzylidene moiety to arrange away from the 2-isopropyl/2-cyclohexyl moieties and to position itself parallel to the second aromatic ring

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(18) In contrast to the synthesis of SIPr-containing second-generation ruthenium catalysts, decomposition of the complex when using MeOH is not observed here.

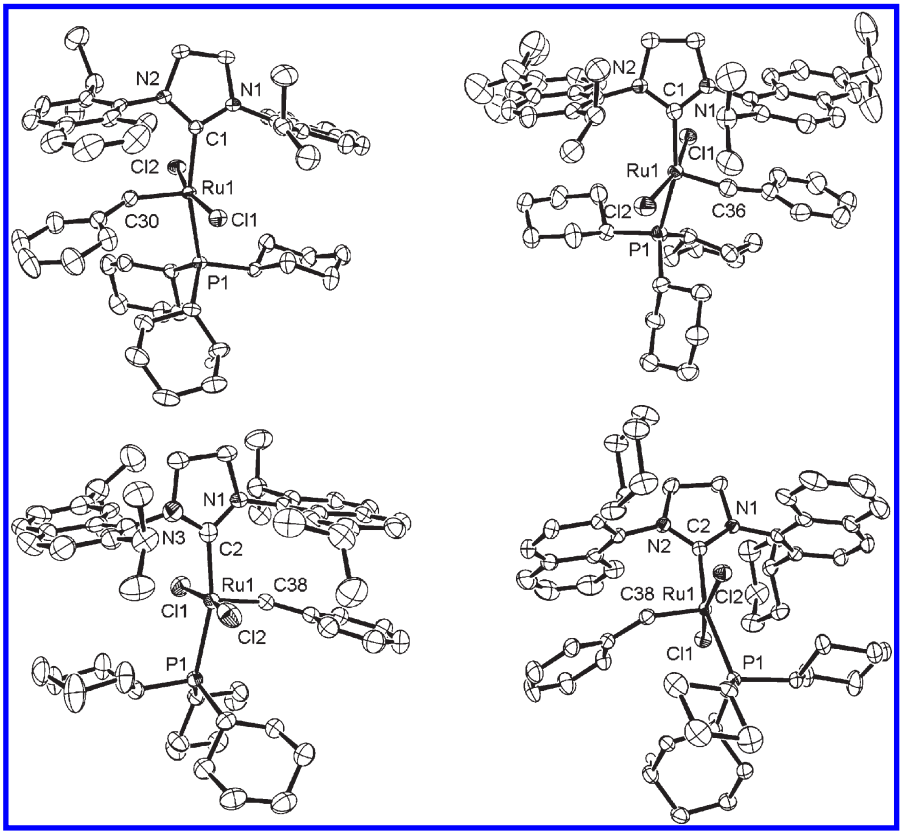
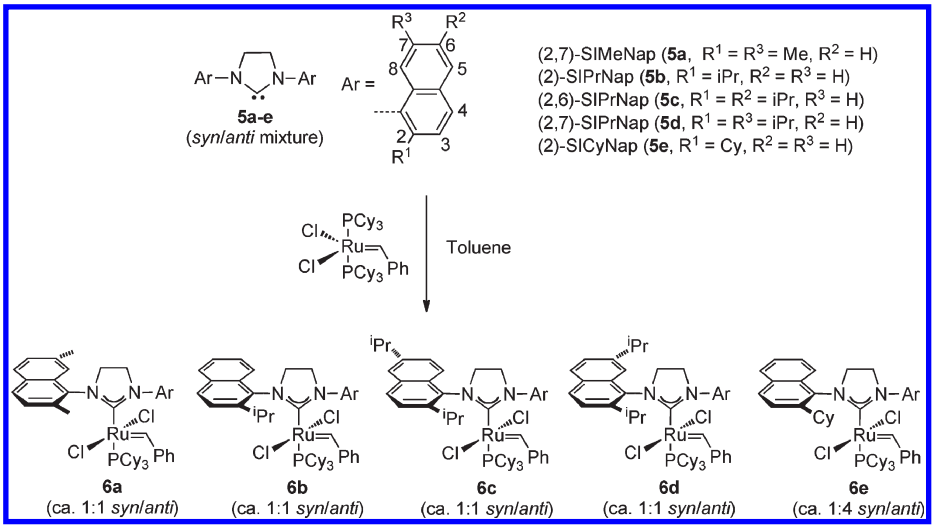



**Figure 1.** ORTEP diagrams (30% probability ellipsoids) of complexes **6b** (top left), **6c** (top right), **6d** (bottom left), and **6e** (bottom right). Selected bond lengths (Å) are as follows. Ru−$C_{NHC}$: **6b**, 2.074(2); **6c**, 2.069(4); **6d**, 2.080(5); **6e**, 2.067(3). Ru−$C_{benzylidene}$: **6b**, 1.847(2); **6c**, 1.830(4); **6d**, 1.846(5); **6e**, 1.834(4). Ru−P: **6b**, 2.4180(5); **6c**, 2.434(1); **6d**, 2.432(1); **6e**, 2.4191(9). Selected bond angles (deg) are as follows. $C_{NHC}$−Ru−$C_{benzylidene}$: **6b**, 99.94(9); **6c**, 98.9(2); **6d**, 100.2(2); **6e**, 99.6(1).

**Scheme 1. Free N-Heterocyclic Carbenes Used (Top) and Grubbs II Type Ruthenium Precatalysts Synthesized (Bottom)**




of the naphthyl moiety. The overall geometry around the transition-metal center and bond lengths and angles in the complexes are similar to those of the parent Grubbs II catalyst [$RuCl_2$(SIMes)(=CHPh)($PCy_3$)] (**GII**).[17,19]

**2.2. Ring-Closing Metathesis (RCM) Activity of Selected Substrates.** The best method to compare the catalytic behavior of different ruthenium precatalysts in the RCM reaction is to directly follow the conversion of standard substrates to product via $^1$H NMR spectroscopy.[13] This allows one not only to understand the overall performance of a catalyst but also to monitor subtle differences such as the ease of initiation of the precatalyst or possible decomposition and differences in stability of the catalysts during the transformation.

We initially studied the behavior of **6a**−**e** in the RCM reactions of diallyltosylamide (**7**) and diethyl diallylmalonate (**8**) using 1 mol % of precatalyst (27 °C, 0.1 M substrate/solvent) and benchmarked the runs against the Grubbs II

(19) Love, J. A.; Sanford, M. S.; Day, M. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 10103.

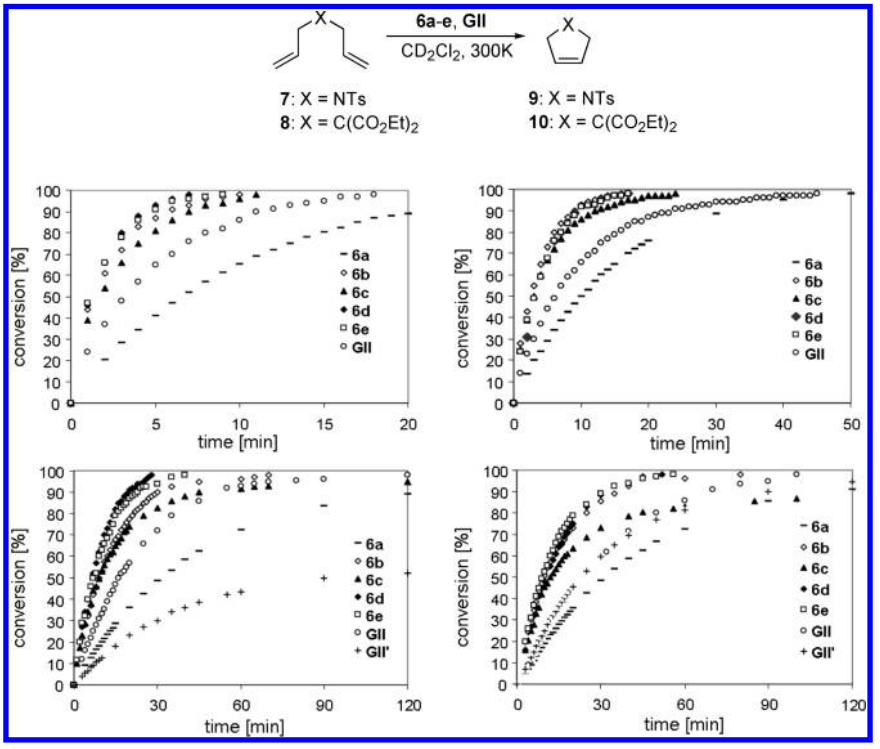



**Figure 2.** Time−conversion plots for the RCM of **7** (left) and **8** (right), using 1 mol % (top) and 0.1 mol % (bottom) of catalyst precursor.

(**GII**) catalyst.[20] The plots of cycloalkene concentration versus time in Figure 2 (top) revealed that the four catalysts **6b**−**e**, namely the ones incorporating bulky isopropyl or cyclohexyl groups on the 2-position of the naphthyl side chains of the NHC ligand, effect the cyclization of substrates **7** and **8** with a markedly increased initial reaction rate compared to **GII**. However, complex **6a** not only turned out to be less active than its congeners but also needed longer reaction times to reach full conversion in comparison to **GII** (30 min for **7**, 50 min for **8**). The shape of the curves indicates that the initial reaction rate for **6a** is significantly slower than for the other precatalysts. This may be directly related to the fact that sterically more demanding NHCs enhance phosphine dissociation and consequently increase initial reaction rates of olefin metathesis. Indeed, **6d**,**e** are the fastest precatalysts for these transformations, with reaction times of $< 20$ min for both substrates.

We therefore wondered whether more detailed information could be gained by lowering the amount of precatalyst by an order of magnitude (0.1 mol %, Figure 2 bottom). For these runs, the catalytic profile of [$RuCl_2${(2)-SIMePh}-(=CHPh)($PCy_3$)] (**GII′**), a slightly less bulky analogue of **GII** recently synthesized by Grubbs et al. for the RCM giving tetrasubstituted olefins,[15b] was also analyzed. These studies uncovered the following trends: first, precatalysts **6e** and especially **6d** are still extremely active and show conversion times comparable to the values obtained for **GII** at 1 mol %. Second, compounds **6b** and especially **6c** are clearly less active under these more demanding conditions. A careful analysis of the shape of the curves shows that while the initial reaction rate is once again higher than for **GII**, the activity of **6c** decreases considerably with increasing conversion and reaction time. This indicates that at least some of the precatalyst is deactivated over time as **6c** reaches complete conversion only after prolonged reaction times. Furthermore, once again, complex **6a** turned out to be slower than the other new catalysts. Nevertheless, and in contrast to the case for **6c**, it does not decompose over time and for both substrates **7** and **8** complete conversion is observed after longer reaction times. Not surprisingly, **GII′**, which behaves very well with bulky diene substrates, also needs longer reaction times than **GII** and apparently decomposes with the tosylamide-derived substrate **7** before complete conversion of the substrate.

