

# Stability of Second Generation Grubbs' Alkylidenes to Primary Amines: Formation of Novel Ruthenium-Amine Complexes

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**Abstract:** The stability of second generation Grubbs' alkylidenes to primary amines relative to the first generation derivatives is investigated. For both Grubbs' alkylidene derivatives, the tricyclohexylphosphine (PCy<sub>3</sub>) ligand is displaced by *n*-butylamine and diethylenetriamine. However, while displacement of PCy<sub>3</sub> in first generation Grubbs' alkylidene derivatives results in decomposition of the catalyst, the N-heterocyclic carbene (NHC) ligand in second generation derivatives is not displaced by primary amines present in up to 100 equivalents. The result is the formation of new stable ruthenium-amine complexes. These complexes are characterized and their catalytic activity is evaluated in ring-closing

metathesis (RCM) and ring-opening metathesis (ROMP) reactions. While the amine complexes evaluated were minimally active in RCM reactions, the ruthenium-butylamine complex was significantly active in ROMP and exhibited an initiation rate constant that was at least an order of magnitude greater than that of the second generation Grubbs' alkylidene from which it was synthesized.

**Keywords:** Grubbs' catalyst stability; primary amines; ring-closing metathesis (RCM); ring-opening metathesis (ROMP); ruthenium; self-healing polymers

## Introduction

One of the most significant advantages of Grubbs' catalysts over other metathesis catalysts is their impressive reactivity with olefinic substrates in the presence of most common functional groups including ketones, aldehydes, alcohols, acids and even water.<sup>[1–4]</sup> However, it has been reported that the first generation Grubbs' alkylidene can be deactivated particularly by functional groups that coordinate strongly to the ruthenium center. For example, the first generation Grubbs' alkylidene is known to decompose rapidly in coordinating solvents such as acetonitrile, dimethyl sulfoxide and dimethylformamide to produce a complex mixture of ruthenium products.<sup>[4]</sup> Furthermore, this complex has been shown to be unstable in the presence of carbon monoxide, to react with hydrogen

gas to produce ruthenium hydrides<sup>[5–7]</sup> and with alcohols to yield carbonyl hydrides.<sup>[8,9]</sup> First generation Grubbs' alkylidenes are also known to be unstable to primary amines<sup>[4]</sup> although no decomposition products have been identified or possible explanations provided for this observation. Instability to primary amines is a significant drawback, particularly in the design of self-healing polymers in which the complex is typically exposed to primary amine curing agents.<sup>[10,11]</sup>

The functional group tolerance of second generation Grubbs' alkylidenes has not yet been evaluated as comprehensively as that of the first generation catalysts. In particular, we have not found mention of the tolerance of second generation Grubbs' complexes to primary amines in the open literature. As mentioned in a previous publication,<sup>[12]</sup> the second generation Grubbs' alkylidene appeared to remain

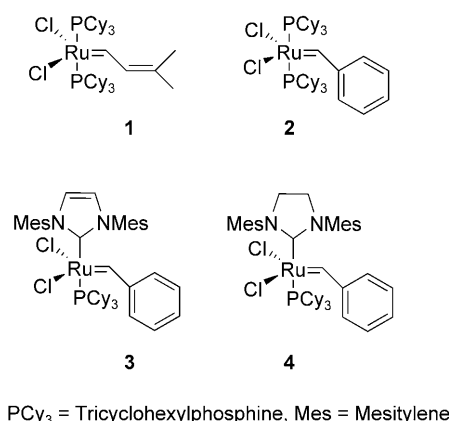
catalytically active after addition to an epoxy prepolymer containing diethylenetriamine (DETA) as the curing agent. In a comparison by *in situ*  $^1\text{H}$  NMR, the second generation Grubbs' complex formed a new carbene that remained active for up to two hours after addition of DETA, while the first generation Grubbs' complex was observed to form a new short-lived carbene complex which decomposed within 10 min of the addition of DETA. For both first and second generation Grubbs' alkylidenes, free tricyclohexylphosphine ( $\text{PCy}_3$ ) was observed in solution by  $^{31}\text{P}$  NMR after addition of DETA, suggesting the displacement of the  $\text{PCy}_3$  by the excess DETA. The  $^{31}\text{P}$  NMR data also showed that while free  $\text{PCy}_3$  was the only product observed with the second generation catalyst, multiple new phosphorus products were observed in addition to the free  $\text{PCy}_3$  after DETA was added to the first generation complex.

A similar observation was made by Ulmann and Grubbs in studying the thermal decomposition of first generation Grubbs' catalyst derivatives.<sup>[13]</sup> Specifically, an evaluation of the reaction mixture for the decomposition of the propylidene derivative,  $(\text{PCy}_3)_2\text{Cl}_2\text{Ru}=\text{CHCH}_2\text{CH}_3$  at  $55^\circ\text{C}$  by  $^{31}\text{P}$  NMR showed that while the predominant product was free  $\text{PCy}_3$ , other small unidentifiable phosphine signals appeared over the course of the catalyst decomposition. Furthermore, Ulmann and Grubbs were able to observe the quantitative formation of *trans*-3-hexene. These observations are consistent with a decomposition mechanism involving the dissociation of a phosphine followed by coupling of the two monophosphine species to yield *trans*-3-hexene and a mixture of inorganic products (Scheme 1). This bimolecular decomposition was observed in early metal-carbene systems<sup>[14,15]</sup> and is generally one of the reasons for the use of more bulky groups in the design of more stable metal-carbene systems.<sup>[4,16]</sup>

