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Widening the Latency Gap in Chelated Ruthenium Olefin Metathesis Catalysts

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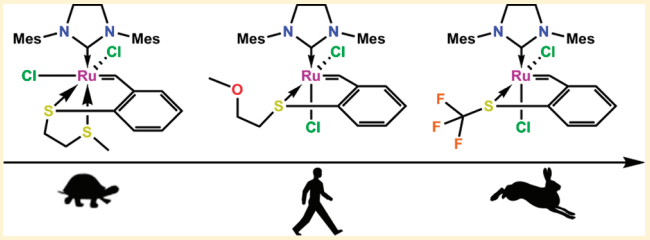
Supporting Information

ABSTRACT: The synthesis of novel sulfur-chelated ruthenium benzylidenes afforded latent catalysts with a wider range of activities and new isomeric forms. A ruthenium complex with a tridentate ligand displayed latency for even one of the most reactive ROMP monomers, dicyclopentadiene, while a room temperature latent trifluoromethyl-substituted thioether derivative was shown to be the most active sulfur-chelated precatalyst to date in several metathesis reactions at higher temperatures. These new complexes widen the spectrum of activity for this family of catalysts, enabling several practical applications and enhancing the understanding for the mechanisms of activation in strongly chelated ruthenium alkylidenes.



INTRODUCTION

Olefin metathesis[1] in the past decade has advanced several synthetic applications, particularly in the synthesis of special polymers by ring-opening metathesis polymerization (ROMP) of strained rings[2] and in the preparation of drugs, where ring-closing metathesis (RCM) is useful in the formation of ubiquitous macrocycles.[3] This recent success is mostly a consequence of the remarkable development of well-defined carbene catalysts based on molybdenum[4] and ruthenium.[5] Nonetheless, several technical problems arise when mixing commercial catalysts with very reactive ROMP monomers.[6] For instance, high reaction rates impede introduction of homogeneous solutions into the desired mold.[7] Thus, several latent olefin metathesis precatalysts were developed.[8,9] When is a catalyst latent? Catalytic latency may be defined as the property of a precatalyst presenting negligible activity at a given temperature (usually room temperature) and significant reaction progress when suitable stimuli are applied. Naturally, several parameters influence the "latency" of a catalyst in a specific reaction, such as substrate and solvent. Activating methods may be divided into two subcategories: chemical[9] and physical.[8] The first case usually presents excellent interconversion between inactive and active forms, but an extra chemical needs to be added to the final product, which may be undesirable in some cases. With regard to the latter, the introduction of foreign products is not necessary, and several recent examples have shown numerous effective ways to activate latent catalysts, such as heat,[8b−g] light,[8h,10] and even ultrasound.[8a]

Even though many latent olefin metathesis catalysts have been studied, the vast majority are not completely inert to most substrates at room temperature, and in many cases the nature of the active species and the mechanism of activation are not fully understood. Complexes **1**[8f] and **6**[8h] are the only physically activated precatalysts reported to be fully inert at room temperature to a series of ROMP monomers such as substituted norbornenes and cyclooctenes. However, prolonged exposure to norbornene and, more importantly, dicyclopentadiene (DCPD), produces polymers even at room temperature.[11] An additional issue with physically activated initiators is that normally only a small fraction of the precatalysts become active,[12] contributing to an overall lower effectiveness of the system.

In this work we present further development of sulfur-chelated precatalysts geared to address two problems: on one hand to make a precatalyst latent to DCPD and on the other hand to enhance the activity of the active form of the dormant catalyst.

RESULTS AND DISCUSSION

We have shown in previous work that sulfur-chelated ruthenium catalysts are latent to several substrates in RCM, cross-metathesis (CM), and ROMP reactions, showing reasonable rates upon heating[8f] or irradiating with UV light.[13] However, DCPD and unsubstituted norbornene are highly active substrates, and their polymerization occurs at room temperature with all known sulfur-chelated complexes. Due to the significance of the high-performance materials derived from these monomers,

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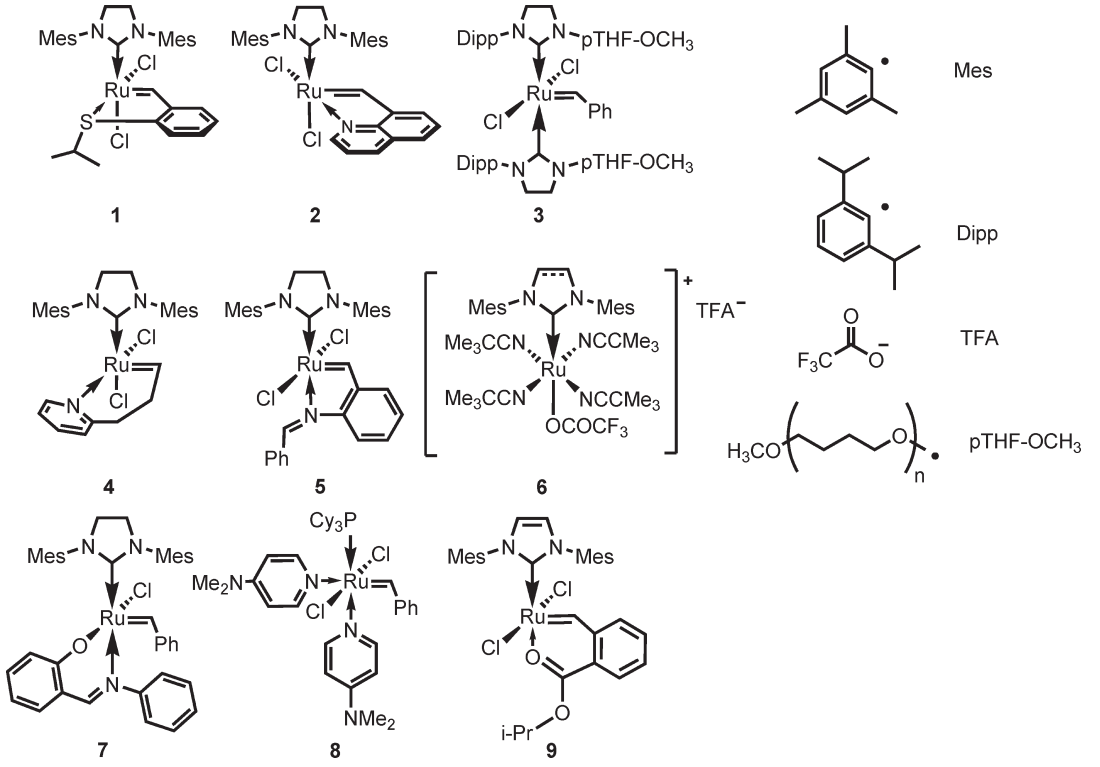
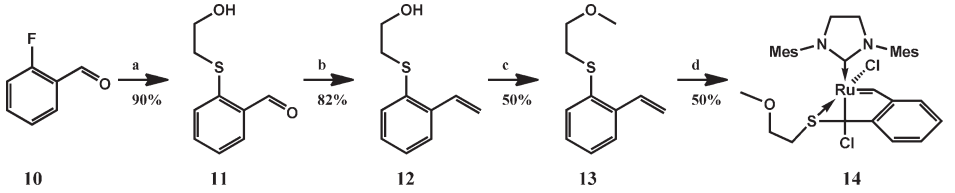


