Chapter 2

Acid- and Photo-Activated Ruthenium Metathesis Catalysts

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Abstract

The use of photoacid generators (PAG) in conjunction with acid-activated ruthenium olefin metathesis catalysts has been explored. The hydrochloric acid generated as a result of irradiation of samples with ultraviolet (UV) light was found to protonate a labile ligand on ruthenium. Displacement of this ligand with chloride anion resulted in the generation of a highly active metathesis catalyst that was effective in catalyzing a variety of reactions, including ring-closing metathesis (RCM) and ring-opening metathesis polymerization (ROMP). Investigations into the mechanism of the activation are also presented.

The preparation of ruthenium alkylidene carbonyl complexes is also described as are chemical and photochemical efforts to induce carbonyl dissociation in order to generate an active metathesis species.

Acetylacetonate (acac) Ruthenium Alkylidene Catalysts

Introduction

Latent olefin metathesis catalysts[1] require an external stimulus (e.g., heat,[2] light,[3–6] acid (see Chapter 3),[7] or mechanical stress) in order to activate.[8] Consequently, they may be stored in the presence of reactive olefins until a metathesis reaction is desired. This attribute makes latent metathesis catalysts critical in a variety of applications including photolithography,[9] roll-to-roll coating,[10] polymer molding,[11] and self-healing materials.[12]

Compared to other methods for catalyst activation, photo-activation is relatively rare. However, photo-initiated ROMP has been reported for catalysts

based on ruthenium (Ru),[3] tungsten (W),[4] molybdenum (Mo),[5] and rhenium (Re).[6] The majority of these systems rely on the *in situ* generation of a reactive alkylidene following ligand dissociation, and thus their catalytic activity is relatively limited. We believed that catalyst activity, especially in more difficult reactions, such as RCM, could be improved via the inclusion of a reactive alkylidene in the pre-catalyst. Here, we validate this approach via the use of coordinatively saturated Ru-*acac* (acac = acetylacetonate) complexes that are activated by the addition of a variety of Brønsted acids, including photoacids. The reactivity of these complexes during RCM and ROMP is presented along with investigations into the mechanism of activation and the nature of the active metathesis species. Selected other approaches to photo-activated olefin metathesis are also presented.

Results and Discussion

Previous work from our group has shown that a metathesis inactive Ru-alkylidene complex ligated by *acac* may be converted into a metathesis active system by protonation and subsequent displacement of the labile *acac* ligands.[7a] These complexes could be easily accessed via transmetalation of the chloride ligands in $(PCy_3)_2Cl_2Ru(=CHPh)$ (**2.1**) with thallium (Tl) *acac* salts (Figure 2.1). Silver (Ag) *acac* salts could also be used in some circumstances, but their use generally resulted in incomplete transmetalation.

Using a similar strategy to that shown in Figure 2.1, several *acac*-containing complexes were prepared, starting from different Ru precursors (Figure 2.2). With these catalysts in hand, we initiated a study into their activity using the RCM of diethyldiallylmalonate (DEDAM, **2.8**) as a test reaction. When **2.8** was exposed to **2.2**-