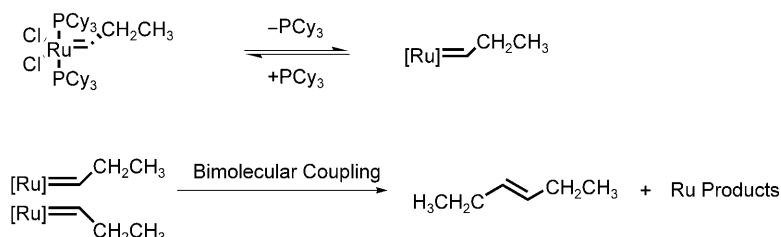
The displacement of  $\text{PCy}_3$  by DETA in both the first and second generation Grubbs' alkylidenes, and the appearance of multiple unidentifiable phosphine peaks in the  $^{31}\text{P}$  NMR spectrum of the first generation Grubbs' complex after addition of DETA, suggest that the reaction of DETA with Grubbs' alkylidenes possibly proceeds by a pathway similar to the bimolecular thermal decomposition of first generation cat-

alysts. If this hypothesis is correct, then second generation Grubbs' alkylidenes would be more stable to DETA than the first generation derivatives as the N-heterocyclic (NHC) ligand is not easily displaced by DETA. Thus, even when the  $\text{PCy}_3$  ligand is displaced by DETA, the NHC ligand remains coordinated to the metal and bulky groups on the NHC ligand sterically hinder the coupling of two ruthenium centers. Furthermore, it is possible that the strength of the coordination of DETA to ruthenium after displacement of the  $\text{PCy}_3$  prevents decomposition *via* nucleophilic attack of an otherwise "naked" complex by a dissociated phosphine to form a dinuclear ruthenium hydride complex similar to that observed by Grubbs et al. in solution at  $55^\circ\text{C}$ .<sup>[17]</sup> Addition of DETA should thus result in the formation of a new, relatively stable ruthenium-amine complex.

If an argument is to be made for bimolecular decomposition as one of the decomposition pathways responsible for the improved stability of second generation Grubbs' complexes to primary amines relative to the first generation complexes, the observations discussed above must be replicated with other primary amines and other derivatives of first and second generation Grubbs' complexes. To this end, this paper begins with a discussion of the effect of a simple primary amine (*n*-butylamine) on the catalytic activity of catalysts **1–4** (Figure 1), followed by the isolation and characterization of reaction product complexes of the



**Figure 1.** Ruthenium catalysts evaluated.



**Scheme 1.** Previously proposed<sup>[13]</sup> pathway for alkylidene decomposition.

second generation Grubbs' complex and both *n*-butylamine and DETA. The isolation of these new complexes makes a strong argument for a decomposition pathway similar to the thermal decomposition of Grubbs' alkylidenes.

## Results and Discussion

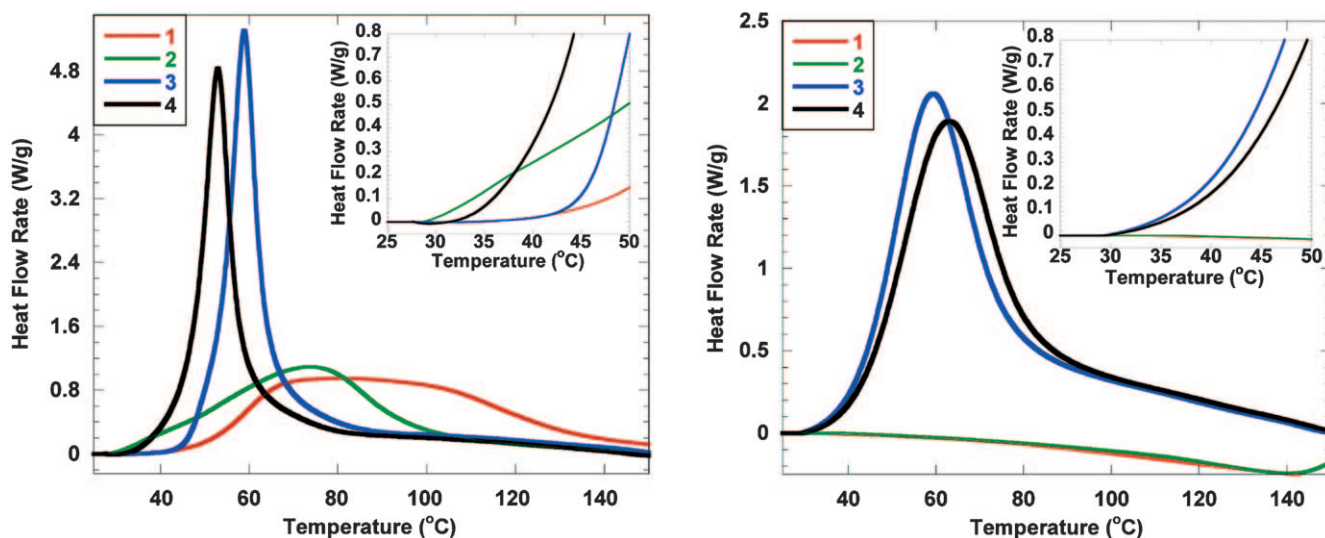
### Effect of *n*-Butylamine on Catalytic Activity

To evaluate whether second generation catalysts are more stable to primary amines due to bulky inert NHC ligands, the catalytic activities of catalysts **1–4** (catalyst loading of 5 mg/mL) were evaluated by monitoring the ring-opening metathesis polymerization (ROMP) of dicyclopentadiene (DCPD) by differential scanning calorimetry (DSC, 25–300 °C, 10 °C min<sup>−1</sup>), before and after addition of *n*-butylamine. All four complexes exhibited an ability to initiate the ROMP of DCPD prior to the addition of the amine, as exotherms associated with ROMP and consistent with the observations of Kessler et al.,<sup>[18]</sup> were observed in all DSC experiments (Figure 2, *left*).

In a separate experiment, each complex was weighed into 20-mL scintillation vials and *n*-butylamine was added to each vial. The amine was observed to dissolve the catalyst in each case, and instantaneous color changes were observed. Complexes **1** and **2**, which generally exhibit light brown and purple colors in solution, respectively, both turned dark brown, while **3** and **4**, both of which are generally brownish red before addition of butylamine were both green afterwards. The vials were immediately placed under house vacuum to remove the excess amine. After 10 min. under vacuum, the vials were removed and

kept in the fume hood until the activity of the catalyst in each vial was evaluated by DSC. The DSC experiments were identical to those performed on the neat untreated catalysts. DCPD (1 mL) was added and after vigorous stirring, a sample was injected into an aluminum crucible, which was then loaded into the DSC and the same method which was used to evaluate the untreated complexes was run. The results are shown in Figure 2 (*right*). While both first generation complexes (**1** and **2**) showed no polymerization activity, both second generation complexes (**3** and **4**) maintained their capability to initiate the ROMP of DCPD even after exposure to *n*-butylamine.