Figure 1. Latent ruthenium olefin metathesis catalysts.[6,7]

Scheme 1. Preparation of Olefin Metathesis Precatalysts 14[a]



[a] Conditions: (a) mercaptoethanol, K_2CO_3, DMF, 60 °C; (b) CH_3PPh_3I, KOtBu, ether; (c) CH_3I, NaH, THF at room temperature; (d) $(SIMes)(PCy_3)(Cl)_2Ru{=}CHPh$, CuCl, CH_2Cl_2, room temperature.

ways to increase the latency of *S*-chelated Ru benzylidenes were explored.

Three-Point Chelates. Thus, with the intent to form an 18*e* precatalyst, a tridentate styrene ligand with both sulfide and ether functionalities was designed (Scheme 1).

Mercaptoethanol was reacted with 2-fluorobenzaldehyde (**10**) in the presence of K_2CO_3 by nucleophilic aromatic substitution using the same conditions previously developed by us.[8f] Wittig olefination of **11** followed by methylation of the hydroxyl group gave the desired styrene ligand precursor (**13**). Commercially available second-generation Grubbs catalyst was reacted with **13** in the presence of CuCl to give new complex **14**. As expected, and according to the ^{1}H NMR analysis, **14** was assigned a *cis*-dichloro geometry.[8f] Unfortunately, structural analysis by X-ray diffraction revealed that only the sulfur atom was bound to the metal (Figure 2), similar to a previous study by Grubbs et al.[14] The insignificant deviation of the O−CH_3 ^{13}C NMR signal in the spectra of free ligand **13** and complex **14** (∼0.1 ppm) also supports the suggestion that there are no significant Ru−O interactions in solution. The strong *trans* influence of the benzylidene ligand likely destabilizes the coordination of the oxygen atom at this position.[15]

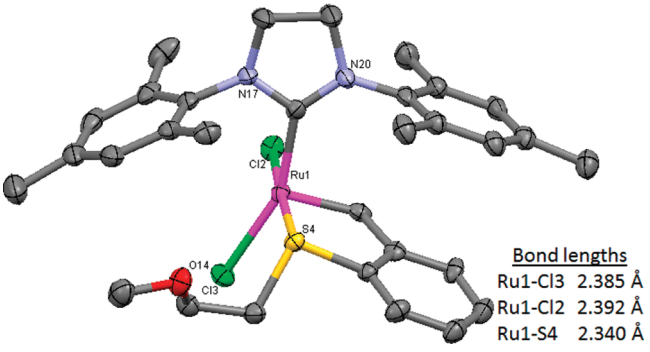


Figure 2. X-ray structure of complex **14**.

In order to enhance the binding of the additional chelating atom, an analogous ligand with an extra sulfur atom (instead of oxygen) was proposed. Thus, methylation of 1,2-ethanedithiol to

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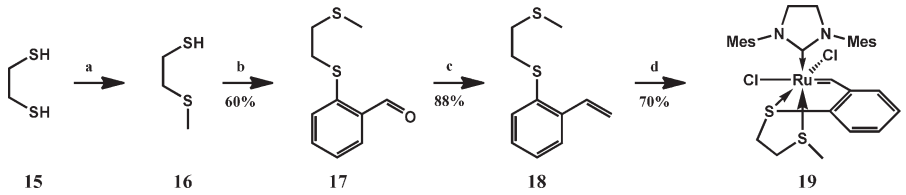
Scheme 2. Preparation of Olefin Metathesis Precatalyst 19[a]



[a] Conditions: (a) CH_3I, NaH, DMF at room temperature; (b) **10**, DMF, 60 °C; (c) CH_3PPh_3I, KOtBu, ether; (d) $(SIMes)(PCy_3)(Cl)_2Ru{=}CHPh$, CuCl, CH_2Cl_2, room temperature.

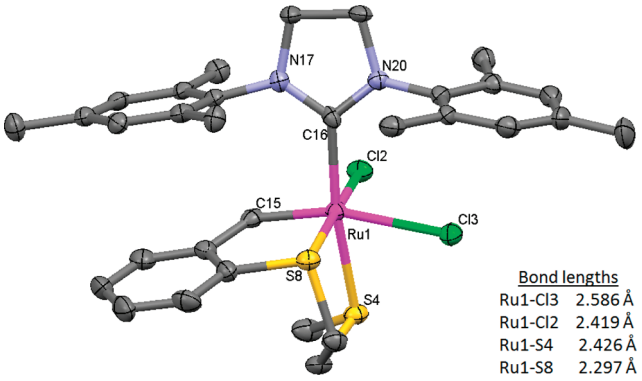


Figure 3. X-ray structure of complex **19**.

afford thioether **16** was followed by nucleophilic aromatic substitution of 2-fluorobenzaldehyde. A Wittig olefination reaction completed the synthesis of styrene **18** in good yields. The novel three-point-chelated ruthenium-based complex **19** was prepared by mixing the ligand precursor with second-generation Grubbs catalyst in the presence of CuCl.

