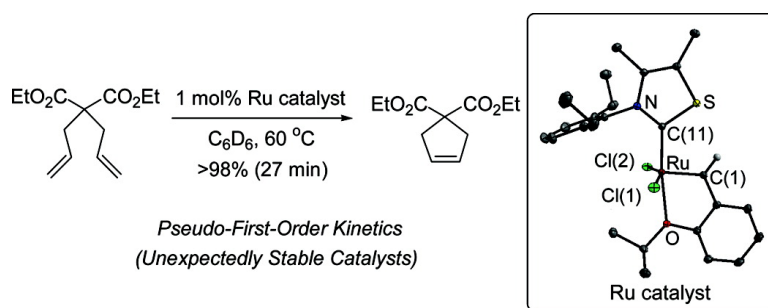


## Synthesis and Activity of Ruthenium Olefin Metathesis Catalysts Coordinated with Thiazol-2-ylidene Ligands

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## Synthesis and Activity of Ruthenium Olefin Metathesis Catalysts Coordinated with Thiazol-2-ylidene Ligands

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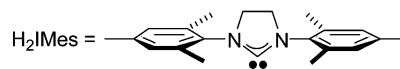
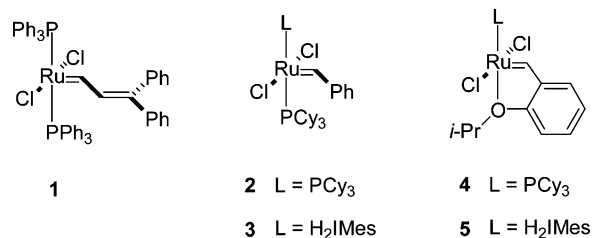
**Abstract:** A new family of ruthenium-based olefin metathesis catalysts bearing a series of thiazole-2-ylidene ligands has been prepared. These complexes are readily accessible in one step from commercially available  $(\text{PCy}_3)_2\text{Cl}_2\text{Ru}=\text{CHPh}$  or  $(\text{PCy}_3)\text{Cl}_2\text{Ru}=\text{CH}(o\text{-}i\text{PrO-Ph})$  and have been fully characterized. The X-ray crystal structures of four of these complexes are disclosed. In the solid state, the aryl substituents of the thiazole-2-ylidene ligands are located above the empty coordination site of the ruthenium center. Despite the decreased steric bulk of their ligands, all of the complexes reported herein efficiently promote benchmark olefin metathesis reactions such as the ring-closing of diethyldiallyl and diethylallylmethyl malonate and the ring-opening metathesis polymerization of 1,5-cyclooctadiene and norbornene, as well as the cross metathesis of allyl benzene with *cis*-1,4-diacetoxy-2-butene and the macrocyclic ring-closing of a 14-membered lactone. The phosphine-free catalysts of this family are more stable than their phosphine-containing counterparts, exhibiting pseudo-first-order kinetics in the ring-closing of diethyldiallyl malonate. Upon removing the steric bulk from the *ortho* positions of the *N*-aryl group of the thiazole-2-ylidene ligands, the phosphine-free catalysts lose stability, but when the substituents become too bulky the resulting catalysts show prolonged induction periods. Among five thiazole-2-ylidene ligands examined, 3-(2,4,6-trimethylphenyl)- and 3-(2,6-diethylphenyl)-4,5-dimethylthiazol-2-ylidene afforded the most efficient and stable catalysts. In the cross metathesis reaction of allyl benzene with *cis*-1,4-diacetoxy-2-butene increasing the steric bulk at the *ortho* positions of the *N*-aryl substituents results in catalysts that are more *Z*-selective.

### Introduction

Olefin metathesis is among the most versatile and powerful methods for the construction of new carbon-carbon double bonds.<sup>1</sup> Over the past decade, olefin metathesis reactions have been elegantly used by chemists working in a wide variety of research fields, including industry and academia, to develop novel synthetic routes and polymeric structures, as well as new materials and industrial processes.<sup>2</sup> The increased popularity of this transformation has resulted from the development of well-defined ruthenium-based catalysts with high air and moisture stability and functional group tolerance.<sup>1</sup>

The synthesis of the first well-defined ruthenium-based olefin metathesis initiator (**1**, Chart 1) was published in 1992.<sup>3</sup> Although the basic structure of the currently used ruthenium-

Chart 1. Ruthenium-Based Olefin Metathesis Catalysts



based catalysts still resembles that original complex, i.e., comprised of a ruthenium alkylidene, two halides, and two neutral ligands, contemporary catalysts (**2–5**, Chart 1) are significantly more reactive and more tolerant of oxygen and moisture. For instance, the commercially available complex **2**, although not as reactive, has much better functional group compatibility than all of the early transition metal olefin metathesis initiators.<sup>4</sup> Substitution of one tricyclohexylphosphine ligand with the bulky *N*-heterocyclic carbene (NHC) ligand H<sub>2</sub>-

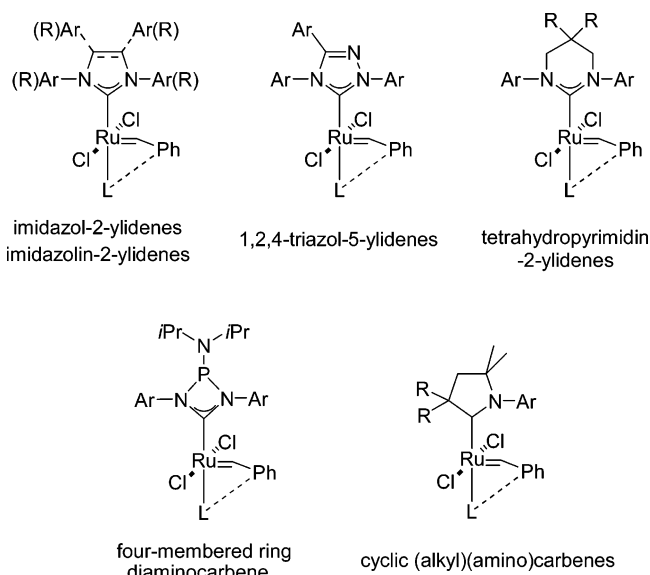
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IMes to produce **3** (Chart 1) led to a significant improvement of catalytic activity, while maintaining the high functional group tolerance and stability of **2**.<sup>5</sup> This improvement has been attributed to the increased affinity of the NHC-substituted ruthenium center for  $\pi$ -acidic olefins relative to  $\sigma$ -donating phosphines.<sup>6</sup> The development of phosphine-free complexes<sup>7</sup> has yielded olefin metathesis catalysts **4** and **5** (Chart 1) that display even higher thermal stability.<sup>8</sup> Subsequent studies led to the development of ruthenium-based catalysts for asymmetric olefin metathesis reactions,<sup>9</sup> and for applications in aqueous and protic solvent systems.<sup>10</sup> Last, the formation of tetrasubstituted carbon-carbon double bonds typically requires high catalyst loadings and elevated reaction temperatures, comprising one of the major limitations for most ruthenium catalysts. Intense effort has recently led to the development of a series of catalysts capable of successfully carrying out this very challenging task.<sup>11</sup>

Herein we report the synthesis and complete characterization of seven new, ruthenium-based olefin metathesis initiators, coordinated with a series of thiazole-2-ylidene ligands. To the best of our knowledge, this is the first report on ruthenium-based olefin metathesis catalysts bearing carbene ligands with only one exocyclic substituent adjacent to the carbenic center. The catalytic performance of these thiazole-2-ylidene-bearing complexes has been evaluated in ring-closing metathesis, cross metathesis, and ring-opening metathesis polymerization reactions. Some complexes display efficiencies similar to the

**Chart 2.** Ruthenium-Based Olefin Metathesis Catalysts Coordinated with Carbene Ligands<sup>a</sup>



<sup>a</sup> The dashed lines in the structures indicate that the coordinating ligand L may or may not be connected to the phenyl ring of the benzylidene.

commercially available second-generation catalysts. The phosphine-free members of this new family of catalysts exhibit unexpectedly high stability. In the cross metathesis reaction of allyl benzene with *cis*-1,4-diacetoxy-2-butene, the bulkier thiazole-2-ylidene ligands afford complexes that display an increased Z-selectivity, compared to the less bulky ones.

## Results and Discussion

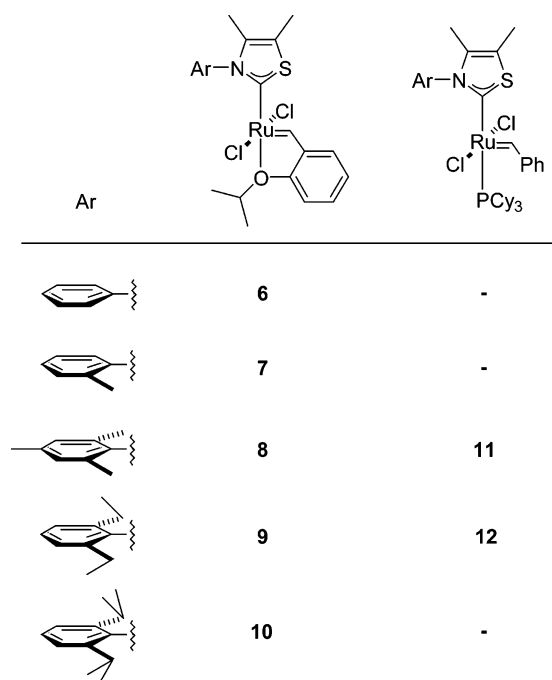
Electron-rich and bulky *N*-heterocyclic carbenes (NHCs) display excellent  $\sigma$ -donating ability and resemble the properties of electron-rich phosphines.<sup>12</sup> As such, they have been extensively utilized in the preparation of many synthetically useful organometallic catalysts.<sup>13</sup> Chart 2 summarizes the carbene frameworks that have been used thus far in ruthenium-based olefin metathesis initiators. The most successful and well-studied catalysts, bear either a symmetrical or unsymmetrical imidazol- or imidazolin-2-ylidene.<sup>14</sup> Triazol-5-ylidenes,<sup>14c,g</sup> tetrahydropyrimidin-2-ylidenes,<sup>15</sup> and a four-membered ring diaminocarbenes<sup>16</sup> have also been used, affording the corresponding complexes (Chart 2). More recently, a series of ruthenium complexes coordinated with cyclic(alkyl)(amino) carbenes, displaying stability and activity comparable to standard olefin metathesis catalysts, have been synthesized.<sup>17</sup>

**Synthesis and Characterization:** Despite the numerous reports concerning carbene-bearing ruthenium-based olefin metathesis initiators,<sup>18</sup> a complex coordinated with a carbene that has only one exocyclic substituent adjacent to the carbenic center has not been reported. While we were initially concerned that the decreased steric protection of such complexes might