It is well-known that a **GII** analogue with a bulky SIPr ligand effects the cyclization of **7** and **8** with an increased reaction rate compared to that for the orginal SIMes-derived **GII** catalyst but fails to completely ring-close substrates that give trisubstituted olefins.[13] This behavior was interpreted in terms of steric effects that render the approach of the bulkier substrate more difficult and thus lead to decomposition of the active ruthenium species during catalysis. It was therefore of interest to see how precatalysts **6a**−**e** behave with such substrates. RCM studies of allylmethallyl tosylamide (**11**) and diethylallylmethallyl malonate (**12**) were performed using 0.5 mol % of the respective precatalyst (27 °C, 0.1 M substrate/solvent) and were once again benchmarked against **GII**. In contrast to the results obtained by Grubbs et al. with the SIPr-modified ruthenium catalyst, the overall catalytic profiles of **6a**−**e** when compared to that of **GII** do not change with substrates **11** and **12** and reactivity trends for these more demanding RCM reactions were found to be similar to those observed for the RCM of **7** and **8**. Thus, especially catalysts **6d**,**e** show excellent activity, being the most efficient catalysts in this study. Reaction times required for full

(20) Syn/anti mixtures of complexes have been used throughout the present study. For preliminary results showing that there are differences in reactivity between the two conformers, see: Gatti, M.; Vieille-Petit, L.; Luan, X.; Mariz, R.; Drinkel, E.; Linden, A.; Dorta, R. *J. Am. Chem. Soc.* **2009**, *131*, 9496.

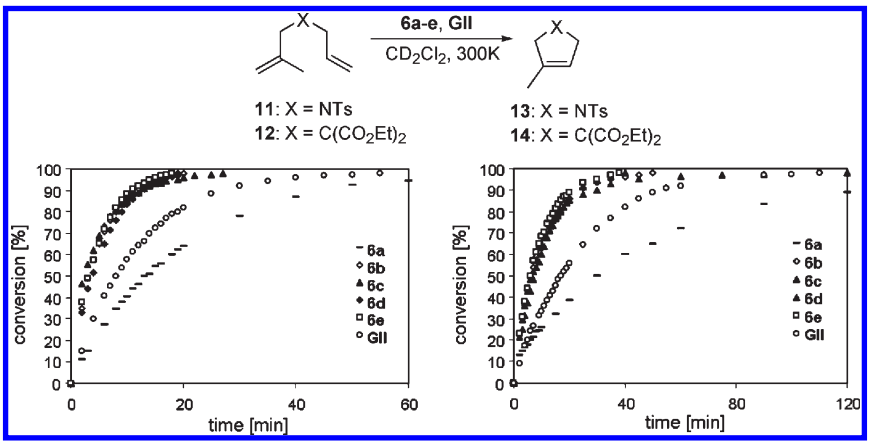



**Figure 3.** Kinetic data for the RCM of **11** (left) and **12** (right), using 0.5 mol % of catalyst precursor.

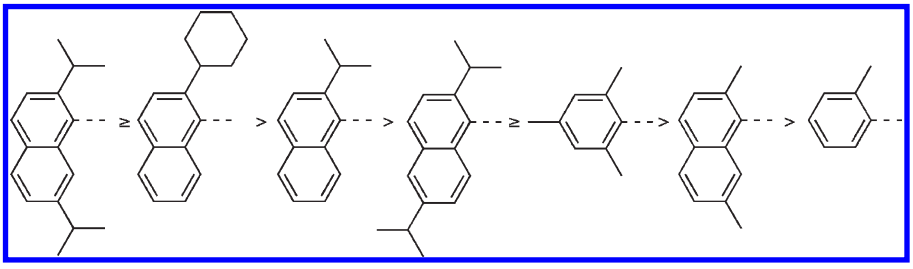
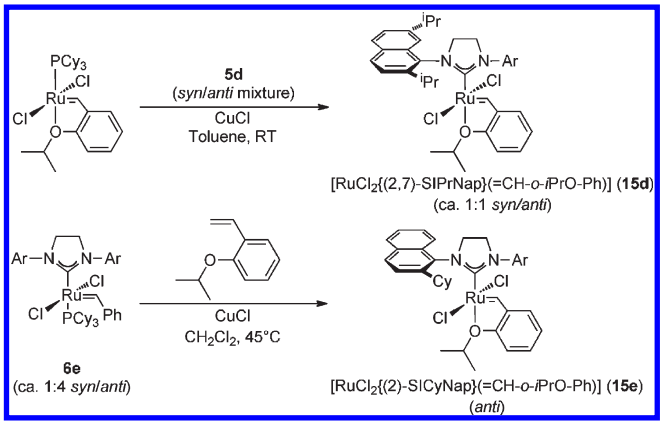


**Figure 4.** Order of catalytic performance for Grubbs II catalysts based on the structure of the side chain of the NHC ligand or RCM giving di- and trisubstituted double bonds.

**Scheme 2. Synthesis of Hoveyda−Grubbs II Type Ruthenium Precatalysts 15d (Top) and 15e (Bottom)**




conversion are typically one-third of what is needed with **GII**. Catalyst **6b** also shows good activities, and only **6c** once again suffers from somewhat lower stability due to its peculiar substitution pattern on the naphthyl side chains. Interestingly, precatalyst **6a** with the less bulky NHC ligand does not perform better with these sterically more demanding substrates and needs longer reaction times for full conversion than does **GII** (full conversion not shown in Figure 3).

Overall, the studies performed for both standard (**7**, **8**) and more challenging (**11**, **12**) substrates show that Grubbs II type precatalysts with NHC ligands containing correctly substituted naphthyl side chains can clearly improve the catalytic behavior of these ruthenium complexes without loss of catalyst stability during the transformation. Figure 4 gives a ranking based on the structure of the side chains in these saturated NHC ligands.

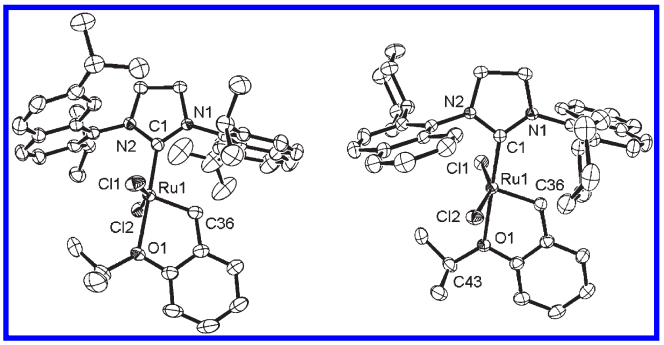
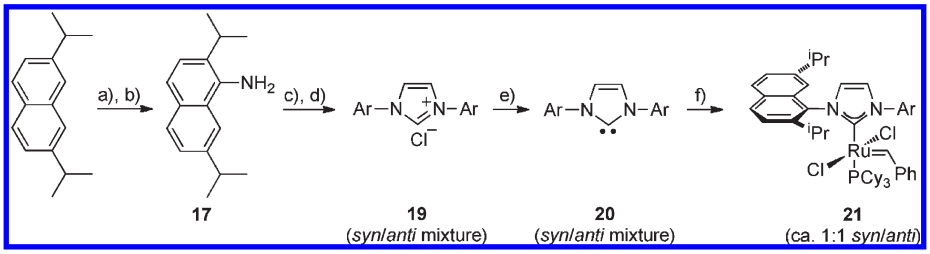



**Figure 5.** ORTEP diagrams (30% thermal ellipsoids) of complexes *anti*-**15d** (left) and *anti*-**15e** (right). Selected bond lengths (Å) are as follows. Ru−$C_{NHC}$: **15d**, 1.970(2); **15e**, 1.972(2). Ru−$C_{benzylidene}$: **15d**, 1.828(3); **15e**, 1.835(2). Ru−O: **15d**, 2.247(2); **15e**, 2.297(1). Selected bond angles (deg) are as follows. $C_{NHC}$−Ru−$C_{benzylidene}$: **15d**, 101.6(1); **15e**, 101.08(7).

**2.3. Synthesis and Characterization of Selected Hoveyda−Grubbs II Type complexes and of a Grubbs II Type Complex with an Unsaturated NHC Ligand.** The studies above showed that the NHC ligands (2,7)-SIPrNap (**5d**) and (2)-SICyNap (**5e**) contain the preferred side chain geometries for ruthenium metathesis precatalysts. We applied this finding to the synthesis of two new Hoveyda−Grubbs II type precatalysts with ligands **5d**,**e** as well as to the synthesis of an analogue of precatalyst **6d** which incorporates an unsaturated NHC counterpart of (2,7)-SIPrNap (**5d**). In the case of Hoveyda−Grubbs II type ruthenium catalysts, the mechanism by which the precatalyst is activated is still unclear and we believed that time−conversion studies with our new NHC ligands might reveal interesting insights into differences between the two catalyst families. Similarly, very different reactivities

**Scheme 3. Synthesis of (2,7)-IPrNap (20)**[a]




[a] Legend: (a) $HNO_3$, AcOH, 0 °C to room temperature; (b) cat. Pd/C, $H_2$, MeOH, room temperature; (c) glyoxal, cat. HCOOH, MeOH, room temperature; (d) $(CH_2O)_n$, HCl/dioxane, EtOAc, 0 °C to room temperature; (e) *t*BuOK, THF, room temperature; (f) $[RuCl_2(=CHPh)(PCy_3)_2]$ (**GI**), toluene, room temperature.

have been reported for SIMes- and IMes-derived second-generation Grubbs II type catalysts,[13] prompting us to synthesize the unsaturated homologue of **5d**.