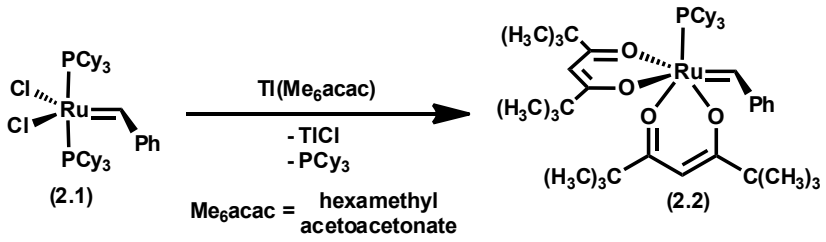


Figure 2.1. General method for preparation of Ru-*acac* complexes

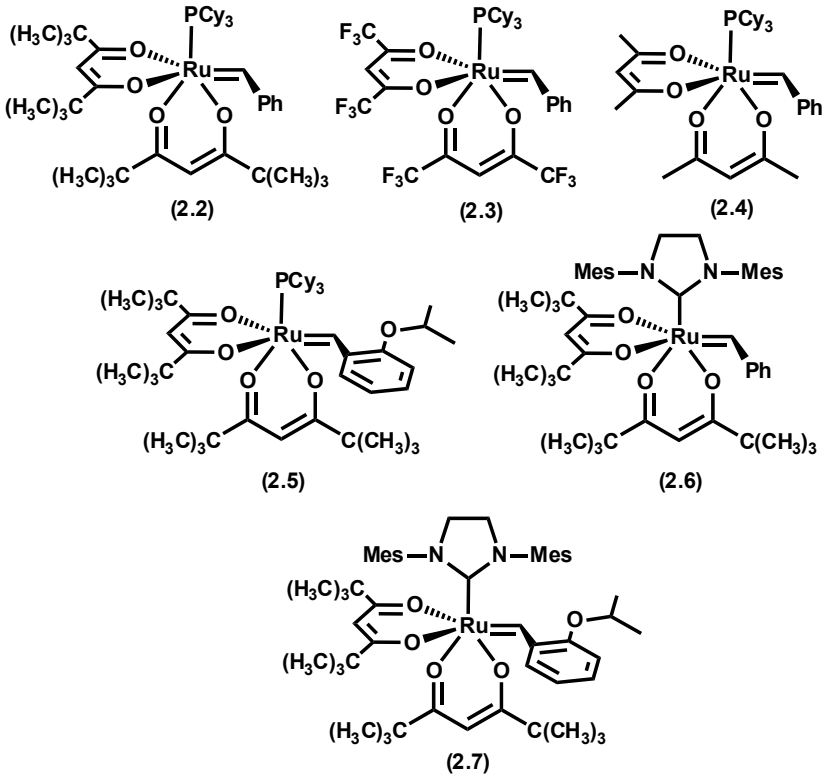


Figure 2.2. *acac*-containing latent metathesis catalysts. Mes = 2,4,6-trimethylbenzene

2.7 in the absence of acid, no conversion to the desired product (**2.9**) was observed. However, addition of 1 eq. of HCl (as a solution in diethyl ether) resulted in complete conversion to **2.9** within 30 min at room temperature (RT). A closer inspection of the RCM reaction revealed that the conversion profile of **2.8** to **2.9** is highly dependent on the amount of acid added and its relative strength (pK_a). For example, addition of 2 eq. of HCl led to faster formation of **2.9**, as did the use of stronger acids, such

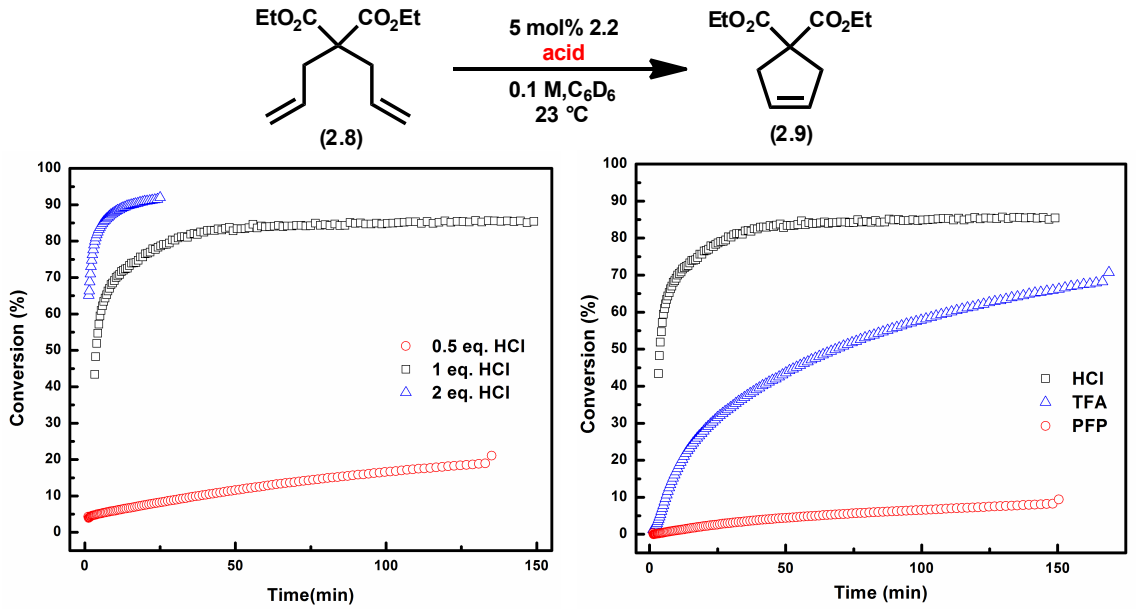


Figure 2.3. RCM of **2.8** to **2.9** with catalyst **2.2** with varying acid concentrations (left) and different acids (right). HCl = hydrochloric acid, TFA = trifluoroacetic acid, PFP = pentafluorophenol

as HCl versus TFA (Figure 2.3). Under our reaction conditions, the conversion of **2.8** was not amenable to simple kinetic analysis, which prevented a quantitative relationship between observed rates and concentration/pK_a. Nevertheless, we were able to gain additional insight into the activation mechanism through the use of acids with noncoordinating conjugate bases. For example, tetrafluoroboric acid (HBF_4), despite its low pK_a, was unable to effectively activate **2.2**. This result suggests that nucleophilic attack by the conjugate base (e.g., Cl^-) is critical to catalyst activation (*vide infra*), an observation that is also consistent with the substitution of *acac* ligands on other metals.[13] Overall, the above results suggest that acid plays a role in the rate-determining step of catalyst activation.