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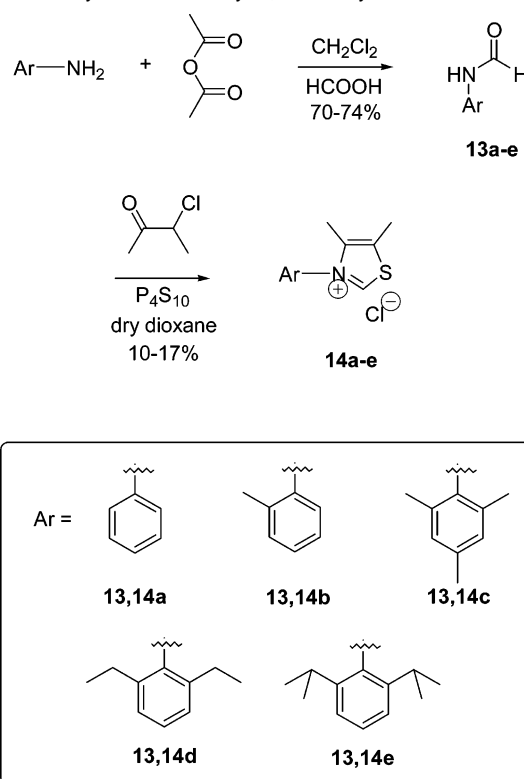
**Chart 3.** New Ruthenium-Based Olefin Metathesis Catalysts Coordinated with Thiazole-2-ylidene Ligands



cause them to be highly unstable and prone to degradation, we were intrigued by this previously unevaluated steric environment. We chose to investigate 3-aryl-4,5-dimethylthiazol-2-ylidenes as ligands, carrying out the synthesis of complexes **6–12** shown in Chart 3. To the best of our knowledge, the only stable thiazol-2-ylidene was reported in 1997 by Arduengo and co-workers.<sup>19</sup> Thiazole-2-ylidenes have been also employed as catalysts in organocatalytic transformations,<sup>20</sup> and some benzothiazolin-2-ylidenes have been used as ligands in other transition metal complexes.<sup>21</sup>

As illustrated in Scheme 1, the synthesis of 3-aryl-4,5-dimethylthiazolium chlorides that were used as carbene precursors is straightforward. *N*-Formylation of commercially available anilines afforded formanilides **13b–13e** in high yields (**13a** is commercially available),<sup>22</sup> which were then reacted with

**Scheme 1.** Synthesis of 3-Aryl-4,5-dimethylthiazolium Chlorides



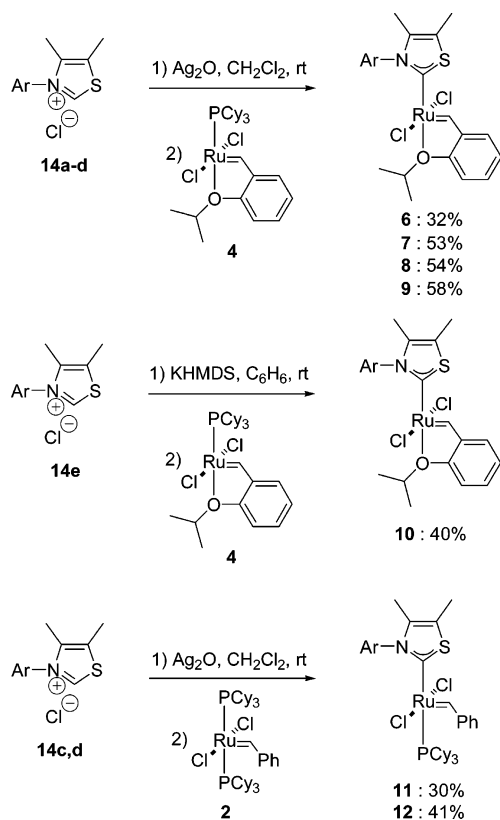
phosphorus pentasulfide and 3-chloro-2-butanone in dry dioxane to afford the desired dimethylthiazolium chlorides **14a–14e**.<sup>23</sup>

Complexes **6–12** were prepared in moderate to high yields from the corresponding 3-aryl-4,5-dimethylthiazole-2-ylidenes, using complexes **2** or **4** as ruthenium sources (Scheme 2). In the case of complex **10**, the appropriate carbene ligand was prepared in situ by deprotonation of dimethylthiazolium salt **14e** with KHMDS. This intermediate carbene is the only reported stable thiazole-2-ylidene at room temperature.<sup>19</sup> For example, the less sterically hindered 3-(2,4,6-trimethylphenyl)-4,5-dimethylthiazol-2-ylidene, derived by the deprotonation of dimethylthiazolium salt **14c**, is not as kinetically stable and dimerizes quickly above 0 °C in solution.<sup>19</sup> Indeed, none of the carbenes formed via deprotonation of the dimethylthiazolium salts **14a–14d** were stable enough to afford the desired ruthenium complexes **6–9** and **11–12** in a satisfactory yield. For instance, the typical isolated yields for complex **11** were lower than 9%, even when the reaction was carried out at 0 °C, or when 2 equiv of **14c**/KHMDS, with respect to the ruthenium source, were

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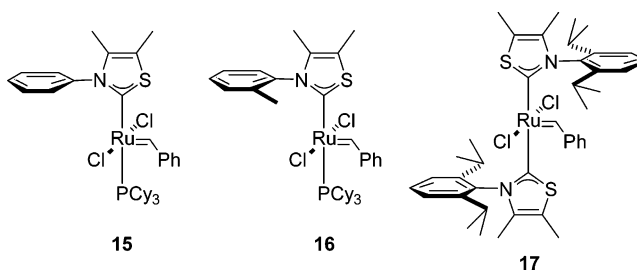
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**Scheme 2.** Synthesis of Ruthenium-Based Olefin Metathesis Catalysts **6–12**

added in portions. To circumvent the formation of the unstable free carbenes (and their concomitant dimerization), the corresponding silver-thiazole-2-ylidene complexes that have been successfully used as NHC transfer reagents in the past were prepared.<sup>24</sup> These silver complexes were formed quantitatively and then reacted in situ (with the ruthenium source) to afford the desired ruthenium complexes **6–9** and **11–12** (see Experimental Section).<sup>25</sup> Interestingly, the same transmetallation conditions do not yield complex **10**, despite the quantitative formation of the corresponding silver-thiazole-2-ylidene complex.<sup>26</sup> As expected, complexes **8** and **9** may also be prepared from **11** and **12**, respectively, via olefin metathesis with *o*-isopropoxy- $\beta$ -methylstyrene, albeit less efficiently compared to their direct preparation using complex **4**.

We also tried to synthesize and isolate the phosphine-containing analogues of complexes **6**, **7**, and **10** via transmetallation between the corresponding silver compounds and

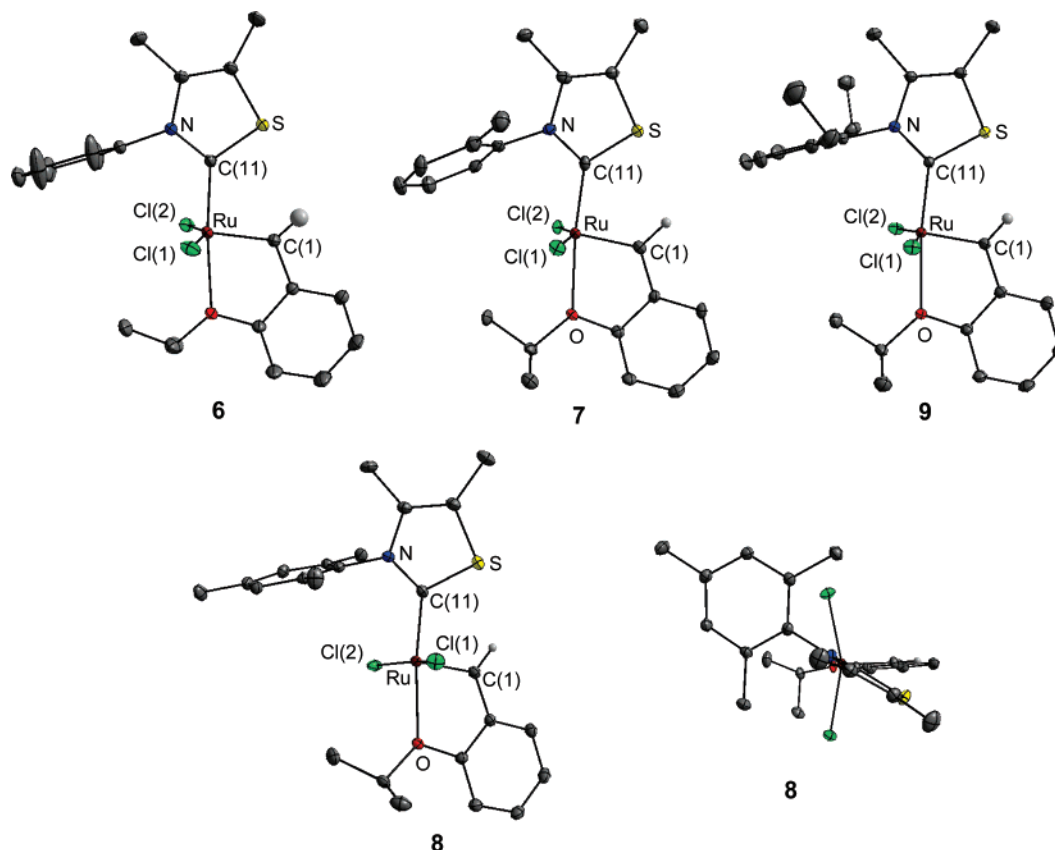
**Chart 4.** Ruthenium-Based Complexes **15–17** (Observed in Situ)

complex **2**. Complexes **15** and **16** (Chart 4) were formed in the course of the reaction, as identified by <sup>1</sup>H and <sup>31</sup>P NMR spectroscopy. However, complete decomposition of complexes **15** and **16** was observed in 2 and 18 h, respectively, at room temperature. The analogous phosphine-containing ruthenium complex bearing a 3-(2,6-diisopropylphenyl)-4,5-dimethylthiazol-2-ylidene was formed neither via transmetallation nor through the in situ generation of the free carbene by deprotonation of the dimethylthiazolium salt **14e**. Instead, only the formation of complex **17** was observed by <sup>1</sup>H NMR and high-resolution mass spectroscopy (Chart 4).<sup>27</sup> Apparently, coordination of the first bulky thiazol-2-ylidene ligand at the ruthenium center, followed by the dissociation of the remaining tricyclohexylphosphine and coordination of a second thiazol-2-ylidene, is favorable due to the formation of an “empty pocket” in the coordination sphere of the intermediate complex. This “empty pocket” accommodates the second unsymmetrical carbene ligand much better relative to the C<sub>3</sub> symmetric tricyclohexylphosphine. Complex **17** is not stable enough to be isolated by column chromatography.