In contrast to previous results where both *cis* and *trans* isomers could be obtained,[8f,16] only one product was observed in this case. The ^{1}H NMR spectrum of the product disclosed the typical asymmetric structure observed for *cis*-dichloro arrangements. In this case the ^{13}C NMR S−CH_3 signal shifted from 15.4 ppm in **18** to 40.6 ppm in **19**, indicative of sulfur binding to ruthenium. Unexpectedly, the X-ray diffraction analysis showed a chloride atom *trans* to the benzylidene moiety. This type of *cis*-dichloro configuration has not been observed to date in ruthenium alkylidenes and possesses a uniquely long Cl−Ru bond of 2.586(1) Å coerced by the *trans* influence of the benzylidene ligand (Figure 3). The other Cl−Ru bond in **19** is of normal length, 2.419(1) Å. For comparison, the Ru−Cl distances observed in other compounds that contain a *cis*-dichloro-ruthenium moiety, with the metal being coordinated in a (pseudo)octahedral environment to two additional C-ligands and two S-ligands, are 2.456, 2.393−2.408, 2.412−2.435, 2.432−2.449, and 2.418−2.432 Å.[17]

New complexes **14** and **19** were tested with respect to their temperature dependency of ROMP and RCM activity. As expected, the sulfur−oxygen complex **14** initiated ROMP of a DCPD solution at room temperature, converting 40% of the monomer after 2 h. In comparison, an insoluble gel was formed after 15 min when the reaction was performed at 80 °C. Most gratifyingly, the sulfur−sulfur chelated complex **19** showed less than 1% monomer conversion after two hours at 20 °C, whereas increased conversion by raising the temperature could be clearly observed (Table 1). At very high temperatures (Table 1, entry 5), decomposition becomes significant and conversion decreases. This type of behavior has been recently observed by Schanz et al. with a Ru vinylvinylidene complex.[18]

Table 1. DCPD Conversion at Various Temperatures in the Presence of 19

entry[a]	temp (°C)	conversion after 1 h (%)	conversion after 3 h (%)
1	20	<1	<1
2	40	<1	8
3	60	20	44
4	80	36	46
5	110	36	37

[a] Conditions: 0.1 mol % **19**.; substrate 0.45 M, in chlorobenzene. Conversion determined by GC-MS using mesitylene as internal standard.

In addition, RCM of diethyldiallylmalonate (DEDAM) with catalysts **14** and **19** was also conducted. As expected no reaction was observed at 25 °C, and both displayed negligible activity also upon heating to 80 °C (<1% for both complexes after 24 h). UV irradiation did not improve RCM conversions either. These results indicate that both initiators are active only toward ROMP reactions. Thus, the goal of reducing the activity of S-chelated ruthenium benzylidenes toward DCPD was achieved by the addition of an additional chelating sulfur atom.

Faster Latent Precatalyst. We have recently advocated that *cis*-dichloro S-chelated olefin metathesis complexes are inactive and reactions occur only through their *trans* counterparts.[13] These precatalysts open an interesting possibility, where active (*trans*) forms may be modified to enhance activity without modifying the latent status of the *cis* forms.[19]

For example, we have shown that a 4-nitro substitution in the benzylidene ring does not influence the latency of complex **1**, while in the latent *trans* N-chelated complex **20** the effect is very significant,[16b] as demonstrated by Grela et al. previously for oxygen-chelated complexes (Figure 4).[20] Thus, we decided to design a highly active sulfur-chelated *trans* dichloro olefin metathesis catalyst, while keeping the *cis* isomer latent. We envisioned that the replacement of methyl with a trifluoromethyl group on the sulfur would significantly weaken the Ru−S bond in **23** and make it a more active catalyst.

Thus, using an optimized version of the Suzuki coupling previously reported by us,[22] commercially available **21** was reacted with vinyl boronic acid ester, giving styrene **22**. Reaction with $(SIMes)py_2(Cl)_2Ru{=}CHPh$[21] gave a new complex, **23**, as a single isomer. Complex **23** was studied in solution by ^{1}H NMR, showing the expected spectrum observed for *cis* isomers. Single-crystal X-ray

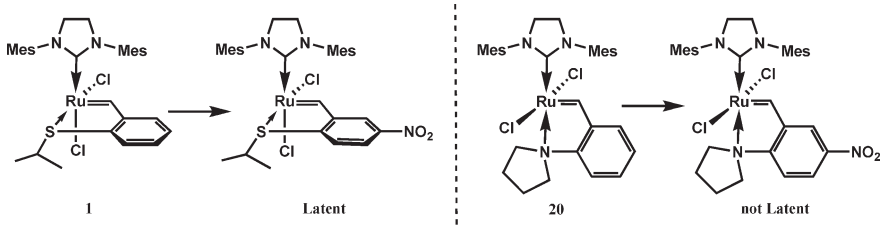
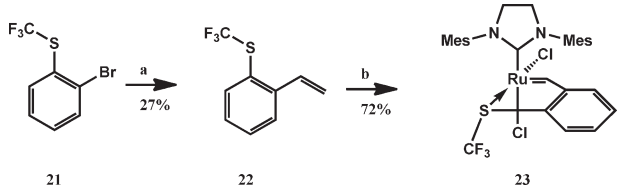


Figure 4. Effects of electron-withdrawing groups on latency of *cis*- versus *trans*-dichloro ruthenium benzylidenes.

Scheme 3. Preparation of Complex 23[a]



[a] Conditions: (a) vinyl boronic acid, di(*n*-butyl)ester, $PdCl_2$, S-Phos, THF, NaOH, 80 °C; (b) $(SIMes)py_2(Cl)_2Ru{=}CHPh$,[19] CH_2Cl_2, 45 °C.

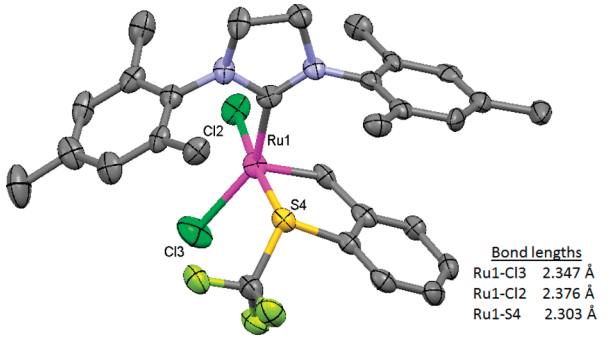


Figure 5. X-ray structure of complex **23** (only one of three crystallographically independent molecular units is shown).

diffraction analysis supported the proposed structure (Figure 5). When dissolved in benzene and irradiated, peaks of the corresponding *trans* isomer could be observed in the ^{1}H NMR spectrum, demonstrating that a significant quantity of a viable active species may be obtained.

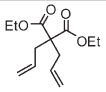
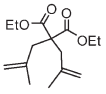
To test the latency of novel precatalyst **23**, it was added to a solution of DEDAM in CH_2Cl_2 and stirred at 27 °C in the dark. After 24 h, less than 1% conversion was observed. After 1 week, only 1.5% product could be found, indicating that the precatalyst displays good latency at room temperature for this substrate.

Table 2 summarizes the results of RCM and CM reactions of the two complexes in hot toluene (the low polarity of toluene compared to CH_2Cl_2 stabilizes the *trans* isomer, increasing the relative amount of the active species in solution).[8c,16a] In order to evaluate the activity of the active form, all metathesis reactions were concurrently carried out with both **23** and **1**.