**2.3.1. Hoveyda−Grubbs II Complexes.** The Hoveyda−Grubbs II type ruthenium complex $[RuCl_2\{(2,7)$-SIPrNap$\}$-$(=$CH-*o*-*i*PrO-Ph$)]$ (**15d**) was prepared from $[RuCl_2(=$CH-*o*-*i*PrO-Ph$)(PCy_3)]$ (Hoveyda−Grubbs I, **HGI**) by simple exchange of the phosphine ligand with (2,7)-SIPrNap (**5d**) in the presence of CuCl (Scheme 2, top). For the synthesis of precatalyst $[RuCl_2\{(2)$-SICyNap$\}(=$CH-*o*-*i*PrO-Ph$)]$ (**15e**), we chose the alternative pathway which starts with the Grubbs II type complex **6e** that subsequently undergoes cross metathesis with 2-isopropoxystyrene in the presence of CuCl (Scheme 2, bottom).[9b−d,21] In both cases, complete reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy (disappearance of the signal corresponding to bound tricyclohexylphosphine). The air-stable complexes **15d**,**e** were purified by column chromatography on silica gel with $CH_2Cl_2$/hexane (1:1) as eluent, leading to pure green microcrystalline products in moderate (51% for **15e**) to good (76% for **15d**) yield. While the syn:anti ratio of the ligands was maintained during the synthesis of these complexes, *syn*-**15e** could not be eluted from the column, justifying the lower overall yield in this case.

Full characterization of the new Hoveyda−Grubbs type complexes included X-ray structure analyses of crystals obtained by slow diffusion of hexane into concentrated solutions of **15d**,**e** in dichloromethane (Figure 5). The overall geometry around the transition-metal center and most of the bond lengths and angles are similar to those of the parent Hoveyda−Grubbs II catalyst $[RuCl_2(SIMes)(=$CH-*o*-*i*PrO-Ph$)]$ (**HGII**).[9b] The Ru−$C_{NHC}$ bond distances in these complexes are slightly shorter than for Grubbs II type complexes, indicating a tighter binding situation due to the replacement of the bulky phosphine trans to the NHC with the chelating ether fragment of the benzylidene moiety.

**2.3.2. Grubbs II Complex Containing an NHC with an Unsaturated N-Heterocycle.** The ligand (2,7)-IPrNap (**20**) featuring an unsaturated central N-heterocycle and its precursor imidazolium salt (2,7)-IPrNap·HCl (**19**) were obtained by adapting literature procedures. Most importantly, the naphthylamine derivative **17** was synthesized via a rather selective nitration step, where the unwanted 4-nitro-2,7-diisopropylnaphthalene derivative was eliminated by column chromatography.[22] Subsequent reduction of 1-nitro-2,7-diisopropylnaphthalene (**16**) under hydrogen pressure in the presence of catalytic amounts of Pd/C[23] gave amine **17** in > 50% yield over these two steps (Scheme 3). Condensation with glyoxal and ring closing with paraformaldehyde using a patented procedure[24] resulted in clean (2,7)-IPrNap·HCl (**19**) that was subsequently deprotonated to give (2,7)-IPrNap (**20**). Not surprisingly, both **19** and **20** were obtained as a ca. 1:1 mixture of syn and anti isomers, as evidenced by $^1H$ and $^{13}C$ NMR spectroscopy.

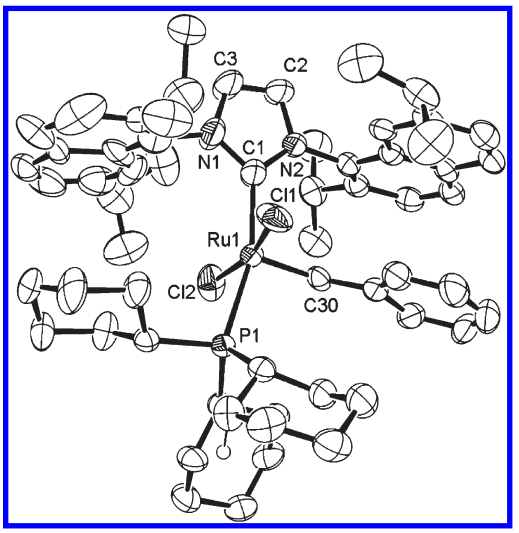



**Figure 6.** ORTEP diagram (30% ellipsoids) of complex **21**. Selected bond lengths (Å): Ru−$C_{NHC}$, 2.091(8); Ru−$C_{benzylidene}$, 1.841(6); C(2)−C(3), 1.33(1). Selected bond angle (deg): $C_{NHC}$−Ru−$C_{benzylidene}$, 99.5(3).

Free carbene **20** was then incorporated into the complex $[RuCl_2\{(2,7)$-IPrNap$\}(=$CHPh$)(PCy_3)]$ (**21**) by following the synthetic procedure reported above for the other Grubbs II type precatalysts (Scheme 3). The structure of **21** was unambiguously assigned by X-ray diffraction studies on single crystals grown by diffusion of methanol into a concentrated dichloromethane solution containing the complex. A representation of *anti*-**21** is shown in Figure 6 together with a list of selected bond lengths and angles. The overall geometry around the transition-metal center and most of the bond lengths and angles in **21** are comparable to those of the parent complex $[RuCl_2(IMes)(=$CHPh$)(PCy_3)]$ (**3**),[6a]

(21) Schoeps, D.; Buhr, K.; Dijkstra, M.; Ebert, K.; Plenio, H. *Chem. Eur. J.* **2009**, *15*, 2960.

(22) For nitration of similar naphthalene derivatives, see: Erichomovitch, L.; Ménard, M.; Chubb, F. L.; Pépin, Y.; Richer, J.-C. *Can. J. Chem.* **1966**, *44*, 2305.

(23) For reduction of *tert*-butyl-substituted nitronaphthalenes, see: Quast, H.; Nüdling, W.; Klemm, G.; Kirschfeld, A.; Neuhaus, P.; Sander, W.; Hrovat, D. A.; Thatcher Borden, W. *J. Org. Chem.* **2008**, *73*, 4956.

(24) Nolan, S. P. International Patent WO 2008/036084 A1, **2008**.

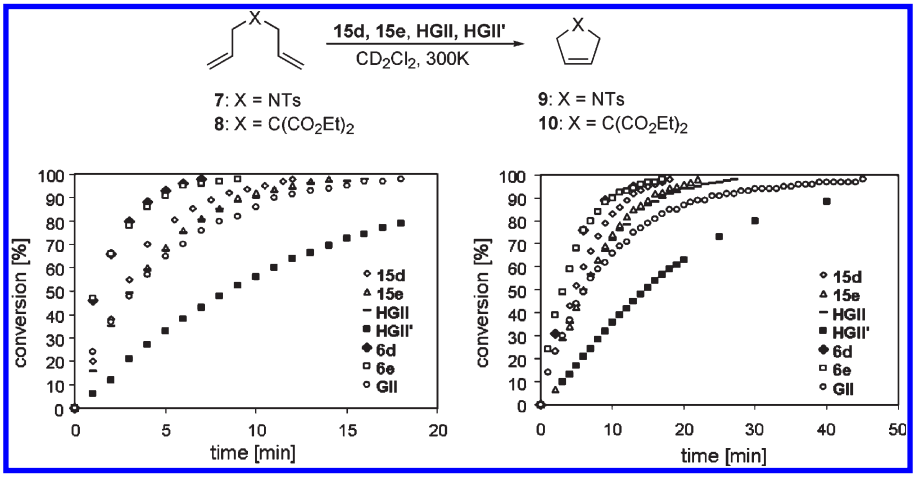



**Figure 7.** Time−conversion plots for the RCM of **7** (left) and **8** (right), using 1 mol % of catalyst precursor.

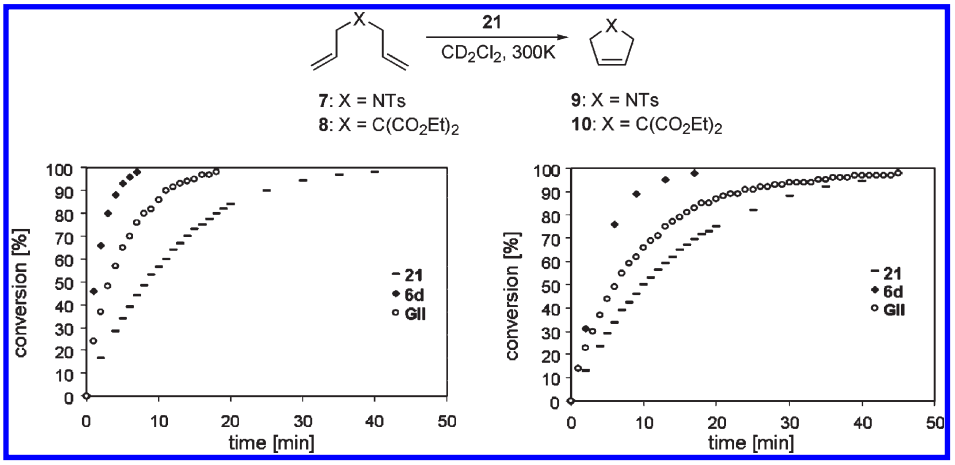


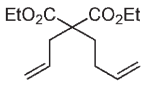
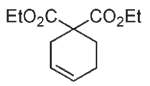
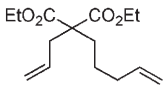
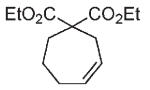
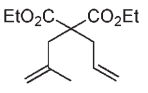
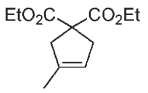
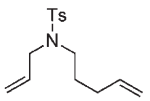
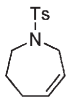
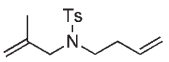
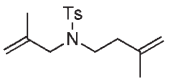
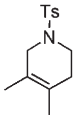
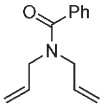
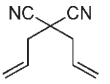
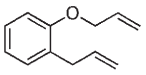
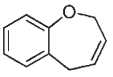
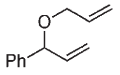
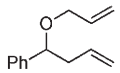
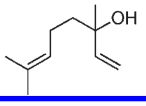

**Figure 8.** Time−conversion plots for the RCM of **7** (left) and **8** (right), using 1 mol % of **21** as catalyst precursor.

and of complexes **6b**−**e** that feature NHC ligands with saturated N-heterocycles. The only noticeable difference consists of the obviously shorter carbon−carbon distance in the backbone of the unsaturated NHC (1.33(1) Å in *anti*-**21** compared to 1.505(8) Å in *anti*-**6d**).

