4528 *Organometallics* **2005,** *24,* 4528−4542

A Convenient System for Improving the Efficiency of First-Generation Ruthenium Olefin Metathesis Catalysts

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Received May 13, 2005

The performance of certain olefin metathesis reactions catalyzed by Grubbs catalysts has been enhanced by the simple addition of phenol. Addition of phenol to self-metathesis reactions catalyzed by **1** produced very small quantities of unwanted byproducts and allowed for room-temperature metathesis at high substrate:catalyst loadings. The efficiency of cross-metathesis reactions between methyl acrylate and 1-decene catalyzed by **2** was also significantly increased by addition of *p*-cresol to the reaction mixture. Mechanistic studies, including NMR spectroscopy and DFT calculations, established that phenol is playing a number of positive roles in the active metathesis cycle, including altering the relative rates of phosphine loss and rebinding, activating the carbene carbon for reaction with olefinic substrate, and hemilabile stabilization of the key 14-electron intermediate species.

Introduction

Since the development of well-defined metal alkylidene complexes, the opportunities for employing olefin metathesis have grown exponentially, to the extent that it is now firmly established as a powerful tool in organic and materials chemistry.[1] In particular, Grubbs' ruthenium catalysts $[Cl_2(PCy_3)_2Ru{=}CHPh]$[2] (**1**) and $[Cl_2(H_2\text{-}IMes)(PCy_3)Ru{=}CHPh]$[3] (**2**) have been used extensively for ring-closing metathesis (RCM), cross-metathesis (CM), and ring-opening polymerization (ROMP) reactions, and their utility is often demonstrated in the synthetic community by incorporation of a metathesis reaction in multistep synthesis of natural products.[4] In this context, self-metathesis (SM) of linear unfunctionalized α-olefins is seemingly one of the simplest possible metathesis reactions; however catalysts **1** and **2** are generally incompatible with these substrates at low catalyst loadings.[5] For SM of linear α-olefins, complex **1** generally displays a short lifetime and is intolerant to reaction temperatures above 50 °C. While the N-heterocyclic carbene (NHC) complex **2** displays significantly enhanced activity and thermal stability relative to **1**, overall selectivity is often compromised by competing olefin isomerization, which can lead to the formation of undesirable secondary metathesis products (SMPs).[6] Within these laboratories DFT calculations have recently predicted that NHC-Ru-catalyzed olefin isomerization, arising from substrate-induced decomposition reaction of second-generation metathesis catalysts, should

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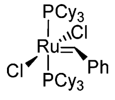
10.1021/om0503848 CCC: \$30.25

be more facile than first-generation catalysts.[7] Consequently, we have focused our efforts toward eliminating olefin isomerization as a competing and complicating process in ruthenium-based olefin metathesis by developing improved first-generation catalyst systems for SM and ethenolysis reactions.[5]

In the industrial context, olefin feedstocks derived from primary processes such as Fischer–Tropsch[8] conversion of synthesis gas often contain numerous impurities that may have the capacity to either retard or completely deactivate various homogeneous catalytic reactions. In this regard, we undertook a study to investigate the effect small quantities of additives have on the performance of catalysts **1** and **2** for the SM of simple linear α-olefins. During this study it was surprisingly found that the addition of relatively low concentrations of phenol had a beneficial effect on the catalyst performance of **1** in SM, instead of the poisoning or retarding effect that was expected. Herein we report a systematic evaluation of the effects of phenol addition on the kinetics and mechanism of olefin metathesis reactions catalyzed by **1**. The influence of phenol addition on the rate of phosphine exchange and kinetics of initiation and propagation in olefin metathesis has been established by NMR spectroscopic techniques and DFT computational studies. From the data a mechanism for olefin metathesis with added phenol is proposed. The implications of these studies on catalyst lifetime, a key issue when performing metathesis in an industrial context,[5] are also discussed.



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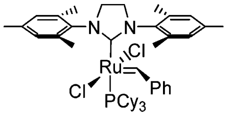

2

Results

Phenol Addition. As depicted in Figure 1, addition of phenol to 1-octene (catalyst **1**:phenol:1-octene = 1:500:9000) solutions containing catalyst **1** results in rapid initial reaction rates, such that conversions achieved within the first 30 min of the reaction are comparable to those obtained with the second-generation catalyst **2**. In addition, the combination of complex **1** with phenol shows excellent selectivity compared with **2**; only 2% secondary metathesis products (SMPs) were obtained after 4 h with complex **1**/phenol, while 37% SMPs were obtained with **2**. Under the standard reaction conditions employed for the current study (1-octene/Ru, 9000:1, neat, 50 °C), 500 equiv of phenol (phenol/Ru, 500:1) provided the optimal enhancement effect (87% conversion after 1 h), although as little as 200 equiv of phenol is capable of providing beneficial catalyst performance (61% conversion after 1 h).

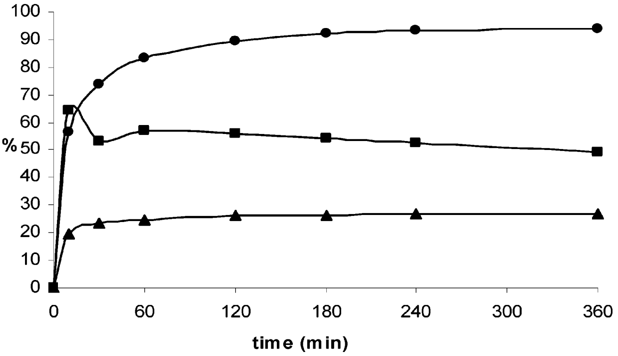

Figure 1. Self-metathesis of 1-octene to 7-tetradecene at 50 °C with catalysts **1**, **2**, and **1**/phenol (substrate/Ru 9000: 1, neat). The progress of the reaction was monitored by GC. ● complex **1** + phenol (500 equiv); ▲ complex **1**; ■ complex **2**. x = conversion.

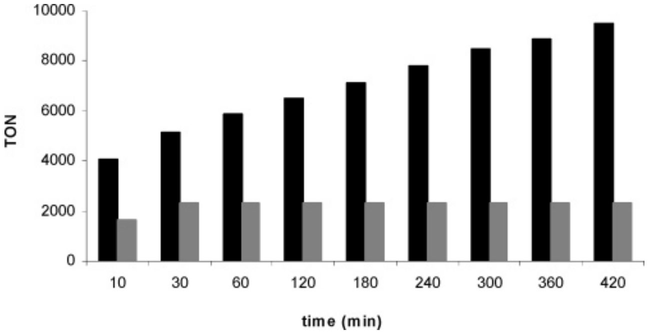

Figure 2. Turnover number (TON) of 7-tetradecene formed from the self-metathesis of 1-octene at 50 °C using catalyst **1** and phenol (substrate/Ru 9000, neat) with 9000 additional equivalents of 1-octene added after 3 h. The progress of the reaction was monitored by GC. (black bars) complex **1** + phenol (500 equiv); (gray bars) complex **1**.

The SM reaction of simple α-olefin substrates with catalyst **1** and phenol is characterized by dramatically enhanced catalyst lifetimes: after 3 h additional quantities of α-olefin are consumed when phenol is present, in contrast to the reaction in the absence of phenol, where catalyst **1** is deactivated after only 30 min. Thus, as depicted in Figure 2, addition of 9000 additional equivalents of 1-octene after 3 h to a 1-octene SM reaction (S/C 9000, 50 °C, neat) catalyzed by catalyst **1**/phenol resulted in a greater overall turnover number (TON). In contrast, when additional amounts of 1-octene were added after 3 h to an equivalent SM reaction catalyzed only by **1**, no additional turnovers were observed. In this context a meaningful method for measuring the lifetime of catalyst **1** in the presence of phenol is by monitoring the *trans*/*cis* ratio of internal olefins formed during SM experiments. Thus, as depicted in Figure 3, using only catalyst **1**, the *trans*/*cis* ratio of 7-tetradecene does not significantly change over the duration of the reaction, but combining catalyst **1** with phenol (500 equiv) gives rise to a significant enrichment to *trans*-7-tetradecene over time. These results can be rationalized in terms of rapid decomposition of catalyst **1** under the reaction conditions, preventing conversion of the sterically more accessible *cis*-7-tetradecene to the *trans*-product. However, with the

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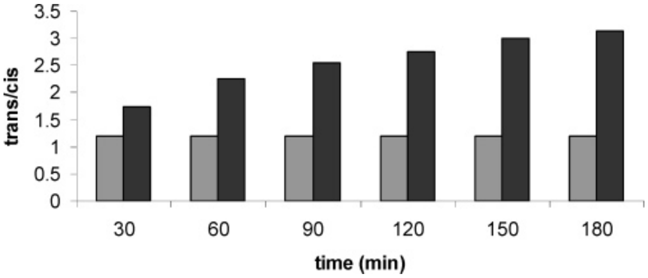


Figure 3. *trans*/*cis* ratio of 7-tetradecene formed from the self-metathesis of 1-octene at 50 °C with catalyst **1** and phenol (substrate/Ru 9000, neat). The progress of the reaction was monitored by GC. (black bars) complex **1** + phenol (500 equiv); (gray bars) complex **1**.

addition of phenol, the lifetime of **1** is significantly extended, which allows for continued reprocessing of *cis*-7-tetradecene.[9]

The reaction can conveniently be performed at room temperature and at substrate/catalyst molar ratios (S/C) up to 100 000. This reaction is also capable of significantly enhancing the efficiency of the in-situ method for generation of an active metathesis catalyst developed by Nubel and Hunt.[10] Thus, in-situ generation of the active catalyst by addition of $RuCl_3$, PCy_3, and 1,4-butynediol diacetate (BDD) to 1-octene in the presence of an intial hydrogen sparge (S/C 9000, 500 equiv phenol/Ru, 60 °C) afforded 68% conversion to 7-tetradecene after 3 h. Without phenol the identical reaction produced only 20% 7-tetradecene.

Ethenolysis of 2-octene (80% *cis*) with added phenol (2-octene:Ru:phenol ratio = 9000:1:500) gives better conversions, extended catalyst lifetime, and less isomerization compared to the identical reaction in which no phenol is added. For example, ethenolysis of 2-octene at 30 °C (15 bar ethylene) with 500 equiv of *ortho*-cresol gave 64% conversion to 1-heptene in 90% selectivity after 5 h. In contrast, in the absence of *ortho*-cresol, only 40% conversion and 80% selectivity to 1-heptene was obtained.

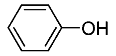
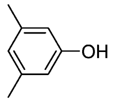
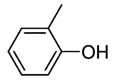
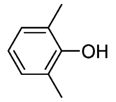
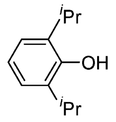
This system is also capable of withstanding numerous impurities present within an α-olefin feedstock. For example, SM of 1-octene at 50 °C using catalyst **1** containing 100 equiv of 2-hexanone provided only 15% 7-tetradecene along with 9% 2-octene after 3 h. The identical reaction with 500 equiv of phenol (1-octene:Ru:2-hexanone:phenol molar ratio = 9000:1:100:500) produced 87% 7-tetradecene, without any detectable amounts of 2-octene being formed. α-Olefin feedstocks that have not been pretreated to remove peroxides by percolation through alumina are generally not compatible with **1** under low catalyst concentrations; however under standard conditions phenol addition gives rise to conversions of up to 70% after 4 h with untreated 1-octene. In addition, the combination of phenol with catalyst **1** allows for greater functional group tolerance relative to catalyst **1** alone. Treatment of 1-octene with acetone (100 equiv/Ru), ethanol (125 equiv/Ru), cycloheptatriene (70 equiv/Ru), cyclooctadiene (60 equiv/Ru), 1-hexanol (60 equiv/Ru), 2-hexanone (60 equiv/Ru), hexenal (60 equiv/Ru), and 3-hexyne (70 equiv/Ru) produced a feedstock that is generally incompatible with catalyst **1** (6% conversion after 3 h). However, using a combination of catalyst **1**/phenol, 33% conversion was obtained with the same feedstock after 3 h.