The RCM of **2.8** also allowed us to investigate the differences in reactivity between **2.2**–**2.7**. In general, when the *acac* ligand was kept constant (**2.2**, **2.5**, **2.6**,

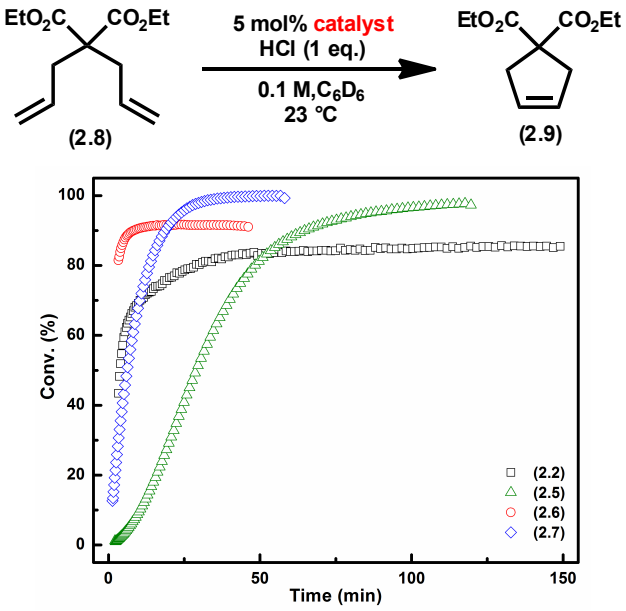


Figure 2.4. Comparison of catalysts **2.2**, **2.5**, **2.6**, and **2.7** in the RCM of 2.8 with 1 eq. HCl

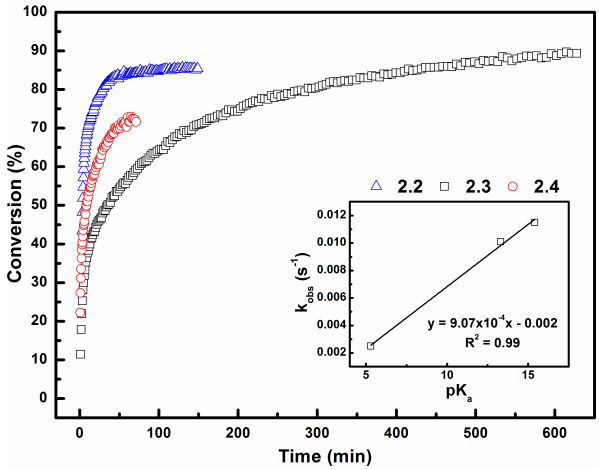
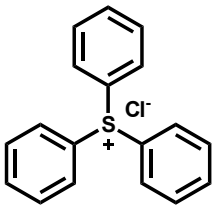
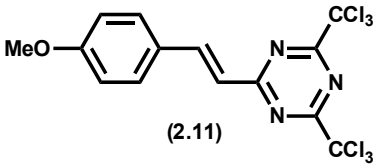


Figure 2.5. Comparison of catalysts **2.2**–**2.4** in the RCM of **2.8** with 1 eq. HCl. Linear plot of k_{obs} versus pK_a of *acac* ligand (inset)

and **2.7**), the trends in catalyst performance were reflective of the reactivity of the parent dichloride complexes (e.g., **2.1** for **2.2**) (Figure 2.4).[14] However, an interesting trend appeared when the RCM of **2.8** was conducted with catalysts **2.2**–**2.4**. In these reactions, we were able to obtain first-order rate constants (k_{obs}) at early reaction times (initial rates). Plotting k_{obs} versus the pKa of the conjugate acids of the *acac*



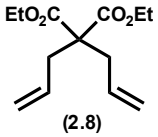
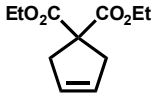
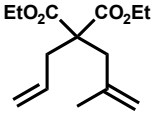
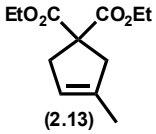
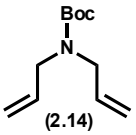
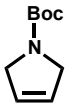
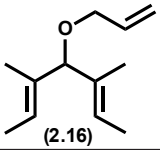
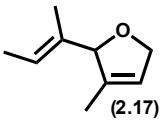
(2.10)



(2.11)

Figure 2.6. Photoacid generators (PAGs) **2.10** and **2.11**

Table 2.1. RCM with catalysts **2.2** and **2.6** with PAG **2.10**[a]

Entry	Substrate	Product	Time, h	Catalyst	Conv.,[b] %	Yield,[c] %
1	 (2.8)	 (2.9)	1	**2.2**	>95	77
			2	**2.6**	>95	83
2	 (2.12)	 (2.13)	1	**2.2**	55	42
			2	**2.6**	93	88
3	 (2.14)	 (2.15)	1	**2.2**	>95	70[d]
			1	**2.6**	>95	93
4	 (2.16)	 (2.17)	3	**2.2**	47	23
			3	**2.6**	71	62