**2.4. Time−Conversion studies of Precatalysts 15d,e and 21 for the RCM of Substrates 7 and 8.** Conversions of the substrates diallyltosylamide (**7**) and diethyl diallylmalonate (**8**) using 1 mol % of catalysts **15d**,**e** (27 °C, 0.1 M substrate/solvent) were once again followed by $^1$H NMR spectroscopy. Parallel reactions were also performed with the SIMes-containing Hoveyda−Grubbs II catalyst [$RuCl_2$(SIMes)-(=CH-*o*-*i*PrO-Ph)] (**HGII**), and kinetic data were also recorded for the more recently reported and commercially available [$RuCl_2${(2)-SIMePh}(=CH-*o*-*i*PrO-Ph)] (**HGII′**).[15b] For better comparison, Figure 7 also contains the kinetic runs of **6d**,**e** and **GII**. Several observations can be made when examining the plots. First, modified **HGII′**, which was developed for RCM of highly substituted dienes,[15b] is clearly not a good candidate for the ring closing of normal substrates. Second and somewhat surprising is the fact that **HGII** performs slightly better than **GII** for both substrates **7** and **8**. The inverse trend is followed with the ruthenium catalysts containing (2,7)-SIPrNap (**5d**) and (2)-SICyNap (**5e**), meaning that an overall lower catalytic activity of Hoveyda−Grubbs type complexes (**15d**,**e**) compared to their Grubbs II analogues (**6d**,**e**) can be observed. It should be noted that Grubbs et al. made the same observation in the RCM of **8** catalyzed by ruthenium complexes bearing unsymmetrical N-heterocyclic carbene ligands.[14b,c] In their study and in contrast to the results presented here, these modified catalysts have been shown to be clearly less active than **HGII**. In our case, **15d**,**e** still perform slightly better than the parent **HGII** complex. Overall, however, the differences in activity are much less pronounced than for phosphine-containing Grubbs II type precatalysts and the curves indicate little difference in the initial reaction rate among **HGII** and **15d**,**e**. The most plausible explanation for this behavior might be that bulky ligands **5d**,**e** lead to a clear initial rate enhancement in the case of phosphine-containing catalysts, where a well-established dissociative mechanism is at work, whereas Hoveyda−Grubbs II type catalysts possibly initiate via an associative mechanism of the olefin and NHC ligand sterics would consequently play a less important role in the activation of the precatalyst.

To complete our time-conversion studies, the catalytic potential of [$RuCl_2${(2,7)-IPrNap}(=CHPh)($PCy_3$)] (**21**) was recorded for diallyltosylamide (**7**) and diethyl diallylmalonate (**8**) using 1 mol % of catalyst loading (27 °C, 0.1 M substrate/solvent). Figure 8 represents the data and compares them to those for both **GII** and its ruthenium analogue **6d**, which features the saturated NHC ligand. The differences in overall activity between saturated and unsaturated NHC-containing ruthenium catalysts (**6d** vs **21**) are truly remarkable. While these activity trends have been reported

**Table 1. Comparative Study in the RCM of Dienes**[a]

| Entry | Substrate | Product | Pre-cat. | Time (h) | Isolated yield (%) |
|---|---|---|---|---|---|
| 1 |  |  | **6a** | 1 | >99 |
| | | | **6d** | 0.3 | 97 |
| | | | **6e** | 0.3 | >99 |
| 2 |  |  | **6a** | 4 | 92 |
| | | | **6d** | 1.5 | 95 |
| | | | **6e** | 1.5 | 94 |
| 3 |  |  | **6a** | 2.5 | 93 |
| | | | **6d** | 1 | 98 |
| | | | **6e** | 1 | >99 |
| | | | **15d** | 2 | 96 |
| | | | **15e** | 2 | >99 |
| | | | **21** | 2.5 | 98 |
| 4 |  |  | **6a** | 2.5 | 93 |
| | | | **6d** | 1 | 98 |
| | | | **6e** | 1 | >99 |
| | | | **15d** | 2 | 96 |
| | | | **15e** | 2 | >99 |
| | | | **21** | 2.5 | 98 |
| 5 |  |  | **6a** | 3 | 96 |
| | | | **6d** | 1 | 98 |
| | | | **6e** | 1 | 95 |
| 6 |  |  | **6a** | 24 | 43[b] |
| | | | **6d** | 24 | 32[b] |
| | | | **6e** | 24 | 48[b] |
| 7 |  |  | **6a** | 1 | 94 |
| | | | **6d** | 0.2 | >99 |
| | | | **6e** | 0.2 | >99 |
| 8 |  |  | **6a** | 2 | 93 |
| | | | **6d** | 1 | 95 |
| | | | **6e** | 1 | 88 |
| | | | **21** | 3 | 90 |
| 9 |  |  | **6a** | 2 | 89 |
| | | | **6d** | 1 | 96 |
| | | | **6e** | 1 | 97 |
| 10 |  |  | **6a** | 2.5 | 93 |
| | | | **6d** | 0.5 | 97 |
| | | | **6e** | 0.5 | 94 |
| | | | **15d** | 0.5 | 97 |
| | | | **15e** | 1 | 98 |
| | | | **21** | 3 | 85 |
| 11 |  |  | **6a** | 1 | 95 |
| | | | **6d** | 0.3 | 91 |
| | | | **6e** | 0.3 | 98 |
| 12 |  |  | **6a** | 0.5 | 92 |
| | | | **6d** | 0.1 | 88 |
| | | | **6e** | 0.1 | 94 |

[a] Reactions performed in $CH_2Cl_2$ at room temperature using 1 mol % of precatalyst, unless noted otherwise. [b] Reaction performed in $CH_2Cl_2$ at 40 °C using 2 mol % of precatalyst.

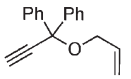
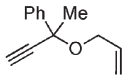
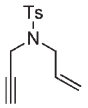
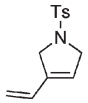
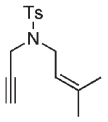
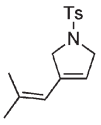
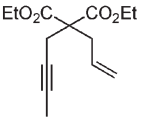
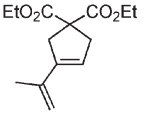
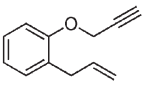
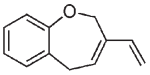
for SIMes/IMes and SIPr/IPr modified benzylidene,[13] indenylidene,[25] and Hoveyda-type complexes,[26] a satisfactory interpretation of these differences remains elusive. Both electronic and steric factors of a given pair of unsaturated and saturated NHCs have been shown for other systems to be practically undistinguishable[27] and cannot explain the kinetic data obtained here. An especially noteworthy feature of the graphs depicted in Figure 8 is the very different initial reaction rates between **6d** and **21**,

(25) Clavier, H.; Nolan, S. P. *Chem. Eur. J.* **2007**, *13*, 8029.

(26) (a) Bieniek, M.; Michrowska, A.; Usanov, D. L.; Grela, K. *Chem. Eur. J.* **2008**, *14*, 806. (b) Clavier, H.; Caijo, F.; Borré, E.; Rix, D.; Boeda, F.; Nolan, S. P.; Mauduit, M. *Eur. J. Org. Chem.* **2009**, 4254.

(27) (a) Dorta, R.; Stevens, E. D.; Scott, N. M.; Costabile, C.; Cavallo, L.; Hoff, C. D.; Nolan, S. P. *J. Am. Chem. Soc.* **2005**, *127*, 2485. (b) Díez-González, S.; Nolan, S. P. *Coord. Chem. Rev.* **2007**, *251*, 874. (c) Kelly, R. A.III; Clavier, H.; Guidice, S.; Scott, N. M.; Stevens, E. D.; Bordner, J.; Samardjiev, I.; Hoff, C. D.; Cavallo, L.; Nolan, S. P. *Organometallics* **2008**, *27*, 2002.

**Table 2. Comparative Study in the RCM of Enynes**[a]

| Entry | Substrate | Product | Pre-cat. | Time (h) | Isolated yield (%) |
|---|---|---|---|---|---|
| 1 |  |  | **6a** | 0.1 | > 99 |
| | | | **6d** | 0.1 | > 99 |
| | | | **6e** | 0.1 | > 99 |
| 2 |  |  | **6a** | 2.5 | 92 |
| | | | **6d** | 1 | 97 |
| | | | **6e** | 1 | 97 |
| | | | **15d** | 1.5 | > 99 |
| | | | **15e** | 1.5 | 97 |
| | | | **21** | 3 | 85 |
| 3 |  |  | **6a** | 24 | < 5 |
| | | | **6d** | 24 | < 5 |
| | | | **6d** | 24 | 18[b] |
| | | | **6e** | 24 | < 5 |
| 4 |  |  | **6a** | 8 | 56 |
| | | | **6d** | 5 | 97 |
| | | | **6e** | 5 | 92 |
| | | | **15d** | 2.5 | 97 |
| | | | **15e** | 2 | 98 |
| | | | **21** | 8 | 91 |
| 5 |  |  | **6a** | 24 | 69[b] |
| | | | **6d** | 24 | 95[b] |
| | | | **6e** | 24 | 98[b] |
| 6 |  |  | **6a** | 24 | < 5 |
| | | | **6d** | 24 | < 5 |
| | | | **6d** | 24 | < 5[b] |
| | | | **6e** | 24 | < 5 |

[a] Reactions performed in $CH_2Cl_2$ at room temperature using 1 mol % of precatalyst, unless noted otherwise. [b] Reaction performed in $CH_2Cl_2$ at 40 °C using 2 mol % of precatalyst.

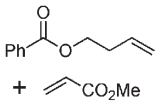
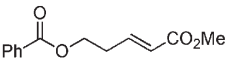
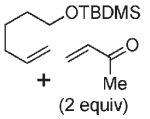
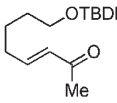
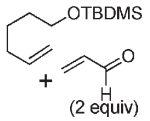
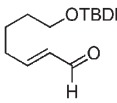
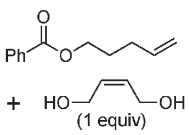
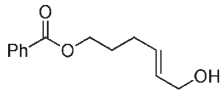
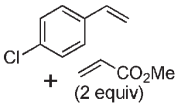
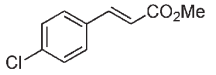
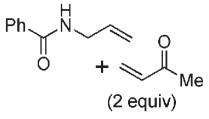
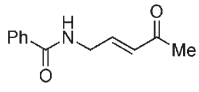
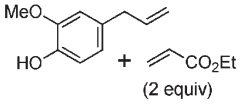
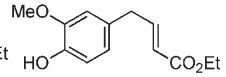
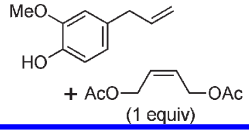
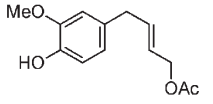
which either suggests that the ease of initial phosphine dissociation is very different for these two catalysts or, perhaps more likely, that the activation step of precatalyst **21** follows an associative mechanism instead. Another intriguing point may be made regarding the activity of **21** toward the two model substrates. While the times needed for full conversion of **8** with **21** or **GII** are similar, the new catalyst does not perform as well with the tosylamide-based substrate **7**. Nonetheless, catalyst **21** seems to be rather robust and does not decompose during these RCM reactions.