Even though latent complex **1** reaches full conversion given enough time, it is very slow even at high temperatures. CF_3-substituted complex **23** displayed improved rates, decreasing the reaction time to full conversion from days to a few hours.

In contrast to complex **1**, the active form of new complex **23** is very active and difficult to isolate, probably indicating that *trans*-**23** readily undergoes decomposition reactions.[8h] Supporting this

Table 2. Comparative Olefin Metathesis Activity of 23 and 1

Entry[a]	Substrate	Cat. Load (mol %)	Conversion with 23 (%)	Conversion with 1 (%)
1		1	75	5
2		5	88	4
3		5	97[b]	16
4[c]		5	<1	<1
5[d]		5	77	65
6[e]		1	70[f]	5

[a] Conditions: 0.5 M substrate in toluene, 1 h at 80 °C. [b] Includes 12% isomerization products. [c] No reaction also after 24 h. [d] Polymerization was also observed. [e] 0.15 M substrate in toluene. [f] Includes 30% isomerization products.

Table 3. Comparative Activity of 23 and 1 at Room Temperature

entry[a]	irradiation[b]	catalyst	conversion (%)[c]
1	dark	**1**	<1
2		**23**	<1[d]
3	350 nm	**1**	<1
4		**23**	86

[a] Conditions: 0.1 M DEDAM with 0.5 mol % precatalyst in CH_2Cl_2 for 2 h at room temperature. [b] Irradiation in a Rayonet apparatus. The "dark" samples were covered with aluminum foil and set inside the Rayonet apparatus for both irradiated and dark samples to be at the same temperature/stirring rate. [c] Determined by GC-MS. [d] Conversion after 1 week was less than 2%.

assumption, ruthenium hydrides (typical ruthenium decomposition products) have been shown to be effective in double-bond isomerization,[23] and this may explain the high quantity of isomerized products observed in entries 6 and 3, Table 2.

As in the case of complex **1**, photoactivation of complex **23** was also determined.[13] Table 3 shows RCM activity under UV irradiation.

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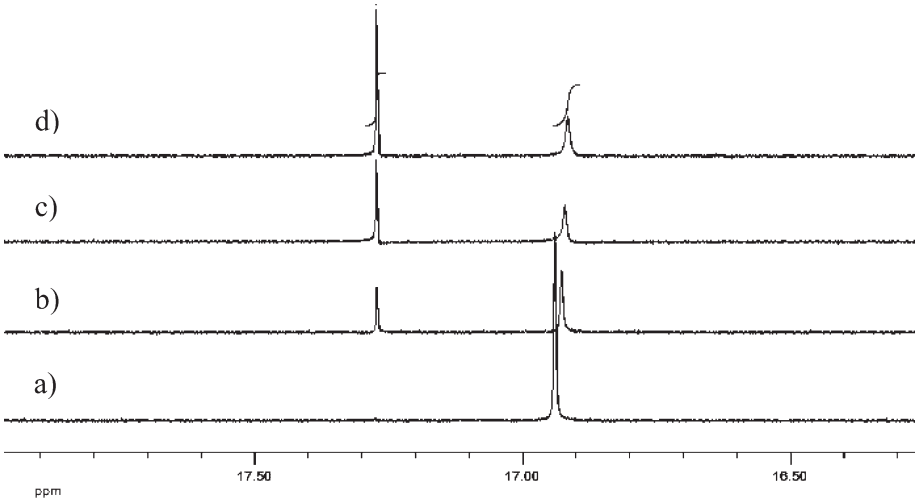

Figure 6. Benzylidene area in ^{1}H NMR of complex **23**: (a) no irradiation; (b) 20 min irradiation; (c) 100 min irradiation; (d) 200 min irradiation.

Table 4. Comparative ROMP Activity of 23 and 1

entry[a]	irradiation[b]	temp (°C)	reaction time (h)	conversion with **1** (%)[c]	conversion with **23** (%)[c]
1	none	~35	24	<1	<1
2	none	80	1.5	32	91
3	350 nm	~35	1	<1	94

[a] Conditions: 0.5 M cyclooctene with 0.3 mol % precatalyst in 1,2-dichloroethane. [b] Irradiation in a Rayonet apparatus. [c] Determined by GC-MS using mesitylene as internal standard.

In order to verify that the *trans* isomer is truly the active species, a solution of **23** in C_6D_6 was irradiated with UV light (350 nm), and a 4:3 *trans*/*cis* mixture was obtained (Figure 6). To this mixture was added hexane to selectively precipitate the *cis* isomer, followed by filtration to remove it from the mixture. The green solid residue after solvent evaporation was redissolved in C_6D_6 and analyzed by ^{1}H NMR, effectively showing that mainly the *trans* isomer was obtained (see the Supporting Information). DEDAM was added to this solution in the glovebox, and the reaction was followed at 25 °C. After 35 min, 15% conversion was observed, which increased to 62% in 15 h.

Finally, the activity of complex **23** for ROMP was also tested. *cis*-Cyclooctene was chosen as a model substrate (Table 4).

As shown in Table 4, complex **23** demonstrated a significantly higher activity than **1** also for ROMP reactions.

CONCLUSIONS

Three new sulfur-chelated ruthenium benzylidenes are presented. These complexes were designed to improve two shortcomings of most latent olefin metathesis catalysts: the lack of true latency toward reactive ROMP monomers and the slow kinetics of the dormant catalysts when activated. To address the first issue, the addition of a second sulfur-chelating atom resulted in a complex (**19**) that displayed high latency at room temperature for dicyclopentadiene ROMP. Moreover, this new complex showed a novel *cis*-dichloro geometry with an unusually long Ru−Cl bond. The use of an additional oxygen-chelating atom instead of sulfur (complex **14**) resulted in a bidentate chelate that did not display enhanced latency, supporting the theory that tridentate chelation is necessary. Seemingly, a strong *trans* influence from the benzylidene ligand disfavors oxygen coordination in this case. In order to enhance the activity of sulfur-chelated ruthenium catalysts, a trifluoromethyl group was attached to the chelating sulfur atom. Indeed, catalyst **23** in its active form was found to be much more active than its sulfur-chelated predecessors.[8g]

Expanding the window of reactivity in dormant precatalysts, on one hand making the resting species less active toward the most reactive substrates and, on the other, improving the active state, advances our understanding of the mechanism of latent catalysis and may result in important practical applications.