The stability of each of the four complexes to butylamine was also evaluated by <sup>1</sup>H and <sup>31</sup>P NMR spectroscopy. Consistent with previous observations made with DETA,<sup>[12]</sup> both **1** and **2** decomposed within 10 min of the addition of *n*-butylamine to a solution of the complex in dichloromethane-*d*<sub>2</sub>, while carbene resonances could be observed for otherwise identical solutions of **3** and **4** for at least up to 1 h after addition of the amine. The <sup>31</sup>P NMR spectra confirmed the displacement of PCy<sub>3</sub> by the amine for all four complexes as free PCy<sub>3</sub> ( $\delta$  = 10.9 ppm) was observed in the reaction mixture. In the case of **4**, no other phosphorus products were observed in the <sup>31</sup>P NMR spectrum, suggesting that this alkylidene might form the most stable complex with *n*-butylamine. The consistent observation of free PCy<sub>3</sub> in solution after addition of primary amines, the decomposition of first generation complexes which have a pair of PCy<sub>3</sub> ligands that can be displaced by primary amines, and the apparent stability of second generation complexes which have bulky NHC ligands that are not easily displaced by primary amines, all seem to suggest that phosphine displacement by primary amines might be

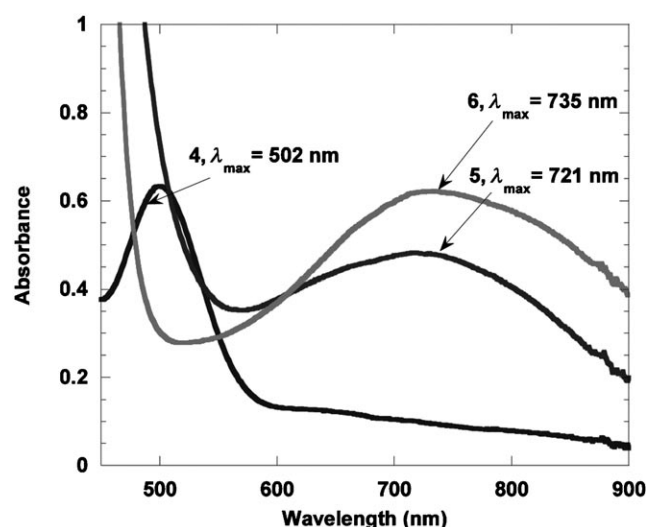


**Figure 2.** Dynamic DSC (25 °C–300 °C, 10 °C min<sup>−1</sup>) for ROMP of DCPD initiated with **1–4**; (*left*) before exposure to *n*-butylamine, and (*right*) after exposure to *n*-butylamine. The exothermic heat flow is in the direction of the positive y axis.

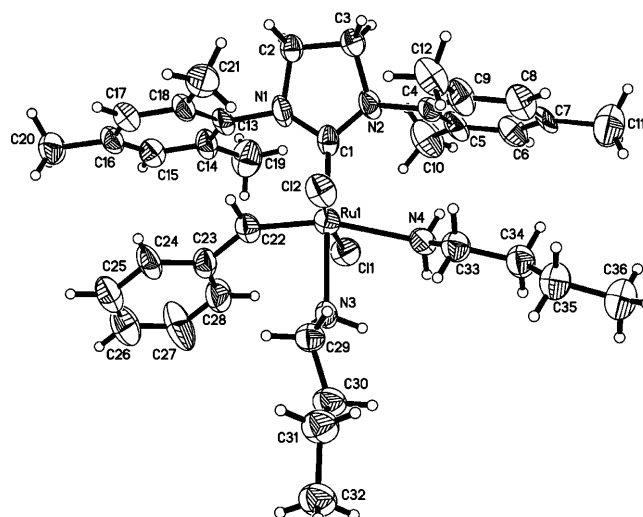
the first step in a decomposition pathway that depends on the bimolecular coupling of two less hindered ruthenium complexes. Furthermore, the improved stability of second generation Grubbs' alkylidene derivatives to primary amines relative to the first generation derivatives is consistent with observations that second generation complexes are more thermally stable than the first generation derivatives. The only possible explanation for this observation given thus far is that the bulky mesitylene groups on the NHC ligand may hinder bimolecular decomposition.<sup>[4]</sup>

### Formation of Ruthenium-Amine Complexes

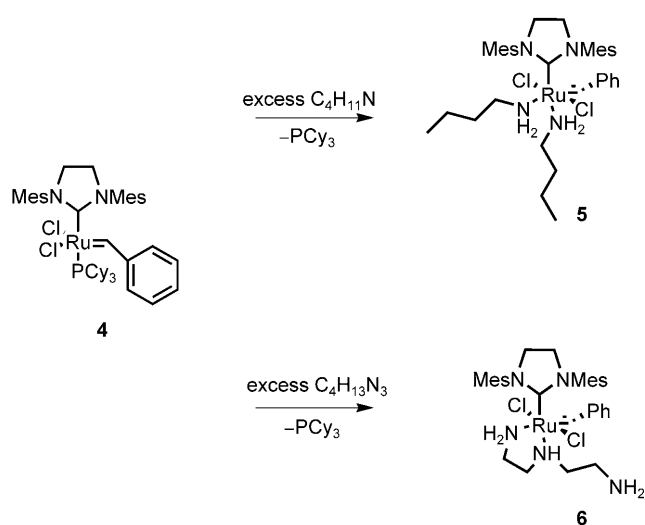
To assert that decomposition of the first generation Grubbs' complex in the presence of primary amines proceeds by a pathway identical to the thermal decomposition pathway shown in Scheme 1 would require the observation of stilbene in the reaction mixture. We have not been able to make such an observation and are unaware of any such reports from other groups. However, if second generation complexes are more stable to primary amines relative to first generation complexes due to the presence of strongly-binding bulky NHC ligands that are not displaced by primary amines, isolation of the ruthenium amine complex and evaluation of its activity could proffer indirect evidence for this decomposition pathway. To this end, two complexes were synthesized by the addition of excess *n*-butylamine or DETA to **4** (Scheme 2). These additions resulted in a color change from brown to green and corresponding 219 nm and 233 nm red shifts, respectively, of the visible metal to ligand charge transfer (MLCT) absorbance were observed by UV-vis spectroscopy (Figure 3). This obser-



**Figure 3.** UV-vis spectra showing the red-shifting of the visible MLCT absorbance of complex **4** upon addition of *n*-butylamine to form complex **5**, and DETA to form complex **6**.