[a] Reaction conditions were catalyst (**2.2** or **2.6**, 5 mol%) and **2.10** (10 mol%) in a quartz NMR tube with CD_2Cl_2 (0.1 M) and substrate. [b] Measured by ^1H NMR spectroscopy. [c] Isolated following column chromatography on silica gel. [d] Average yield over three runs

ligands in **2.2**–**2.4** revealed a linear trend consistent with acid involvement in the rate-determining step (Figure 2.5, inset). Qualitatively, hexafluoroacetylacetonate (**2.3**) is a weaker base (stronger conjugate acid) and thus, protonation of this ligand is more difficult compared to more electron-donating *acac*-type ligands (**2.2** and **2.4**). As a consequence of this effect, we are able to finely control the activity of the catalyst by adjusting either the pK_a of the exogenous acid or that of the *acac*-type ligand.

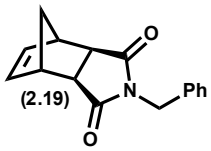
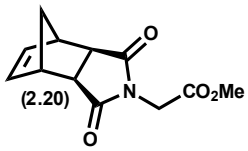
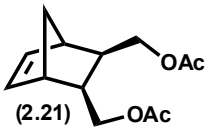
Having established the acid-activated nature of catalysts **2.2**–**2.7**, we

turned our attention to the use of photoacid generators (PAG) as sources of exogenous acid.[15] The majority of PAGs used in applications such as photolithography generate acids with noncoordinating counter-ions;[9] we desired a nucleophilic counterion having previously demonstrated that nucleophilic substitution is necessary to achieve catalyst activation. Therefore, PAGs **2.10** and **2.11** were selected for their ability to produce HCl upon irradiation with sub-300-nm light (Figure 2.6). Having selected appropriate PAGs, we examined the reactivity of our tandem activation system in RCM, since this reaction has been historically difficult for photo-activated metathesis catalysts.

The tandem system of PAG **2.10** and catalyst **2.2/2.6** was found to be very efficient in the RCM of **2.8**, reaching >95% conversion within 1 h of UV irradiation (Table 2.1, entry 1). Reactions run in the absence of UV light or PAG showed no metathesis activity, while irradiation of a solution containing only **2.10** and **2.2** or **2.6** resulted in eventual catalyst decomposition. For the RCM of **2.8**, the combination of catalyst **2.2** and PAG **2.11** was also effective, but required longer reaction times (ca. 2 h) to reach high conversions (80%), likely due to the lower quantum yield of **2.11** (Φ_f = 0.01[16] compared to Φ_f = 0.6[17] for **2.10**). More difficult RCM substrates, including tri-substituted olefins, cyclized in moderate conversion using PAG **2.10** (Table 1, entries 2 and 4). In these cases, catalyst **2.6** was found to be more active, which is consistent with the substitution of the phosphine in **2.2** with an N-heterocyclic carbene (NHC).[18] Overall, the combination of PAG **2.10** and catalysts **2.2** and **2.6** was found to be very effective at the RCM of a variety of substrates.

Having established the effectiveness of PAG **2.10** at activating *acac*-

Table 2.2. ROMP of various monomers with catalysts **2.2** and **2.6** with PAG **2.10**[a]

Entry	Monomer	Catalyst	Time, h	Conv.,[b] %	Theo M_n, kDa	Exp M_n,[c] kDa	PDI[c]
1	 (2.18)	**2.2**	2	>95	2.2	13.9	1.38
		2.6	2	>95	2.2	8.5	1.56
2	 (2.19)	**2.2**	1	>95	5.2	57.5	1.33
		2.6	1	>95	5.8	127	1.25
3	 (2.20)	**2.2**	1	>95	4.7	59.9	1.44
		2.6	1	>95	4.9	157	1.29
4	 (2.21)	**2.2/2.6**	1	>95	4.6	-[d]	-

[a] Reaction conditions were catalyst (5 mol%) and **2.10** (10 mol%) in a quartz NMR tube with CD_2Cl_2 (0.1 M) and substrate. [b] Determined by ^1H NMR spectroscopy. [c] Measured by multi-angle laser light scattering (MALLS) GPC. [d] Insolubility of polymer precluded GPC analysis

ligated catalysts for RCM, we turned our attention to ROMP. Many common ROMP monomers, such as norbornene derivatives and cyclooctene (**2.18**), underwent ROMP in excellent conversion using the combination of **2.2** and **2.10** (Table 2.2). Molecular weights (M_n), measured by GPC were consistently higher than predicted, which is indicative of incomplete catalyst initiation. Indeed, after irradiation for 2 h, a catalyst solution under ROMP reaction conditions displayed peaks in both ^1H and ^{31}P NMR spectra characteristic of catalyst **2.2**. Integration relative to the free *acac* ligand in solution revealed that ca. 10% of the catalyst was activated during the reaction time, which is consistent with the higher M_n's obtained by GPC. It is worth noting that addition of excess HCl (as a solution in Et_2O) also resulted in incomplete catalyst activation. Thus, the