**2.5. Scope Investigation in Ring-Closing Metathesis and Cross-Metathesis.** The detailed studies above indicate that Grubbs II type complexes **6d**,**e** show the best activity in the RCM of standard substrates leading to five-membered rings, outperforming both the Hoveyda−Grubbs II type compounds **15d**,**e** and the unsaturated benzylidene-type precatalyst **21**. To assess the overall metathesis performance of these new compounds, we therefore investigated their catalytic behavior in RCM of a wider range of substrates. At the same time, we tested them in a range of enyne ring-closing metathesis reactions as well as in the cross-metathesis of selected olefins. Precatalysts **6d**,**e** were directly compared to the less active **6a** in order to assess whether some substrates preferentially lead to RCM product with **6a** containing a less bulky NHC ligand. An abridged study was performed for precatalysts **15d**,**e** and benzylidene-type catalyst **21** containing the unsaturated NHC ligand. In order to facilitate assessment, all catalytic runs were carried out at standard dilution (0.1 M) and at room temperature unless noted otherwise.[28] As can be seen from the results below, catalytic data with the different precatalysts follow the same trends observed for the runs shown above.

**2.5.1. Ring-Closing Metathesis.** Special attention was focused on tolerance toward functional groups, on the influence of ring size as well as the degree of substitution of the unsaturated bonds. The results are depicted in Table 1. As a general trend, differences between precatalysts **6d**,**e** were found to be minute, which confirms the results obtained through kinetic studies. On the other hand, the (2,7)-SIMe-Nap-containing ruthenium complex **6a** displayed a significantly reduced activity compared to **6d**,**e**. This could be directly related to the fact that sterically demanding NHCs enhance phosphine dissociation and consequently increase the rate of the initiation step of olefin metathesis. As commonly encountered, RCM leading to the formation of seven-membered rings necessitated longer reaction times (entries 2, 4, and 9).[25] Excellent product yields with trisubstituted olefins were isolated after short reaction times (entries 3 and 5), confirming the precedent study. RCM leading to a tetrasubstituted cyclic olefin was found to be more difficult, and reactions were carried out at 40 °C using 2 mol % of catalyst (entry 6). Despite this, product yields were moderate and entry 6 highlights a current shortcoming of these new catalysts. Interestingly, complex **6e** with a bulky NHC ligand surpassed **6a** (and **6d**) in this transformation. While an interpretation is rather speculative at this point, it should be noted that in contrast to **6a**,**d**, which are present as a 1:1 mixture of syn and anti NHC isomers, **6e**

(28) Higher concentrations seem to be beneficial in metathesis reactions; see ref 20.

**Table 3. Comparative Study in Cross-Metathesis[a]**

| Entry | Substrate | Product | Pre-cat. | Time (h) | Isolated yield (%) | *E*/*Z* |
|---|---|---|---|---|---|---|
| 1 |  |  | **6a** | 5 | 79 | > 20:1 |
| | | | **6d** | 5 | 85 | > 20:1 |
| | | | **6e** | 5 | 91 | > 20:1 |
| | | | **15d** | 5 | 69 | > 20:1 |
| | | | **21** | 5 | 77 | > 20:1 |
| 2 |  |  | **6a** | 3 | 70 | > 20:1 |
| | | | **6d** | 3 | 85 | > 20:1 |
| | | | **6e** | 3 | 80 | > 20:1 |
| 3 |  |  | **6a** | 5 | 12 | > 20:1 |
| | | | **6d** | 5 | 31 | > 20:1 |
| | | | **6e** | 5 | 25 | > 20:1 |
| 4 |  |  | **6a** | 5 | 75 | > 20:1 |
| | | | **6d** | 5 | 85 | > 20:1 |
| | | | **6e** | 5 | 84 | > 20:1 |
| 5 |  |  | **6a** | 3 | 72 | > 20:1 |
| | | | **6d** | 3 | 83 | > 20:1 |
| | | | **6e** | 3 | 77 | > 20:1 |
| 6 |  |  | **6a** | 6 | 8 | > 20:1 |
| | | | **6d** | 6 | 17 | > 20:1 |
| | | | **6e** | 6 | 15 | > 20:1 |
| 7 |  |  | **6a** | 5 | 68[b] | > 20:1 |
| | | | **6d** | 5 | 89[b] | > 20:1 |
| | | | **6e** | 5 | 92[b] | > 20:1 |
| 8 |  |  | **6a** | 5 | 80[b] | 10:1 |
| | | | **6d** | 5 | 78[c] | 10:1 |
| | | | **6e** | 5 | 86[b] | 10:1 |

[a] Reactions performed in $CH_2Cl_2$ at room temperature using 1 mol % of precatalyst. [b] Traces of dimer ($E/Z$ = 5:1) were isolated (4−8%). [c] 20% of the dimer ($E/Z$ = 5:1) was isolated.

consists of predominantly *anti*-(2)-SICyNap ligand and this spatial arrangement of the NHC has already been shown to be beneficial for these challenging substrates.[20] In addition to ester- and tosylamide-based substrates, catalysts **6a**,**d**,**e** were found to be tolerant to various functional groups such as amides (entry 7), nitriles (entry 8), ethers (entries 9−11), and alcohols (entry 12). Three of the substrates in Table 1 were also tested with precatalysts **15d**,**e** and **21** (entries 3, 4, and 10). Product yields are high when these catalysts are employed, but in accordance with the results obtained above, slightly longer reaction times were needed to reach full conversion.

**2.5.2. Ring-Closing Enyne Metathesis.** Ring-closing enyne metathesis represents a powerful method for the synthesis of exocyclic 1,3-dienes, which can go on to react further in Diels−Alder reactions or Claisen rearrangements.[1a,29] We investigated the RCM of various enynes (Table 2). The substrate presented in entry 1 reacts in a straightforward manner, and consequently no activity difference could be observed between the catalysts. Overall, the same trend was found as for the RCM of dienes; i.e., catalysts **6d**,**e** exhibited activities superior to that of **6a** (entries 2 and 4). Enormous reactivity differences exist, though, which are not linked to the differences in precatalyst structure but originate from subtle changes in both the double and triple bonds of the substrates. Introducing a fully methylated double bond into tosylamide-derived substrates (entry 4) surprisingly leads to high conversions to product, in comparison to the very poor reactivities seen for the double bond featuring a methylene end group (entry 3). Likewise, introduction of a terminal methyl group onto the triple bond leads to enhanced reactivity in comparison to the parent triple bond (entry 5 vs 3).[30] Entry 5 also indicates that especially **6e** performs better than other second-generation ruthenium catalysts, which for this and similar substrates show various amounts of side

(29) (a) Poulsen, C. S.; Madsen, R. *Synthesis* **2003**, *1*, 18. (b) Clark, D. A.; Kulkarni, A. A.; Kalbarczyk, K.; Schertzer, B.; Diver, S. T. *J. Am. Chem. Soc.* **2006**, *128*, 15632.

(30) (a) Kitamura, T.; Sato, Y.; Mori, M. *Adv. Synth. Catal.* **2002**, *344*, 678. For a discussion on the reaction mechanism in enyne metathesis, see: (b) Lloyd-Jones, G. C.; Marque, R. G.; de Vries, J. G. *Angew. Chem., Int. Ed.* **2005**, *44*, 7442.

products.[31] Unfortunately, in the case of the ether-containing substrate depicted in entry 6, only traces of product were observed with **6a**,**d**,**e**, as analyzed by $^1$H NMR of the crude reaction mixture. Interestingly, Hoveyda−Grubbs II type precatalysts **15d**,**e** give slightly better results in enyne metathesis reactions than their Grubbs II analogues **6d**,**e**. This is apparent in entry 4, where their higher reactivity allowed reduction of the reaction time required for the isolation of the product in quantitative yields. Unsaturated **21** once again performed well but showed lower overall reactivity.

**2.5.3. Cross-Metathesis.** In comparison to RCM, cross-metathesis (CM) is certainly an underutilized olefin metathesis transformation.[2c] The basic reason for this underutilization lies in the fact that CM lacks the entropic driving force of RCM and often leads to relatively low statistical yields of the desired cross-product, as well as poor *E*/*Z* cross-product selectivity.[32] Table 3 gives an overview on the scope and limitations of the new catalysts in cross-metathesis reactions of terminal alkenes and α,β-unsaturated olefins. Of note, for all reactions carried out, the secondary reaction product was isolated and identified as the starting material except where noted. Overall, examples shown in Table 3 corroborate the trend observed in the RCM of dienes and enynes, as we see noticeably superior catalytic performances of catalysts **6d**,**e** in comparison to **6a**. Whereas methyl acrylate and methyl vinyl ketone were well tolerated (entries 1 and 2), the use of acrolein as a less activated olefin partner led to a dramatic reduction of the isolated yields (entry 3). On the other hand, *cis*-2-butene-1,4-diol (only 1 equiv used) gave excellent yields without any traces of isomerization (entry 4). In addition to aliphatic partners, we engaged a styrene derivative in the cross-metathesis, with methyl acrylate leading to good isolated yields with **6d**,**e** and slightly lower ones with complex **6a** (entry 5). An allylamide-type olefin has been tried as a coupling partner but provided poor yields (entry 6). Eugenol (entries 7 and 8) can also be used to good effect as a CM partner, although some dimeric material was formed due to self-cross-metathesis. It is interesting to note that the amount of byproducts in the CM in entries 7 and 8 is lowest for **6e** and highest for **6d**. Finally, entry 1 also shows that the less active benzylidene-type complex **21** is still a better choice for cross-metathesis reactions than the Hoveyda−Grubbs II precatalyst **15d**.

## 3. Conclusions

A series of second-generation ruthenium-based olefin metathesis catalysts bearing *N*-naphthyl-substituted N-heterocyclic carbene (NHC) ligands has been prepared and completely characterized. The starting point of the present investigation was the synthesis of a series of Grubbs II type precatalysts with NHCs containing naphthyl side chains alkylated at the ortho position (2-position) and optionally at the second aromatic ring (6- or 7-position). Detailed kinetic data on the RCM reactions revealed how these substitution patterns affect the catalytic performance of the catalysts and identified two preferred NHC architectures. This finding was then applied to the synthesis of the corresponding Hoveyda−Grubbs II type complexes and for the synthesis of a Grubbs II catalyst featuring an unsaturated NHC ligand. Better reactivity combined with at least equal stability makes the best NHC structures reported here very interesting alternatives to commercially available SIMes-derived precatalysts. A more scalable synthesis of these ligands that does not require chromatographic purification steps and further fine-tuning of the substitution pattern on the naphthyl side chains are underway and will be reported in due course.