Table 1. Self-Metathesis of 1-Octene via Catalyst 1/Substituted Phenols

entry[a]	phenol type[b]	phenol pK_a[11]	conv (%)[c]
1	–	–	26
2	4-Cl-phenol	9.42	58
3	4-I-phenol	9.33	71
4	4-F-phenol	9.89	86
5	4-H-phenol	9.99	87
6	4-Me-phenol	10.28	91

[a] Catalyst **1** and phenol (substrate/Ru 9000, neat). [b] 500 equiv/Ru, 50 °C. [c] Determined by GC after 3 h.

Table 2. Self-Metathesis of 1-Octene via Catalyst 1/Substituted Phenols

Entry[a]	**Phenol Type**[b]	**Conv. (%)**[c]
1	-	26
2		87
3		81
4		79
5		74
6		67

[a] Catalyst **1** and phenol (substrate/Ru 9000, neat). [b] 500 equiv/Ru, 50 °C. [c] Determined by GC after 3 h.

The observation that catalyst **1**/phenol provides a more reactive system for the SM of α-olefins prompted efforts to assess the effect of substituted phenols on the formation of 7-tetradecene in 1-octene metathesis, the results of which are summarized in Tables 1 and 2. These results suggest that the combination of catalyst **1** with *less* acidic phenols, such as cresol (entry 6, Table 1), generally gives rise to superior catalyst performance than when more acidic phenols, such as 4-chlorophenol (entry 2, Table 1), are used. As indicated in Table 2, for the SM of 1-octene, the combination of more sterically encumbered phenols, such as 2,6-di-isopropylphenol (entry 6, Table 2), with catalyst **1** gives inferior catalyst performance relative to less encumbered phenols (entry 2, Table 2). Other phenols, including naphthols, biphenols, hydroquinones, catechols, and 2,6-di-*tert*-butyl-4-methylphenol (BHT), were all found to give significantly improved reaction rates and catalyst lifetime when combined with catalyst **1**. Other additives, including anilines, thiophenol, anisoles, cyclohexanols, pyridines, benzoquinones, TEMPO, simple alcohols, and quaternary amine salts all failed to give any significant rate enhancement when added to catalyst **1**.

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(9) A similar enrichment of *trans*-tetradecene is observed for the cyclohexylphoban catalyst **5** relative to **1**: unpublished results.

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Table 3. Self-Metathesis of 1-Octene via Catalyst 1/Acidic Alcohols

entry[a]	additive[b]	additive pK_a[11]	conv. (%)[c]
1	–	–	26
2	CF_3CH_2OH	12.3	45
3	$(CF_3)_3COH$	9.52	70
4	$(CF_3)_2CHCOH$	9.3	78
5	phenol	9.99	87

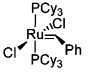
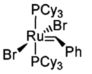
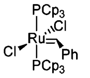
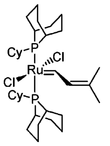
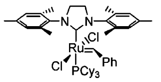
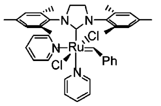
[a] Catalyst **1** and phenol (substrate/Ru 9000, neat). [b] 500 equiv/Ru, 50 °C. [c] Determined by GC after 3 h.

The observation that catalyst **1**/phenol is more reactive for the SM of α-olefins suggested that acidic alcohols with a pK_a similar to phenol[11] (pK_a = 9.0−10.5) may be capable of producing a similar rate-enhancing effect. In this regard, 1-octene SM reactions were performed with catalyst **1** and a number of acidic alcohols (500 equiv/Ru), and the results are shown in Table 3. Interestingly, with catalyst **1**, the SM of 1-octene was accelerated by the addition of trifluoroethanol (entry 2, Table 3), perfluoro-*tert*-butyl alcohol (entry 3, Table 3), and hexafluoro-2-propanol (entry 4, Table 3), although end conversions were not as high as those obtained when phenol was used as additive (entry 5, Table 3). On the basis of these data, it was apparent that the acidity of the promoting additive is essential for increasing catalyst performance. Although acidic alcohols do provide an alternative to phenols for enhancing the SM of α-olefins, their relative volatility and toxicity prevents their use in practical large-scale applications.

In an attempt to probe the general applicability of phenol addition to SM reactions of α-olefins, a number of different Ru alkylidene metathesis catalysts were tested, and the results are outlined in Table 4. Using **3**, the SM of 1-octene is enhanced with added phenol (entry 2), although overall conversions are lower than those achieved with the dichloride analogue **1** (entry 1). These results are consistent with the observation by Grubbs and co-workers that although initiation rates are generally faster for Br-containing metathesis catalysts, overall conversions are poorer than those obtained with Cl-containing catalysts.[12] The bis-cyclopentylphosphine complex **4** appears to be a very poor catalyst for α-olefin SM, giving only 2% conversion after 3 h (entry 3). However, addition of 500 equiv of phenol/Ru gives rise to a 10-fold increase in conversion relative to the experiment where no phenol is added (24% after 3 h, entry 3). Perhaps surprisingly, no significant improvement in catalyst activity is observed for α-olefin SM when phenol is added to complexes **5** and **2** (entries 5 and 6, Table 5). However, it is worthy of note that in the case of complexes **5** and **2** it was observed that phenol addition significantly slows initiation of both **5** and **2** (vide infra).

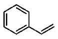
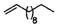
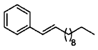
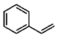
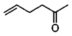
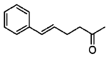
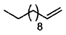
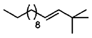
As mentioned above, the addition of phenol to SM reaction mixtures containing the second-generation catalyst **2** results in lower activity relative to the experiment where no phenol is added. Despite this, added phenol can have a positive effect on selectivity of SM reactions using catalyst **2**. For example, the SM of 1-octene (1-octene/Ru 40 000, 50 °C) produced 30% unwanted secondary SMPs after 6 h. However, for the identical reaction where 500 equiv of phenol was added, only 5% SMPs were formed after 6 h. Perhaps surprisingly, added phenol has the capacity to significantly improve the performance of certain CM reactions catalyzed by **2**. For example, with 0.1 mol % of catalyst **2**, the CM of methyl acrylate with untreated Aldrich 1-decene was achieved in 100% conversion after only 15 min with added *p*-cresol (500 equiv), whereas only 28% conversion was obtained in the absence of *p*-cresol (Figure 4).

Table 4. Self-Metathesis of 1-Octene via Ru Alkylidene Complexes and Phenol

Entry[a]	Catalyst[b]		Conv. (%)[c] in Absence of Phenol	Conv. (%)[c] in Presence of Phenol
1		**1**	26	87
2		**3**[2d]	15	52
3		**4**	2	24
4		**5**[5]	59	44
5		**2**	55	50
6		**6**[13]	14	4

[a] Catalyst **1** and phenol (substrate/Ru 9000, neat). [b] 500 equiv/Ru, 50 °C. [c] Determined by GC after 3 h.

Table 5. Cross-Metathesis Reactions via Ru−Alkylidene Catalysts

Entry	Substrate[a]	Cross-Partner[a]	Product	Cat (Mol%)	Conv (%)[b]
1[c]				**1** (0.015) **1**/Phenol[d] (0.015)	49 76
2[c]				**1** (0.015) **1**/Phenol[d] (0.015)	23 65
3[e]				**1** (1.0) **1**/Phenol[d] (1.0)	- 57

[a] Purified by passing through alumina before use. [b] Determined by GC. [c] Substrate:cross-partner = 3:1, 50 °C, 4 h. [d] 1000 equiv of phenol. [e] Excess cross-partner, 40 °C, 8 h.

As depicted in Table 5, added phenol can also enhance CM reactions catalyzed by **1**, although the system shows no appreciable activity toward traditionally inactive substrates such as acrylates or 1,1-disubstituted olefins. The combination of catalyst **1** and phenol shows good activity for the RCM of diethyldiallyl malonate (Figure 5), although the high dilution required for efficient RCM reactions appears to limit the effectiveness of phenol in this instance.

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[11] Mihailović, M. L; Čeković, Z. In *The Chemistry of the Hydroxyl Group*; Patai, S., Ed.; Wiley-Interscience: New York, 1971; Vol. 1, p 506.

[12] Sanford, M. S.; Love, J. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 6543−6554.

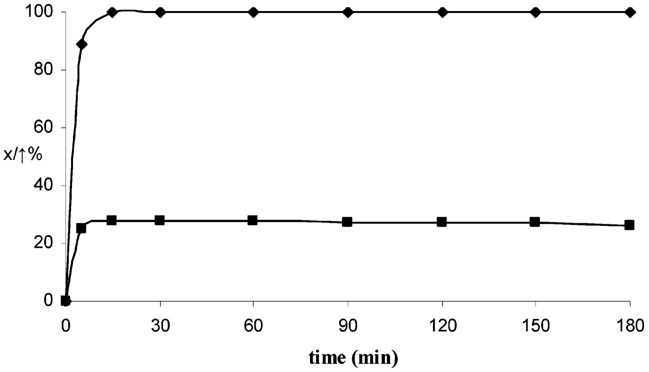


Figure 4. Cross-metathesis (CM) of methyl acrylate with 1-decene at 50 °C with catalysts **2** and **2**/*p*-cresol (methyl acrylate/1-decene/Ru 2000:1000:1, neat). The progress of the reaction was monitored by GC. ● complex **2** + *p*-cresol (500 equiv); ■ complex **2**. x = conversion.

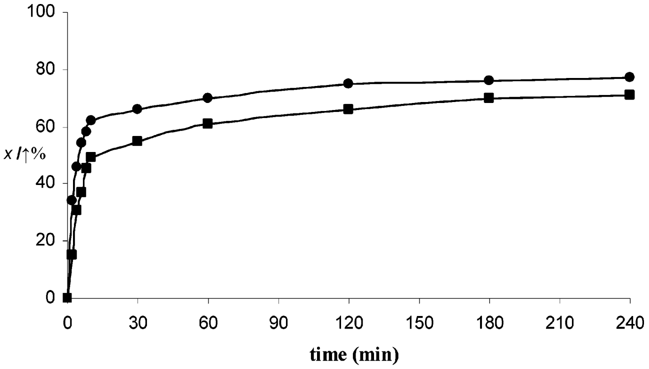


Figure 5. RCM of diethyl diallylmalonate at 50 °C with catalysts **1** and **1**/phenol (substrate/Ru 3440:1, [Ru] = 0.20 mM in toluene). The progress of the reaction was monitored by GC. ● complex **1**/phenol (1500 equiv); ■ complex **1**. x = conversion.

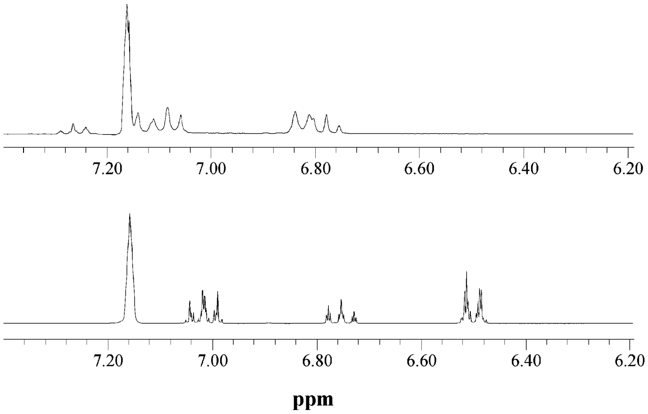


Figure 6. ^{1}H NMR of (a, lower spectrum) phenol in benzene-d_6; (b, upper spectrum) complex **1** and phenol (1:2) in benzene-d_6.