EXPERIMENTAL SECTION

General Procedures. All reagents were of reagent grade quality, purchased commercially from Sigma-Aldrich, Alfa-Aesar, or Fluka, and used without further purification. All solvents were dried and distilled prior to use. Purification by column chromatography was performed on Davisil chromatographic silica media (40−60 μm). TLC analyses were performed using Merck precoated silica gel (0.2 mm) aluminum [backed] sheets. NMR spectra were recorded on Bruker DPX_{200}, DPX_{400}, or DMX_{500} instruments; chemical shifts, given in ppm, are relative to Me_4Si as the internal standard or to the residual solvent peak. HR-MS data were obtained using a Thermoscientific LTQU XL Orbitrap HRMS equipped with APCI (atmospheric-pressure chemical ionization). Gas chromatography data were obtained using an Agilent 6850 GC equipped with an Agilent 5973 MSD working under standard conditions and an Agilent HP5-MS column. Purification on preparative HPLC was carried out on a Jasco instrument equipped with an MD-1515 photodiode array detector and a Phenomenex normal phase Luna 10 μm column (250 × 21.2 mm) working at a 20 mL/min flow.

2-(2-Hydroxyethylthio)benzaldehyde (11). 2-Mercaptoethanol (1.2 mL, 16.6 mmol) was added to K_2CO_3 (2.45 g, 7.8 mmol) in 10 mL of DMF. 2-Fluorobenzaldehyde (2.0 g, 16.1 mmol) was added, and the mixture was stirred overnight at 60 °C. After cooling, the mixture

was poured into 20 mL of saturated $NaHCO_3$ and extracted with ether (3 × 25 mL). The extracts were washed with water and dried over $MgSO_4$, and the solvent was removed under reduced pressure. The crude product was purified by chromatography on silica gel (petroleum ether−ethyl acetate gradient from 10:1 to 4:1) to yield **11** as a colorless oil (90%). ^{1}H NMR (200 MHz, $CDCl_3$, ppm): δ 2.06 (bs, 1H), 3.17 (t, J = 6.1 Hz, 2H), 3.83 (t, J = 6.1 Hz, 2H), 7.29−7.37 (m, 2H), 7.45−7.57 (m, 1H), 7.55−7.51 (m, 2H), 7.83 (d, J = 7.6 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 36.1, 60.3, 125.8, 128.7, 132.2, 134.0, 134.2, 140.4, 191.6. $C_9H_{10}O_2S$ GC-MS (EI): m/z 182.00 (M^+), calcd 182.04.

2-(2-Vinylphenylthio)ethanol (12). Methyl triphenylphosphonium iodide (8.6 g, 21.3 mmol) was dissolved in 25 mL of ether before KOtBu (2.6 g, 23.2 mmol) was added in one portion at 0 °C. After stirring for 10 min at room temperature, **11** (2.75 g, 15.1 mmol) was added in one portion at 0 °C, and the reaction stirred at room temperature until complete disappearance of the reactants (2−3 h). The mixture was poured into 50 mL of saturated $NaHCO_3$ and extracted with ether (3 × 50 mL). The extract was dried over $MgSO_4$, and the solvent removed under reduced pressure. The crude product was further purified by chromatography on silica gel (petroleum ether−ethyl acetate gradient from 10:1 to 4:1) to yield **12** as a colorless oil (82%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 2.25 (s, 1H), 3.03 (t, J = 6.0 Hz, 2H), 3.67 (s, 2H), 5.36 (dd, J = 11.0, 1.2 Hz, 1H), 5.70 (dd, J = 17.4, 1.2 Hz, 1H), 7.28−7.19 (m, 2H), 7.30 (dd, J = 17.4, 11.0 Hz, 1H), 7.46−7.42 (m, 1H), 7.55−7.51 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 37.7, 60.2, 116.2, 126.3, 127.5, 128.1, 132.0, 132.8, 134.6, 139.5. $C_{10}H_{12}OS$ GC-MS (EI): m/z 180.06 (M^+), calcd 180.06.

(2-Methoxyethyl)(2-vinylphenyl)sulfane (13). NaH (115 mg, 4.8 mmol) was added in one portion to **12** (433 mg, 2.40 mmol) in DMF and stirred for 10 min. CH_3I (450 μL, 7.2 mmol) was then added dropwise, and the mixture stirred overnight at room temperature. The mixture was poured into 20 mL of saturated $NaHCO_3$ and extracted with ether (3 × 25 mL). The extracts were washed with water and dried over $MgSO_4$, and the solvent was removed under reduced pressure. The crude product was purified by chromatography on silica gel (petroleum ether−ethyl acetate gradient from 10:1 to 4:1) to yield as a colorless oil (50%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 3.04 (t, J = 6.7 Hz, 2H), 3.34 (s, 3H), 3.53 (t, J = 6.7 Hz, 2H), 5.34 (dd, J = 11.0, 1.3 Hz, 1H), 5.69 (dd, J = 17.4, 1.3 Hz, 1H), 7.24−7.20 (m, 2H), 7.28 (dd, J = 17.4, 11.3 Hz, 1H), 7.44−7.40 (m, 1H), 7.54−7.50 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 33.8, 58.7, 70.9, 115.9, 126.1, 127.1, 128.1, 131.2, 133.9, 134.8, 139.2. $C_{11}H_{14}OS$ GC-MS (EI): m/z 194.10 (M^+), calcd. 194.08.

2-(2-(Methylthio)ethylthio)benzaldehyde (17). Ethanedithiol (0.84 mL, 1.25 mmol) was added to K_2CO_3 (3.00 g, 21 mmol) in 10 mL of DMF. CH_3I (0.69 mL, 1.35 mmol) was then added dropwise, and the mixture stirred overnight at room temperature. 2-Fluorobenzaldehyde (2.0 g, 16.1 mmol) was added, and the mixture was stirred overnight at 60 °C. After cooling, the mixture was poured into 20 mL of saturated $NaHCO_3$ and extracted with ether (3 × 25 mL). The extracts were washed with water and dried over $MgSO_4$, and the solvent was removed under reduced pressure. The crude product was purified by chromatography on silica gel (petroleum ether−ethyl acetate gradient from 10:1 to 4:1) to yield **17** as a colorless oil (60%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 2.15 (s, 3H), 2.79−2.72 (m, 2H), 3.21−3.13 (m, 2H), 7.34 (t, J = 7.2, 7.2 Hz, 1H), 7.44 (d, J = 7.9 Hz, 1H), 7.53 (dt, J = 8.0, 7.9, 1.6 Hz, 1H), 7.85 (dd, J = 7.7, 1.2 Hz, 1H), 10.40 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 15.6, 32.9, 33.0, 125.9, 128.7, 131.9, 134.0, 134.4, 140.4, 191.4. $C_{10}H_{12}OS_2$ GC-MS (EI): m/z 212.00 (M^+), calcd 212.03.