**Figure 4.** ORTEP diagram of **5** with 50% probability ellipsoids.



**Scheme 2.** Synthesis of ruthenium-amine complexes.

vation is consistent with similar observations made in which the displacement of  $\text{PCy}_3$  in the second generation Grubbs' complex by pyridine<sup>[16]</sup> and bromopyridine<sup>[17]</sup> resulted in red shifting of the visible MLCT absorbance. Complexes **5** and **6** (Scheme 2) were precipitated from solution by addition of cold pentane ( $-30^\circ\text{C}$ ) and cold diethyl ether ( $-30^\circ\text{C}$ ), respectively. The resulting precipitated complexes were both green powders. While complex **5** was soluble in common solvents such as dichloromethane, benzene, THF, and toluene, complex **6** was only mildly soluble in non-polar solvents such as benzene and toluene.

The structure of **5** was determined by X-ray crystallography (Figure 4) and representative bond lengths and bond angles are reported in Table 1. Several



**Table 1.** Selected bond lengths (Å) and angles (deg) for complex **5**.

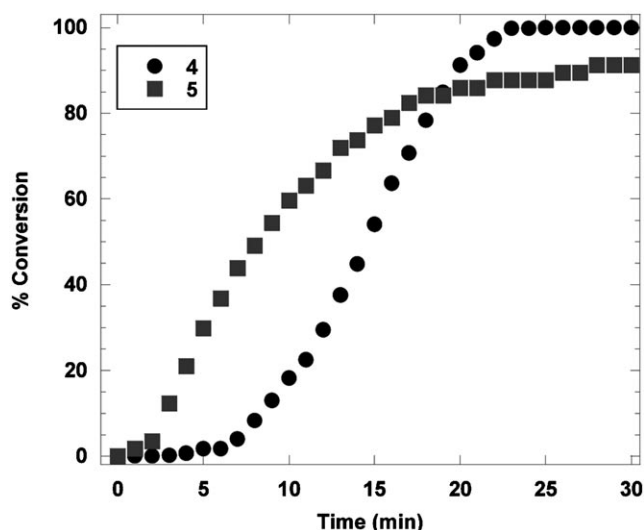
Bond Lengths (Å)			
Ru–C(1)	2.018(5)	Ru–C(22)	1.879(6)
Ru–N(3)	2.231(5)	Ru–N(4)	2.317(6)
Ru–Cl(1)	2.407(2)	Ru–Cl(2)	2.387(2)
Bond Angles (deg)			
C(1)–Ru–C(22)	95.9(3)	C(22)–Ru–N(3)	84.5(3)
C(1)–Ru–N(3)	176.1(3)	C(22)–Ru–N(4)	163.3(3)
C(1)–Ru–N(4)	100.4(3)	C(22)–Ru–Cl(1)	101.2(2)
C(1)–Ru–Cl(1)	92.4(2)	C(22)–Ru–Cl(2)	86.5(2)
C(1)–Ru–Cl(2)	89.6(2)	Cl(1)–Ru–Cl(2)	171.8(4)

structural isomers of this bis-butylamine adduct can be envisioned. However, the solid-state structure shows that, as is the case for previously reported ruthenium-pyridine adducts,<sup>[16,19]</sup> one amino group occupies the coordination sites *trans* to the benzylidene and the N-heterocyclic carbene ligand. The Ru=C(22) (benzylidene carbon) bond length of 1.879(6) Å and the Ru–C(1) (N-heterocyclic carbene) bond length of 2.018(5) Å are remarkably consistent with the corresponding bond lengths measured for the ruthenium-pyridine adduct.<sup>[16]</sup> The difference between the two Ru–N bond lengths is also consistent with observations made for the Ru-pyridine adduct and has been attributed to a larger *trans* influence exerted by the benzylidene ligand relative to the N-heterocyclic carbene ligand.

A solid state structure could not be obtained for complex **6**. The structure for complex **6** shown in Scheme 2 is proposed based on elemental analysis, ESI mass spectrometry and by analogy to **5**. The HR-ESI mass spectrum of complex **6** was within 4 ppm of the mass of the suggested structure. In addition, a comparison of the isotopic patterns of the HR-ESI mass spectrum of complex **6** and a simulated spectrum of a complex with the proposed structure, showed good agreement (see Supporting Information). The benzylidene and the N-heterocyclic carbene ligand were assigned in the NMR spectrum. However, all other proton resonances were broad, not well resolved, and could not be used to determine connectivity. The broad resonances in the <sup>1</sup>H NMR could be indicative of the presence of several diastereomers and/or fluxional binding of the secondary amine in DETA.