Table 6. Rate Constants for Initiation and Phosphine Exchange[13,14]

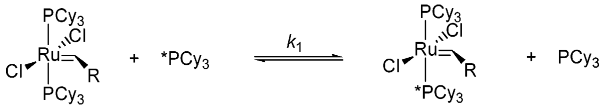
entry	phenol	initiation rate constant k_{init} (s^{-1})^a	exchange rate[15,16] constant k_B (s^{-1})^b
1	no phenol	0.35	–
2	BHT	0.30	0.29
3	2,6-dimethylphenol	0.25	–
4	phenol	0.09	0.19
5	4-chlorophenol	0.03	0.14

[a] Reactions were referenced using a phosphoric acid/D$_2$O capillary, [Ru] = 1 equiv, [phenol] = 50 equiv, and [1-octene] (2 mL), phosphoric acid/D$_2$O, 15 °C. [b] Reactions were carried out in toluene-d_8, [Ru] = 1 equiv, [phenol] = 50 equiv, and [PCy$_3$] = 1.5 equiv, 50 °C.

NMR Spectroscopy. Initial NMR investigations of catalyst **1** and phenol were focused on observing direct PhO–H··Cl–Ru interactions by ^{31}P NMR. When a standard stock solution of phenol in benzene-d_6 was transferred to an NMR tube containing complex **1**, such that the ratio of phenol:complex **1** was 2:1, no significant difference in chemical shift was observed in the ^{31}P NMR (δ = 37.6 ppm, complex **1**, δ = 37.8 ppm, complex **1**/phenol). However, when the same sample was measured by ^{1}H NMR spectroscopy (Figure 6), a significant shift in the resonances of the phenol protons were observed. Thus, the *ortho*-protons present on the phenol ring (δ = 6.5 ppm, benzene-d_6) were shifted downfield to δ = 6.83 ppm upon interaction with complex **1**, while the magnitude of the downfield shift observed for the *meta*-protons and *para*-proton was significantly smaller.

Previously it has been shown to be difficult to investigate ligand displacement of Ru-alkylidene complexes directly in solution, because the putative Ru-olefin adduct cannot be isolated.[12] As a result, degenerate exchange of free and bound phosphine has been identified as the most reliable method for measuring phosphine/ligand substitution.[12] We undertook a study to compare initiation kinetics of **1** with added phenol by measuring the rate of disappearance of starting complex **1**/phenol in the presence of substrate and by degenerate ^{31}P NMR magnetization transfer experiments. Initiation kinetics were measured by dissolving the desired phenol (50 equiv) in octene (2 mL), and complex **1** (1 equiv) was added to the octene/phenol solution with vigorous stirring. Approximately 1 mL of this solution was transferred to a degassed NMR tube containing a phosphoric acid/D$_2$O capillary. The NMR tube was transferred to a spectrometer (internal temperature 15 °C), and ^{31}P NMR spectra were recorded at 2 min intervals. Using the phosphoric acid capillary as an internal standard, the relative mole fraction of complex **1** was measured against time, and the initiation rate constant extrapolated. As summarized in Table 6, the initiation rate constants at 15 °C for ruthenium complex **1** with different substituted phenols surprisingly ranged over 1 order of magnitude and show that phenol addition has, perhaps surprisingly, a significant effect on phosphine loss. The most striking effect in the series involves 4-chlorophenol (entry 5, Table 6), which displays an initiation rate constant 13.5 times slower than when no phenol is added (entry 1, Table 6). These results suggest that phosphine loss in catalyst **1** is very sensitive to the electronic nature of the substituents on the phenol and the corresponding pK_a of the phenolic proton. The large difference in initiation rate constantswhen phenol is present (entry 4, Table 6) is notable, because catalyst **1**/phenol exhibits much higher olefin metathesis activity than **1** alone (entry 1, Table 6), despite initiating about 4 times slower. Adding steric bulk to the 2,6-position of phenol has the effect of increasing the initiation rate constant to the extent that catalyst **1**/BHT displays an initiation rate constant similar to that where no phenol is added (entry 2, Table 6). When a similar experiment was repeated with the

Scheme 1



second-generation catalyst **2**, catalyst initiation appeared to be severely slowed at room temperature. For example, catalyst **2** (20 mg, 0.0235 mmol) was dissolved in 1 mL of C_6D_6 and 1-octene (1 mL, 6.38 mmol) was added to this solution, and the ^{31}P NMR spectra were recorded at regular intervals at room temperature. After 5 min the corresponding heptylidene had rapidly formed; however when the same experiment was repeated in the presence of 50 equiv of phenol, after 90 min the only species observed was the starting benzylidene complex **2**.

In an effort to reinforce the conclusions drawn from the initiation kinetic studies (above), and more accurately measure k_1 (Scheme 1),[12] ^{31}P NMR magnetization transfer experiments were carried out with catalyst **1**, the results of which are summarized in Table 6. Thus, using a selnogp.3 pulse sequence, phosphine exchange experiments were carried out at 50 °C in toluene-d_8 and with 1.5 equiv of PCy_3 and 50 equiv of phenol. The time-dependent magnetization data were analyzed, and the rate constants (k_1) for the exchange between bound and free phosphine were obtained (Scheme 1). These experiments confirm that phosphine dissociation is significantly affected by the type of phenol present in the solution and parallel those obtained from the initiation kinetic studies. For example, catalyst **1**/BHT (entry 2, Table 6) shows the fastest rate of exchange between free and bound phosphine, while catalyst **1**/4-chlorophenol (entry 2, Table 6) showed the slowest rate of exchange. In the present study, ^{31}P NMR magnetization transfer experiments also showed that the exchange rate constant (k_1) was dependent on the concentration of phenol present in solution. For example, catalyst **1**/BHT (17 equiv/Ru) displayed a phosphine exchange rate of 0.61 s^{-1}, but a more concentrated BHT solution (60 equiv/Ru) displayed a phosphine exchange rate of 0.29 s^{-1}.

In an effort to investigate possible interactions between liberated PCy_3 and phenol, the chemical shift of PCy_3 in the presence of various phenols was investigated. ^{31}P NMR spectroscopy showed that while PCy_3 has a chemical shift in toluene-d_8 of $\delta = 11.0$ ppm, addition of 50 equiv of 4-chlorophenol resulted in a downfield shift to approximately $\delta = 30.0$ ppm. However, in the presence of only 10 equiv of 4-chlorophenol the aforementioned downfield shift was not observed. This effect was also observed for other phenols and implies that under high concentrations phenol may be capable of "sequestering" free phosphine so as to form species of the type $(PhOH)_nPCy_3$. As a consequence, PCy_3 recoordination to catalyst **1** could be slowed (vide infra), which is evidenced experimentally by rapid initial reaction rates, allowing for room-temperature SM of α-olefins (Table 1).

One important implication of the presented ^{1}H and ^{31}P NMR data is that it does not account for the significant extension in catalyst lifetime observed when phenol is combined with catalyst **1**. Thus, it was clear that phenol must play an additional role in stabilizing the active metathesis catalyst during the catalytic cycle. Although ^{1}H and ^{31}P NMR studies showed that phenol does not significantly retard the thermal decomposition of catalyst **1** in the absence of substrate, dramatic improvements in lifetime were observed by ^{31}P NMR in the *presence* of substrate. Thus, the ethenolysis of 2-octene (80% *cis*) using **1** was monitored in a high-pressure NMR cell (15 bar ethylene, 30 °C) by ^{31}P NMR. The results in the presence and absence of phenol are shown in Figures 7 and 8, respectively.

As depicted in Figure 7, in the absence of phenol after 5 min the primary species observed were the propagating methylidene ($\delta = 44.0$ ppm), ethylidene ($\delta = 36.0$ ppm), and hexylidene ($\delta = 36.5$ ppm). Within 8 h, the methylidene and alkylidene resonances had disappeared and were replaced by a major decomposition species observed as a broad singlet at about 38.0 ppm, as well as numerous other small resonances. The addition of phenol (Figure 8) totally inhibits the formation of the resonances corresponding to deactivation products of the propagating methylidene and alkylidenes ($\delta = 38.0$, 40.5, and 41.0 ppm), and after 8 h, the predominant species is the methylidene at $\delta = 44.0$ ppm. These results illustrate the dramatic impact phenol has on the lifetime of catalyst **1** for various SM and ethenolysis reactions.[17]

UV−Visible Specroscopy. In an effort to further delineate the interaction of phenol with ruthenium-alkylidene complexes, the electronic spectra of benzylidene **1** in the presence of various substituted phenols were measured. As depicted in Figure 9, the electronic spectrum of complex **1** in toluene shows a long-wavelength absorption at $\lambda_{max} = 527.7$ nm (spectrum C). This relatively weak band, which is likely due to the metal to ligand charge transfer (MLCT) into the π^* orbital of the ruthenium−carbon bond,[18−20] was found to provide a useful diagnostic handle for determining the interaction of phenol with catalyst **1** in toluene solution. Although metal to carbene (π^*) absorptions are in principle solvent dependent,[20] the magnitude of the solvent shift observed is dependent on the magnitude of the delocalization of the donor and acceptor orbitals.[18] In this instance, the spectrum of benzylidene **1** remained essentially unchanged in other solvents.

When various substituted phenols were mixed with complex **1**, the metal → π^* (carbene) MLCT transition was shifted to shorter wavelengths by up to 5 nm (Figure 9). For example, when catalyst **1** was mixed with

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[13] Sanford, M. S.; Love, J. A.; Grubbs, R. H. *Organometallics* **2001**, *20*, 5314−5318.

[14] Grubbs and co-workers used a DANTE pulse sequence and a CIFIT program to extract exchange rate constants, and reported the data per coordinated phosphine (see ref 12). Using this methodology, an exchange value of 0.381 at 50 °C using 3 equiv of phosphine was obtained.

[15] Because the NMR pulse sequences used by Grubbs and ourselves for measuring phosphine exchange rates were not the same (see ref 13), a direct comparison between the two sets of results is not possible.

[16] The $k_{(obs)}$ exchange rate value was multiplied by 2 because of a symmetrical transition state as described by Green and co-workers: Green, M. L. H.; Wong, L.-L.; Sella, A. *Organometallics* **1992**, *11*, 2660−2668.

[17] The nature of the decomposition species observed in these reactions is the subject of further investigation.

[18] Kunkely, H.; Vogler, A. *Inorg. Chim. Acta* **2001**, *325*, 179−181.

[19] Hansen, S. M.; Rominger, F.; Eisenträger, F.; Metz, M.; Hofmann, P. *Chem.−Eur. J.* **1999**, *5*, 557−566.

[20] Wright, R. E.; Vogler, A. *J. Organomet. Chem.* **1978**, *160*, 197−205.

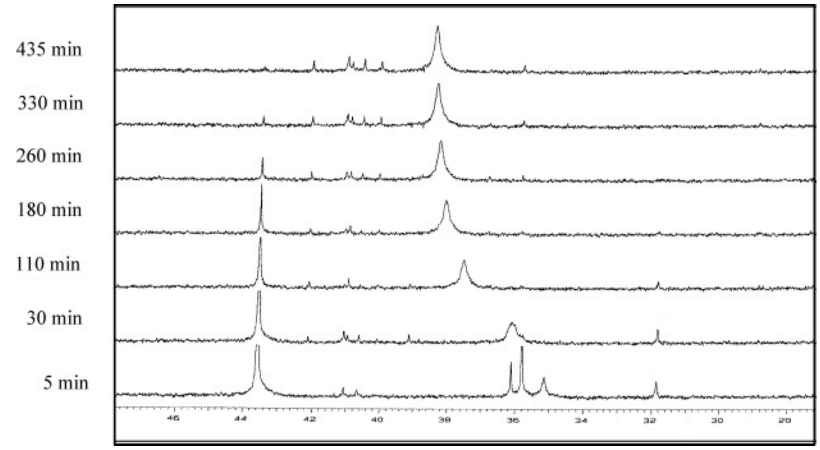

Figure 7. ^{31}P NMR ($CDCl_3$) of the ethenolysis of 2-octene (80% *cis*) using catalyst **1** (15 bar ethylene, 30 °C). Methylidene, $\delta = 43.8$ ppm; alkylidenes, $\delta = 35.8$, 36.2 ppm.