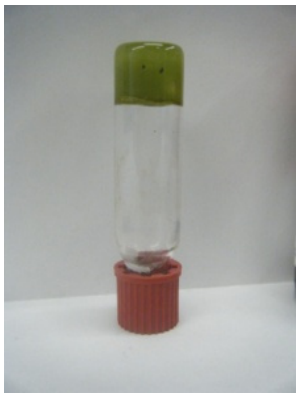


Figure 2.7. Quartz vial containing gel resulting from ROMP of **2.22** using catalyst **2.2** and PAG **2.10**

relatively small degree of catalyst activation is a result of limitations inherent to the *acac*-type ligand, and not a reflection of the efficiency of the PAG.

Despite the low degree of catalyst activation, we believed that the success of the tandem system in ROMP demonstrated its potential for industrial polymer molding applications. Therefore, with an eye toward potential industrial applications, we attempted to form a cross-linked solid from the ROMP of dicyclopentadiene (DCPD, **2.22**). Irradiation of a solution of **2.22**, **2.2**, and **2.10** in a minimal amount of CH_2Cl_2 (for solubility) resulted in complete gelation within 1 h (Figure 2.7). Attempted melting and solvation confirmed that the gel was not solidified monomer.

Having demonstrated the potential of the tandem system of acid-activated catalyst and PAG **2.10**, we focused on the nature of the active species. As was already discussed, the conjugate base of the activating acid was found to be critical in obtaining a highly active catalyst. This result implies that substitution of the *acac* ligands is an essential step in catalyst activation. To verify that the substitution process was occurring, we designed a trapping experiment for the active species, which consisted of irradiation of **2.2** in the presence of a reactive

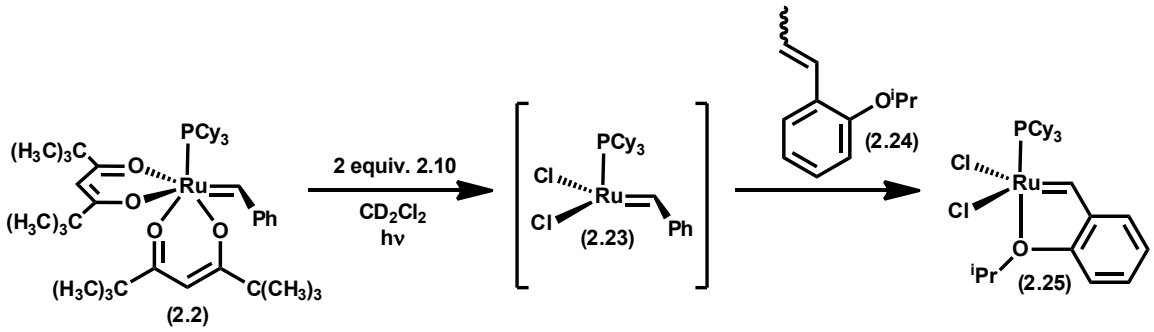


Figure 2.8. Trapping of reactive intermediate.

olefin (**2.24**) that would generate a stable catalyst upon cross-metathesis (**2.25**). Indeed, after a solution consisting of the preceding reagents was irradiated for 5 h, catalyst **2.25** was observed in both the ^{1}H and ^{31}P NMR spectra (Figure 2.8). This result indicates that at least one of the catalytically active species is the 14 electron complex **2.23**. Also recall the enhanced activity of catalyst **2.6** versus **2.2**; this result is also consistent with a 14 electron, dichloride active species. While the evidence for an active species such as **2.23** is strong, at this time we cannot rule out the presence of other active metathesis species which may be present in solution.[19]

Conclusion and Future Outlook

In summary, we have described a robust acid-activated catalytic system based on *acac*-ligated Ru-alkylidene complexes that are capable of both RCM and ROMP in good to excellent conversions. Mechanistic studies indicated that the identity of the exogenous acid and the electronics of the *acac* ligand play a critical role in catalyst activation. With this knowledge in hand, we were able to develop a photo-activated olefin metathesis system, via the use of a photoacid generator

(PAG) that was effective at RCM and ROMP. Notably, the combination of a PAG and acid-activated catalyst is not limited to *acac*-ligated complexes, but should be applicable to other acid-activated metathesis catalysts.[7] For example, the acid activated catalyst can be modified to increase activity in addition to improving stability (especially towards O_2), latency, and ease of synthesis (see Chapter 3). Alternatively, the PAG may be modified to create a complex with improved solubility and a chromophore tuned to a specific wavelength of light. Exogenous sensitizers can also be added to further improve the sensitivity and quantum yield of the PAG.[20]