The molecular structure of complexes **6–9** was confirmed by single-crystal X-ray crystallographic analysis (Figure 1).<sup>28</sup> All complexes exhibit a distorted square pyramidal geometry with the Ru=C benzylidene bond occupying the apical position and the Cl atoms *trans* to one another. The bond lengths and angles of **6–9** are quite similar to those of complex **5** (Table 1). However, the Ru–C<sub>thiazol-2-ylidene</sub> bond distance in **6–9** is 0.026–0.037 Å shorter than the Ru–C<sub>NHC</sub> bond distance in **5**. This difference is most likely due to the decreased steric bulk of the thiazole-2-ylidene ligands compared to the H<sub>2</sub>IMes. This hypothesis is supported by the increased Ru–C<sub>thiazol-2-ylidene</sub> bond distance as the ligand increases in steric bulk (namely going from **6** to **9**). The dihedral angles between the thiazole-2-ylidene and the isopropoxy styrene planes in complexes **6**, **7**, and **9** range between 5° and 13° (Table 1, entry 8). This dihedral angle is much larger in **8** (34°) as illustrated in the top view of complex **8** shown in Figure 1. In the solid state, the aryl substituent of the thiazole-2-ylidene ligand in complexes **6–9** is located above the empty coordination site of the ruthenium center.<sup>28</sup> This is rather interesting since the phosphine-free ruthenium complexes reported thus far, bearing unsymmetrical carbenes with only one exocyclic aryl substituent adjacent to the carbenic center, are isolated with this aryl group being directly above the benzylidene proton.<sup>14i,14l,17</sup>

- (24) (a) Wang, H. M. J.; Lin, I. J. B. *Organometallics* **1998**, *17*, 972–975. (b) Lin, I. J. B.; Vasam, C. S. *Comm. Inorg. Chem.* **2004**, *25*, 75–129. (c) de Frémont, P.; Scott, N. M.; Stevens, E. D.; Ramiial, T.; Lightbody, O. C.; Macdonald, C. L. B.; Clyburne, J. A. C.; Abernethy, C. D.; Nolan, S. P. *Organometallics* **2005**, *24*, 6301–6309. (d) Yu, X. Y.; Patrick, P. O.; James, B. R. *Organometallics* **2006**, *25*, 2359–2363.
- (25) 3-(3,5-Di-*tert*-butylphenyl)-4,5-dimethylthiazolium chloride was also prepared; however, we were unable to generate its silver complex under the conditions reported for the other dimethylthiazolium salts. Its deprotonation with KHMDS in the presence of complex **2** did not afford any new benzylidene species (NMR spectroscopy). When complex **4** was used as the ruthenium source we were able to identify a new product in situ, most probably derived from carbene bis-addition to the ruthenium center. This species is not stable enough to be isolated by column chromatography. For other reported ruthenium complexes derived from carbene bis-addition, see ref 27.
- (26) Formation of **10** was observed, although only after refluxing the silver-thiazole-2-ylidene complex with complex **4** in CH<sub>2</sub>Cl<sub>2</sub> overnight. Since **10** can be efficiently formed via the in situ deprotonation of dimethylthiazolium salt **14e**, we did not study the transmetallation route further.

- (27) Carbene bis-substitution in analogous ruthenium complexes has been reported in the past: refs 14a and 14e,f. Also see: Ledoux, N.; Allaert, B.; Linden, A.; Van Der Voort, P.; Verpoort, F. *Organometallics* **2007**, *26*, 1052–1056.
- (28) Low quality crystals of complex **10** were also obtained. Although highly disordered, X-ray analysis on different samples of these single crystals showed the same connectivity and orientation of the ligands as in the crystal structures of the complexes **6–9**.



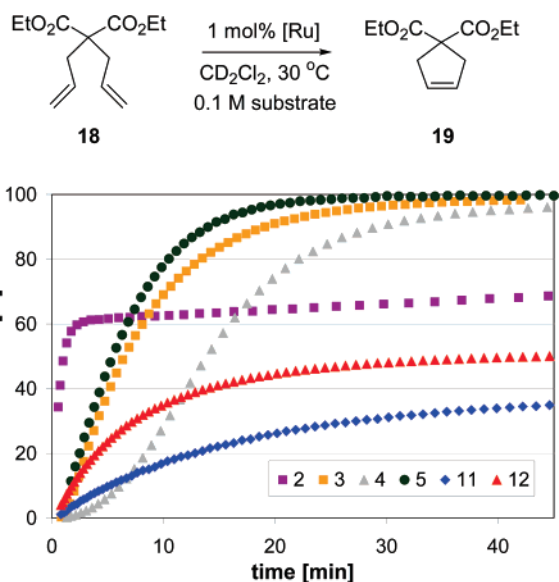
**Figure 1.** Side view of the structures of complexes 6–9 and top view of complex 8 are shown. Displacement ellipsoids are drawn at 50% probability. For clarity, most hydrogen atoms have been omitted.

**Table 1.** Selected Bond Lengths, Bond Angles, and Dihedral Angles for Complexes 5–9<sup>a</sup>

entry		5	6	7	8	9
Bond Lengths (Å)						
1	Ru–C(1)	1.828	1.832	1.826	1.830	1.832
2	Ru–C(11)	1.981	1.944	1.947	1.953	1.955
3	Ru–O	2.261	2.265	2.270	2.275	2.268
Bond Angles (deg)						
4	C(1)–Ru–C(11)	101.5	94.7	94.7	95.8	94.6
5	C(11)–Ru–O	176.2	174.3	173.9	173.0	173.2
6	Cl(1)–Ru–Cl(2)	156.5	154.4	155.7	159.0	154.6
7	S–C(11)–Ru	n/a	126.6	127.8	121.0	124.4
Dihedral Angles (deg)						
8	S–C(11)–Ru–C(1)	n/a	8.2	13.2	34.0	5.1

<sup>a</sup> For a complete list of bond lengths and bond angles, refer to the Supporting Information.

**Ring-Closing Metathesis (RCM) Activity:** RCM is the first widely used olefin metathesis reaction in organic synthesis<sup>1b</sup> and has been used to evaluate the efficiency of most ruthenium-based catalysts.<sup>29</sup> We initially studied the catalytic activity of the new phosphine-containing complexes in the RCM of diethyldiallyl malonate (**18**) to substituted cycloalkene **19** (Figure 2). Interestingly, the plots of cycloalkene **19** concentration vs time, for the RCM of **18** using catalysts 2–5 and 11–12 in Figure 2, reveal that both **11** and **12** effect the cyclization of **18**. Nevertheless, these two new catalysts are less efficient than complexes 2–5 due to their high decomposition rate, clearly illustrated from the curvature in the logarithmic plot (ln-

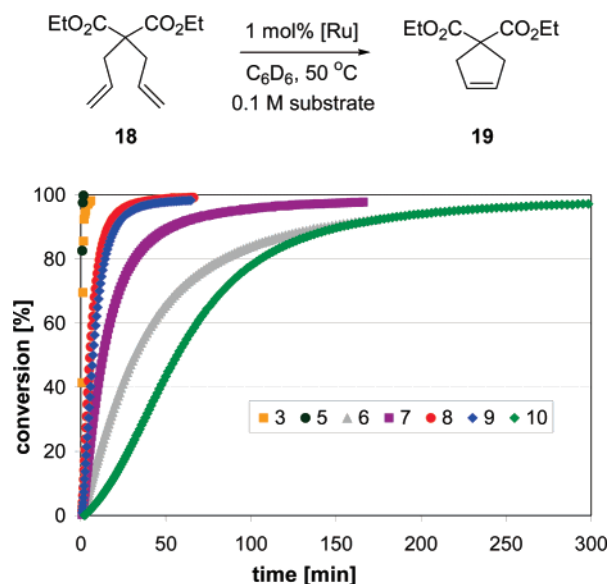


**Figure 2.** RCM of diene **18** to disubstituted cycloalkene **19**, using catalysts 2–5, **11**, and **12**.

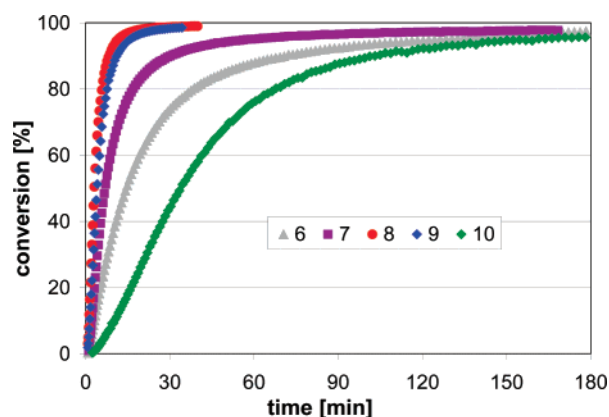
([starting material]) vs time) for both **11** and **12** (Supporting Information, SI).

We next studied the same RCM reaction with the phosphine-free complexes 6–10 (Figure 3). Due to the slower initiation of these catalysts, we carried out the RCM reactions at 50 °C. Despite their decreased steric protection, complexes 6–10 were found to be very efficient catalysts for the RCM of **18**. All of them led to >97% conversion at 1 mol % catalyst loading. The most efficient catalysts (**8** and **9**) demonstrated activity com-

(29) See: Ritter, T.; Hejl, A.; Wenzel, A. G.; Funk, T. W.; Grubbs, R. H. *Organometallics* **2006**, *25*, 5740–5745 and literature cited therein.



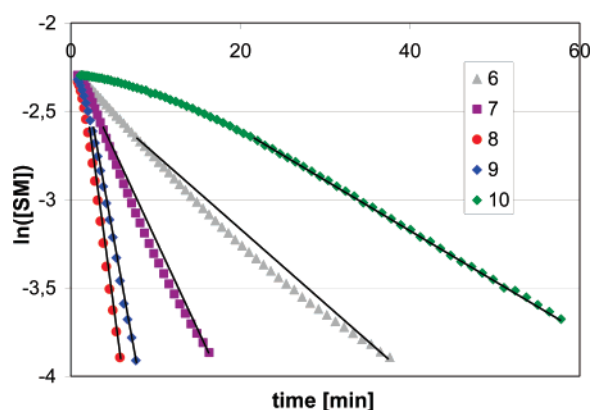
**Figure 3.** RCM of diene **18** to disubstituted cycloalkene **19** at 50 °C, using catalysts **3**, **5**, and **6–10**.



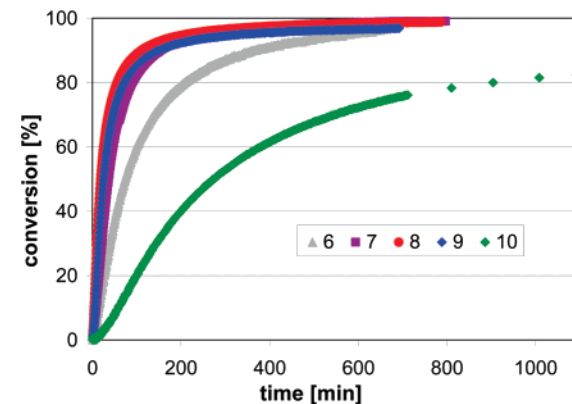
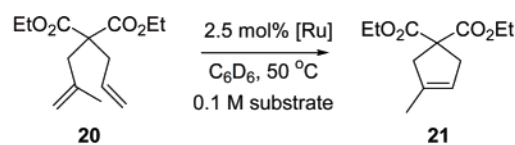
**Figure 4.** RCM of diene **18** with catalysts **6–10** at 60 °C (1 mol % catalyst loading).

parable to the second-generation catalysts **3** and **5**. As illustrated in Figure 3, complex **10** bearing the bulkiest thiazole-2-ylidene ligand in this catalysts family has the longest induction period. This poor catalyst initiation upon increasing the steric bulk of the carbene ligand is a general trend for all *o*-isopropoxy-styrene catalysts.<sup>30</sup> When 2.5 mol % catalyst loading was used at 50 °C in benzene (SI), catalysts **8** and **9** displayed >97% conversion in 20 min (40 min at 1 mol % loading).