## 4. Experimental Section

**4.1. Materials and General Considerations.** All manipulations were carried out under an inert atmosphere of nitrogen using Schlenk or glovebox (Mecaplex or Innovative Technology) techniques, unless otherwise noted. Solvents were either distilled from appropriate drying agents or purged with argon and collected after passage through alumina columns in a solvent purification system (Innovative Technology). Deuterated NMR solvents were purchased from Armar Chemicals, degassed, and dried over activated molecular sieves of appropriate size. NMR spectra were recorded using Bruker ARX-300, AV2-400, and AV-500 spectrometers and treated with MestReC or 1D WINNMR. Mass spectra and elemental analyses were recorded by the analytical services of the Institute of Organic Chemistry (UZH). $[RuCl_2(=CHPh)(PCy_3)_2]$ (**GI**), $[RuCl_2(=CH\text{-}o\text{-}i\text{PrO-Ph})(PCy_3)]$ (**HGI**), $[RuCl_2(SIMes)(=CH\text{-}o\text{-}i\text{PrO-Ph})]$ (**HGII**), and $[RuCl_2\{(2)\text{-SIMePh}\}(=CH\text{-}o\text{-}i\text{PrO-Ph})]$ (**HGII′**) were purchased from Aldrich and used as received. $[RuCl_2(SIMes)(=CH\text{-Ph})(PCy_3)]$ (**GII**),[7,33] $[RuCl_2\{(2)\text{-SIMePh}\}(=CH\text{-Ph})(PCy_3)]$ (**GII′**)[15b] and 2-isopropoxystyrene[34] were prepared according to literature procedures. The syntheses of compounds $[RuCl_2\{(2,7)\text{-SIMeNap}\}(=CH\text{-Ph})(PCy_3)]$ (**6a**),[16a] $[RuCl_2\{(2)\text{-SIPrNap}\}(=CH\text{-Ph})(PCy_3)]$ (**6b**),[17] $[RuCl_2\{(2,6)\text{-SIPrNap}\}(=CH\text{-Ph})(PCy_3)]$ (**6c**),[17] $[RuCl_2\{(2,7)\text{-SIPrNap}\}(=CH\text{-Ph})(PCy_3)]$ (**6d**),[17] $[RuCl_2\{(2)\text{-SICyNap}\}(=CH\text{-Ph})(PCy_3)]$ (**6e**),[17] and (2,7)-SIPrNap (**5d**)[16a] were reported elsewhere. 2,7-Diisopropylnaphthalene was purchased from TCI Laboratory Chemicals, and all other chemicals were obtained from Aldrich or Acros and used without further purification. Silica gel for flash chromatography was purchased from Macherey-Nagel. The data for the crystal structure determinations were collected on a Nonius KappaCCD area-detector diffractometer using graphite-monochromated Mo Kα radiation ($\lambda$ = 0.710 73 Å) and an Oxford Cryosystems Cryostream 700 cooler. Data reduction was performed with HKL Denzo and Scalepack.[35] The SHELXL97 program was used for structure refinement.[36] Detailed crystallographic data for complexes **6b**−**e** can be found in ref 17. The CCDC files 749672−749674 contain the supplementary crystallographic data for compounds **15d**−**f**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. For the structures of **6b**−**e**, see ref 17.

**4.2. Synthetic Procedures. 4.2.1. [$RuCl_2$\{(2,7)-SIPrNap\}(=CH-*o*-*i*PrO-Ph)] (15d; ca. 1:1 Syn/Anti).** In 20 mL of toluene, a mixture of the free carbene (2,7)-SIPrNap (**5d**, mixture of isomers; 120 mg, 0.245 mmol), $[RuCl_2(=CH\text{-}o\text{-}i\text{PrO-Ph})(PCy_3)]$ (**HGI**; 100 mg, 0.166 mmol), and CuCl (18 mg, 0.182 mmol) was stirred at room temperature. After 40 h, the $^{31}$P NMR spectrum of the dark solution showed complete consumption of $[RuCl_2(=CH\text{-}o\text{-}i\text{PrO-Ph})(PCy_3)]$ and the solution was filtered and evaporated to dryness. The green-brown residue was dissolved

(31) Sashuk, V.; Grela, K. *J. Mol. Catal. A* **2006**, *256*, 59.
(32) Chatterjee, A. K.; Choi, T. L.; Sanders, D. P.; Grubbs, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 11360.
(33) Trnka, T. M.; Morgan, J. P.; Sanford, M. S.; Wilhelm, T. E.; Scholl, M.; Choi, T.-L.; Ding, S.; Day, M. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 2546.
(34) Krause, J. O.; Nuyken, O.; Wurst, K.; Buchmeiser, M. R. *Chem. Eur. J.* **2004**, *10*, 777.
(35) Otwinowski, Z.; Minor, W. In *Macromolecular Crystallography*, Part A; Carter, C. W., Jr., Sweet, R. M., Eds.; Academic Press: New York, 1997; Methods in Enzymology Vol. *276*, pp 307−326.
(36) Sheldrick, G. M. SHELXL97. *Acta Crystallogr.* **2008**, *A64*, 112.

in a minimum amount of $CH_2Cl_2$/hexane (1:1), and this solution was subjected to column chromatography on silica gel, in air, using the same system of solvent for the elution. The green fraction was collected and evaporated to dryness to give **15d** as a fine green powder. Yield: 103 mg (76%). Crystals suitable for X-ray structure analysis were obtained by slow diffusion of hexane into a concentrated solution of **15d** in $CH_2Cl_2$. $^1$H NMR (400 MHz, $CD_2Cl_2$, 27 °C): $\delta$ 16.40 and 16.22 (2s, 1H, Ru=C*H*), 8.39−6.64 (series of m, 14H, $H_{arom}$), 4.69 (m, 1H, OC*H*$(CH_3)_2$), 4.59−4.32 (m, 4H, N(C$H_2$)N), 4.13 (m, 1H, ArC*H*$(CH_3)_2$), 3.69 (m, 1H, ArC*H*$(CH_3)_2$), 3.25 (m, 1H, ArC*H*$(CH_3)_2$), 3.13 (m, 1H, ArC*H*$(CH_3)_2$), 1.43−1.37 (series of d, 24H, ArCH(C$H_3)_2$), 1.11−0.90 (series of d, 6H, OCH(C$H_3)_2$) ppm. $^{13}$C{$^1$H} NMR ($CD_2Cl_2$, 125 MHz, 27 °C): $\delta$ 291.7, 291.1, 213.8, 213.4, 152.1, 152.0, 146.8, 146.5, 146.1, 144.3, 131.8, 131.4, 129.5, 129.3, 129.0, 127.6, 127.5, 126.1, 125.3, 123.4, 123.3, 122.1, 121.8, 112.7, 74.9, 35.8, 35.6, 34.8, 34.4, 32.0, 30.1, 29.7, 29.4, 29.1, 29.0, 27.9, 27.8, 26.4, 25.5, 24.0, 23.4, 23.3, 23.2, 22.6, 22.4, 21.9, 21.1, 20.9, 20.7. 14.0 ppm. MS ($CHCl_3$/MeOH): *m*/*z* 775.4 [M − Cl]$^+$. Anal. Calcd for $C_{45}H_{55}Cl_2N_2ORu\cdot 0.5C_6H_{12}$: C, 67.43; H, 7.31; N, 3.28. Found: C, 67.43; H, 7.24; N, 3.33.

**4.2.2. [RuCl$_2${(2)-SICyNap}(=CH-*o*-*i*PrO-Ph)] (15e; Anti Isomer).** The complex [RuCl$_2${(2)-SICyNap}(=CH-Ph)(PCy$_3$)] (**6e**; 200 mg, 0.195 mmol) and CuCl (22 mg, 0.222 mmol) were placed in a Schlenk tube, and $CH_2Cl_2$ (10 mL) was added. 2-Isopropoxystyrene (56.9 mg, 0.390 mmol) dissolved in $CH_2Cl_2$ (10 mL) was then added, and the resulting bright violet solution was stirred at 45 °C for 90 min. During that time, the color changed to brown and then to dark green. After evaporation to dryness, the green residue was dissolved in a minimum amount of $CH_2Cl_2$/hexane (1:1) and this solution was subjected to column chromatography on silica gel, in air, using the same system of solvent for the elution. The green fraction was collected and evaporated to dryness to give **15e** as a fine green powder. Yield: 80 mg (51%). Crystals suitable for X-ray structure analysis were obtained by slow diffusion of hexane into a concentrated solution of **15e** in $CH_2Cl_2$. $^1$H NMR (400 MHz, $CD_2Cl_2$, 27 °C): $\delta$ 16.08 (s, 1H, Ru=C*H*), 8.32−6.52 (series of m, 16H, $H_{arom}$), 4.73 (sept, 1H, OC*H*$(CH_3)_2$), 4.46−4.32 (m, 4H, N(C$H_2$)N), 3.67 (m, 2H, Ar($C_6H_{11}$)), 2.03−1.28 (series of m, 20H, Ar($C_6H_{11}$)), 1.10 (d, 3H, OCH(C$H_3)_2$), 1.03 (d, 3H, OCH-(C$H_3)_2$) ppm. $^{13}$C{$^1$H} NMR ($CD_2Cl_2$, 125 MHz, 27 °C): $\delta$ 290.8, 214.3, 152.1, 145.2, 144.1, 134.2, 133.1, 132.1, 129.6, 129.2, 127.6, 126.5, 125.9, 125.6, 125.2, 122.1, 121.8, 112.8, 74.9, 54.6, 39.7, 36.3, 32.4, 27.5, 26.7, 26.4, 21.2, 21.0 ppm. MS ($CHCl_3$/MeOH): *m*/*z* 771.3 [M − Cl]$^+$. Anal. Calcd for $C_{45}H_{51}Cl_2N_2ORu\cdot 0.33CH_2Cl_2$: C, 65.12; H, 6.23; N, 3.35. Found: C, 65.22; H, 6.33; N, 3.35.