Ruthenium Carbonyl Alkylidene Complexes

Introduction

The photo-induced dissociation of carbonyl (CO) ligands is a well-known reaction in coordination and organometallic chemistry.[21] In general, a d-d transition populates a M-CO antibonding orbital (σ*), which weakens the M-CO bond and results in favorable conditions for CO dissociation. We believed that this chemistry could be used to generate an open coordination site on a Ru metathesis catalyst and serve as the basis for a photo-activated catalyst system. However, a number of challenges are inherent to such an approach. First, Ru-CO complexes containing alkylidenes are relatively rare because CO coordination often induces C-H activation and subsequent insertion into the alkylidene.[22,23] For example, Diver et al. has reported that exposure of Grubbs' 2nd generation catalyst (**2.26**) to an atmosphere of CO results in CO coordination followed by alkylidene insertion into

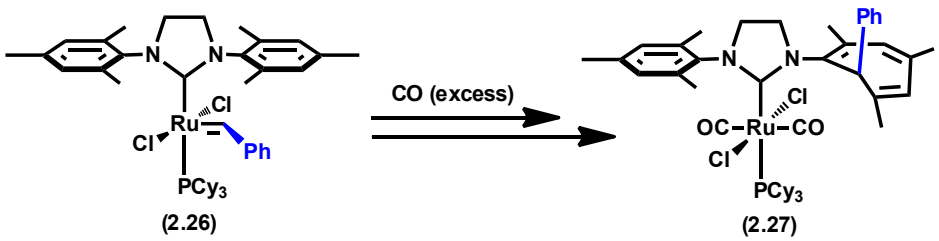


Figure 2.9. CO-induced insertion of alkylidene ligand into Mes substituent

the Mes substituent of the NHC (Figure 2.9).[24] A second problem arises from the fact that going from a 16 electron (e^-) complex, such as **2.26**, to an analogous CO-containing complex requires the generation of a cationic catalyst. This is the only viable approach since the alternative substitution of the phosphine ligand in **2.26** with CO was just shown to be infeasible. Fortunately, cationic Ru-based metathesis catalysts are known, although they are often less active than their neutral counterparts.[25] A final obstacle inherent to the use CO dissociation as a method for photo-activation is the fact that Ru^{2+} photochemistry is dominated by metal-to-ligand charge transfer (MLCT) transitions.[26] Despite this complication, and the others mentioned above, we believed that an investigation into the use of Ru-CO dissociation as the basis for a photo-activated metathesis system was a worthwhile endeavor.

Results and Discussion

The generation of alkylidene-containing cationic Ru^{2+} complexes via chloride abstraction in the presence of an L-type ligand (phosphine, pyridine, etc.) is well-known.[27] We believed that a similar approach could be used to generate a stable CO complex. Indeed, reaction of catalyst **2.26** with $AgBF_4$ at –78 °C

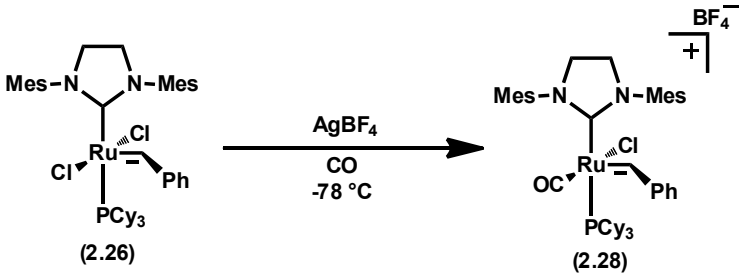


Figure 2.10. Preparation of CO complex **2.28**

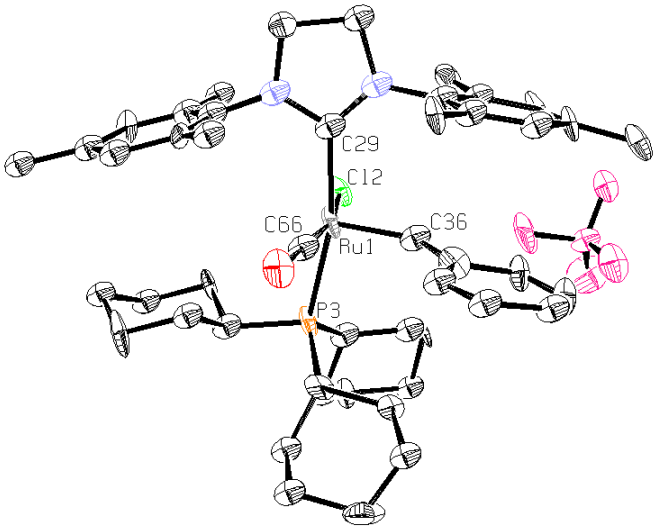


Figure 2.11. Solid-state structure of **2.28** with ellipsoids drawn at 50% probability. Selected bond lengths (Å) : Ru-C29 = 2.124, Ru-C36 = 1.881, Ru-C66 = 1.779, Ru-P3 = 2.427, Ru-Cl2 = 2.372