Methyl(2-(2-vinylphenylthio)ethyl)sulfane (18). Methyl triphenylphosphonium iodide (1.54 g, 3.81 mmol) was dissolved in 25 mL of ether before KOtBu (0.458 g, 4.08 mmol) was added in one portion at 0 °C. After stirring for 10 min at room temperature, **17** (0.578 g, 2.72 mmol) was added in one portion at 0 °C and the reaction stirred at room temperature until complete disappearance of the reactants (2−3 h). The mixture was poured into 50 mL of saturated $NaHCO_3$ and extracted with ether (3 × 50 mL). The extract was dried over $MgSO_4$, and the solvent removed under reduced pressure. The crude product was further purified by chromatography on silica gel (petroleum ether−ethyl acetate gradient from 10:1 to 4:1) to yield **18** as a colorless oil (88%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 2.12 (s, 3H), 2.72−2.64 (m, 2H), 3.11−3.03 (m, 2H), 5.37 (dd, J = 11.0, 1.2 Hz, 1H), 5.72 (dd, J = 17.4, 1.2 Hz, 1H), 7.26 (ddt, J = 1.3, 6.8, 9.3, Hz, 2H), 7.31 (dd, J = 17.5, 11.0 Hz, 1H), 7.46−7.42 (m, 1H), 7.58−7.54 (m, 1H). ^{13}C NMR (MHz, $CDCl_3$, ppm): δ 15.4, 33.5, 33.9, 115.9, 126.2, 127.3, 128.1, 131.6, 133.4, 134.7, 139.3. $C_{11}H_{14}S_2$ GC-MS (EI): m/z 210.00 (M^+), calcd 210.05

General Procedure for *cis*-Dichloro Catalysts (14, 19). In a glovebox, Grubbs second-generation catalyst (50 mg, 0.059 mmol) was added to 2 equiv of the ligand (**13** or **18**) in 10 mL of CH_2Cl_2 in one portion. The solution was stirred for 1 h at room temperature before CuCl (10 mg, 0.101 mmol) was added, and the mixture was stirred for 24 h. The solvent was removed by evaporation, and the product purified by silica gel chromatography (hexane−acetone gradient from 5:1 to 1:1). The fraction containing the product was evaporated, and the product was recrystallized from DCM−pentane at −18 °C.

14: blue solid (19.0 mg, 50%). Crystals suitable for X-ray analysis were obtained by slow diffusion of hexanes over a CH_2Cl_2 solution of **14** at −18 °C. ^{1}H NMR (500 MHz, CD_2Cl_2, ppm, 256 K):[23] δ 1.58 (s, 3H), 2.15 (s, 3H), 2.38 (s, 3H), 2.46 (s, 3H), 2.53 (s, 3H), 2.64 (s, 3H), 2.78 (ddd, J = 13.0, 8.8, 4.6 Hz, 1H), 3.46 (s, 3H), 3.58−3.47 (m, 3H), 4.21−3.76 (m, 4H), 5.96 (s, 1H), 6.76 (d, J = 7.7 Hz, 1H), 6.91 (s, 1H), 7.05 (s, 1H), 7.13 (s, 1H), 7.17 (t, J = 7.4 Hz, 1H), 7.51 (t, J = 7.5 Hz, 1H), 7.60 (d, J = 7.8 Hz, 1H), 17.05 (s, 1H). ^{13}C NMR (125 MHz, CD_2Cl_2, ppm): δ 13.9, 18.7, 20.9, 22.7, 26.0, 27.3, 31.6, 36.7, 123.3, 129.2, 129.4, 129.7, 130.1, 135.3, 137.3, 138.7, 139.8, 155.1, 213.8, 285.6. $C_{31}H_{38}Cl_2N_2ORuS$ HR-MS (ESI): m/z 623.1423 ($M - Cl$)$^+$, calcd 623.1431.

19: dark green solid (27.0 mg, 70%). Crystals suitable for X-ray analysis were obtained by slow diffusion of hexanes over a CH_2Cl_2 solution of **19** at −18 °C. ^{1}H NMR (500 MHz, CD_2Cl_2, ppm): δ 1.75 (s, 3H), 2.12 (s, 6H), 2.26 (s, 6H), 2.29 (m, 1H), 2.52 (s, 6H), 2.66 (m, 1H), 2.94 (m, 1H), 3.63 (m, 1H), 3.93 (s, 4H), 6.52 (s, 2H), 6.80 (d, J = 7.5 Hz, 1H), 6.99 (s, 2H), 7.30 (t, J = 7.2 Hz, 1H), 7.70 (dt, J = 7.5, 7.2 Hz, 2H), 16.91 (s, 1H). ^{13}C NMR (125 MHz, CD_2Cl_2, ppm): δ 18.7, 19.0, 21.2, 29.5, 31.9, 40.6, 52.2, 125.0, 129.7, 130.0, 130.2, 131.0, 131.3, 131.8, 135.6, 135.8, 136.5, 137.2, 137.4, 139.1, 156.0, 210.8, 302.0. $C_{31}H_{38}Cl_2N_2RuS_2$ HR-MS (ESI): m/z 639.1196 ($M - Cl$)$^+$, calcd 639.1203.

1-(Trifluoromethylsulfanyl)-2-vinylbenzene (22). Palladium acetate (32.0 mg, 48 μmol) and 2-dicyclohexylphosphimo-2′,6′-dimethoxy-1,1′-biphenyl (39.0 mg, 95 μmol) were dissolved in 2.0 mL of THF. **21** (120.0 μL, 0.460 mmol) was added, and the mixture was stirred for 15 min. Vinylboronic acid di-*n*-butyl ester (0.50 mL, 23.1 mmol) was added, followed by 1.0 mL of a 3.75 M NaOH aqueous solution, and the reaction mixture was heated to reflux (ca. 70 °C) for 4 h. After cooling, the mixture was extracted with 20 mL of *n*-hexane. The extract was washed once with 10 mL of 1 M sodium hydroxide, followed by a 3 × 10 mL wash with deionized water (to neutral pH). The organic layer was filtrated over silica, dried over $MgSO_4$, and evaporated. The yellow oil residue of the crude product was further purified by normal phase preparative HPLC using *n*-pentane as eluent to afford **22** as a pale yellow oil (25.5 mg, 27% overall). ^{1}H NMR(400 MHz, $CDCl_3$, ppm): δ 5.43 (dd, J = 1.0, 11.0 Hz, 1H), 5.77 (dd, J = 1.0, 17.5 Hz, 1H), 7.32 (dt, J = 1.5, 7.6 Hz, 1H), 7.38 (dd, J = 11.0, 17.5 Hz, 1H), 7.45 (tdd, J = 0.65, 1.4, 7.9 Hz, 1H), 7.69 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 77.2, 117.2, 122.7, 126.4, 128.5, 131.6, 134.4, 138.5, 143.0. ^{19}F NMR (375.5 MHz, $CDCl_3$, ppm): δ −42.4. $C_9H_7F_3S$ GC-MS (EI): m/z 244.00 (M^+), calcd 204.02.