**4.2.3. 1-Nitro-2,7-diisopropylnaphthalene (16).** In air, acetic acid (glacial, 20 mL) and fuming $HNO_3$ (2 mL) were mixed at 0 °C. (2,7)-Diisopropylnaphthalene (5 g, 23.5 mmol) was added dropwise while the temperature was kept at 0 °C. The mixture was kept at 0 °C for an additional 1 h, stirred for 1 h at room temperature, and then neutralized with NaOH (2 N). The pH was raised to 9−10 and the mixture extracted twice with dichloromethane. The organic phase was washed with water, dried over anhydrous $MgSO_4$, filtered, and concentrated. The resulting crude yellow-orange oil was subjected to column chromatography on silica gel (hexane/$CH_2Cl_2$, 10/0.1 to 10/0.5), and the first fraction contained pure **16** as a yellow oil after evaporation of volatiles (4.26 g, 70%). $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.89 (d, $J$ = 8.6 Hz, 1H, $H_{ar}$), 7.80 (d, 8.6 Hz, 1H, $H_{ar}$), 7.47−7.41 (m, 3H, $H_{ar}$), 3.08 (m, 2H, 2 × C*H*$(CH_3)_2$), 1.34 (d, $^3J$ = 6.8 Hz, 6H, C*H*$(CH_3)_2$), 1.31 (d, $^3J$ = 6.8 Hz, 6H, C*H*$(CH_3)_2$) ppm. $^{13}$C{$^1$H} NMR ($CDCl_3$, 125 MHz): $\delta$ 149.3, 146.7, 136.6, 130.9, 130.2, 127.8, 126.4, 124.4, 122.3, 117.6 ($C_{ar}$), 34.5, 29.4 (*C*H$(CH_3)_2$), 23.6, 23.3 (CH(*C*$H_3)_2$) ppm. HRMS (EI): *m*/*z* calcd for $C_{16}H_{19}NO_2$ 257.1416, found 257.1415.

**4.2.4. 1-Amino-2,7-diisopropylnaphthalene (17).** In air, nitronaphthalene **16** (4.7 g, 18.3 mmol) was dissolved in 100 mL of technical methanol. This solution was transferred into a high-pressure autoclave, and Pd on carbon (5% wt. Pd, 210 mg) was added. After it was purged repeatedly with hydrogen, the autoclave was charged with 30 bar of $H_2$. After the mixture was stirred at room temperature for 24 h, the pressure was released and the reaction mixture filtered through Celite. After concentration, the residue was dissolved in a minimum amount of hexane and the solution filtered on a silica gel plug, first washing with hexane/$CH_2Cl_2$ (10/0.1 to 10/1) and subsequently eluting the expected product with $CH_2Cl_2$. Evaporation of volatiles and drying under vacuum led to **17** as a red-brown oil (3.37 g, 81%). $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ 7.67 (d, 1H, $H_{ar}$), 7.58 (m, 1H, $H_{ar}$), 7.30−7.22 (m, 3H, $H_{ar}$), 4.13 (br, 2H, N$H_2$), 3.08 (m, 2H, 2 × C*H*$(CH_3)_2$), 1.31 (d, $^3J$ = 6.9 Hz, 6H, C*H*$(CH_3)_2$), 1.30 (d, $^3J$ = 6.8 Hz, 6H, C*H*$(CH_3)_2$) ppm. $^{13}$C{$^1$H} NMR ($CDCl_3$, 125 MHz): $\delta$ 145.4, 137.1, 131.3, 128.4, 126.5, 124.5, 123.8, 123.0, 118.6, 117.0 ($C_{ar}$), 34.7, 27.9 (*C*H$(CH_3)_2$), 24.0, 22.5 (CH(*C*$H_3)_2$) ppm. HRMS (ESI): *m*/*z* calcd for $C_{16}H_{22}N$ [M + H]$^+$ 228.174 68, found 228.174 30.

**4.2.5. *N*,*N*′-Bis(2,7-diisopropylnaphthalene)ethylenediimine (18).** In air, amine **17** (3.71 g, 16.3 mmol) was dissolved in 100 mL of technical methanol and treated with aqueous glyoxal solution (40 wt %, 1.18 g) and a few drops of formic acid. The reaction mixture was stirred overnight at room temperature. The yellow precipitate was filtered off, washed with cold methanol, and dried under vacuum to give **18** as a fine yellow powder (2.7 g, 69%). $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ 8.26 (s, 2H, N(CH)$_2$N), 7.81−7.39 (series of m, 10H, $H_{ar}$), 3.31 (sept, $^3J$ = 6.9 Hz, 2H, C*H*$(CH_3)_2$), 3.07 (sept, $^3J$ = 6.9 Hz, 2H, C*H*$(CH_3)_2$), 1.34 (d, $^3J$ = 6.9 Hz, 12H, CH(C$H_3)_2$), 1.33 (d, $^3J$ = 6.9 Hz, 12H, CH(C$H_3)_2$) ppm. $^{13}$C{$^1$H} NMR ($CDCl_3$, 75 MHz): $\delta$ 164.7 (N(*C*H)$_2$N), 146.6, 144.7, 132.4, 131.2, 127.8, 125.3, 125.1, 123.2, 119.3 ($C_{ar}$), 34.5, 28.3 (*C*H$(CH_3)_2$), 23.9, 23.5 (CH(*C*$H_3)_2$) ppm. HRMS (ESI): *m*/*z* calcd for $C_{34}H_{40}N_2Na$ [M + Na]$^+$ 499.308 37, found 499.308 24.

**4.2.6. 1,3-Bis(2,7-diisopropylnaphthalen-1-yl)imidazolium Chloride [(2,7)-IPrNap·HCl] (19; ca. 1:1 Syn/Anti).** In air, diimine **18** (1 g, 2.1 mmol) was dissolved/suspended in 20 mL of technical ethyl acetate and the resulting mixture was cooled to 0 °C. Separately, paraformaldehyde (82 mg, 2.7 mmol) was suspended in HCl (4 N in dioxane, 1 mL) and the reaction mixture was stirred until complete dissolution. The resulting clear solution was added dropwise to the solution of **18** at 0 °C. After addition, the mixture was stirred for 1 h at 0 °C and 2 h at room temperature. Then, the resulting brown solution/suspension was evaporated to dryness; the dark brown residue was dissolved in 10 mL of methanol and the solution treated with $NaHCO_3$. After filtration and concentration to around 2 mL, the concentrate was precipitated into ether (ca. 100 mL). The pale brown precipitate was filtered off and washed several times with ether until a white powder was obtained, which was dried under vacuum. **19** was thus obtained with yields ranging from 18% to 40%. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ 9.81 (s, 0.45H, N−C*H*=N of the minor isomer), 9.44 (s, 0.55H, N−C*H*=N of one isomer), 8.60−7.52 (series of m, 10H, $H_{ar}$), 7.06 (s, 0.9H, N(C*H*)$_2$N of the minor isomer), 6.89 (s, 1.1H, N(C*H*)$_2$N of the major isomer), 3.12−2.69 (series of sept, 4H, C*H*$(CH_3)_2$), 1.47−1.29 (series of d, 24H, CH(C$H_3)_2$) ppm. $^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$): $\delta$ 149.8, 149.7, 143.5, 143.1, 138.8, 138.0, 131.9, 131.8, 131.1, 131.0, 129.4, 129.1, 128.7, 128.5, 128.0, 127.5, 127.0, 126.3, 126.2, 126.1, 122.6, 122.5, 117.0, 116.2 ($C_{ar}$), 35.0, 34.5, 29.4, 29.3 (*C*H$(CH_3)_2$), 24.1, 24.0, 23.8, 23.7, 23.2 (CH(*C*$H_3)_2$) ppm. HRMS (ESI): *m*/*z* calcd for $C_{35}H_{41}N_2$ [M]$^+$ 489.326 43, found 489.326 91.

**4.2.7. 1,3-Bis(2,7-diisopropylnaphthalen-1-yl)imidazol-2-ylidene [(2,7)-IPrNap] (20; ca. 1:1 Syn/Anti).** [(2,7)-IPrNap·HCl] (**19**; 200 mg, 0.38 mmol) was suspended in 5 mL of THF, and the suspension was stirred for 15 min at room temperature. Freshly sublimed KO$^t$Bu (46 mg, 0.42 mmol) was added. The initial suspension turned instantaneously to a yellow solution. After 2 h of stirring at room temperature, the reaction mixture was filtered through Celite and evaporated to dryness and the residue

was extracted with toluene. After filtration of the toluene solution through Celite and evaporation to dryness, **20** was obtained as a yellow-orange powder (128 mg, 69%). $^1$H NMR ($C_6D_6$, 400 MHz): $\delta$ 7.84−7.35 (series of m, 10H, $H_{ar}$), 6.87 (s, 0.9H, N(C*H*)$_2$N of one isomer), 6.86 (s, 1.1H, N(C*H*)$_2$N of other isomer), 3.63−3.00 (series of m, 4H, C*H*(CH$_3$)$_2$), 1.55−1.37 (series of d, 24H, CH(C*H*$_3$)$_2$) ppm. $^{13}$C{$^1$H} NMR (125 MHz, $C_6D_6$): $\delta$ 221.6, 221.3 (N-*C*-N), 147.4, 147.3, 143.1, 143.0, 135.9, 135.8, 132.7, 132.3, 131.9, 131.8, 128.6, 128.3, 128.1, 127.9, 126.1, 125.3, 123.3, 123.2, 122.4, 122.3, 120.7, 120.0 ($C_{ar}$), 35.2, 34.8, 29.0, 28.9 (*C*H(CH$_3$)$_2$), 24.4, 24.3, 24.25, 24.2, 24.1, 23.9, 23.7, 23.6 (Ar−CH(*C*H$_3$)$_2$) ppm.

**4.2.8. [RuCl$_2$\{(2,7)-IPrNap\}(=CHPh)(PCy$_3$)] (21; ca. 1:1 Syn/Anti).** In 20 mL of toluene, a mixture of the free carbene (2,7)-IPrNap (**20**; 128 mg, 0.262 mmol) and [RuCl$_2$(=CHPh)-(PCy$_3$)$_2$] (**GI**; 166 mg, 0.201 mmol) was stirred at room temperature. After 24 h, complete consumption of [RuCl$_2$(=CHPh)-(PCy$_3$)$_2$] was observed by $^{31}$P NMR spectroscopy; the solution was evaporated to dryness and dried overnight under vacuum. The dark red residue was washed with 10 mL of methanol and dissolved in a minimum of $CH_2Cl_2$. Diffusion of MeOH into this concentrated solution gave **21** as dark red crystals suitable for X-ray structure analysis. Yield: 100 mg (48%). $^1$H NMR (400 MHz, $CD_2Cl_2$, 27 °C): $\delta$ 19.43 (s, 1H, Ru=C*H*-Ph), 8.03−6.61 (m, 17H, $H_{arom}$ and N(C*H*)$_2$N), 3.98−3.01 (series of m and sept, 4H, ArC*H*(CH$_3$)$_2$), 2.03−0.55 (series of m, 57H, ArCH(C*H*$_3$)$_2$ and P(C$_6$*H*$_{11}$)$_3$) ppm. $^{13}$C{$^1$H} NMR (125 MHz, $CD_2Cl_2$): $\delta$ 192.2, 191.6, 150.6, 150.5, 147.2, 146.4, 146.2, 146.1, 145.5, 143.7, 143.5, 133.7, 133.6, 132.1, 131.5, 131.4, 131.3, 131.2, 130.8, 130.7, 130.5, 130.3, 129.7, 127.2, 127.0, 126.8, 126.6, 126.5, 126.3, 126.2, 125.9, 125.8, 125.4, 124.8, 123.8, 122.9, 122.1, 122.0, 121.5, 119.9, 34.7, 34.3, 34.2, 34.1, 31.7, 31.6, 31.55, 31.5, 29.4, 29.2, 28.9, 28.6, 28.1, 27.7, 27.65, 27.6, 27.5, 26.2, 26.0, 25.8, 25.4, 25.0, 23.75, 23.7, 23.6, 23.5, 23.4, 23.0, 22.8, 22.5, 22.4, 21.9, 13.8. $^{31}$P{$^1$H} (162 MHz, $CD_2Cl_2$, 27 °C): $\delta$ 31.37 and 31.19 (2s). MS (ESI, MeOH/$CH_2Cl_2$): *m*/*z* 995.6 [M − Cl]$^+$. Anal. Calcd for $C_{60}H_{79}Cl_2N_2PRu\cdot 1.5MeOH$: C, 68.44; H, 7.94; N, 2.60. Found: C, 68.11; H, 7.80; N, 2.74.