under an atmosphere of CO resulted in the isolation of a stable cationic Ru-CO complex (Scheme 4, **2.28**). Complex **2.28** possesses a single infrared (IR) CO stretch at 1961 cm^{-1} which shifts to 1915 cm^{-1} upon ^{13}CO isotopic substitution. This result is in good agreement with the shift to 1917 cm^{-1} predicted from a simple harmonic oscillator approximation. In C_6D_6, the benzylidene resonance of **2.28** is observed at 15.75 ppm in the ^{1}H spectrum while a single resonance at 41 ppm is observed by ^{31}P NMR spectroscopy. Finally, the structure of **2.28** was confirmed by single-crystal x-ray diffraction (Figure 2.11). Curiously, the use of precursors

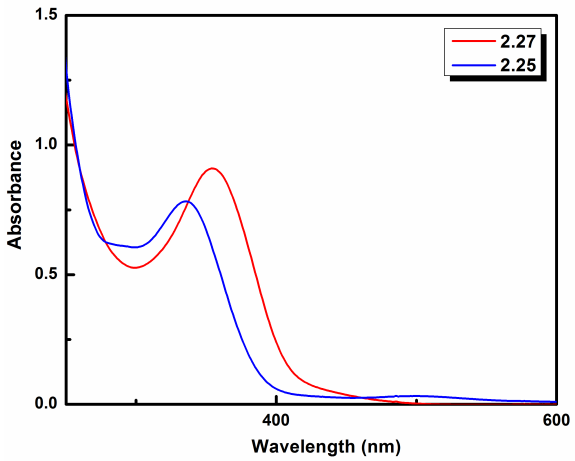


Figure 2.12. UV-vis spectrum of **2.26** and **2.28** in THF at RT

similar to **2.26** (e.g., **2.2**) did not result in the formation of stable CO complexes.

As expected, the UV-Vis spectra of **2.26** and **2.28** (in THF) are characterized by intense MLCT bands, which are assigned to a Ru→CHPh transition (Figure 2.12).[18] The λ_{max} (354 nm) of **2.28** is slightly red-shifted with respect to the λ_{max} (336 nm) **2.26**, consistent with stabilization provided by the CO ligand. No ligand field transitions (d-d) in either **2.26** or **2.28** are obvious in Figure 2.12. Accordingly, UV irradiation of **2.28** produced no evidence of CO dissociation and the starting complex was recovered quantitatively. Irradiation in the presence of excess phosphine ligand (PCy_3) did not produce any bis-phosphine product. Our attempts to chemically induce CO dissociation using triethylamine oxide also failed, as did attempts to generate the neutral 18 e^- complex via reaction of **2.28** with a variety of halide salts. This latter result is particularly surprising, since the closely analogous $(H_2IMes)(PCy_3)(CO)Cl_2Ru{=}CH(CHC(CH_3)_2)$ [H_2Imes = 1,3-dimesitylimidazolidine-2-ylidene] has been previously reported.[28] Interestingly, when **2.28** was reacted with MeLi followed by the alkylating agent $Et_3O^+BF_4^-$, complex **2.29** was recovered

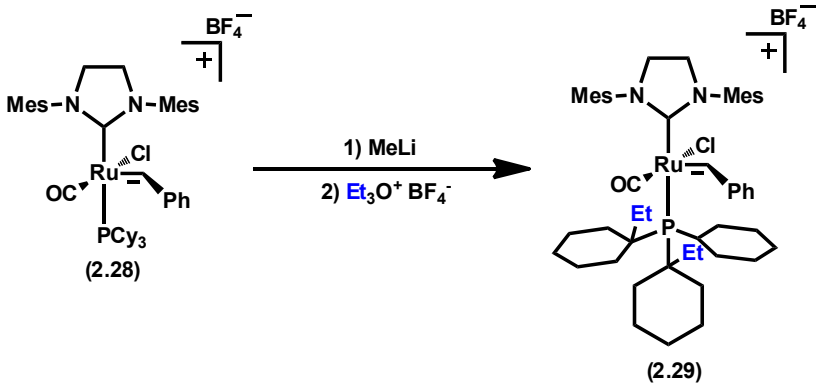


Figure 2.13. Reaction of **2.28** with MeLi followed by alkylating agent ($Et_3O^+BF_4^-$)