Catalyst (23). **22** (25.5 mg, 0.125 mmol) and pyridine third-generation Grubbs catalyst (1.1 equiv) were dissolved in 4 mL of chloroform. The resulting solution was refluxed for 4.5 h and then evaporated to dryness. The crude product was purified by chromatography on silica gel using acetone−CH_2Cl_2 (1:10) as eluent to give **23** as an indigo solid after evaporation (126.4 mg, 72%). Crystals suitable for X-ray analysis were obtained by slow diffusion of hexanes over a CH_2Cl_2 solution of **23** at 4 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 1.56 (s, 3H), 2.10 (s, 3H), 2.28 (s, 3H), 2.38 (s, 3H), 2.52 (s, 3H), 2.61 (s, 3H), 3.86 (m, 2H), 4.09 (m, 2H), 5.92 (s, 1H), 6.71 (d, J = 7.1, 1H), 6.81 (s, 1H), 6.97 (2, 1H), 7.0 (s, 1H), 7.21 (t, J = 7.1 Hz, 1H), 7.53 (dt, J = 1.0, 7.8 Hz, 1H), 7.65 (d, J = 7.19, 1H), 16.85 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 17.3, 18.6, 19.2, 20.3, 20.9, 21.2, 51.3, 51.4, 124.0, 124.5 (q, J = 325 Hz), 128.8, 129.2, 129.6, 129.7, 129.8, 129.8 130.0, 131.0, 131.0, 134.7, 134.7, 135.9, 137.7, 138.6, 139.6, 140.9, 154.7, 210.5, 284.9. ^{19}F NMR (375.5 MHz, $CDCl_3$, ppm): δ −39.0. $C_{29}H_{31}Cl_2F_3N_2RuS$ HR-MS (ESI): m/z 633.0873 $(M - Cl)^+$, calcd 633.0887.

General Procedure for ROMP of DCPD. A 4 mL vial was charged with initiator (0.45 μmol, 0.1%), DCPD (60 μL, 0.45 mmol), mesitylene (internal standard, 50 μL), and chlorobenzene (1 mL). The reaction mixture was stirred at the appropriate temperature. Monomer conversion was monitored by GC-MS.

General Procedure for RCM and CM Reactions. A 4 mL vial was charged with initiator (0.50 mmol, 1%), substrate (0.50 mmol), and solvent (1 mL). The reaction mixture was stirred at the defined temperature and irradiation (none or UV light at 350 nm) for the defined time. Product formation was monitored by GC-MS.

■ ASSOCIATED CONTENT

Supporting Information. NMR and MS spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) (a) Vougioukalakis, G. C.; Grubbs, R. H. *Chem. Rev.* **2010**, *110*, 1746–1787. (b) Samojlowicz, C.; Bieniek, M.; Grela, K. *Chem. Rev.* **2009**, *109*, 3708–3742. (c) Boeda, F.; Clavier, H.; Nolan, S. P. *Chem. Commun.* **2008**, 2726–2740. (d) Diesendruck, C. E.; Tzur, E.; Lemcoff, N. G. *Eur. J. Inorg. Chem.* **2009**, *28*, 4185–4203. (e) Monfette, S.; Fogg, D. E. *Chem. Rev.* **2009**, *109*, 3783–3816. (f) Dunbar, M. A.; Balof, S. L.; LaBeaud, L. J.; Yu, B.; Lowe, A. B.; Valente, E. J.; Schanz, H.-J. *Chem.—Eur. J.* **2009**, *15*, 12435–12446.

(2) (a) Freitas, E. R.; Gum, C. R. *Chem. Eng. Prog.* **1979**, *75*, 73–76. (b) Phillips Petroleum Company. *Hydrocarbon Process.* **1967**, *46*, 232. (c) Caster, K. C.; Tokas, E. F.; Keck, C. G.; Hontz, M. E. *J. Mol. Catal. A: Chem.* **2002**, *190*, 65. (d) Slugovc, C. *Macromol. Rapid Commun.* **2004**, *25*, 1283–1297. (e) Leitgeb, A.; Wappel, J.; Slugovc, C. *Polymer* **2010**, *51*, 2927–2946.

(3) (a) Nicolaou, K. C.; Bulger, P. G.; Sarlah, D. *Angew. Chem., Int. Ed.* **2005**, *44*, 4490–4527. (b) Wallace, D. J.; Goodman, J. M.; Kennedy, D. J.; Davies, A. J.; Cowden, C. J.; Ashwood, M. S.; Cottrell, I. F.; Dolling, U.; Reider, P. J. *Org. Lett.* **2001**, *3*, 671–674. (c) Yun, S. Y.; Hansen, E. C.; Volchkov, I.; Cho, E. J.; Lo, W. Y.; Lee, D. *Angew. Chem., Int. Ed.* **2010**, *49*, 4261–4263. (d) Kanada, R. M.; Itoh, D.; Nagai, M.; Niijima, J.; Asai, N.; Mizui, Y.; Abe, S.; Kotake, Y. *Angew. Chem., Int. Ed.* **2007**, *46*, 4350–4355.

(4) Schrock, R. R.; Murdzek, J. S.; Bazan, G. S.; Robbins, J.; DiMare, M.; O'Regan, M. *J. Am. Chem. Soc.* **1990**, *112*, 3875–3886.

(5) (a) Schwab, P.; France, M. B.; Ziller, J. W.; Grubbs, R. H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2039–2041. (b) Scholl, M.; Ding, S.; Lee, C. W.; Grubbs, R. H. *Org. Lett.* **1999**, *1*, 953–956.

(6) (a) Sinner, F. M.; Gatschelhofer, C.; Mautner, A.; Magnesa, C.; Buchmeiser, M. R.; Pieber, T. R. *J. Chromatogr. A* **2008**, *1191*, 274–281. (b) Mol, J. C. *J. Mol. Catal. A: Chem.* **2004**, *213*, 39–45.