Moreover, when the RCM reaction of **18** with the phosphine-free catalysts **6–10** was carried out at 60 °C (Figures 4 and 5), the reaction was completed in less time. Under these conditions, catalysts **8** and **9** led to >97% conversion in 20 min (40 min at 50 °C). Complex **10** was once again the slowest initiating catalyst. Surprisingly, catalysts **8–10** did not show signs of decomposition even at this elevated temperature, following pseudo-first-order kinetics over the course of the reaction after the end of the initial induction period (Figure 5). On the other hand, catalysts **6** and **7**, bearing the less bulky thiazole-2-ylidene ligands, showed some curvature in their logarithmic plots, consistent with a decrease in activity during the course of the reaction due to decomposition.



**Figure 5.** Log plots for catalysts **6–10** in the RCM of diethylallylmalonate (**18**) at 60 °C (1 mol % catalyst loading).

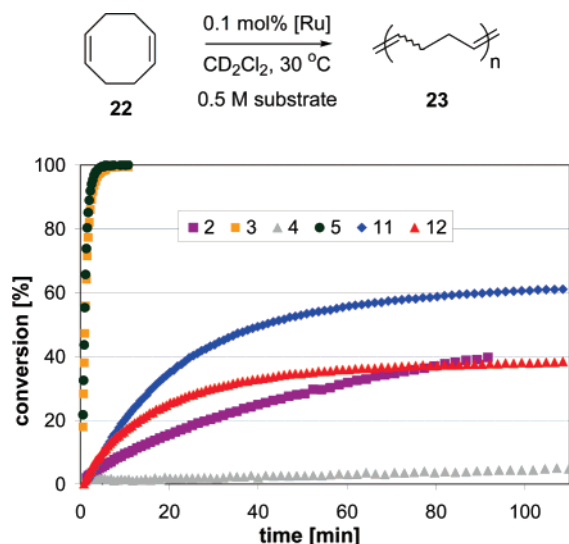


**Figure 6.** RCM of diene **20** to disubstituted cycloalkene **21** at 50 °C, using catalysts **6–10**.

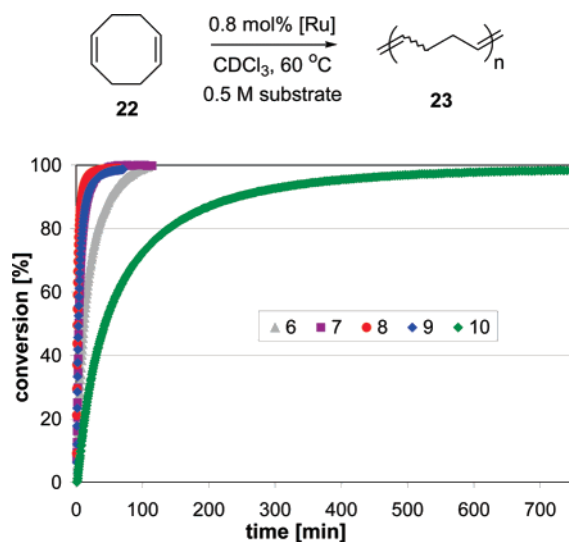
The RCM of diethylallylmethylmalonate (**20**, Figure 6) leads to the formation of a trisubstituted cyclic olefin (**21**). Due to steric effects, this reaction is more demanding than the corresponding RCM of diethylallyl malonate (**18**). As depicted in Figure 6, complexes **6–10** efficiently catalyze this more challenging ring-closing. Catalysts **6–9** lead the reaction to >96% conversion in 6.5 h, whereas complex **10** is again the least efficient catalyst due to its prolonged induction period (73% conversion in 6.5 h). It should be also noted that the reactivities of catalysts **7**, **8**, and **9** in this RCM reaction are very similar. Phosphine-containing catalysts **11** and **12** ring-close substrate **20** as well (SI), slightly surpassing in efficiency the first-generation phosphine-containing catalyst **2** (2.5 mol % catalyst loading, 0.1 M **20**, 30 °C, CD<sub>2</sub>Cl<sub>2</sub>). Nevertheless, both **11** and **12** suffer from a high decomposition rate reaching a plateau of 25% and 27% maximum conversion, respectively.

The formation of tetrasubstituted double bonds via RCM is very challenging and typically requires high catalyst loadings and elevated reaction temperatures due to the increased steric bulk of the substrates.<sup>11,29</sup> In this context, complexes **8–10** do not ring-close diethyltrimethylmalonate, even after 7 days at 60 °C (5 mol % catalyst loading, 0.1 M substrate, C<sub>6</sub>D<sub>6</sub>), although the catalysts are still present in the solution without any evidence of decomposition (<sup>1</sup>H NMR spectroscopy). On

(30) Hejl, A. H. Ph.D. Thesis, California Institute of Technology, Pasadena, 2007.



**Figure 7.** ROMP of 1,5-cyclooctadiene (**22**) using catalysts **2–5**, **11**, and **12**.



**Figure 8.** Monitoring the ROMP of 1,5-cyclooctadiene with catalysts **6–10**.

the contrary, initiators **6** and **7** slowly ring-close diethyldimethylallyl malonate (3% and 5% conversion, respectively, 7 days, 60 °C, 5 mol % catalyst loading, 0.1 M substrate,  $C_6D_6$ ) simultaneously undergoing complete decomposition.

**Ring-Opening Metathesis Polymerization (ROMP) Activity:** The ROMP of monomers containing strained, unsaturated rings is one of the earliest commercial applications of olefin metathesis.<sup>1,31</sup> We initially studied the catalytic activity of the new thiazole-2-ylidene-bearing complexes in the ROMP of 1,5-cyclooctadiene (**22**) by  $^1H$  NMR spectroscopy. Overall, the reactivity trends for ROMP were found to be similar to those observed for RCM. The phosphine-containing complexes (**11** and **12**) promote the ROMP of **22**, leveling off at 61% and 38% conversion, respectively, after 110 min at 30 °C (Figure 7). Both catalysts initiate quickly, but their decomposition rate is also high, as evidenced by their decreasing catalytic activity over the course of the reaction. As illustrated in Figure 8, phosphine-free initiators **6–10** polymerize **22** as well. Catalysts **7–9** lead to the complete conversion of **22** to the polyalkenamer **23** in

(31) Slugovc, C. *Macromol. Rapid Commun.* **2004**, *25*, 1283–1297.

**Table 2.** ROMP of Norbornene (**24**) Using Catalysts **6–10**

catalyst	yield [%]	$M_n^a$	PDI <sup>a</sup>	<i>cis/trans</i> ratio <sup>b</sup>
<b>6</b>	83	45 000	3.8	45/55
<b>7</b>	77	41 000	4.2	42/58
<b>8</b>	79	53 000	4.2	44/56
<b>9</b>	74	32 000	4.8	43/57
<b>10</b>	77	70 000	4.4	36/64

<sup>a</sup> Determined by GPC (THF). <sup>b</sup> Determined by NMR spectroscopy; catalysts **3** and **5** afforded polymers with a 46/54 and 66/34 *cis/trans* ratio, respectively.

less than 1 h, while catalysts **6** and **10** are less efficient. The reason for the low efficiency of complex **10** is its prolonged induction period even at 60 °C, as observed in the RCM studies.

The ROMP of highly strained molecules such as norbornene and norbornene derivatives takes place with a significantly higher reaction rate relative to **22**.<sup>32</sup> As shown in Table 2, catalysts **6–10** efficiently polymerize norbornene (**24**) at catalyst loadings as low as 0.2 mol %. Although the polymerization reactions were carried out at –20 °C, the polydispersity indices (PDIs) of the resulting polymers were rather high (3.8–4.8). This suggests slow initiation (relative to propagation) and/or that extensive chain transfer occurred either inter- or intramolecularly. Last, all initiators afforded a predominantly *trans*-olefin microstructure with catalyst **10** being the most selective (*cis/trans* ratio: 36/64).

**Cross Metathesis (CM) Activity:** CM is more challenging than either RCM or ROMP, because it lacks the entropic driving force of RCM and the ring-strain release of ROMP. Moreover, statistically, CM reactions often lead to relatively low yields of the desired cross-product, as well as poor *E/Z* cross-product selectivity.<sup>33</sup> In CM, the *E/Z* selectivity at high conversion is governed by thermodynamic factors; namely, secondary metathesis promotes isomerization of the product to the thermodynamically favored *E* isomer. The development of catalysts that could efficiently control *E/Z* selectivity in CM reactions still represents a major challenge.

We chose to evaluate the phosphine-free thiazole-2-ylidene catalysts in the CM of allyl benzene (**26**) with *cis*-1,4-diacetoxy-2-butene (**27**, Figure 9). Apart from the heterocoupled product (**28**), *trans*-1,4-diacetoxy-2-butene as well as both *E* and *Z* homocoupled allylbenzene were also formed and monitored during the course of the reaction via GC analysis. The conversion to the heterocoupled product **28** vs time, catalyzed by **6–10**, is shown in Figure 9. Catalysts **7** and **9** demonstrated exactly the same reactivity, while catalyst **8** proved to be slightly more efficient affording a higher yield of the desired cross-

- (32) (a) Amir-Ebrahimi, V.; Corry, D. A.; Hamilton, J. G.; Thompson, J. M.; Rooney, J. J. *Macromolecules* **2000**, *33*, 717–724. (b) Bielawski, C. W.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2000**, *39*, 2903–2906. For representative examples on the use of other transition metal complexes in the ROMP of highly strained monomers, see: (c) Gilliom, L. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 733–742. (d) Petasis, N. A.; Fu, D. K. *J. Am. Chem. Soc.* **1993**, *115*, 7208–7214. (e) Totland, K. M.; Boyd, T. J.; Lavoie, G. G.; Davis, W. M.; Schrock, R. R. *Macromolecules* **1996**, *29*, 6114–6125. For two review articles on living ROMP, see: (f) Schrock, R. R. *Acc. Chem. Res.* **1990**, *23*, 158–165. (g) Bielawski, C. W.; Grubbs, R. H. *Prog. Polym. Sci.* **2007**, *32*, 1–29.
- (33) For a general model on the selectivity of CM reactions, see: Chatterjee, A. K.; Choi, T. L.; Sanders, D. P.; Grubbs, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 11360–11370.