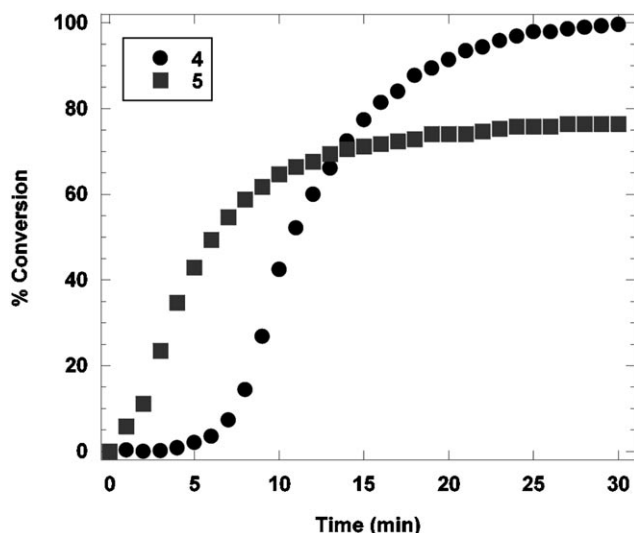
### Reactivity of Ruthenium-Amine Complexes with Selected Substrates

The reactivity of complexes **5** and **6** with representative ROMP and ring-closing metathesis (RCM) sub-

**Figure 5.** ROMP of DCPD in dichloromethane-*d*<sub>2</sub> with complexes **4** and **5** at 23 °C. [Ru] = 0.5 mM, [DCPD] = 0.25 M.

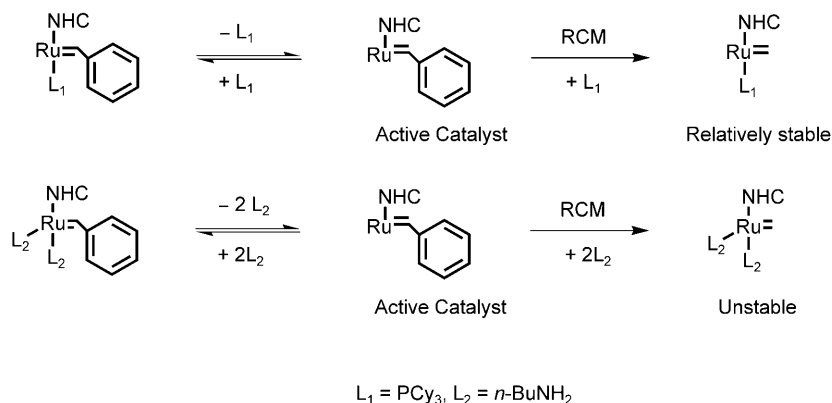
strates was evaluated. In a comparison of the ROMP of DCPD with complexes **4**, **5** and **6**, complex **5** exhibited the fastest ROMP initiation with greater than 50% conversion occurring at 23 °C within the first 10 min (Figure 5) and proceeded up to *ca.* 90% in 30 min. Less than 20% conversion was observed for **4** and no conversion was observed for **6** within the first 10 min. However, initiation of the ROMP of DCPD was observed with catalyst **4** after about 10 min and 100% conversion was achieved after about 23 min. ROMP of DCPD was not observed with complex **6** under these conditions. A similar observation was made in the ROMP of 1,5-cyclooctadiene (COD). Complex **5** exhibited superior initiation of the ROMP of COD (conversion of *ca.* 40% in the first 5 min) and a conversion of about 70% in 30 min, while initiation was significantly slower with catalyst **4** (conversion of *ca.* 2% after 5 min.), a conversion of close to 100% observed after 30 min (Figure 6).

Diethyl diallylmalonate is commonly used for the evaluation of RCM activity of new ruthenium catalysts.<sup>[19,20]</sup> Complex **5** showed minimal activity in the RCM of diethyl diallylmalonate with a conversion of only about 10% after 30 min, compared to about 90% in the case of **4** (Figure 7). Furthermore, no carbene protons were observed in the reaction mixture by <sup>1</sup>H NMR after 10 min. This observation is consistent with decomposition of a similar ruthenium-bromopyridine complex observed during the RCM of diethyl diallylmalonate.<sup>[21]</sup> Presumably, these catalysts are not well suited to RCM reactions which require the formation of relatively stable methylidenes. Steric bulk is lost around the ruthenium center in going from the benzylidene to the methylidene complex during RCM (Scheme 3). Therefore, it is likely that bimolecular decomposition (Scheme 1) occurs much more readily in

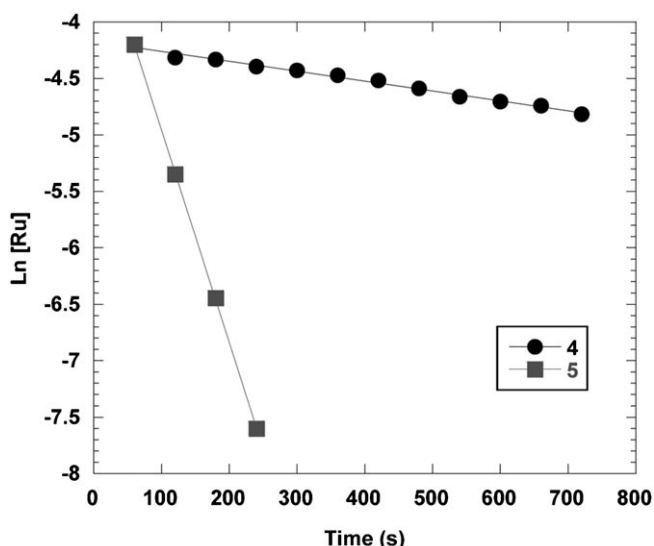


complex **5**, which contains the less sterically bulky and weaker-binding primary amine ligands relative to complex **4**, which contains the more sterically bulky and stronger binding tricyclohexylphosphine ligand. No activity was observed in solution for **6** in any of the reactions discussed above. No conversion of starting material was observed in RCM or ROMP even after 12 h at 23 °C. Increasing the reaction temperature to 60 °C did not result in conversion of starting material in either ROMP or RCM. These observations are likely due to the chelate effect of the bidentate coordination of DETA to the ruthenium in the proposed structure of complex **6**, which would significantly slow down dissociation of the amine ligands and hinder binding of the substrate.