(7) Breslow, D. S. *Prog. Polym. Sci.* **1993**, *18*, 1141–1195.

(8) (a) Piermattei, A.; Karthikeyan, S.; Sijbesma, R. P. *Nat. Chem.* **2009**, *1*, 133–137. (b) Barbasiewicz, M.; Szadkowska, A.; Bujok, R.; Grela, K. *Organometallics* **2006**, *25*, 3599–3604. (c) Ung, T.; Hejl, A.; Grubbs, R. H.; Schrodi, Y. *Organometallics* **2004**, *23*, 5399–5401. (d) Slugovc, C.; Burtscher, D.; Mereiter, K.; Stelzer, F. *Organometallics* **2005**, *24*, 2255–2258. (e) Furstner, A.; Thiel, O. R.; Lehmann, C. W. *Organometallics* **2002**, *21*, 331–335. (f) Ben-Asuly, A.; Tzur, E.; Diesendruck, C. E.; Sigalov, M.; Goldberg, I.; Lemcoff, N. G. *Organometallics* **2008**, *27*, 811–813. (g) Kost, T.; Sigalov, M.; Goldberg, I.; Ben-Asuly, A.; Lemcoff, N. G. *J. Organomet. Chem.* **2008**, *693*, 2200–2003. (h) Wang, D.; Wurst, K.; Knolle, W.; Decker, U.; Prager, L.; Naumov, S.; Buchmeiser, M. R. *Angew. Chem., Int. Ed.* **2008**, *47*, 3267–3270.

(9) (a) Allaert, B.; Dieltens, N.; Ledoux, N.; Vercaemst, C.; Van Der Voort, P.; Stevens, C. V.; Linden, A.; Verpoort, F. *J. Mol. Catal. A: Chem.* **2006**, *260*, 221–226. (b) Dunbar, M. A.; Balof, S. L.; Roberts, A. N.; Valente, E. J.; Schanz, H. J. *Organometallics* **2011**, *30*, 199–203.

(10) Vidavsky, Y.; Lemcoff, N. G. *Beilstein J. Org. Chem.* **2010**, *6*, 1106–1119.

(11) DCPD polymerization is very exothermic and is rapidly finished after the initial induction period seen in partially latent catalysts (catalysts latent for less reactive substrates). For example, gel formation is clearly observed after a few minutes of addition of **1** to a DCPD solution in methylene chloride.

(12) Diesendruck, C. E.; Vidavsky, Y.; Ben-Asuly, A.; Lemcoff, N. G. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 4209–4213.

(13) Ben-Asuly, A.; Aharoni, A.; Diesendruck, C. E.; Vidavsky, Y.; Goldberg, I.; Straub, B. F.; Lemcoff, N. G. *Organometallics* **2009**, *28*, 4652–4654.

(14) (a) Hejl, A.; Day, M. W.; Grubbs, R. H. *Organometallics* **2006**, *25*, 6149–6154. Additional tridentate ligands in ruthenium benzylidenes have been previously reported:(b) Bieniek, M.; Bujok, R.; Cabaj, M.; Lugan, N.; Lavigne, G.; Arlt, D.; Grela, K. *J. Am. Chem. Soc.* **2006**, *128*, 13652–13653.

(15) (a) Toledo, J. C.; Neto, B. S. L.; Franco, D. W. *Coord. Chem. Rev.* **2005**, *249*, 419–431. (b) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335–422.

(16) (a) Diesendruck, C. E.; Tzur, E.; Ben-Asuly, A.; Goldberg, I.; Straub, B. F.; Lemcoff, N. G. *Inorg. Chem.* **2009**, *48*, 10819–10825. (b) Tzur, E.; Szadkowska, A.; Ben-Asuly, A.; Makal, A.; Goldberg, I.; Wozniak, K.; Grela, K.; Lemcoff, N. G. *Chem.—Eur. J.* **2010**, *16*, 8726–8737.

(17) (a) Bierbach, U.; Barklage, W.; Saak, W.; Pohl, S. *Z. Naturforsch., B: Chem. Sci.* **1992**, *47*, 1593–1601. (b) Alessio, E.; Bolle, M.; Milani, B.; Mestroni, G.; Faleschini, P.; Todone, F.; Geremia, S.; Calligaris, M. *Inorg. Chem.* **1995**, *34*, 4722–4734. (c) Taimisto, M.; Oilunkaniemi, R.; Laitinen, R. S.; Ahlgren, M. *Z. Naturforsch., B: Chem. Sci.* **2003**, *58*, 959–964. (d) Chutia, P.; Kumari, N.; Shatma, M.; Woollins, J. D.; Slawin, A. M. Z.; Dutta, D. K. *Polyhedron* **2004**, *23*, 1657–1661. (e) Maiti, B. K.; Gorls, H.; Klobes, O.; Imhof, N. *Dalton Trans.* **2010**, *39*, 5713–5720.

(18) Hudson, D. M.; Valente, E. J.; Schachner, J.; Limbach, M.; Müller, K.; Schanz, H. *J. Chem. Cat. Chem.* **2011**, *3*, 297–301.
(19) Diesendruck, C. E.; Iliashevsky, O.; Ben-Asuly, A.; Goldberg, I.; Lemcoff, N. G. *Macromol. Symp.* **2010**, *293*, 33–38.
(20) (a) Grela, K.; Harutyunyan, S.; Michrowska, A. *Angew. Chem., Int. Ed.* **2002**, *41*, 4038–4040. (b) For an earlier study on the electronic effects in ether benzylidenes see: Zaja, M.; Connon, S. J.; Dunne, A. M.; Rivard, M.; Buschmann, N.; Jiricek, J.; Blechert, S. *Tetrahedron* **2003**, *59*, 6545–6558.
(21) Sanford, M. S.; Love, J. A.; Grubbs, R. H. *Organometallics* **2001**, *20*, 5314–5318.
(22) Aharoni, A.; Vidavsky., Y.; Diesendruck, C. E.; Ben-Asuly, A.; Goldberg, I.; Lemcoff, N. G. *Organometallics* **2011**, *30*, 1607–1615.
(23) (a) Yamamoto, Y.; Nakagai, Y.; Ohkoshi, N.; Itoh, K. *J. Am. Chem. Soc.* **2001**, *123*, 6372–6380. (b) Schmidt, B. *Angew. Chem., Int. Ed.* **2003**, *42*, 4996–4999. (c) Hong, S.; Sanders, D. P.; Lee, C. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2005**, *127*, 17160–17161.
(24) NMR shown at low temperature for enhanced identification of hydrogen signals.