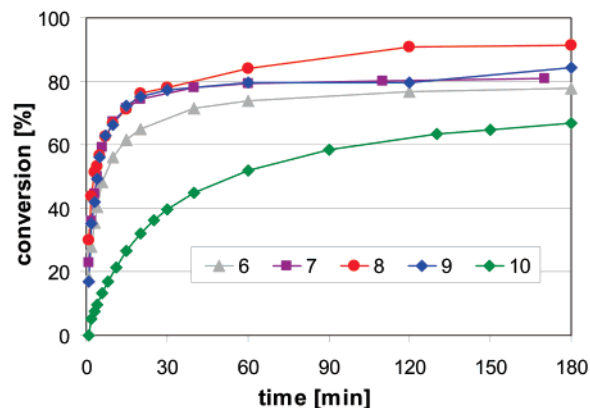
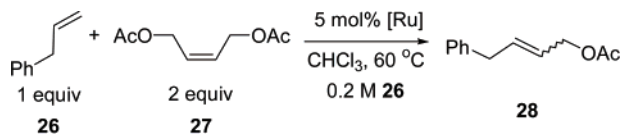


Figure 9. Conversion to heterocoupled product **28** using catalysts **6–10**.

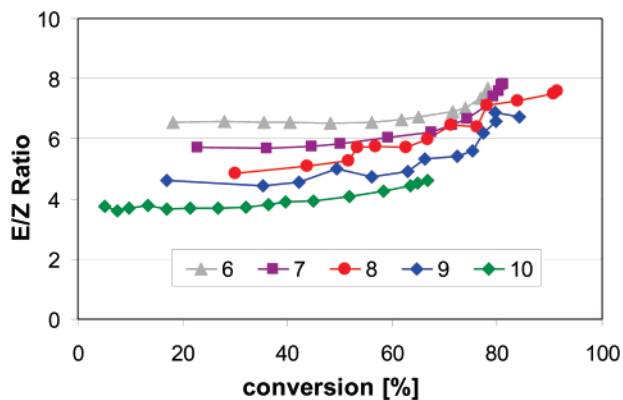


Figure 10. *E/Z* selectivity versus conversion in the CM reaction of allyl benzene (**26**) with *cis*-1,4-diacetoxy-2-butene (**27**).

product. Catalyst **10** was the least reactive catalyst in the series due to its poor initiation. More importantly, these new catalysts produce more *Z*-olefin upon increasing the bulkiness of the *N*-aryl substituents of the thiazole-2-ylidene ligand, as illustrated in the plots of the *E/Z* ratio of cross-product vs conversion to cross-product (Figure 10). Complex **6** is the least *Z*-selective catalyst, affording a relatively constant 6.5 *E/Z* ratio for a heterocoupled product conversion up to 60%. Increasing the bulkiness of the *N*-aryl group on the thiazole-2-ylidene ligand, catalysts become more *Z*-selective with complex **10** being the most selective of all, affording an *E/Z* ratio that is smaller than 4 for up to 50% heterocoupled product yield. The *E/Z* selectivity differences among the catalysts are more pronounced at low conversion levels, where the inherent diastereoselectivity of the catalyst seems to determine the *E/Z* outcome of the reaction. At conversions higher than 60%, the catalysts isomerize the product to the thermodynamically favored *E* isomer, ultimately reaching an *E/Z* ratio of about 8.<sup>34</sup> The same trend is also observed for catalysts **6–9** at 25 °C (catalyst **10** has a very long induction period at this temperature), although the selectivity differences are smaller (see SI).

(34) The *E/Z* ratio of the first-generation catalysts **2** and **4** in the same reaction is ~5. Second-generation catalysts **3** and **5** give lower *E/Z* ratios (~3) at low conversion, but when the conversion increases above 60% the product *E/Z* ratios increase dramatically (see ref 29).

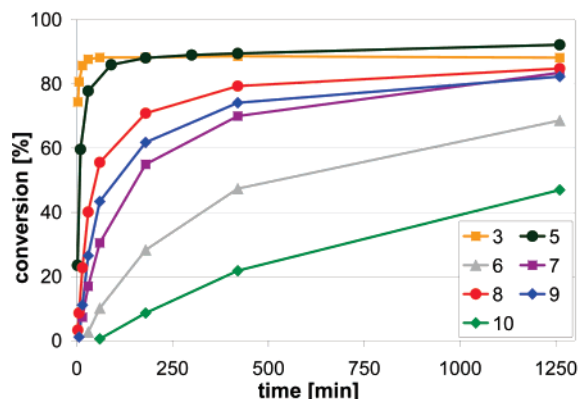
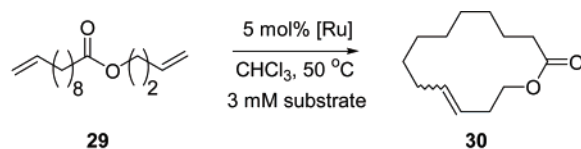


Figure 11. Conversion of lactone **29** to the 14-membered ring-closed product **30** using catalysts **3** and **5–10**.

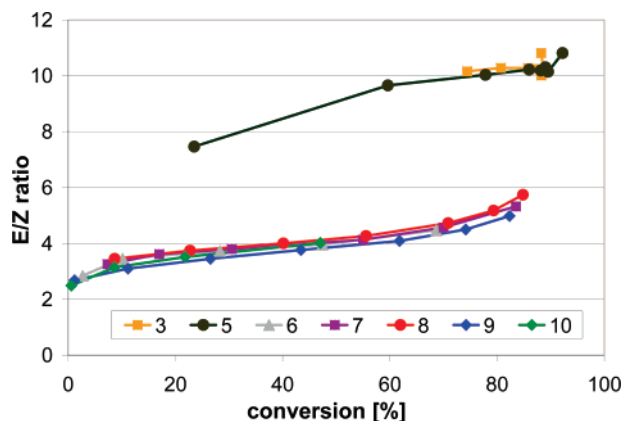


Figure 12. *E/Z* selectivity versus conversion in the macrocyclic ring-closing reaction of **29**.

**Macrocyclic Ring-Closing Metathesis Activity:** A variety of macrocyclic (>seven-membered) lactones, lactams, ketones, and ethers, some of which are alkaloids, perfume ingredients, and antibiotics, can be efficiently synthesized via macrocyclic ring-closing reactions of the corresponding  $\alpha,\omega$ -dienes.<sup>35</sup> To further exploit the potential of complexes **6–10** in olefin metathesis, we studied their catalytic activity in the macrocyclic ring-closing of the 14-membered lactone **29** (Figure 11).<sup>36</sup> Initiators **7–9** were the most reactive catalysts in this family, showing reactivity comparable to that of the second-generation catalysts **3** and **5**. Catalysts **6–10** display almost identical stereoselectivity in this reaction, producing macrocyclic product **30** with an *E/Z* ratio that begins at ~3 and finally reaches the value of ~6 at 85% conversion (Figure 12). Moreover, as clearly illustrated in Figure 12, the *E/Z* profile of catalysts **6–10** is

(35) Review articles: (a) Fürstner, A.; Langemann, K. *Synthesis* **1997**, 792–803. (b) Gaich, T.; Mulzer, J. *Curr. Top. Med. Chem.* **2005**, *5*, 1473–1494. (c) Van de Weghe, P.; Eustache, J. *Curr. Top. Med. Chem.* **2005**, *5*, 1495–1519. (d) Nicolaou, K. C.; Bulger, P. G.; Sarlah, D. *Angew. Chem., Int. Ed.* **2005**, *44*, 4490–4527.

(36) This macrocyclic ring-closing reaction has been performed in the past with other ruthenium-based olefin metathesis initiators: (a) Lee, C. W.; Grubbs, R. H. *Org. Lett.* **2000**, *2*, 2145–2147. (b) Conrad, J. C.; Eelman, M. D.; Duarte Silva, J. A.; Monfette, S.; Parnas, H. H.; Snelgrove, J. L.; Fogg, D. E. *J. Am. Chem. Soc.* **2007**, *129*, 1024–1025.

completely different than that of catalysts **3** and **5** and more similar to the stereoselectivity displayed by the first-generation catalyst **2** in the same reaction.<sup>36a</sup>

## Conclusions

A series of ruthenium-based olefin metathesis initiators, coordinated with thiazole-2-ylidene ligands, have been synthesized and completely characterized. Despite their decreased steric protection, these complexes are competent catalysts for ring-closing metathesis, cross metathesis, and ring-opening metathesis polymerization. Especially the phosphine-free thiazole-2-ylidene-bearing catalysts are unexpectedly robust, showing stability and activity comparable to those of the existing NHC-containing ruthenium catalysts. The most stable of these new complexes follow pseudo-first-order kinetics in the ring-closing of diethylallyl malonate even at 60 °C. Increasing the size of the *ortho* substituents on the *N*-aryl group of the thiazole-2-ylidene ligand from H to Et leads to phosphine-free catalysts with increased stability; however, increasing the steric bulk further to *i*-Pr results in slower catalyst initiation. Unlike previously evaluated catalysts, the steric bulk of these new thiazole-2-ylidene-containing complexes is correlated to the observed *E/Z* ratio of the cross-product in the cross metathesis reaction of allyl benzene with *cis*-1,4-diacetoxy-2-butene. Thus, decreasing the steric demand of the *ortho* substituents on the *N*-aryl groups from *i*-Pr to H results in an increased *E*-selectivity from ~4 to ~6.5.

## Experimental Section

**Materials and General Procedures:** Unless otherwise indicated, all compounds were purchased from Aldrich or Fisher. Catalysts **2** and **4** were obtained from Materia, Inc. Silica gel used for the purification of organometallic complexes was obtained from TSI Scientific, Cambridge, MA (60 Å, pH 6.5–7.0). 3-(2,6-Diisopropylphenyl)-4,5-dimethylthiazolium chloride (**14e**) was prepared according to literature methods.<sup>18,21,22</sup> All reactions involving metal complexes were conducted in oven-dried glassware under an argon atmosphere with anhydrous solvents, using standard Schlenk and glovebox techniques. Anhydrous solvents were obtained via elution through a solvent column drying system.<sup>37</sup> NMR chemical shifts are reported in ppm downfield from Me<sub>4</sub>Si, by using the residual solvent peak as internal standard for <sup>1</sup>H and <sup>13</sup>C and H<sub>3</sub>PO<sub>4</sub> ( $\delta$  0.0) for <sup>31</sup>P. Data for NMR spectra are reported as follows: chemical shift ( $\delta$  ppm), multiplicity, coupling constant (Hz), and integration. Gas chromatography data were obtained using an Agilent 6850 FID gas chromatograph equipped with a DB-Wax Polyethylene Glycol capillary column (J&W Scientific). Gel permeation chromatography (GPC) was carried out in THF on two PLgel 5  $\mu$ m mixed-B columns (Polymer Labs) connected in series with a DAWN EOS multiangle laser light scattering (MALLS) detector and an Optilab DSP differential refractometer (both from Wyatt Technology). No calibration standards were used, and  $dn/dc$  values were obtained for each injection by assuming 100% mass elution from the columns. X-ray crystallographic structures were obtained by Larry M. Henling and Dr. Michael W. Day of the California Institute of Technology Beckman Institute X-ray Crystallography Laboratory. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K., and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers 642800 (**6**), 642801 (**7**), 639435 (**8**), and 634944 (**9**).