Grubbs' and co-workers have used the rate constants of the stoichiometric reaction of ruthenium complexes with ethyl vinyl ether to quantify the initiation rates of these complexes.<sup>[16,22,23]</sup> Ethyl vinyl ether has been shown to react rapidly, quantitatively, and irreversibly with ruthenium complexes similar to those evaluated in this work.<sup>[24]</sup> Complex **5** exhibited the fastest initiation rate of  $1.88 \times 10^{-2} \text{ s}^{-1}$  at 23 °C in benzene-*d*<sub>6</sub> at an olefin/catalyst ratio of 38/1 (Figure 8). A rate constant of  $8.6 \times 10^{-4} \text{ s}^{-1}$  was observed for **4**, which is in the previously reported range of  $4.6 \times 10^{-4} \text{ s}^{-1}$ ,  $6.1 \times 10^{-4} \text{ s}^{-1}$  and  $1.0 \times 10^{-3} \text{ s}^{-1}$  measured in toluene-*d*<sub>8</sub>, dichloromethane-*d*<sub>2</sub> and THF-*d*<sub>8</sub>, respectively, at an olefin/catalyst ratio of 29/1.<sup>[23]</sup> The initiation rate constant for **5** is therefore at least an order of magnitude greater than that of **4**, and at least an order of magnitude less than the  $2 \times 10^{-1} \text{ s}^{-1}$  reported for the ruthenium bromopyridine complexes.<sup>[16]</sup> A likely explanation for the slower initiation rate observed for **5** relative to the ruthenium bromopyridine complexes is that the primary amines coordinate more strongly to the ruthenium center than pyridines and are therefore less easily displaced by an olefin. No catalytic activity was observed for complex **6** under these conditions, most likely due to a lack of



**Scheme 3.** Ring-closing metathesis (RCM) using ruthenium-phosphine and ruthenium-amine adducts.



**Figure 8.** Reaction of **4** and **5** with ethyl vinyl ether.  $[\text{Ru}] = 14 \text{ mM}$ ,  $[\text{ethyl vinyl ether}] = 529 \text{ mM}$ .  $[\text{olefin}]/[\text{complex}]$  ratio = 38/1. Reactions were performed at  $23^\circ\text{C}$  in benzene- $d_6$ .

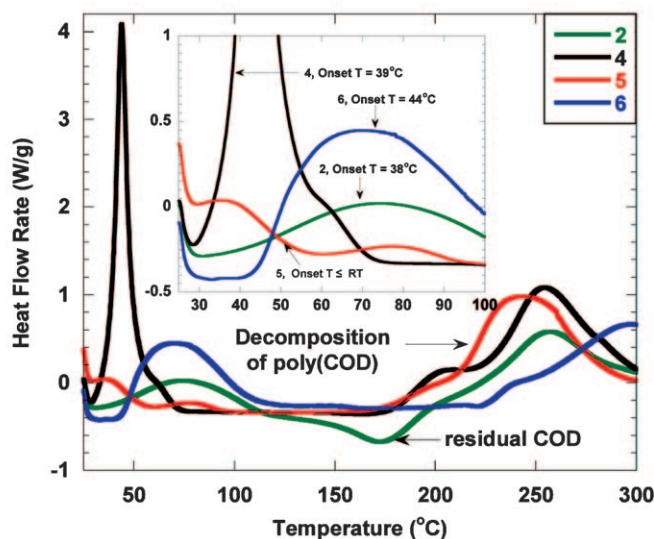
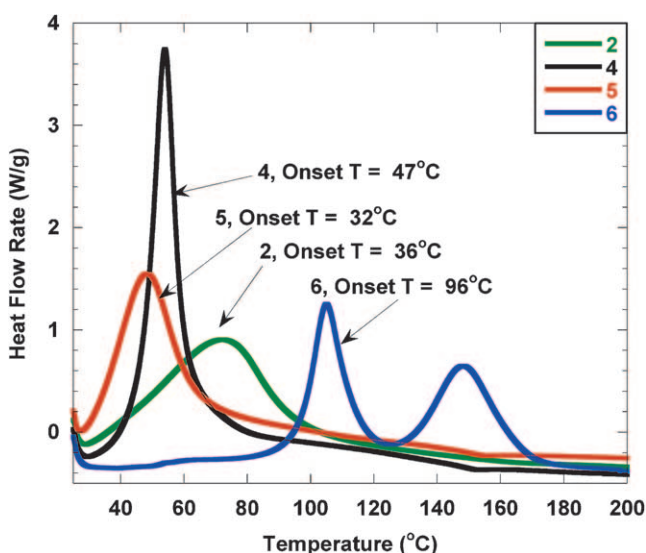
the complete dissociation of DETA required for initiation as discussed above.

The activities of complexes **5** and **6** were also compared to those of **2** and **4** in dynamic DSC evaluations of the bulk ROMP of DCPD and COD. Separate mixtures of each monomer and one of each of the four complexes were loaded into the DSC and heated from  $25$ – $300^\circ\text{C}$  at a rate of  $10^\circ\text{Cmin}^{-1}$ . For both DCPD (Figure 9, *left*) and COD (Figure 9, *right*), **5** exhibited the fastest initiation of bulk polymerization.

Bulk ROMP of COD proceeded so fast that a significant amount of conversion of the monomer had occurred in the time taken to transfer the monomer/catalyst mixture into the DSC. The polymerization exotherm observed for **5** is therefore significantly lower than would be expected. Onset temperatures of polymerization of both DCPD and COD were consistent with the initiation rate constants measured in solution. ROMP of both DCPD and COD was observed with **6**, albeit at significantly elevated temperatures. The onset temperature for ROMP of DCPD with **6** was  $96^\circ\text{C}$ , while ROMP of COD with **6** exhibited a much smaller but earlier exotherm (onset  $T = 44^\circ\text{C}$ ).

## Conclusions

Primary amines appear to displace phosphine ligands in first and second generation Grubbs' catalyst. In the case of first generation catalysts, primary amines likely displace both phosphine ligands to form transient bis-amine complexes that decompose *via* bimolecular pathways similar to those reported for thermal decomposition. In the case of second generation Grubbs' catalysts, the NHC ligand remains in place after displacement of the phosphine ligand by a primary amine. The bulky groups on the NHC ligand sterically hinder bimolecular decomposition. The result is the formation of new, relatively stable ruthenium amine complexes. *n*-Butylamine complexes were significantly more active than standard second generation catalysts both in solution and bulk polymerization conditions, while DETA complexes were only active at elevated temperatures.