**4.3. Time−Conversion Studies. 4.3.1. General Remarks.** All catalytic samples were prepared under an inert atmosphere of nitrogen using gloveboxes. All reactions were run in NMR tubes equipped with a screw-cap septum top at 300 K (27 °C) at a 0.1 M substrate/solvent ratio, and the conversions were followed by $^1$H NMR spectroscopy. Substrates **7**,[36] **8**,[12] **11**,[38] and **12**[39] were synthesized according to literature procedures.

**4.3.2. RCM of Diallyltosylamide (7) and Diethyl Diallylmalonate (8). 4.3.2.1. Catalyst Loading of 1 mol %.** To obtain the required catalyst amount, a solution of the appropriate ruthenium complex ($4 \times 10^{-3}$ mmol) in 2 mL of $CH_2Cl_2$ was prepared. A 400 $\mu$L portion of this solution was transferred to a NMR tube and evaporated to dryness, and the residue was dried for 1 h under vacuum. The tube was then closed with a screw-cap septum top. Separately, in a small vial, substrates **7** and **8** (0.08 mmol, 20.1 and 19.2 mg, respectively) were dissolved in 0.8 mL (0.1 M) of $CD_2Cl_2$ and then transferred via syringe to the respective NMR tubes containing the catalyst. The tube was vigorously stirred for a few seconds (the reaction time was started at this point) and introduced into the spectrometer, and conversions were obtained by $^1$H NMR.

**4.3.2.2. Catalyst Loading of 0.1 mol %.** To obtain the required catalyst amount, a solution of the appropriate ruthenium complex ($8 \times 10^{-3}$ mmol) in 10 mL of $CH_2Cl_2$ was prepared. A 100 $\mu$L portion of this solution was transferred to a NMR tube and evaporated to dryness, and the residue was dried for 1 h under vacuum. The tube was then closed with a screw-cap septum top. Separately, in a small vial, substrates **7** and **8** (0.08 mmol, 20.1 and 19.2 mg, respectively) were dissolved in 0.8 mL (0.1 M) of $CD_2Cl_2$ and then transferred via syringe to the respective NMR tube containing the catalyst. The tube was vigorously stirred for a few seconds (the reaction time was started at this point) and introduced to the spectrometer, and conversions were obtained by $^1$H NMR.

**4.3.3. RCM of Allylmethallyl Tosylamide (11) and Diethyl Allylmethallylmalonate (12). 4.3.3.1. Catalyst Loading of 0.5 mol %.** To obtain the required catalyst amount, a solution of the appropriate ruthenium complex ($4 \times 10^{-3}$ mmol) in 2 mL of $CH_2Cl_2$ was prepared. A 200 $\mu$L portion of this solution was transferred to a NMR tube and evaporated to dryness, and the residue was dried for 1 h under vacuum. The tube was then closed with a screw-cap septum top. Separately, in a small vial, substrates **11** and **12** (0.08 mmol, 21.2 and 20.3 mg, respectively) were dissolved in 0.8 mL (0.1 M) of $CD_2Cl_2$ and then transferred via syringe to the respective NMR tubes containing the catalyst. The tube was vigorously stirred for a few seconds (the reaction time was started at this point) and introduced to the spectrometer, and conversions were obtained by $^1$H NMR.

**4.4. Preparative Metathesis Reactions. 4.4.1. General Remarks.** A Schlenk flask, under argon, was charged with the substrate (0.5 mmol) and dry dichloromethane (5 mL, $C = 0.1$ M), and then the precatalyst (0.005 mmol) was added. The progress of the reaction was monitored by TLC. The solvent was removed under vacuum, and the crude residue was purified by flash column chromatography to yield the pure product. Most substrates and products have been previously described.[3b,24,37−40] Characterization of new catalytic products is as follows.

**4.4.2. (*E*)-6-Hydroxyhex-4-enyl benzoate (Table 3, Entry 4).** Colorless oil. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.98−7.94 (m, 2H, *H*$^{Ph}$), 7.50−7.44 (m, 1H, *H*$^{Ph}$), 7.38−7.32 (m, 2H, *H*$^{Ph}$), 5.64−5.60 (m, 2H, C*H*=C*H*), 4.24 (t, *J*(H,H) = 6.5 Hz, 2H, O−C*H*$_2$), 4.00 (d, *J*(H,H) = 4.3 Hz, 2H, C*H*$_2$−OH), 2.16−2.10 (m, 2H, C*H*$_2$−CH=CH), 1.97 (s bd, 1H, OH), 1.78 (quint, *J*(H,H) = 7.0 Hz, 2H, CH$_2$−C*H*$_2$−CH$_2$) ppm. $^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$): $\delta$ 167.1 (C), 133.3 (CH), 131.7 (CH), 130.7 (C), 130.5 (CH), 129.9 (CH), 128.8 (CH), 64.7 (CH$_2$), 58.7 (CH$_2$), 29.0 (CH$_2$), 28.5 (CH$_2$) ppm. HRMS (ESI): *m*/*z* calcd for $C_{13}H_{16}O_3Na$ 243.0997 [M + Na]$^+$, found 243.0991.

**4.4.3. (*E*)-*N*-(4-Oxopent-2-enyl)benzamide (Table 3, Entry 6).** Colorless oil. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.74−7.72 (m, 2H, *H*$^{Ph}$), 7.48−7.43 (m, 1H, *H*$^{Ph}$), 7.39−7.35 (m, 2H, *H*$^{Ph}$), 6.74 (td, *J*(H,H) = 16.1 and 5.1 Hz, 1H, C*H*=CH−CO), 6.57 (s br, 1H, N*H*), 6.11 (td, *J*(H,H) = 16.1 and 1.7 Hz, 1H, CO−C*H*=CH), 4.19 (dt, *J*(H,H) = 6.0 and 0.9 Hz, 2H, C*H*$_2$−NH), 2.18 (s, 2H, C*H*$_3$) ppm. $^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$): $\delta$ 198.6 (C), 167.9 (C), 143.3 (CH), 134.2 (C), 132.3 (CH), 131.4 (CH), 129.1 (CH), 128.9 (CH), 127.4 (CH), 41.2 (CH$_2$), 27.6 (CH$_3$) ppm. HRMS

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(ESI): *m*/*z* calcd for $C_{12}H_{13}NO_3Na$ 226.0844 $[M + Na]^+$, found 226.0844.

**4.4.4. (*E*)-Ethyl 4-(4-Hydroxy-3-methoxyphenyl)but-2-enoate (Table 3, Entry 7).** Colorless oil. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.00 (dt, *J*(H,H) = 15.5 and 6.7 Hz, 1H, $CH_2-CH{=}CH$), 6.77 (d, *J*(H,H) = 8.1 Hz, 1H, $H^{Ph}$), 6.60−6.57 (m, 2H, $H^{Ph}$), 5.72 (dt, *J*(H,H) = 15.5 and 1.7 Hz, 1H, $CH_2-CH{=}CH$), 5.62 (s, 1H, O*H*), 4.10 (q, *J*(H,H) = 7.1 Hz, 2H, $CH_2-CH_3$), 3.77 (s, 3H, $CH_3$), 3.36 (dd, *J*(H,H) = 6.7 and 1.7 Hz, 2H, $CH_2-CH{=}CH$), 1.19 (t, *J*(H,H) = 7.1 Hz, 3H, $CH_3$) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): $\delta$ 167.1 (C), 148.2 (CH), 147.1 (C), 144.8 (C), 129.9 (C), 122.4 (CH), 121.9 (CH), 115.0 (CH), 111.7 (CH), 60.2 ($CH_2$), 56.3 ($CH_3$), 38.6 ($CH_2$), 14.7 ($CH_3$) ppm. HRMS (ESI): *m*/*z* calcd for $C_{13}H_{16}O_3Na$ 259.0946 $[M + Na]^+$, found 259.0943.

**4.4.5. (*E*)-4-(4-Hydroxy-3-methoxyphenyl)but-2-enyl Acetate (Table 3, Entry 8).** Colorless oil. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 6.78−6.76 (m, 1H, $H^{Ph}$), 6.60−6.57 (m, 2H, $H^{Ph}$), 5.88−5.77 (m, 1H, CH=C*H*), 5.58 (s, 1H, O*H*), 5.58−5.48 (m, 1H, CH=C*H*), 4.45 (dd, *J*(H,H) = 6.3 and 1.0 Hz, 2H, $CH_2-O$), 3.79 (s, 3H, $CH_3$), 3.24 (d, *J*(H,H) = 6.7 Hz, 2H, $CH_2-CH{=}CH$), 1.97 (s, 3H, $CH_3$) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): $\delta$ 171.3 (C), 147.0 (C), 144.5 (C), 135.4 (CH), 131.8 (C), 125.4 (CH), 121.6 (CH), 114.8 (CH), 111.6 (CH), 65.4 ($CH_2$), 56.3 ($CH_3$), 38.7 ($CH_2$), 21.4 ($CH_3$) ppm. HRMS (ESI): *m*/*z* calcd for $C_{13}H_{16}O_4Na$ 259.0946 $[M + Na]^+$, found 259.0948.

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**Supporting Information Available:** CIF files giving crystallographic data for **15d**,**e** and **21**. This material is available free of charge via the Internet at http://pubs.acs.org.