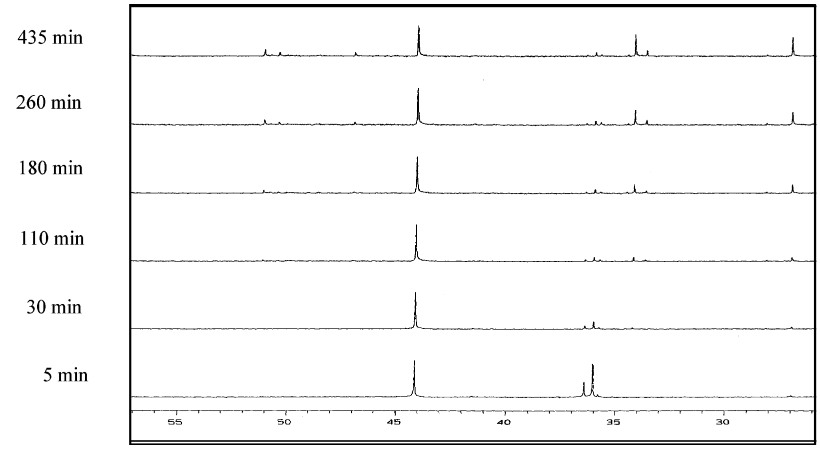

Figure 8. ^{31}P NMR ($CDCl_3$) of the ethenolysis of 2-octene (80% *cis*) using catalyst **1** and 60 equiv of phenol (15 bar ethylene, 30 °C). Methylidene, $\delta = 44.0$ ppm; alkylidenes, $\delta = 36.0$, 36.5 ppm.

p-cresol (1000 equiv) in toluene ([*p*-cresol] = 0.5 M), the long-wavelength absorption was shifted to $\lambda_{max} = 522.4$ nm (spectrum A), and a similar effect was also observed with 4-chlorophenol (spectrum E). Importantly, the magnitude of the hypsochromic shift was also concentration dependent. As shown in Figure 9, when catalyst **1** was mixed with *p*-cresol (200 equiv) in toluene ([*p*-cresol] = 0.1 M), the long-wavelength absorption was only $\lambda_{max} = 525.6$ nm (spectrum D). Notably, when BHT was added to toluene solutions of **1** ([BHT] = 0.5 M), only a very small hypsochromic shift was observed ($\lambda_{max} = 527.1$ nm, spectrum B). These results suggest that interaction of phenol with catalyst **1** is altering the electrophilic character of the carbene carbon, which in turn results in the metal → π^* (carbene) MLCT transition being shifted to shorter wavelengths.

EPR Spectroscopy. In the course of various SM reactions of α-olefins catalyzed by **1** in the presence of some phenols, *intensely colored reaction mixtures* were observed. For example, when catalyst **1** was added to a solution of 1-octene containing 500 equiv of catechol at 50 °C, a deep purple color was observed after 10 min. Similarly, with 500 equiv of 4-methoxyphenol, an intense blue color was observed. The relevance of this observation is supported by the relative ease at which phenols are oxidized to phenoxy radicals[11] and a report[21] that catalyst **1** has the ability to generate persistent radical anions on treatment with π-acceptors such as *p*-benzoquinones. On the basis of the foregoing, a series of EPR spectra were measured to determine the ability of phenol, or derivatives thereof, to act as radical scavengers in olefin metathesis reactions. Thus, when 1 mL of a solution of **1** in 1-octene (20 mL) containing 500 equiv of phenol was transferred to an EPR vial, and the EPR spectrum measured at room temperature, a very broad and weak spectrum was observed. However, when the identical reaction was performed with BHT, a phenol capable of producing a long-lived radical species,[11] a well-defined spectrum was obtained (Figure 10). The spectrum obtained was compared to a known EPR spectrum of the BHT radical (Figure 11) and was found to be identical. In addition, EPR spectra measured in the absence of either catalyst **1** or BHT were found to give no detectable signals. Under similar reaction conditions, catechol and hydroquinone also gave strong, albeit less defined EPR spectra. These results suggest that under the reaction conditions BHT is capable of sequestering a radical from catalyst **1** and is oxidized to a stable BHT radical. The actual role ruthenium radicals play in olefin metathesis is however less clear, and the ability of phenols to sequester Ru-radical species formed during olefin metathesis continues to be investigated.[22]

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(21) Amir-Ebrahimi, V.; Hamilton, J. G.; Nelson, J.; Rooney, J. J.; Thompson, J. M.; Beaumont, A. J.; Rooney, A. D.; Harding, C. J. *J. Chem Soc., Chem. Commun.* **1991**, 1621–1622.

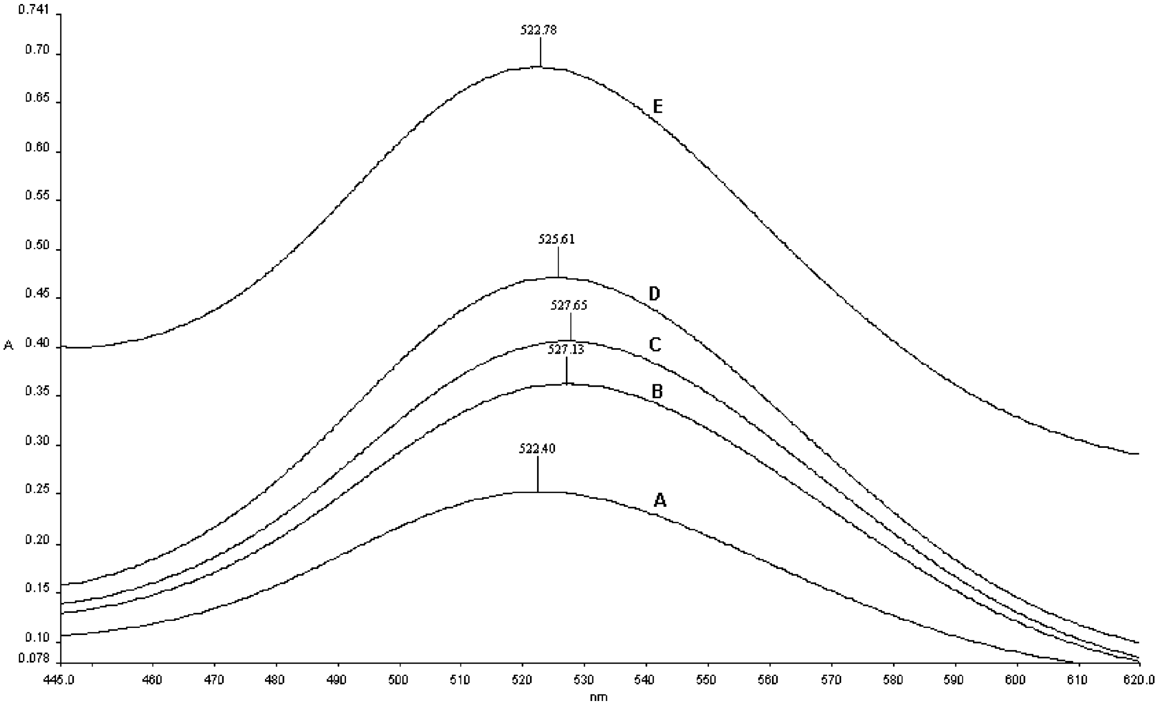

Figure 9. UV−visible spectrum of catalyst **1** in toluene: (A) catalyst **1** with *p*-cresol (1000 equiv) in toluene ([*p*-cresol] = 0.5 M); (B) catalyst **1** with BHT (1000 equiv) in toluene ([BHT] = 0.5 M); (C) catalyst **1** in toluene ([**1**] = 0.05 M); (D) catalyst **1** with *p*-cresol (200 equiv) in toluene ([*p*-cresol] = 0.1 M); (E) catalyst **1** with 4-chlorophenol (1000 equiv) in toluene ([4-chlorophenol] = 0.1 M).

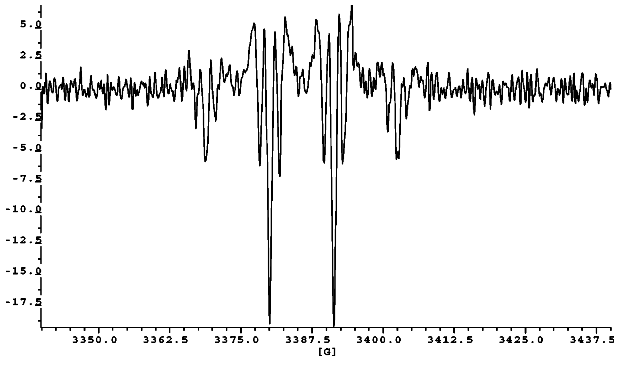

Figure 10. EPR spectrum of catalyst **1** with BHT, recorded at 20 °C.

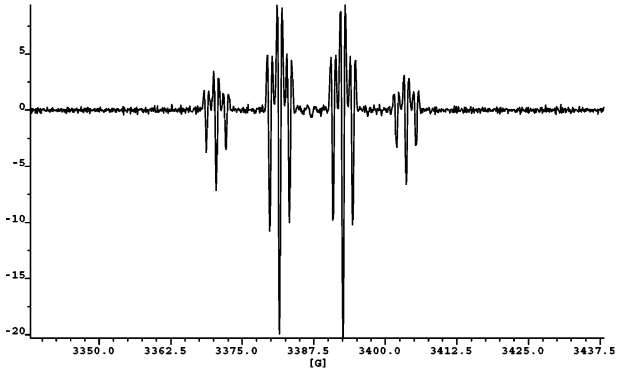

Figure 11. EPR spectrum of BHT radical (prepared by reaction of BHT with H_2O_2), recorded at 20 °C.

Computational Investigation. To gain insight into the possible roles played by phenol, prior and during Ru-catalyzed olefin metathesis, a DFT study focusing on (i) phenol coordination modes and energies to suitable Ru-carbene models, (ii) phenol effect on catalyst initiation, and (iii) correlation of charge distribution effects with catalyst activity was conducted. In all calculations trimethylphosphine (PMe_3) was used as a model for tricyclohexylphosphine (PCy_3), whereas the stripped-down heterocyclic carbene, IMe, was used as a model for the real H_2IMes ligand for calculations on second-generation catalyst systems. This approach was deemed appropriate for the calculation of accurate relative effects exerted by phenol while simultaneously ensuring expedient calculations.

Phenol Coordination to Unsaturated Ru-Carbene. The Ru-carbene-catalyzed olefin metathesis mechanism is widely agreed to involve dissociation of PCy_3 in $Cl_2Ru(PCy_3)_2{=}CHPh$ (**1**), yielding the unsaturated and active intermediate $Cl_2Ru(PCy_3){=}CHPh$. The latter species (R = H, Ph, or alkyl) represents the active form of the catalyst, and subsequent olefin coordination leads to the formation of the corresponding ruthenacyclobutane known to be an important intermediate in the active metathesis mechanism.[23] $Cl_2Ru(PCy_3){=}CHR$ represents a high-energy intermediate, as is evident from a number of theoretical studies.[24] Consequently, it was considered appropriate to initiate a DFT study on phenol affinity for $Cl_2Ru(PCy_3){=}CHR$ with subsequent correlation to experimentally observed reactivity trends.