**RCM Activity Tests.<sup>38</sup> Preparation of the Stock Solutions:** Two stock solutions can be prepared that contain enough catalyst for all

RCM reactions. Inside a glovebox, a volumetric flask was charged with the catalyst (0.016 mmol) and C<sub>6</sub>D<sub>6</sub> (or CD<sub>2</sub>Cl<sub>2</sub>) was added to prepare 1.0 mL of stock solution **A** (0.016 M). A 0.5 mL aliquot of **A** was then transferred to another 2 mL volumetric flask and diluted to 2 mL with C<sub>6</sub>D<sub>6</sub> (or CD<sub>2</sub>Cl<sub>2</sub>) to prepare stock solution **B** (0.004 M).

**RCM of Diethylallyl Malonate (18):** An NMR tube with a screw-cap septum top was charged inside a glovebox with catalyst stock solution **B** (200  $\mu$ L, 0.80  $\mu$ mol, 1.0 mol % or 500  $\mu$ L, 2  $\mu$ mol, 2.5 mol %) and C<sub>6</sub>D<sub>6</sub> (or CD<sub>2</sub>Cl<sub>2</sub>) (600 or 300  $\mu$ L, respectively). The sample was equilibrated at 30, 50, or 60 °C in the NMR probe before **18** (19.3  $\mu$ L, 19.2 mg, 0.080 mmol, 0.1 M) was added via syringe. Data points were collected over an appropriate period of time using the Varian array function. The conversion to **19** was determined by comparing the ratio of the integrals of the methylene protons in the starting material,  $\delta$  2.83 (dt), with those in the product,  $\delta$  3.13 (s). (These are the chemical shifts in C<sub>6</sub>D<sub>6</sub>; in CD<sub>2</sub>Cl<sub>2</sub> the corresponding chemical shifts are  $\delta$  2.61 (dt) and  $\delta$  2.98 (s).)

**RCM of Diethylallylmethyl Malonate (20):** An NMR tube with a screw-cap septum top was charged inside a glovebox with catalyst stock solution **B** (200  $\mu$ L, 0.80  $\mu$ mol, 1.0 mol % or 500  $\mu$ L, 2  $\mu$ mol, 2.5 mol %) and C<sub>6</sub>D<sub>6</sub> (or CD<sub>2</sub>Cl<sub>2</sub>) (600 or 300  $\mu$ L, respectively). The sample was equilibrated at 30, 50, or 60 °C in the NMR probe before **20** (20.5  $\mu$ L, 20.4 mg, 0.080 mmol, 0.1 M) was added via syringe. Data points were collected over an appropriate period of time using the Varian array function. The conversion to **21** was determined by comparing the ratio of the integrals of the methylene protons in the starting material,  $\delta$  2.91 (s), 2.88 (dt), with those in the product,  $\delta$  3.15 (s), 3.05 (m). (These are the chemical shifts in C<sub>6</sub>D<sub>6</sub>; in CD<sub>2</sub>Cl<sub>2</sub>, the corresponding chemical shifts are  $\delta$  2.67 (s), 2.64 (dt) for the starting material and  $\delta$  2.93 (s), 2.88 (m) for the product.)

**ROMP Activity Tests.<sup>38</sup> ROMP of 1,5-Cyclooctadiene (22):** An NMR tube with a screw-cap septum top was charged inside a glovebox with a catalyst stock solution in CD<sub>2</sub>Cl<sub>2</sub> or CDCl<sub>3</sub> (0.004 M, 800  $\mu$ L, 3.2  $\mu$ mol, 0.8 mol % or 100  $\mu$ L of the 0.004 M stock solution (**B**), 0.1 mol %, along with 700  $\mu$ L of solvent). The sample was equilibrated at 30 or 60 °C in the NMR probe before **22** (49.1  $\mu$ L, 43.3 mg, 0.40 mmol, 0.5 M) was added via syringe. Data points were collected over an appropriate period of time using the Varian array function. The conversion to **23** was determined by comparing the ratio of the integrals of the methylene protons in the starting material,  $\delta$  2.31 (m), with those in the product,  $\delta$  2.05 (br m), 2.00 (br m).

**ROMP of Norbornene (24):** Typically, **24** (47.1 mg, 0.5 mmol) and dry, degassed CH<sub>2</sub>Cl<sub>2</sub> (2 mL) were added in a flame-dried 4 mL vial equipped with a screw-cap septum top, under an atmosphere of argon. In a glovebox, the catalyst (0.002 mmol) and CH<sub>2</sub>Cl<sub>2</sub> (1 mL) were combined in another 4 mL vial with a screw-cap septum top and the vial was taken out of the glovebox. Both solutions were equilibrated at –20 °C for 5 min before 0.5 mL of the catalyst solution (0.001 mmol of catalyst, monomer/catalyst = 500) was added to the monomer solution via a syringe. The reaction was allowed to stir at –20 °C for 90 min under an argon atmosphere and then quenched with ethyl vinyl ether (500  $\mu$ L). The reaction was stirred at –20 °C for 10 more min and then left to reach room temperature. This solution was added dropwise to 50 mL of MeOH under vigorous stirring. Polynorbornene (**25**) completely precipitated after 5–10 min of stirring. It was then collected, washed with MeOH (3  $\times$  2 mL), and dried under high vacuum overnight, before analyzed by GPC and NMR.

**CM Activity Tests.<sup>38</sup> Cross Metathesis of Allylbenzene (26) with *cis*-1,4-Diacetoxy-2-butene (27):** **26** (1.00 mL, 7.55 mmol) and tridecane (internal standard, 0.920 mL, 3.77 mmol) were combined in a flame-dried, 4 mL vial under an atmosphere of argon. The mixture was stirred before taking a  $t_0$  time point. The catalyst (10  $\mu$ mol) and CHCl<sub>3</sub> (1 mL) were added in a 4 mL vial inside a glovebox. The vial was taken out of the glovebox, and **27** (64  $\mu$ L, 0.40 mmol) and the allylbenzene/tridecane mixture (51  $\mu$ L) were added simultaneously via syringe. The reaction was allowed to stir at 25 or 60 °C. Samples for

(37) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518–1520.

(38) All reactions were performed at least in duplicate to confirm reproducibility.

GC analysis were obtained by adding a 30  $\mu\text{L}$  reaction aliquot to 500  $\mu\text{L}$  of a 3M solution of ethyl vinyl ether in dichloromethane. The sample was shaken, allowed to stand for at least 5 min, and then analyzed via GC.

**Macrocyclic Ring-Closing Metathesis Activity Tests.**<sup>38</sup> **Macrocyclic Ring-Closing Metathesis of Diene 29:** 14-Membered lactone **29** (410  $\mu\text{L}$ , 1.5 mmol) and tridecane (internal standard, 500  $\mu\text{L}$ , 2.05 mmol) were combined in a flame-dried, 4 mL vial under an atmosphere of argon. The mixture was stirred before taking a  $t_0$  time point. The catalyst (1.5  $\mu\text{mol}$ ) and dry, degassed  $\text{ClCH}_2\text{CH}_2\text{Cl}$  (6 mL) were added in a 20 mL vial in a glovebox. The vial was taken out of the glovebox and equilibrated at 50  $^\circ\text{C}$  for 5 min under argon, and the 14-membered lactone/tridecane mixture (18  $\mu\text{L}$ ) was then added via syringe. The reaction was allowed to stir at 50  $^\circ\text{C}$ . Samples for GC analysis were obtained by adding a 400  $\mu\text{L}$  reaction aliquot to 100  $\mu\text{L}$  of a 3M solution of ethyl vinyl ether in dichloromethane. The sample was shaken, allowed to stand for at least 5 min, and then analyzed via GC.

**3-Phenyl-4,5-dimethylthiazolium chloride 14a:**<sup>22</sup> A mixture of *N*-formyl-aniline (**13a**) (3.634 g, 30 mmol) and phosphorus pentasulfide (1.351 g, 3.04 mmol) in dry 1,4-dioxane (4 mL) was stirred at room temperature for 15 min under an argon atmosphere. 3-Chloro-2-butanone (2.131 g, 20 mmol) was added, and the resulting slurry was heated at 100  $^\circ\text{C}$ . The reaction mixture was refluxed for 50 min, initially becoming clear yellow and finally deep red. After cooling at room temperature, the crude mixture was diluted with  $\text{H}_2\text{O}$  (20 mL).  $\text{Na}_2\text{CO}_3$  was added to the reaction mixture until  $\text{pH} \approx 7$ . The solvent was evaporated under reduced pressure, and the resulting solid was suspended in  $\text{CH}_2\text{Cl}_2$  and purified by column chromatography eluting with  $\text{EtOH}/\text{CH}_2\text{Cl}_2$  (15/85). Upon concentration of the last yellowish band, a viscous orange oil was obtained. This was solidified when washed under vigorous stirring with diethyl ether (3  $\times$  2 mL) to afford **14a** as a light pink solid (770 mg, 11%).  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 300 MHz):  $\delta = 11.13$  (s, 1H), 7.67–7.60 (m, 3H), 7.53–7.49 (m, 2H), 2.57 (s, 3H), 2.23 (s, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 75 MHz):  $\delta = 161.03$ , 142.08, 141.75, 137.19, 132.10, 130.84, 126.34, 13.10, 12.86. HRMS ( $\text{FAB}^+$ ): calculated for  $\text{C}_{11}\text{H}_{12}\text{NS}$  [ $\text{M}]^+$  190.0690, observed 190.0693.

***N*-Formyl-2-methylaniline 13b:**<sup>21</sup> A mixture of formic acid (14.361 g, 0.312 mol) and acetic anhydride (12.659 g, 0.124 mol) was stirred at room temperature for 1 h under an argon atmosphere. This mixture was added to a solution of 2-methylaniline (10.710 g, 0.1 mol) in dry dichloromethane (60 mL) at such a rate that the temperature of the reaction mixture was kept between 5 and 10  $^\circ\text{C}$ . The reaction was stirred at room temperature for 16 h and then refluxed for 4 h. The solvent was evaporated under reduced pressure, and the residue was dissolved in  $\text{CHCl}_3$  (200 mL) and washed with a saturated aqueous  $\text{NaHCO}_3$  solution (3  $\times$  200 mL) and water (200 mL). The organic layer was dried over  $\text{Na}_2\text{SO}_4$ , and the solvent was evaporated under reduced pressure. The remaining yellow solid was washed with a mixture of hexanes/diethyl ether (2  $\times$  10 mL) and then with hexanes (3  $\times$  5 mL) to afford **13b** as a white solid (9.70 g, 72%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta = 9.03$ –8.18 (m, 2H, CHO, NH), 7.77–7.03 (m, 4H), 2.30–2.22 (m, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta = 164.41$ , 160.32, 135.50, 134.99, 131.45, 130.82, 130.50, 129.87, 127.25, 126.80, 126.34, 125.84, 123.75, 121.32, 18.05, 17.99. HRMS ( $\text{FAB}^+$ ): calculated for  $\text{C}_8\text{H}_{10}\text{NO}$  [ $\text{M}]^+$  136.0762, observed 136.0783.