**Figure 9.** Dynamic DSC ( $25^\circ\text{C}$  –  $300^\circ\text{C}$ ,  $10^\circ\text{Cmin}^{-1}$ ) evaluation of the bulk polymerizations of DCPD (*left*) and COD (*right*) using **2**, **3**, **5** and **6**. The exothermic heat flow is in the direction of the positive y axis. Since the polymerization of COD using **5** had started prior to inserting the sample into the DSC, the onset  $T$  was estimated to be less than or equal to  $RT$ .

## Experimental Section

Complexes **1** and **3** were obtained from Materia Inc. Complexes **2** and **4**, COD, diethyl diallylmalonate, mesitylene, benzene-*d*<sub>6</sub> and dichloromethane-*d*<sub>2</sub> were obtained from Sigma–Aldrich. DCPD was obtained from Acros Chemicals. DCPD and mesitylene were distilled before use, diethyl diallylmalonate was eluted through a plug of activated alumina and COD was used as received from a sure-seal reagent bottle. All reagents were degassed by three consecutive freeze-pump-thaw cycles. DSC experiments were performed on a Mettler-Toledo DSC 821<sup>e</sup> instrument connected to a computer equipped with STAR<sup>e</sup> (version 6.0) evaluation software. <sup>1</sup>H NMR kinetic experiments were performed on a Varian UNITY INOVA 500 NB instrument. All other <sup>1</sup>H NMR and <sup>31</sup>P NMR experiments were performed on a Varian UNITY 500 instrument. All air- or moisture-sensitive procedures were carried out in a glove box under an argon atmosphere.

### Effect of *n*-Butylamine on Catalysts

A 5 mg sample of each of **1–4** was weighed into 20-mL scintillation vials. DCPD (1 mL) was added to each vial and the vial was vigorously stirred using a vortex before injecting approximately 15 mg of the mixture into an aluminum pan, which was then hermetically sealed and inserted into the DSC. The sample was then heated from 25 °C to 300 °C at a rate of 10 °C min<sup>−1</sup>. In a separate experiment, approximately 20 mg of each catalyst were weighed into a separate vial. *n*-Butylamine (1 mL) was added to each catalyst and the resulting mixture was immediately put under vacuum. After 10 min, the butylamine had evaporated and DCPD was added to each vial and the mixture was vigorously stirred using a vortex before injecting a sample into a DSC pan, which was then loaded into the DSC. The sample was evaluated using the same method described above.

### Synthesis of the (IMesH<sub>2</sub>)(C<sub>4</sub>H<sub>11</sub>N)<sub>2</sub>Ru=CHPh (**5**)

Complex **4** (247 mg, 0.291 mmol) was weighed into a 20-mL vial in an argon-filled glove box. Dry dichloromethane (1 mL) was added to the vial and the mixture was vigorously shaken to dissolve the catalyst. *n*-Butylamine (3 mL, 30.4 mmol) was added to the vial. A color change from brown to green was observed instantaneously. Cold pentane (−30 °C) was added to the vial and a green precipitate was observed to begin forming almost immediately. The vial was kept at −30 °C in the glove box for 12 h. The precipitate was then filtered, washed with 4 × 5 mL of pentane and dried under vacuum to afford **5** as a green powder; yield: 127 mg (61%).

A sample of this product was used for crystal structure determination. Samples for elemental analysis were prepared by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/pentane followed by drying under vacuum. These samples analyzed as the monobutyl amine adduct (IMesH<sub>2</sub>)(C<sub>4</sub>H<sub>11</sub>N)(Cl<sub>2</sub>)Ru=CHPh probably due to loss of butylamine under vacuum.<sup>[16]</sup> <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, −30 °C): δ = 18.96 (s, 1 H, CHPh), 7.82–6.57 (multiple peaks, Ar-H, 9 H), 4.14–3.92 (m, 4 H, CH<sub>2</sub>CH<sub>2</sub>), 2.56 (s, 6 H, Mes CH<sub>3</sub>), 2.30 (s, 3 H, Mes CH<sub>3</sub>), 2.26 (m, 2 H, NH<sub>2</sub>), 2.14 (s, 3 H, Mes CH<sub>3</sub>), 2.08 (s, 6 H, Mes CH<sub>3</sub>), 1.90 (m, 2 H,

CH<sub>2</sub>), 1.09–1.05 (m, 4 H, CH<sub>2</sub>), 0.75 (m, 3 H, CH<sub>3</sub>); <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, −30 °C): δ = 305.81 (m, Ru=CHPh), 219.45 [s, Ru–C(N)<sub>2</sub>], 151.12, 151.1, 140.02, 138.89, 138.03, 137.17, 136.30, 134.08, 129.49, 129.09, 129.08, 128.26, 54.17, 53.99, 53.80, 53.63, 53.44, 51.49, 50.41, 39.58, 33.79, 20.96, 20.85, 20.82, 20.16, 19.84, 17.85, 13.44; Anal. calcd. for C<sub>32</sub>H<sub>41</sub>Cl<sub>2</sub>N<sub>3</sub>Ru: C 60.07, H 6.47, N 6.57; found: C 59.87, H 6.88, N 6.66.