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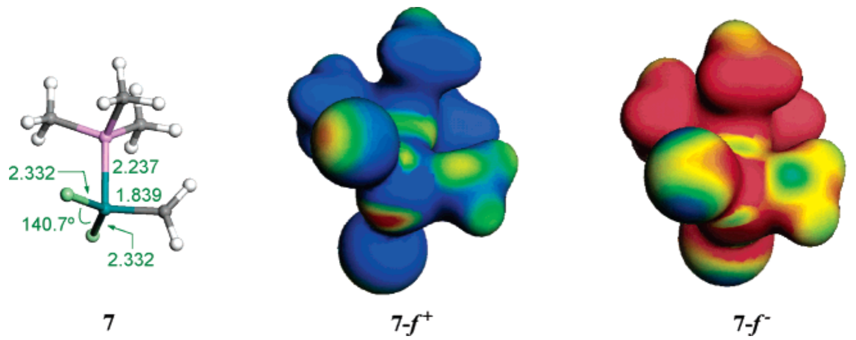
(22) Turk and Ford have reported the oxidation of 2,6-di-*tert*-butylphenol catalyzed by CoPcTs is pH and temperature dependent: Turk, H.; Ford, W. T. *J. Org. Chem.* **1988**, *53*, 461−462.

(23) Grubbs, R. H. *Tetrahedron* **2004**, *126*, 7117−7140.

(24) (a) Adlhart, C.; Chen, P. *J. Am. Chem. Soc.* **2004**, *126*, 3496−3510. (b) Suresh, C. H.; Koga, N. *Organometallics* **2004**, *23*, 76−80. (c) Burdett, K. A.; Harris, L. D.; Margl, P.; Maughon, B. R.; Mokhtar-Zadeh, T.; Saucier, P. C.; Wasserman, E. P. *Organometallics* **2004**, *23*, 2027−2047. (d) Fomine, S.; Martinez Vargas, S.; Tlenkopatchev, M. A. *Organometallics* **2003**, *22*, 93−99. (e) Cavallo, L. *J. Am. Chem. Soc.* **2002**, *124*, 8965−8973. (f) Vyboishcikov, S. F.; Bühl, M.; Thiel, W. *Chem. Eur. J.* **2002**, *8*, 3962−3975.



7 **7-*f*⁺** **7-*f*⁻**

Figure 12. Optimized geometry of **7** together with maps of the nucleophlic (**7-*f***$^+$) and electrophilic (**7-*f***$^-$) Fukui functions on the electron isodensity surface of **7**.

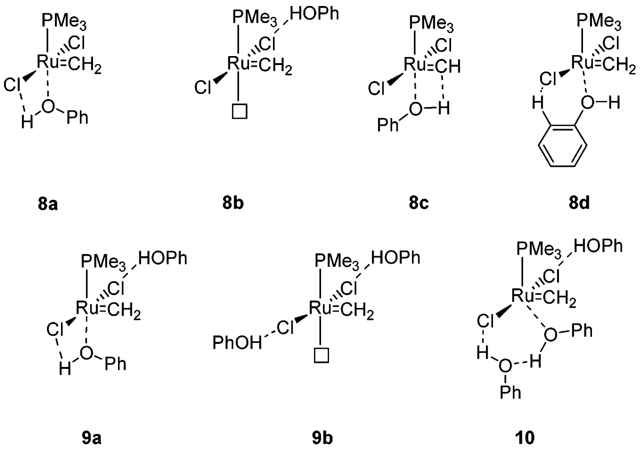


Figure 13. Proposed structures for coordination of phenol to the active catalyst intermediate **8**.

The DFT-optimized geometry of the PMe_3 Ru-methylidene analogue of $Cl_2Ru(PCy_3){=}CHR$ is illustrated as **7** in Figure 12. The calculated geometrical parameters for this PMe_3 model are in excellent agreement with a recently reported DFT study.[24d] The reactivity of a molecule with respect to electrophilic and nucleophilic attack may elegantly be calculated by the frontier molecular orbital (FMO) Fukui function as developed by Parr and Yang.[25] The calculated positions in **7** exhibiting nucleophilic Fukui functions (f^+; i.e., positions activated for nucleophilic attack) are illustrated by the map of f^+ on the electron isodensity surface of **7** (**7-*f***$^+$ in Figure 12).

The relative concentration of red in **7-*f***$^+$ indicates that Ru, Cl, and the methylidene carbon (in decreasing order) should in principle be susceptible to favorable interaction with a nucleophile. Similarly the relative concentration of blue in **7-*f***$^-$, largely positioned on either side of the Cl ligands, points toward areas activated for electrophilic interaction. From this qualitative picture it is thus predicted that the δ^- oxygen of phenol should preferentially interact with Ru in **7**, while the δ^+ phenolic hydrogen should interact via possible hydrogen bonding with the Cl ligands in **7**.

Consequently, the monophenol coordination complexes **8a**–**8d** (Figure 13) were suggested as possible candidates for phenol coordination. The favorable calculated coordination energy of phenol in **8a** of −11.7 kcal/mol is contrasted by the relatively lower coordination energy (−3.9 kcal/mol) for PhOH··Cl coordination in **8b**, effectively suggesting that formation of the Ru··O and H··Cl metallacycle complex **9a** will be the more favored coordination mode of phenol to **7** (Figure 14). This is in agreement with a computational study by Morokuma et al. in which it was found that a similar coordination mode for MeOH coordination to sterically unhindered $OsHCl(CO)(PH_3)_2$ is favored.[26] This result was further confirmed by the spontaneous optimization of starting geometries for **8c** and **8d** to the geometry of **8a**, effectively dismissing the importance of the proposed coordination modes of phenol in **8c** and **8d** in Figure 13. The relevance of phenol hydrogen bond coordination to Cl in **8b** is highlighted by the prevalence of D−H···Cl−M (D = O, N, etc.) interactions in a number of crystal structures.[27] Expansion of the monophenol coordination complexes to incorporate two phenol units led to the successful optimization of **9a** and **9b**. The respective phenol coordination energies for **9a** and **9b** are −16.6 and −8.0 kcal/mol, while incorporation of a second phenol unit in the metallacycle fragment of **9a** leads to the six-membered metallacycle complex **10** with a total phenol coordination energy of −26.3 kcal/mol (Figure 14). From these calculated phenol coordination energies it is evident that increasing stabilization of **7** is achieved upon increase of the coordinating phenol units.

The coordination position of phenol oxygen in **9a** also represents the olefin coordination site in the mechanism of metathesis. Consequently, it is conceivable that an equilibrium between **9a** and **9b** exists, providing for hemilabile stabilization of the active Ru species **7**. This equilibrium favors **9a** by 7.8 kcal/mol, ensuring a low-energy intermediate that inhibits the decomposition of **7**, with simultaneous activation of the Ru-carbene carbon for interaction with coordinating olefin (vide infra). Furthermore, it is also anticipated that this hemilabile stabilization effect is more likely to incorporate a larger number of phenol units as is evident from enhanced stabilization found for increase in number of phenol units. This hemilabile stabilization effect is schematically represented in Scheme 2.

Calculation of Phenol Effect on Catalyst Initiation. To assess the influence of phenol complexation on

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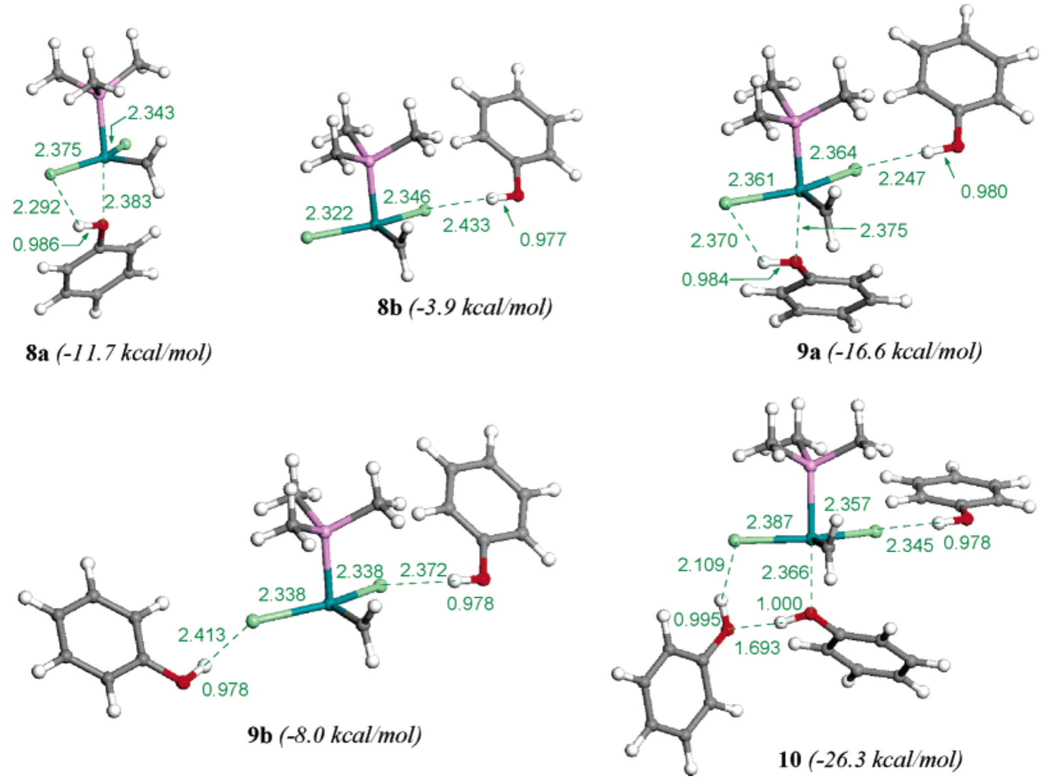
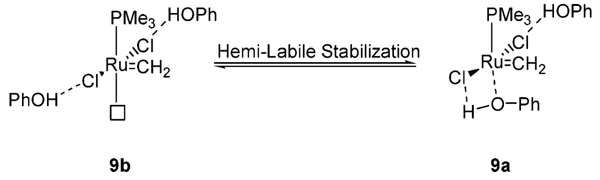


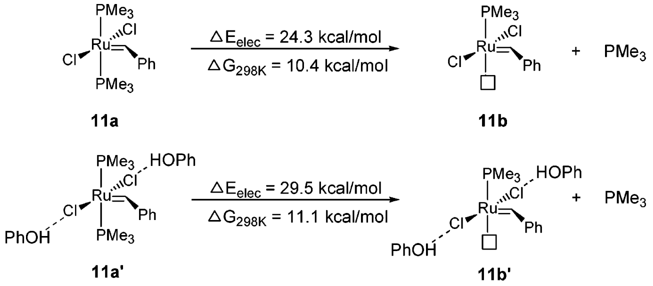
8a *(-11.7 kcal/mol)* **8b** *(-3.9 kcal/mol)* **9a** *(-16.6 kcal/mol)* **9b** *(-8.0 kcal/mol)* **10** *(-26.3 kcal/mol)*

Figure 14. Optimized geometries and phenol coordination energies for **8a**, **8b** and **9a**, **9b**, and **10**.