**3-(2-Methylphenyl)-4,5-dimethylthiazolium Chloride 14b:** This dimethylthiazolium chloride was prepared and purified as described for **14a**. Upon concentration of the last yellowish band from the chromatography column, a viscous orange oil was obtained. This was solidified when washed under vigorous stirring with diethyl ether to afford **14b** as a tan solid (17% yield).  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 300 MHz):  $\delta = 11.09$  (s, 1H), 7.53–7.31 (m, 4H), 2.57 (s, 3H), 2.08 (s, 3H), 2.04 (s, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 75 MHz):  $\delta = 160.77$ , 142.05, 136.10,

134.60, 134.30, 132.23, 132.00, 128.08, 126.55, 17.23, 12.90, 11.98. HRMS ( $\text{FAB}^+$ ): calculated for  $\text{C}_{12}\text{H}_{14}\text{NS}$  [ $\text{M}]^+$  204.0847, observed 204.0845.

***N*-Formyl-2,4,6-trimethylaniline 13c:** This formamide was prepared as described for **13b**. After the solvent was evaporated under reduced pressure, the obtained yellow solid was washed with hot diethyl ether to afford **13c** as a white solid (70% yield).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta = 8.39$ –8.03 (m, 1H, CHO), 7.26–6.91 (m, 2H), 6.75 (broad s, 1H, NH), 2.29–2.21 (m, 9H);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta = 165.48$ , 160.05, 137.75, 137.61, 135.37, 135.16, 130.92, 130.74, 129.53, 129.16, 21.15, 21.12, 18.84, 18.64. HRMS ( $\text{FAB}^+$ ): calculated for  $\text{C}_{10}\text{H}_{14}\text{NO}$  [ $\text{M}]^+$  164.1075, observed 164.1116.

**3-(2,4,6-Trimethylphenyl)-4,5-dimethylthiazolium Chloride 14c:** This dimethylthiazolium chloride was prepared and purified as described for **14a**. Upon concentration of the last yellowish band from the chromatography column, a viscous yellow oil was obtained. This was solidified when washed under vigorous stirring with diethyl ether to afford **14c** as a tan solid (17% yield).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta = 10.84$  (s, 1H), 6.96 (s, 2H), 2.57 (s, 3H), 2.27 (s, 3H), 2.02 (s, 3H), 1.85 (s, 6H);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta = 160.81$ , 142.18, 141.58, 134.95, 133.65, 132.86, 130.36, 21.35, 17.57, 13.21, 11.62. HRMS ( $\text{FAB}^+$ ): calculated for  $\text{C}_{14}\text{H}_{18}\text{NS}$  [ $\text{M}]^+$  232.1160, observed 232.1158.

***N*-Formyl-2,6-diethylaniline 13d:** This formamide was prepared as described for **13b**. After the solvent was evaporated under reduced pressure, the remaining yellow solid was washed with hot diethyl ether to afford **13d** as a white solid (74% yield).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta = 8.15$ –8.02 (m, 1H, CHO), 7.86 (broad s, 1H, NH), 7.25–7.06 (m, 3H), 2.65 (q,  $J = 7$  Hz, 2H), 2.53 (q,  $J = 7$  Hz, 2H), 1.20 (t,  $J = 7$  Hz, 3H), 1.14 (t,  $J = 7$  Hz, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta = 165.97$ , 161.00, 142.13, 141.52, 132.15, 131.66, 128.65, 128.37, 127.09, 126.49, 25.18, 25.04, 15.00, 14.62. HRMS ( $\text{EI}^+$ ): calculated for  $\text{C}_{11}\text{H}_{15}\text{NO}$  [ $\text{M}]^+$  177.1154, observed 177.1159.

**3-(2,6-Diethylphenyl)-4,5-dimethylthiazolium Chloride 14d:**<sup>22</sup> A mixture of **13d** (3.545 g, 20 mmol) and phosphorus pentasulfide (0.900 g, 2.02 mmol) in dry 1,4-dioxane (5 mL) was stirred at room temperature for 15 min under an argon atmosphere. 3-Chloro-2-butanone (1.422 g, 20 mmol) was added, and the resulting slurry was heated at 100  $^\circ\text{C}$ . The reaction mixture was refluxed for 50 min, initially becoming clear yellow and finally deep red. After cooling at room temperature, the crude mixture was diluted with  $\text{H}_2\text{O}$  (20 mL), and  $\text{Na}_2\text{CO}_3$  was added to the reaction mixture until  $\text{pH} \approx 7$ . The solvent was evaporated under reduced pressure, and the resulting solid was suspended in  $\text{CH}_2\text{Cl}_2$  and purified by column chromatography eluting with  $\text{EtOH}/\text{CH}_2\text{Cl}_2$  (15/85). Upon concentration of the last band, a viscous brownish oil was obtained. This was solidified when washed under vigorous stirring with diethyl ether (3  $\times$  2 mL) to afford **14d** as a tan solid (560 mg, 10%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta = 10.97$  (s, 1H), 7.52 (t,  $J = 8$  Hz, 1H), 7.30 (d,  $J = 8$  Hz, 2H), 2.63 (s, 3H), 2.16 (q,  $J = 8$  Hz, 4H), 2.06 (s, 3H), 1.14 (t,  $J = 8$  Hz, 6H);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta = 161.92$ , 141.63, 139.62, 135.04, 134.20, 132.30, 127.65, 23.97, 14.18, 13.16, 11.82. HRMS ( $\text{FAB}^+$ ): calculated for  $\text{C}_{15}\text{H}_{20}\text{NS}$  [ $\text{M}]^+$  246.1316, observed 246.1326.

**[RuCl<sub>2</sub> (3-Phenyl-4,5-dimethylthiazol-2-ylidene) (=CH-*o*-iPrO-Ph)] 6:** In a glovebox, 3-phenyl-4,5-dimethylthiazolium chloride (**14a**) (113.0 mg, 0.50 mmol, 1 equiv), silver(I) oxide (58.0 mg, 0.25 mmol, 0.5 equiv), and 4 Å molecular sieves (113 mg) were suspended in  $\text{CH}_2\text{Cl}_2$  (7 mL) in the dark. The reaction mixture was stirred at room temperature for 1 h. Complex **4** (270 mg, 0.45 mmol, 0.9 equiv) was added as a solid in one portion, and the reaction flask was taken out of the glovebox and stirred under a nitrogen atmosphere at room temperature for 1.5 h in the dark. The solvent was removed in vacuo, and the remaining solid was dissolved in a minimum amount of  $\text{C}_6\text{H}_6$  and poured onto a column packed with TSI Scientific silica gel. The complex was eluted with pentanes/diethyl ether (1/1) as a brown-green band. The solvent was removed in vacuo, and the obtained solid was



transferred in a glovebox, dissolved in the minimum amount of benzene, and lyophilized to afford the desired complex as a brown-yellow solid (75 mg, 0.147 mmol, 32% yield). The complex is stable in air in the solid state and soluble in  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ , benzene, toluene, and THF. Crystals suitable for X-ray crystallography were grown at room temperature by slow diffusion of hexanes into a solution of **6** in benzene.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 500 MHz):  $\delta = 17.93$  (s, 1H), 7.90–7.88 (m, 2H), 7.79–7.77 (m, 1H), 7.70–7.58 (m, 4H), 7.15–7.08 (m, 2H), 5.14 (septet,  $J = 6$  Hz, 1H), 2.42 (s, 3H), 2.12 (s, 3H), 1.52 (d,  $J = 6$  Hz, 6H);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 125 MHz):  $\delta = 287.26$ , 215.05, 154.90, 143.81, 143.80, 142.49, 139.96, 130.36, 129.71, 129.57, 129.18, 122.95, 122.26, 113.68, 75.67, 21.72, 12.97, 12.71. HRMS (FAB<sup>+</sup>): calculated for  $\text{C}_{21}\text{H}_{25}\text{Cl}_2\text{NORuS}$  [ $\text{M}$ ]<sup>+</sup> 508.9921, observed 508.9900.

**[RuCl<sub>2</sub> (3-(2-Methylphenyl)-4,5-dimethylthiazol-2-ylidene) (=CH-*o*-iPrO-Ph)] 7:** This ruthenium complex was prepared and purified as described for complex **6** (53% yield). Crystals suitable for X-ray crystallography were grown at room temperature by slow diffusion of hexanes into a solution of **7** in benzene.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 500 MHz):  $\delta = 17.92$  (s, 1H), 8.09–8.07 (m, 1H), 7.79–7.77 (m, 1H), 7.70–7.67 (m, 1H), 7.53–7.49 (m, 2H), 7.44–7.42 (m, 1H), 7.15–7.07 (m, 2H), 5.12 (septet,  $J = 6$  Hz, 1H), 2.42 (s, 3H), 2.16 (s, 3H), 2.01 (s, 3H), 1.53 (d,  $J = 6$  Hz, 3H), 1.44 (d,  $J = 6$  Hz, 3H);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 125 MHz):  $\delta = 287.59$ , 215.39, 155.27, 144.32, 144.30, 141.81, 140.49, 138.46, 130.70, 130.04, 129.90, 129.52, 123.29, 122.59, 114.02, 76.01, 22.13, 22.07, 19.13, 13.17, 12.36. HRMS (FAB<sup>+</sup>): calculated for  $\text{C}_{22}\text{H}_{25}\text{Cl}_2\text{NORuS}$  [ $\text{M}$ ]<sup>+</sup> 523.0078, observed 523.0069.

**[RuCl<sub>2</sub> (3-(2,4,6-Trimethylphenyl)-4,5-dimethylthiazol-2-ylidene) (=CH-*o*-iPrO-Ph)] 8:** In a glovebox, 3-(2,4,6-trimethylphenyl)-4,5-dimethylthiazolium chloride (**14c**) (93.8 mg, 0.35 mmol, 1 equiv), silver(I) oxide (40.6 mg, 0.175 mmol, 0.5 equiv), and 4 Å molecular sieves (95 mg) were suspended in  $\text{CH}_2\text{Cl}_2$  (5 mL) in the dark. The reaction mixture was stirred at room temperature for 1 h. Catalyst **4** (189 mg, 0.315 mmol, 0.9 equiv) was added as a solid in one portion, and the reaction flask was taken out of the glovebox and stirred under a nitrogen atmosphere at room temperature for 1 h in the dark. The solvent was removed in vacuo, and the remaining solid was dissolved in a minimum amount of  $\text{C}_6\text{H}_6$  and poured onto a column packed with TSI Scientific silica gel. The complex was eluted with pentanes/diethyl ether (1/1) as a brown band. The solvent was removed in vacuo, and the obtained solid was transferred in a glovebox, dissolved in the minimum amount of benzene, and lyophilized to afford the desired complex as a brown solid (93 mg, 0.168 mmol, 54% yield). The complex is stable in air in the solid state and soluble in  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ , benzene, toluene, and THF. Crystals suitable for X-ray crystallography were grown at room temperature by slow diffusion of hexanes into a solution of **8** in benzene.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 500 MHz):  $\delta = 17.27$  (s, 1H), 7.67–7.59 (m, 2H), 7.12–7.07 (m, 4H), 5.17 (septet,  $J = 6$  Hz, 1H), 2.43 (s, 6H), 2.09 (s, 6H), 1.87 (s, 3H), 1.61 (d,  $J = 6$  Hz, 6H);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 125 MHz):  $\delta = 284.03$ , 211.33, 154.36, 143.92, 140.58, 139.78, 138.08, 137.00, 130.82, 130.10, 129.31, 122.81, 122.43, 113.62, 75.93, 21.74, 21.19, 18.71, 12.69, 11.90. HRMS (FAB<sup>+</sup>): calculated for  $\text{C}_{24}\text{H}_{29}\text{Cl}_2\text{NORuS}$  [ $\text{M}$ ]<sup>+</sup> 551.0382, observed 551.0382.