### Synthesis of the (IMesH<sub>2</sub>)(C<sub>4</sub>H<sub>13</sub>N<sub>3</sub>)Ru=CHPh (**6**)

Complex **4** (166 mg, 0.195 mmol) was dissolved in 2 mL of dichloromethane. DETA (528 μL, 4.89 mmol) was added to the solution whereby the color changed in several seconds from medium brown to green. Diethyl ether (10 mL) was added and the solution became somewhat turbid. The vial was kept in −30 °C for 12 h. The solution was then decanted into a different vial and concentrated under vacuum to ca. 3 mL. During concentration a green precipitate formed. The solids were washed twice with 10 mL and two times with 20 mL of cold diethyl ether. The green solid residue was dissolved in benzene (5 mL) and lyophilized to afford pure complex **6** as light green powder; yield: 91.3 mg (70%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, −30 °C): δ = 18.57 (s, 1 H, CHPh), 9.28 (d, 1 H, NH), 7.58–6.95 (multiple peaks, 8 H, Ar-H), 6.03 (s, 1 H, Ar-H), 4.10–3.93 (m, 4 H, CH<sub>2</sub>CH<sub>2</sub>), 3.92–3.74 (m, 2 H, NH<sub>2</sub>), [2.93–2.99 (m, 1 H), 2.82–2.72 (m, 1 H), 2.59 (m, 1 H), 2.49 (m, 1 H), 2.25–2.05 (m, 2 H), 1.99 (m, 1 H), 1.86 (m, 1 H), 1.37–1.12 (m, 2 H)], (total of 10 protons, combination of CH<sub>2</sub> and NH<sub>2</sub>), 2.91 (s, 3 H, Mes CH<sub>3</sub>), 2.63 (s, 3 H, Mes-CH<sub>3</sub>), 2.48 (s, 3 H, Mes-CH<sub>3</sub>), 2.43 (s, 3 H, Mes-CH<sub>3</sub>), 2.03 (s, 3 H, Mes CH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, −30 °C): δ = 310.43 (s, Ru=CHPh), 219.47 [s, Ru–C(N)<sub>2</sub>], 154.17, 138.85, 138.63, 138.23, 137.94, 137.83, 137.68, 137.40, 130.77, 130.10, 130.05, 130.00, 129.97, 129.87, 129.36, 129.19, 128.89, 128.51, 127.81, 52.85, 51.49, 50.85, 46.62, 41.02, 37.97, 21.21, 20.93, 19.45, 19.02, 18.78, 18.12; HR-ESI-MS: *m/z* = 636.2382, calcd for C<sub>32</sub>H<sub>45</sub>ClN<sub>5</sub>Ru<sup>+</sup> (M<sup>+</sup>–Cl): 636.2407; anal. calcd. for C<sub>32</sub>H<sub>45</sub>Cl<sub>2</sub>N<sub>5</sub>Ru: C 57.22, H 6.75, N 10.43; found: C 57.29, H 6.56, N 10.24.

### RCM of Diethyl Diallylmalonate

A 5.0 mM stock solution of ruthenium catalyst was prepared by dissolving the appropriate catalyst (0.0099 mmol) in a 2.0-mL volumetric flask with the appropriate solvent. Exactly 0.75 mL of the Ru catalyst solution was added to an NMR tube which was then capped with a septum and wrapped with Teflon tape. The solution was allowed to come to thermal equilibrium inside the NMR probe for 5 min. The tube was then ejected and 25 μL of diethyl diallylmalonate (roughly 0.25 M and 50 equiv. relative to [Ru]) were added *via* syringe. Reactions were monitored by integrating the resonances associated with the terminal vinyl protons (δ = 5.87 ppm) of the substrate over time, using mesitylene as an internal standard.

### NMR Evaluation of Solution ROMP of DCPD and COD

A 0.5 mM solution of ruthenium complex was prepared by adding 0.2 mL of a 5.00 mM solution of the complex to a 2.0-mL volumetric flask and diluting to 2 mL with the appropriate solvent. Exactly 0.75 mL was added to an NMR



tube which was then capped with a septum and wrapped with Teflon tape. The solution was allowed to come to thermal equilibrium inside the NMR probe for 5 min. The tube was then ejected and 25  $\mu$ L of the appropriate ROMP monomer (roughly 0.25 M and 500 equiv. relative to [Ru]) were added *via* syringe. Reactions were monitored by integrating the resonances associated with the vinyl protons of DCPD ( $\delta$  = 6.20 ppm) and the vinyl COD ( $\delta$  = 5.77 ppm) over time, using mesitylene as an internal standard.

### Initiation Kinetics

A 15.0 mM solution of ruthenium complex was prepared by dissolving the complex (0.015 mmol) in a 1.0-mL volumetric flask, diluting to 1 mL with the appropriate solvent. Exactly 0.75 mL of the Ru solution was added to an NMR tube which was then capped with a septum and wrapped with Teflon tape. The solution was allowed to come to thermal equilibrium inside the NMR probe for 5 min. The tube was then ejected and 40  $\mu$ L of ethyl vinyl ether (roughly 0.529 M and 38 equiv. relative to [Ru]) were added *via* syringe. Reactions were monitored by integrating the resonances associated with the carbene protons (around  $\delta$  = 19.0 ppm) over time, using mesitylene as an internal standard.

### DSC Evaluation of Bulk ROMP of DCPD and COD

Catalysts **2**, **4–6** were weighed into separate 20-mL vials and 1 mL of the appropriate monomer was added such that each resulting solution contained 0.05 mol% of catalyst. Approximately 15 mg of each solution was injected into an aluminum pan, which was then hermetically sealed and inserted into the DSC. Each sample was then heated from 25 °C to 300 °C at a rate of 10 °C min<sup>-1</sup>. A total of 30–45 s elapsed from the time the monomer and the catalyst were mixed to the start of the DSC experiments. Onset temperatures were calculated using the STAR<sup>e</sup> (version 6.0) data evaluation software, which calculates onset T as the point of intersection between the baseline before the thermal transition and the inflectional tangent of the transition.

### Crystallographic Data

CCDC 719519 contains the supplementary crystallographic data (excluding structure factors) for complex **5** reported in this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data\_request/cif or on CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax.: (internat.)] + 44 1223/336–033; e-mail: deposit@ccdc.cam.ac.uk].

### Supporting Information

<sup>1</sup>H NMR and <sup>31</sup>P NMR spectra for complexes **1–4** before and after addition of butylamine, HR-ESI-MS for complex **6**, and a comparison of the isotopic pattern of HR-ESI-MS for complex **6** with a theoretical simulated spectrum with for the same complex are available as Supporting Information.

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