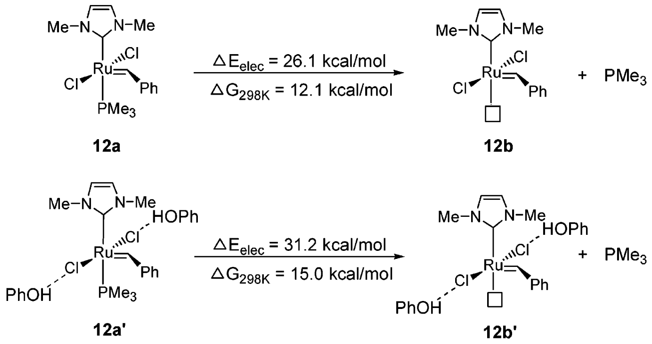
Scheme 2



Scheme 3. Calculated PMe$_3$ Dissociation Energies (ΔE_{elec} and ΔG_{298K}) from the First-Generation Model 11a in Both the Absence and Presence of Hydrogen-Bonded Phenol



Scheme 4. Calculated PMe$_3$ Dissociation Energies (ΔE_{elec} and ΔG_{298K}) from the Second-Generation Model 12a in Both the Absence and Presence of Hydrogen-Bonded Phenol



catalyst initiation, comparative phosphine dissociation energies in both the absence and presence of coordinated phenol were calculated for the first- [$Cl_2(PMe_3)_2Ru{=}CHPh$ (**11a**)] and second-generation [$Cl_2(PMe_3)(IMe)Ru{=}CHPh$ (**12a**)] benzylidene models. Hydrogen bond coordination modes of two phenol units to **11a** and **12a** were considered as illustrated by complexes **11a′** and **12a′** in Schemes 3 and 4, respectively. The calculated phosphine dissociation energies in the absence (i.e., **11a** → **11b** + PMe$_3$ and **12a** → **12b** + PMe$_3$) and presence of phenol (i.e., **11a′** → **11b′** + PMe$_3$ and **12a′** → **12b′** + PMe$_3$) are also summarized in Schemes 3 and 4. In addition to the inclusion of the electronic energies (ΔE, 0 K) for PMe$_3$ dissociation the corrected Gibbs free energies (ΔG) at 298.15 K and 1 atm are also included. The calculated electronic energies (ΔE) for PMe$_3$ dissociation in the *absence* of phenol is calculated to be 24.3 and 26.1 kcal/mol for the first- and second-generation benzylidene models, respectively, emphasizing the known property of second-generation catalysts to initiate slower than the corresponding first-generation catalysts.[12] Incorporation of favorable entropy ($T\Delta S$) contributions in both cases results in calculated Gibbs free energies of dissociation of 10.4 and 12.1 kcal/mol, respectively. These calculated PMe$_3$ dissociation energies are in good agreement with previously reported theoretical studies in which PMe$_3$ was used as model.[24d,f]

For both the first- and second-generation benzylidene models an increase in PMe$_3$ dissociation energies is found when phenol is coordinated. The electronic dissociation energies for first- and second-generation models increase to 29.5 and 31.2 kcal/mol, respectively, when phenol is coordinated, which amounts to ΔG_{298K} dis-

Table 7. Calculated Hirshfeld Charge Analysis on Ru, Cl, and Methylidene C for 7, 8a, 8b, 9a, 9b, and 10

	Hirshfeld charge (e)		
structure	Ru	Cl	Ru=CH_2
7	0.257	−0.413	−0.312
8a	0.259	−0.258 (−0.253)[a]	−0.138
8b	0.279	−0.222	−0.135
9a	0.262	−0.201 (−0.246)[a]	−0.130
9b	0.285	−0.202	−0.124
10	0.263	−0.212 (−0.241)[a]	−0.134

[a] Values in parentheses refer to the Hirshfeld charge on Cl participating in the four- or six-membered coordination mode of phenol.

sociations of 11.1 and 15.0 kcal/mol, respectively, upon incorporation of favorable entropy corrections. The calculated phosphine dissociation energies indicate that catalyst initiation should be slowed upon coordination of phenol, in agreement with experimental observations. In addition, the relatively sluggish phosphine dissociation of the second-generation system is further enhanced upon coordination of phenol, making the inhibition of this catalyst system upon addition of phenol in experiment conceivable.

Charge Distribution Analysis. In a paper by Rooney et al.[28] the increase in Grubbs first-generation catalyst activity for ROMP upon addition of phenol as solvent is postulated to be regulated by metal to halide charge transfer. In this hypothesis the chloride ligands in **1** coordinate via phenolic hydrogen bonds to phenol, effectively resulting in a net flow of negative charge away from ruthenium. This in turn enhances the electrophilic nature of the carbene carbon in **1**, making the Ru=C bond more Lewis acidic and enhancing its reactivity toward Lewis-basic electron-rich olefins.[29] To assess this hypothesis theoretically, the changes in charge distribution at the Ru, Cl, and carbene carbon atoms for different coordination modes of phenol were studied by using the Hirshfeld charge analysis method.[30] The Hirshfeld charge localizations on Ru, Cl, and methylidene C for PMe_3 models, with and without coordinated phenol, are summarized in Table 7.

The calculated Hirshfeld charges located on Ru, Cl, and methylidene C of **7**, containing no coordinated phenol, are 0.257, −0.413, and −0.312e, respectively. The nature of these charges is in agreement with the relative electrophilic nature of Ru and nucleophilic character of Cl and methylidene C, as was also suggested from the maps of the Fukui functions (vide supra). Coordination of one phenol fragment through a hydrogen bond interaction to Cl in **8b** results in a loss of localized negative charge on Ru, Cl, and methylidene C to 0.279, −0.222, and −0.135e, respectively. The loss of −0.177e charge on methylidene C is calculated to be the most pronounced, effectively demonstrating a significant enhancement of electrophilic nature of the carbene carbon. Upon hydrogen bond coordination of two phenol fragments to two Cl ligands in **9b**, a further reduction of negative charge is found, yielding localized Hirshfeld charges of 0.285, −0.202, and −0.124e for Ru, Cl, and methylidene C, respectively. The loss of −0.188e on the methylidene C of **9b** compared to **7** represents the largest electrophilic activation found for the Ru-carbene carbon in the current study.

The four-membered coordination mode of a single phenol unit in **8a** also results in the delocalization of negative charge on Ru (0.259e), Cl (−0.253e), and methylidene C (−0.138e) compared to **7**. However, the comparative delocalization of only −0.002e on Ru is attributable to a counter introduction of negative charge on Ru due to the O → Ru interaction, effectively balancing the delocalization of negative charge from Ru through the hydrogen bond. The relatively greater negative charge on Cl (−0.253e) for **8a** compared to **8b** (−0.222e) is attributable to more effective negative charge delocalization from Cl for the latter pure hydrogen bond adduct (linear O−H··Ru interaction).[26] This phenomenon is also reflected in the relatively less electrophilic character of the carbene carbon in **8a** compared to **8b**. Introduction of a second linear hydrogen-bonded phenol to **8a**, to yield **9a**, leads to a further reduction of negative charge on Ru (0.262e), both Cl's (−0.201 and −0.246e), and methylidene C (−0.130e). Expansion of the four-membered metallacycle in **9a** to the six-membered adduct **10** has essentially no effect on the charge localizations on Ru, Cl, and methylidene C.

Despite the charge distribution differences pointed out above for different coordination modes of phenol, it is evident that all coordination modes of phenol lead to a significant enhancement of the electrophilic character of the carbene carbon. This suggests that coordinated phenol not only stabilizes the active metathesis complex **7** (via the proposed hemilabile interaction; vide supra) but also activates the carbene carbon for subsequent reaction with an olefinic substrate. These charge decomposition results are thus in perfect agreement with the proposals put forward by Rooney to explain enhanced metathesis activity of $Cl_2Ru(PCy_3)$=CHPh catalysts in phenolic solvents.[28] In general, it is thus anticipated that although phenol coordination retards phosphine loss during catalyst initiation, the competitive equilibrium toward olefin incorporation into a ruthenacyclobutane intermediate (k_{-1}/k_2; vide infra) should necessarily be favored (due to olefin interaction with an *activated* carbene carbon) compared to the conventional catalyst in the absence of phenol.

Discussion

Solvent and Additive Effects in Olefin Metathesis. While there are numerous reports outlining solvent selection as being crucial in influencing the outcome of a Ru-catalyzed metathesis reactions, there are few studies devoted to investigating this effect. Grubbs et al. has shown that solvent effects have a dramatic impact on the initiation rates of Ru-alkylidene complexes.[12] In particular, k_{Init} was found to be roughly proportional to the dielectric constant of the reaction medium, with the initiation rate increasing by 30% upon moving from toluene to CH_2Cl_2 as solvent. These effects were attributed to possible stabilization of the four-coordinate intermediate or PCy_3, although no evidence

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[28] Amir-Ebrahimi, V.; Corry, D. A.; Hamilton, J. G.; Thompson, J. M.; Rooney, J. J. *Macromolecules* **2000**, *33*, 717−724.

[29] A similar argument applies upon changing the Cl ligands in **1** with trifluoro acetyl fragments, see: Wu, Z.; Nguyen, S. T.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1995**, *117*, 5503−5511.

[30] (a) Hirshfeld, F. L. *Theor. Chim. Acta B* **1977**, *44*, 129. (b) Delley, B. *Chem. Phys. Lett.* **1986**, *110*, 329.

Table 8. Self-Metathesis of 1-Octene via Catalyst 1/Phenol in Various Solvents

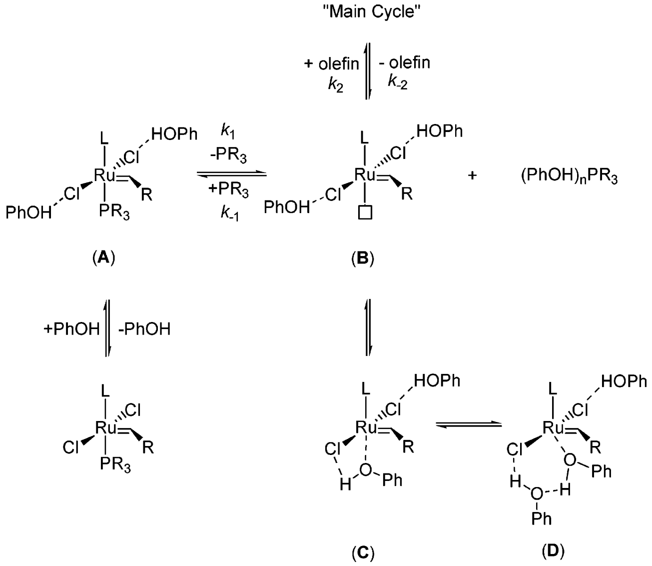
entry[a]	solvent	dielectric constant (ϵ)[36]	conv (%)[b,c] without phenol	conv (%)[c] with phenol
1	neat	2.1	26	87
2	THF	7.3	3	5
3	toluene	2.4	13	62
4	decane	2.0	19	76
5	cyclohexane	2.0	22	77
6	Ph_2O	3.9	29	78
7	CH_2Cl_2	9.1	35	76
8	$CHCl_3$	4.8	54	85

[a] Catalyst **1** (1-octene/Ru 9000, 50 °C), 20 mL of solvent. [b] 500 equiv/Ru. [c] Determined by GC after 2 h.

of solvento adducts were detected by ^{1}H or ^{31}P spectroscopy. For the SM of simple olefins, it has been reported that reactions are best performed neat or in a halogenated solvent, while polar aprotic solvents are often least compatible. For example, Mol et al. have shown that for the SM of *trans/cis*-4-nonene reactions performed in 1,2-dichloroethane gives conversions greater than reactions performed neat, while reactions performed in diethyl ether give poorest conversions.[31] Rooney and co-workers reported that the nature of the polymer formed by the ROMP reaction of two cyclic monomers using catalyst **1** was altered by performing the reaction in chlorophenol as a solvent, and this change was attributed to an unquantified increase in catalyst activity.[28,32] Similar solvent effects in ROMP reactions using catalyst **2** reveal that molecular weights and molecular weight distributions are affected by nitriles, amines, thiocyanates, and pyridines in solution.[33] The activity of various Ru-carbene olefin metathesis reactions is reported to be enhanced by addition of copper(I) chloride,[2d,34] although the higher activity that results from use of a phosphine scavenger such as copper(I) chloride often results in more rapid catalyst decomposition. Nolan, Prunet, and co-workers have also reported that tricyclohexylphosphine oxide when combined with a suitable solvent can eliminate unwanted isomerization observed in certain RCM reactions catalyzed by **2**.[35]