**[RuCl<sub>2</sub> (3-(2,6-Diethylphenyl)-4,5-dimethylthiazol-2-ylidene) (=CH-*o*-iPrO-Ph)] 9:** In a glovebox, 3-(2,6-diethylphenyl)-4,5-dimethylthiazolium chloride (**14d**) (70.5 mg, 0.25 mmol, 1 equiv), silver(I) oxide (29.0 mg, 0.125 mmol, 0.5 equiv), and 4 Å molecular sieves (71 mg) were suspended in  $\text{CH}_2\text{Cl}_2$  (3.5 mL) in the dark. The reaction mixture was stirred at room temperature for 1 h. Catalyst **4** (135 mg, 0.225 mmol, 0.9 equiv) was added as a solid in one portion, and the reaction flask was taken out of the glovebox and stirred under a nitrogen atmosphere at room temperature for 16 h in the dark. The solvent was removed in vacuo, and the remaining solid was dissolved in a minimum amount of  $\text{C}_6\text{H}_6$  and poured onto a column packed with TSI Scientific silica gel. The complex was eluted with pentanes/diethyl

ether (1/1) as a brown band. The solvent was removed in vacuo, and the obtained solid was transferred in a glovebox, dissolved in the minimum amount of benzene, and lyophilized to afford the desired complex as a brown solid (74 mg, 0.131 mmol, 58% yield). The complex is stable in air in the solid state and soluble in  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ , benzene, toluene, and THF. Crystals suitable for X-ray crystallography were grown at room temperature by slow diffusion of hexanes into a solution of **9** in benzene.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 500 MHz):  $\delta = 17.27$  (s, 1H), 7.66–7.62 (m, 2H), 7.54 (t,  $J = 8$  Hz, 1H), 7.34 (d,  $J = 8$  Hz, 2H), 7.11–7.06 (m, 2H), 5.16 (septet,  $J = 6$  Hz, 1H), 2.62 (m, 2H), 2.43 (s, 3H), 2.24 (m, 2H), 1.88 (s, 3H), 1.59 (d,  $J = 6$  Hz, 6H), 1.17 (t,  $J = 7$  Hz, 6H);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 125 MHz):  $\delta = 282.90$ , 210.53, 154.52, 143.77, 142.20, 140.93, 139.54, 131.26, 130.09, 130.00, 125.80, 122.79, 122.42, 113.65, 75.91, 31.52, 27.39, 27.30, 26.08, 24.06, 21.76, 13.23, 12.71, 12.28. HRMS (FAB<sup>+</sup>): calculated for  $\text{C}_{25}\text{H}_{30}\text{Cl}_2\text{NORuS}$  [ $\text{M}$ ]<sup>+</sup> 564.0469, observed 564.0461.

**[RuCl<sub>2</sub> (3-(2,6-Diisopropylphenyl)-4,5-dimethylthiazol-2-ylidene) (=CH-*o*-iPrO-Ph)] 10:** 3-(2,6-Diisopropylphenyl)-4,5-dimethylthiazolium chloride (**14e**) (190.8 mg, 0.616 mmol, 2.2 equiv) was stirred with an equimolar quantity of KHMDS (122.8 mg, 0.616 mmol) in benzene (15 mL) inside a glovebox at room temperature for 30 min. Catalyst **4** (168.2 mg, 0.28 mmol, 1.0 equiv) was added as a solid in one portion, and the reaction flask was taken out of the glovebox and stirred under a nitrogen atmosphere at room temperature for 1 h. The solution was concentrated to 2 mL in vacuo and poured onto a column packed with TSI Scientific silica gel. The complex was eluted with hexanes/diethyl ether (1/1) as a brown band. The solvent was removed in vacuo, and the obtained solid was transferred in a glovebox, dissolved in the minimum amount of benzene, and lyophilized to afford the desired complex as a brown solid (66 mg, 0.11 mmol, 40% yield). The complex is stable in air in the solid state and soluble in  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ , benzene, toluene, and THF.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 500 MHz):  $\delta = 16.60$  (s, 1H), 7.63–7.57 (m, 2H), 7.38 (d,  $J = 8$  Hz, 2H), 7.07–7.02 (m, 3H), 5.19 (septet,  $J = 6$  Hz, 1H), 2.50 (septet,  $J = 7$  Hz, 2H), 2.42 (s, 3H), 1.91 (s, 3H), 1.70 (d,  $J = 6$  Hz, 6H), 1.12 (d,  $J = 7$  Hz, 6H), 1.03 (d,  $J = 7$  Hz, 6H);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 125 MHz): 280.83, 209.03, 162.87, 154.15, 146.64, 143.30, 141.88, 138.53, 130.42, 129.81, 124.75, 122.63, 122.29, 113.50, 75.93, 28.41, 24.46, 24.12, 22.02, 12.99, 12.58. HRMS (FAB<sup>+</sup>) calculated for  $\text{C}_{27}\text{H}_{35}\text{NOCl}_2\text{RuS}$  [ $\text{M}$ ]<sup>+</sup> 593.0860, observed 593.0875.

**[RuCl<sub>2</sub> (3-(2,4,6-Trimethylphenyl)-4,5-dimethylthiazol-2-ylidene) (=CH-Ph) (PCy<sub>3</sub>)] 11:** In a glovebox, 3-(2,4,6-trimethylphenyl)-4,5-dimethylthiazolium chloride (**14c**) (134 mg, 0.5 mmol, 1 equiv), silver(I) oxide (58 mg, 0.25 mmol, 0.5 equiv), and 4 Å molecular sieves (135 mg) were suspended in  $\text{CH}_2\text{Cl}_2$  (2.5 mL) in the dark. The reaction mixture was stirred at room temperature for 1 h. Catalyst **2** (370 mg, 0.45 mmol, 0.9 equiv) was added as a solid in one portion, and the reaction flask was taken out of the glovebox and stirred under a nitrogen atmosphere at room temperature for 30 min in the dark. The solvent was removed in vacuo, and the remaining solid was dissolved in a minimum amount of  $\text{C}_6\text{H}_6$  and poured onto a column packed with TSI Scientific silica gel. The complex was eluted with diethyl ether/pentanes (15/85) as a green band. The solvent was removed in vacuo, and the obtained solid was transferred in a glovebox, dissolved in the minimum amount of benzene, and lyophilized to afford the desired complex as a brown solid (105 mg, 0.136 mmol, 30% yield). The complex is stable in air in the solid state and soluble in  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ , benzene, toluene, and THF.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 500 MHz):  $\delta = 19.61$  (d,  $J = 6$  Hz, 1H), 8.16 (d,  $J = 8$  Hz, 2H), 7.59 (t,  $J = 8$  Hz, 1H), 7.29 (t,  $J = 8$  Hz, 2H), 6.84 (s, 2H), 2.34–2.24 (m, 9H), 2.11 (s, 6H), 1.77 (s, 3H), 1.71–1.12 (m, 30H);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 125 MHz):  $\delta = 299.80$ , 220.39, 152.21, 140.31, 139.14, 137.94, 136.21, 131.24, 129.71, 129.46, 128.44, 107.27, 32.53, 32.40, 29.96, 28.08, 28.00, 27.21, 26.66, 21.08, 18.88, 12.35, 11.67;  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 202 MHz)  $\delta = 30.96$ . HRMS (FAB<sup>+</sup>): calculated for  $\text{C}_{39}\text{H}_{56}\text{Cl}_2\text{NPSRu}$  [ $\text{M}$ ]<sup>+</sup> 773.2292, observed 773.2316.



**[RuCl<sub>2</sub> (3-(2,6-Diethylphenyl)-4,5-dimethylthiazol-2-ylidene) (=CH-Ph) (PCy<sub>3</sub>)] 12:** In a glovebox, 3-(2,6-diethylphenyl)-4,5-dimethylthiazolium chloride (**14d**) (70.5 mg, 0.25 mmol, 1 equiv), silver(I) oxide (29.0 mg, 0.125 mmol, 0.5 equiv), and 4 Å molecular sieves (71 mg) were suspended in CH<sub>2</sub>Cl<sub>2</sub> (3.5 mL) in the dark. The reaction mixture was stirred at room temperature for 1 h. Catalyst **2** (185 mg, 0.225 mmol, 0.9 equiv) was added as a solid in one portion, and the reaction flask was taken out of the glovebox and stirred under a nitrogen atmosphere at room temperature for 1.5 h in the dark. The solvent was removed in vacuo, and the remaining solid was dissolved in a minimum amount of C<sub>6</sub>H<sub>6</sub> and poured onto a column packed with TSI Scientific silica gel. The complex was eluted with diethyl ether/pentanes (15/85) as a brown band. The solvent was removed in vacuo, and the obtained solid was transferred in a glovebox, dissolved in the minimum amount of benzene, and lyophilized to afford the desired complex as a brown solid (72 mg, 0.091 mmol, 41% yield). The complex is stable in air in the solid state and soluble in CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, benzene, toluene, and THF. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 500 MHz): δ = 19.67 (d, *J* = 7 Hz, 1H), 8.16–8.14 (m, 2H), 7.60 (t, *J* = 7 Hz, 1H), 7.36–7.27 (m, 3H), 7.19–7.17 (m, 2H), 2.92 (m, 2H), 2.33–2.22 (m, 6H), 2.19–2.07 (m, 2H), 1.80 (s, 3H), 1.67–1.09 (m, 36H); <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 125 MHz): δ = 301.65, 219.36, 152.36, 141.37, 140.42, 140.39, 139.31, 131.28, 129.82, 129.78, 128.88, 128.52, 127.84, 126.65, 125.58, 32.53, 32.41, 31.16, 29.90, 28.08, 28.00, 27.63, 27.59, 26.65, 26.40, 24.19,

12.74, 12.35, 12.03; <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 202 MHz) δ = 29.38. HRMS (FAB<sup>+</sup>): calculated for C<sub>40</sub>H<sub>58</sub>RuNPSCl<sub>2</sub> [M]<sup>+</sup> 787.2449, observed 787.2460.

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**Supporting Information Available:** <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR spectra of catalysts **6–12**. Text, tables, and figures giving details of the X-ray analysis of catalysts **6–9**; crystal data are also available as CIF files. GPC chromatograms for the ROMP of norbornene with catalysts **6–10**. Plots with additional catalytic evaluation data for **6–12**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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