A series of α-olefin SM experiments were performed using **1** as catalyst in the presence and absence of phenol in various solvents to determine the role solvent effects have in altering the performance of α-olefin SM, the results of which are shown in Table 8. Consistent with previous literature,[12] a large solvent effect was observed for the SM of 1-octene using catalyst **1**. For example, using THF as solvent (entry 2, Table 7), only 3% conversion was observed after 2 h, while using $CHCl_3$ as solvent (entry 8, Table 8), 54% conversion was observed. With phenol addition (500 equiv/Ru) end conversions were substantially higher than reactions performed in the absence of phenol. Perhaps surprisingly, SM reactions of α-olefins in neat phenol (>10 000 equiv/Ru) did not provide any improvements in end conversions or catalyst lifetime. As summarized in Table 8, there does not appear to be any significant relationship between dielectric constant[36] and conversion of 1-octene using catalyst **1**, although conversions are slightly higher in diphenyl ether ($\epsilon = 3.9$, entry 6, Table 8) and CH_2Cl_2 ($\epsilon = 9.1$, entry 7, Table 8). In this instance the dielectric constant of the solvent appears to be less important than solvent acidity. For example, $CHCl_3$ is a weak acid ($pK_a = 13.6$, $\epsilon = 4.8$)[37] and gives rise to conversions that are comparable to when trifluoroethanol ($pK_a = 12.3$, $\epsilon = 26$, conversion = 45%) is used as solvent.

Scheme 5



Mechanism of Ruthenium-Catalyzed Olefin Metathesis Reactions with Added Phenol. On the basis of the foregoing data, we can propose a general mechanism for olefin metathesis reactions catalyzed by catalysts **1** and **2** with added phenol. ^{31}P NMR magnetization transfer experiments, initiation kinetic studies, and DFT calculations indicate that added phenol is slowing phosphine loss to afford the 14-electron intermediate **B** (Scheme 5). Furthermore, DFT calculations suggest phenol interacts with the ruthenium olefin metathesis catalyst via a PhO−H··Cl−Ru interaction in which the ruthenium-bound chloride acts as a hydrogen bond acceptor to the acidic PhO−H proton of the phenol. Although phenols are well-known for reacting with organometallic complexes,[38] in this instance the Ru-carbene complexes **1**−**5** appear to remain chemically unchanged when treated with phenol in the presence and absence of substrate. For example, com-

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[37] Scharlin, P. *Acta Chem. Scan.* **1986**, *A40*, 207−209.

[38] For selected examples, see: (a) Cole-Hamilton, D. J.; Young, R. J.; Wilkinson, G. *J. Chem Soc., Dalton Trans.* **1976**, 1995−2001. (b) Braga, D.; Sabatino, P.; Di Bugno, C.; Leoni, P.; Pasquali, M. *J. Organomet. Chem.* **1987**, *334*, C46−C48. (c) Heppert, J. A.; Boyle, T. J.; Takusagawa, F. *Organometallics* **1989**, *8*, 461−467. (d) Atwood, D. A.; Cowley, A. H.; Schluter, R. D.; Bond, M. R.; Carrano, C. *J. Inorg. Chem.* **1995**, *34*, 2186−2189. (e) Hirano, M.; Kurata, N.; Marumo, T.; Komiya, S. *Organometallics* **1998**, *17*, 501−503. (f) Brandts, J. A. M.; Boersma, J.; Spek, A. L.; Van Koten, G. *Eur. J. Inorg. Chem.* **1999**, *10*, 1727−1733.

plexes **2** and **5** were isolated unchanged (MS, NMR) after stirring in phenol for 24 h. In addition, only **5** was isolated after reaction with 1-octene/phenol (**5**:1-octene: phenol ratio = 1:1000:200, 65 °C) for 1 h. In addition, there appears to be no evidence for Cl abstraction and concomitant formation of Ru aryloxide complexes.[39] As previously noted, complex **1** remains unchanged, even at elevated temperatures, in the presence of phenol, and the aforementioned rate enhancement effect is not inhibited by added Cl ions.

The relevance of the proposed PhO−H··Cl−Ru interaction is supported by a detailed investigation by Orpen,[27a] who concluded that M−Cl-containing complexes have a strong propensity to interact with hydrogen bond donors, due in part to the large negative charge on the chloride in the partly ionic M−Cl bonds. In the present study, these proposals are reinforced by UV−visible and NMR spectroscopy, as well as a map of the electrophilic Fukui function (positions activated for electrophilic attack) on the electron isodensity surface, which suggests the δ^+ phenolic hydrogen should interact via hydrogen bonding with the Cl ligands in **7**. A similar effect has been observed by Van Koten and co-workers for the self-assembly of aryldiamineplatinum complexes via a repeating RO−H··Cl−Pt interaction.[27b]

The magnitude in which phosphine loss is retarded upon phenol addition is dependent on the relative strength of the PhO−H··Cl−Ru interaction. Consequently, in this system the actual degree to which k_1 is inhibited is determined by both the acidity and steric properties of the phenol. Initiation kinetics and degenerate ^{31}P NMR magnetization transfer experiments indicate phenols that are *less* acidic, such as cresol (pK_a = 10.28), do not retard phosphine loss to the degree that more acidic phenols, such as 4-chlorophenol (pK_a = 9.42), do. As indicated by DFT theory, a greater PhO−H··Cl−Ru interaction pulls electron density away from the Ru center, creating a stronger Ru−PR$_3$ bond and slowing phosphine loss (k_1). ^{31}P NMR magnetization transfer experiments and initiation kinetic studies indicate that increased steric bulk, particularly at the 2,6-position of the phenol, gives rise to a weaker PhO−H··Cl−Ru interaction, resulting in a faster phosphine dissociation rate (k_1) than when less bulky phenols of similar acidity are combined with catalyst **1**.

Grubbs and co-workers have previously shown that recoordination of free PR$_3$ (k_{-1}) in first-generation catalysts is competitive with substrate binding, the net effect being the active 14-electron species is returned to the "inactive" 16-electron species **A** (Scheme 5).[12] In the present study, large downfield shifts observed when PCy$_3$ and excess 4-cholorophenol interact observed by ^{31}P NMR suggest that excess phenol may be capable of sequestering dissociated phosphine so as to form species of the type (PhOH)$_n$PCy$_3$. Notably, DFT calculations predict that phenol interaction also gives rise to a significant enhancement in the electrophilic character of the carbene carbon, resulting in activation of the carbene carbon for reaction with an olefinic substrate. The net result of these combined effects would be to make olefin coordination followed by ruthenacyclobutane formation more facile, despite phosphine loss being relatively inefficient with added phenol. Thus, in the case of the first-generation catalyst **1**, without added phenol, $k_{-1}/k_2 \gg 1$, essentially making recoordination of PR$_3$ competitive with substrate binding. With added phenol however, despite k_1 being slowed and k_{-1} retarded, a competitive increase in k_2 results from more favored olefin coordination and subsequent interaction with activated Ru-carbene carbon. Interestingly, a similar effect was noted by Grubbs and co-workers for NHC-containing complexes.[12]

DFT calculations indicate that an equilibrium between **B** and **C** most likely exists, resulting in hemilabile stabilization of the active Ru species in the absence of substrate. The equilibrium favors **C** by 7.8 kcal/mol, ensuring the formation of a low-energy intermediate that inhibits decomposition of the 14-electron species **B**. Incorporation of additional phenol units is predicted by DFT calculations to give rise to further enhanced stabilization. In this instance hemilabile stabilization is proposed to be occurring in the presence of an active alkylidene or methylidene species, in contrast to the recently reported Hoveyda catalyst,[40] and derivatives thereof,[41] in which stabilization of the active catalyst must result in a return to the parent benzylidene species.

Experimentally, these observations are evidenced by faster reaction rates and increased catalyst stability for the first-generation catalyst **1**, particularly for simple SM and CM of α-olefins. For SM reactions catalyzed by **2**, added phenol results in slower reaction rates relative to when phenol is not present. In this instance, phosphine loss (k_1), which is already slow in catalyst **2**, appears to become rate limiting when phenol is added. Phenol addition to α-olefin SM reactions catalyzed by **2** can also result in fewer unwanted SMPs, giving rise to greater overall selectivity.

Conclusion

In summary, this report has shown that the activity and lifetime of certain SM, CM, and ethenolysis reactions catalyzed by **1** may be enhanced by the simple addition of phenol. This system is particularly relevant for industrial scale SM reactions of simple α-olefin substrates, where high levels of catalyst efficiency are required. For example, phenol addition to SM reactions catalyzed by **1** allows the reaction to take place smoothly at room temperature and at high S/C loadings, while producing very small quantities of unwanted byproducts. In some instances addition of phenol leads to a 10-fold increase in catalyst lifetime and significantly increases the overall turnover number (TON) of the reaction. Added phenol is also capable of increasing the

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[39] Fogg and co-workers have recently reported the synthesis of new alkylidene complexes in which aryloxide groups function as pseudohalide groups: Conrad, J.; Amoroso, D.; Czechura, P.; Yap, G. P. A.; Fogg, D. *Organometallics* **2003**, *22*, 3634−3636.

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efficiency of certain CM reactions catalyzed by the second-generation catalyst **2**. For example, with 0.1 mol % of catalyst **2**, the CM of methyl acrylate with 1-decene was achieved in 100% conversion after only 15 min with added *p*-cresol (500 equiv), whereas only 28% conversion was obtained in the absence of *p*-cresol. Although the full scope and generality of phenol addition to CM reactions catalyzed by **2** remains to be fully explored, a natural consequence of the greater catalyst efficiency imparted by phenol addition is lower catalyst loadings and more economical metathesis processes.[42] NMR studies and DFT calculations establish that phenol is playing a number of positive roles in the active metathesis cycle, including altering the relative rates of phosphine loss and rebinding (k_1/k_{-1}), activating the carbene carbon for reaction with olefinic substrate (k_3) and hemilabile stabilization of the key 14-electron intermediate species. Studies aimed at further increasing the efficiency of Ru-carbene metathesis catalysts are ongoing.[43]

Experimental Section

General Procedures. Manipulations of organometallic compounds were performed using standard Schlenk techniques under an atmosphere of dry argon or in a nitrogen-filled mBraun Unilab 3702 glovebox (O_2 < 1 ppm). All reactions were conducted in oven-dried (150 °C) glassware. NMR spectra were recorded on either a Bruker Avance 300 MHz or a Varian Unity Plus 500 MHz spectrometer. Unless otherwise stated, ^{31}P NMR were referenced using H_3PO_4 ($\delta = 0$ ppm) as an internal standard. Gas chromatography was performed on an Agilent Technologies 6890N Network GC system using either a Pona column for nonpolar samples or a MDN column for polar samples.

Materials and Methods. Toluene, tetrahydrofuran, diethyl ether, and hexanes were dried by passage through an Innovative Technologies solvent purification system. AR grade methylene chloride and pentane were purchased from Aldrich chemicals and degassed before use. Ruthenium complexes **3**,[12] **5**,[5] and **6**[13] were prepared according to literature procedures. Ruthenium complexes **1**, **2**, and **4** were obtained from Strem or Aldrich Chemicals. α-Olefin feedstocks were percolated through a pad of alumina prior to use.[44]

General Experimental Procedure for Self-Metathesis Experiments with Added Phenol. A stock 1-octene solution was degassed with argon 30 min before use, and 20 mL (0.127 mmol) was transferred to a 250 mL three-necked round-bottom flask fitted with a dry ice reflux condenser, thermometer, and septum, and the phenol (200−1000 equiv) was added in one portion. The solution was heated to 50 °C, and catalyst **1** (11.6 mg, 0.014 mmol) was weighed into a custom-made miniature aluminum weighing tray. The weighing tray containing the catalyst was added to the flask, and the reaction stirred for 6 h. Samples were taken after 10, 30, 60, 120, 180, 240, and 360 min and analyzed by GC-FID. Conversions are reported as the molar % 1-octene that was converted to the desired 7-tetradecene product.

General Experimental Procedure for Ring-Closing Metathesis (RCM) of Diethyl Diallyl Malonate with Phenol. A 250 mL three-necked round-bottom flask was fitted with a reflux condenser, thermometer, and septum. A needle was inserted through the septum and connected to a gas supply via a needle valve to ensure a slow and steady stream of argon through the reaction solution. Toluene (60 mL), diethyldiallylmalonate (10.0 g, 42 mmol), and phenol (1.70 g, 18 mmol) were added to the reaction vessel, and the reaction was heated to 50 °C. Complex **1** (10 mg, 0.012 mmol) was weighed into a custom-made aluminum weighing tray and added to the reaction mixture. Samples were taken at regular intervals via syringe through the septum. Samples were analyzed by GC with a Pona column.

General Experimental Procedure for Cross-Metathesis (CM) of 1-Dodecene with Styrene (Representative Procedure). A 250 mL three-necked round-bottom flask was fitted with a reflux condenser, thermometer, and septum. A needle was inserted through the septum and connected to a gas supply via a needle valve to ensure a slow and steady stream of argon through the reaction solution. Styrene (13.8 mL, 123 mmol), phenol (570 mg, 6.4 mmol), and 1-dodecene (7.8 mL, 41 mmol) were added to the reaction vessel, and the reaction was heated to 50 °C. Complex **1** (5.0 mg, 0.006 mmol) was weighed into a custom-made aluminum weighing tray and added to the reaction mixture. Samples were taken at regular intervals via syringe through the septum. Samples were analyzed by GC with a Pona column and by GC-MS with an MDN column.

General Experimental Procedure for Cross-Metathesis (CM) of 1-Dodecene with 5-Hexene-2-one (Representative Procedure). A 250 mL three-necked round-bottom flask was fitted with a dry ice reflux condenser, thermometer, and septum. A needle was inserted through the septum and connected to a gas supply via a needle valve to ensure a slow and steady stream of argon through the reaction solution. 5-Hexene-2-one (14.0 mL, 68.8 mmol), 1-dodecene (7.8 mL, 41 mmol), and phenol (1.20 g, 12.8 mmol) were added to the reaction vessel, and the reaction was heated to 50 °C. Complex **1** (10 mg, 0.012 mmol) was weighed into a custom-made aluminum weighing tray and added to the reaction mixture. Samples were taken at regular intervals via syringe through the septum. Samples were analyzed by GC with a Pona column and by GCMS with an MDN column.

General Experimental Procedure for Cross-Metathesis (CM) of 3,3-Dimethyl-1-butene with 4-Hexen-1-yl acetate (Representative Procedure). A 250 mL three-necked round-bottom flask was fitted with a dry ice reflux condenser, thermometer, and septum. A needle was inserted through the septum and connected to a gas supply via a needle valve to ensure a slow and steady stream of argon through the reaction solution. 4-Hexen-1-yl acetate (8.4 g, 58.0 mmol), phenol (545 mg, 0.58 mmol), and 3,3-dimethyl-1-butene (18 mL, excess) was added to the reaction vessel and the reaction was heated to reflux. Complex **1** (47 mg, 0.058 mmol) was weighed into a custom-made aluminum weighing tray and added to the reaction mixture. Samples were taken at regular intervals via syringe through the septum. Samples were analyzed by GC with a Pona column and by GC-MS with an MDN column.

Self-Metathesis of 1-Octene Using the in-Situ Method for Preparing a Metathesis Catalyst with Added Phenol. Reactions were carried out in a 100 mL three-necked flask fitted with a reflux condenser, thermometer, and septum. The reflux condenser was connected to a cooling bath set at 5 °C to ensure a constant flow of chilled water through the jacket, thereby preventing loss of octene. The top of the condenser was connected to a bubbler in order to monitor liquid losses and gas emissions. The thermometer was positioned below the level of the reaction solution to ensure correct temperature monitoring. A needle inserted through the septum and connected to a gas supply via a needle valve was used to ensure a slow and steady stream of argon or hydrogen bubbles through the reaction solution. Argon was used during the initial phase to purge the system. Phenol (6.831 M in chlorobenzene), tricyclohexylphosphine (0.372 M in chlorobenzene),

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[42] A report detailing the full scope and generality of phenol addition to CM reactions catalyzed by **2** will be published shortly.

[43] Forman, G. S.; Tooze, R. P. (Sasol Technology UK), World Patent, WO 2004056728, 2004.

[44] Armarego, W. L. F.; Perrin, D. D. *Purification of Laboratory Chemicals*, 4th ed; Butterworth Heinemann: Oxford, 2002.

1,4-butynediol diacetate (BDD) (0.983 M in chlorobenzene), and $RuCl_3{\cdot}3H_2O$ (0.081 M in EtOH) stock solutions were prepared using degassed solvents passed over basic alumina and stored under basic alumina under an Ar atmosphere. The reagents were added in the following sequence; 1-octene (20 mL, 0.127 mmol), phenol (1.07 mL, 7.3 mmol), PCy_3 (0.10 mL, 0.037 mmol), BDD (0.15 mL, 0.15 mmol), and $RuCl_3{\cdot}3H_2O$ (0.18 mL, 0.015 mmol). After all the reagents were added, the gas flow was changed to hydrogen and the reaction was heated at the desired temperature by means of a preheated oil bath, and stirred using a magnetic stirrer bar. Samples were taken at regular intervals via syringe through the septum and analyzed by GC-FID. 1-Octene (20 mL) was employed in all experiments, and catalyst, solvent, and additive amounts were calculated relative to this and octadecane (0.5 mL) was used as internal standard.

General Method for Ethenolysis of 2-Octene with Added Phenol. Reactions were carried out in a 50 mL Parr autoclave fitted with a stirrer, a diptube for gas entrainment, and an outlet (vent) line. The reactor was flushed with argon, sealed and flushed with ethylene. 2-Octene (80% *cis*, 16 mL, 1.0 mmol) was transferred via syringe to an ethylene flushed sample bomb and introduced to the reactor under a few bar of ethylene pressure. Stirring was initiated (1000 rpm), and the autoclave contents were heated to 45 °C. The catalyst (8.23 mg, 0.01 mmol) was weighed into a sample tube, dissolved in 8 mL of octane, transferred via syringe to the sample bomb, and introduced to the reactor under ethylene pressure so as to reach the desired reaction pressure in the autoclave. As ethylene dissolved in the mixture and reactor pressure dropped, the pressure was maintained by opening the gas inlet line. Once the desired pressure could be maintained with no further pressure drop, the system was closed and left to stir for 15 h. Samples were taken at the end of the run and analyzed by GC-FID.

Cross-Metathesis (CM) of 1-Decene with Methyl Acrylate Using 2 and *p*-Cresol. A 250 mL three-necked round-bottom flask was fitted with a dry ice reflux condenser, thermometer, and septum. A needle was inserted through the septum and connected to a gas supply via a needle valve to ensure a slow and steady stream of argon through the reaction solution. Methyl acrylate (8.7 mL, 97 mmol), untreated Aldrich 1-decene (9.0 mL, 48 mmol), and *p*-cresol (2.5 g, 23 mmol) were added to the reaction vessel and the reaction was heated to 50 °C. Complex **2** (40 mg, 0.048 mmol) was weighed into a custom-made aluminum weighing tray and added to the reaction mixture. Samples were taken at regular intervals via syringe through the septum. Samples were analyzed by GC with a Pona column and by GC-MS with an MDN column.

General Method for Measuring Initiation Rate Constants. The desired phenol (50 equiv) was dissolved in 1-octene (2 mL). Complex **1** (1 equiv) was added to the octene/phenol solution with vigorous stirring. Approximately 1 mL of this solution was immediately transferred to a degassed NMR tube containing a phosphoric acid/D_2O capillary. The NMR tube was placed into a beaker of water at 15 °C and immediately transferred to a Varian 500 NMR machine (internal temperature 15 °C). An NMR routine was set up where ^{31}P NMR spectra were recorded at regular intervals. The average amount of time that elapsed between addition of the catalyst to the solution and collection of the first ^{31}P NMR spectrum was 6 min.

General Method for Measuring Phosphine Exchange Rates. The desired phenol (50 equiv), PCy_3 (1.5 equiv), and complex **1** (1 equiv) were dissolved in toluene-d_8 (1.5 mL). The exchange rate between free and bound phosphine was measured at 50 °C using a selnogp.3 pulse sequence. ^{31}P NMR spectra were calculated at variable mixing times and time-dependent magnetization data were analyzed to give the desired rate constants. The pulse sequence used causes the selective inversion of a single line (PCy_3), which puts the magnetization of the free phosphine along the Z axis. Both the new signals for complex **1** and for PCy_3 (from dissociation) are detected. With increasing mixing time, the signal for complex **1** increases and the signal for PCy_3 decreases.

Computational Details. All geometry optimizations were performed with the DMol^3 density functional theory (DFT) code[45] as implemented in the MaterialsStudio (Version 3.0) program package of Accelrys Inc. The nonlocal generalized gradient approximation (GGA) functional by Perdew and Wang (PW91)[46] was used for all geometry optimizations. The convergence criteria for these optimizations consisted of threshold values of 2×10^{-5} Ha, 0.00189 Ha/Å, and 0.00529 Å for energy, gradient, and displacement convergence, respectively, while a self-consistent field (SCF) density convergence threshold value of 1×10^{-6} Ha was specified. DMol^3 utilizes a basis set of numeric atomic functions, which are exact solutions to the Kohn–Sham equations for the atoms.[47] These basis sets are generally more complete than a comparable set of linearly independent Gaussian functions and have been demonstrated to have small basis set superposition errors.[47] In the present study a polarized split valence basis set, termed double numeric polarized (DNP) basis set has been used. All geometry optimizations employed highly efficient delocalized internal coordinates.[48] Selected optimized geometries were subjected to full frequency analyses at the same GGA/PW91/DNP level of theory to afford calculation of Gibbs free energy corrections to the total electronic energies at 298.15 K and 1 atm with the inclusion of zero-point energy (ZPE) corrections. All energies reported in the text are total electronic energies except when explicitly stated to the contrary. The calculation of phenol coordination energies was performed according to the following general reaction: $[Ru] + n PhOH \rightarrow [Ru][PhOH]_n$ with $\Delta E(\text{coordination}) = E\{[Ru][PhOH]_n\} - E\{[Ru]\} - \{n \times E(PhOH)\}$.

Acknowledgment. We gratefully acknowledge the assistance of Mrs. Melanja Smith of the University of St Andrews Chemistry Department NMR Service, Dr. John Walton for assistance with EPR experiments, Dr. Simon Duckett (University of York) for assistance with phosphorus exchange experiments, Dr. Ronan Bellabarba (Sasol, St Andrews) for stimulating discussions and Mr. Ivan Bester (Information Management, Sasol, Sasolburg) for infrastructure support to the Sasol Molecular Modeling group.

OM0503848

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