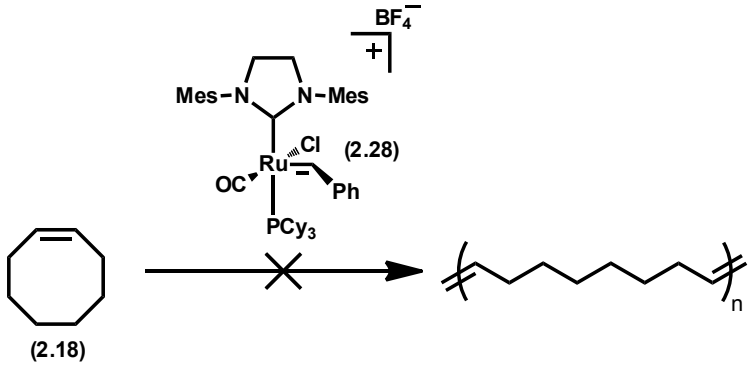


Figure 2.14. Failed ROMP reaction of **2.18** with **2.28**

(Figure 2.13). Complex **2.29** results from deprotonation at C1 of the cyclohexyl groups of PCy_3 and subsequent alkylation at this position. A similar transformation was observed by Piers et al. with a PMe_3 ligated tungsten carbyne complex.[29]

Despite the lack of reactivity between **2.28** and various small molecules, we believed that it could potentially undergo traditional phosphine dissociation in order to enter the metathesis catalytic cycle. Unfortunately, under a variety of forcing conditions, no conversion to polymer was observed when a solution of ROMP monomer **2.18** was exposed to **2.28** (Figure 2.14).

Conclusion and Future Outlook

The preparation of a stable CO-containing Ru-alkylidene complex was described. This complex was prepared in an attempt to develop a photo-active metathesis catalyst based on photoinduced CO dissociation and represents a rare example of a stable Ru-CO carbene complex. Unfortunately, UV irradiation of the complex (**2.28**) did not result in CO dissociation or indeed, any change in the complex. Similarly, our efforts to use **2.28** as a catalyst for ROMP were also unsuccessful. Despite these setbacks, the preparation and stability of **2.28** demonstrates the feasibility of combining Ru-CO and Ru-carbene chemistry.

Experimental Section

General: All reactions unless otherwise specified were carried out in dry glassware under argon using standard Schlenk techniques or in a Vacuum Atmospheres Glovebox under a nitrogen atmosphere. Solvents were purified by passage through solvent purification columns and further degassed with bubbling argon. NMR solvents were dried over CaH_2 and vacuum transferred to a dry Schlenk flask and subsequently degassed with argon. Commercially available reagents were used as received with the following exceptions. Triphenylsulfonium chloride (**2.10**) was dissolved in CH_2Cl_2, passed through a column of basic alumina and concentrated *in vacuo*. Diethyldiallylmalonate (**2.8**), cyclooctene (**2.18**), *t*-butyldiallyl carbamate (**2.14**), dicyclopentadiene (**2.21**), and diethyl 2-allyl-2-(2-methylallyl)malonate (**2.12**) were distilled prior to use. Norbornene monomers were prepared by modification of literature procedures. Triphenylsulfonium nonaflate was acquired from Midori

Kaguku Inc.^{1}H, ^{13}C, and ^{31}P spectra were recorded on a Varian Mercury 300 Spectrometer and the chemical shifts are reported in ppm relative to the appropriate solvent. High-resolution mass spectra were provided by the California Institute of Technology Mass Spectrometry Facility. Gel Permeation Chromatography was carried out in THF on two I-Series MBLMW ViscoGel columns (Viscotek) connected in series with a DAWN EOS multi-angle laser light scattering (MALLS) detector and an Optilab DSP differential refractometer. No standards were used, and dn/dc values were obtained for each injection by assuming 100% mass recovery from the columns. Photoreactions were performed in quartz glassware using a 450 W medium pressure mercury arc lamp (Hanovia PC4510-50) surrounded by a water cooled quartz jacket. The reaction vessel was positioned ca. 5 cm from the center of the irradiating lamp. In some cases, a handheld UV lamp typically used for TLC illumination was used as the light source. IR spectra were taken on a PerkinElmer Spectrum BX FT-IR (NaCl). X-ray quality crystals were grown as indicated. The crystals were mounted on a glass fiber with Paratone-N oil. X-ray diffraction studies were carried out in the Beckman Institute Crystallographic Facility on a Bruker Smart 1000 CCD diffractometer. Structures were determined using direct methods with standard Fourier techniques using the Bruker AXS software package.

Caution! Thallium complexes are extremely toxic and should be handled with extreme care.

Preparation of 2.2: In a glovebox, **2.1** (69 mg, 0.084 mmol) and 2,2,6,6-tetramethyl-3,5-heptanedionato thallium (65.6 mg, 0.168 mmol) were combined in a 20 mL scintillation vial and dissolved in 5 mL of benzene. The resulting green solution

was stirred at RT for 24 hours after which it was filtered through a plug of celite. CuCl (115 mg, 1.16 mmol) was added to the filtered solution and stirred for 2 h at room temperature. The solution was frozen at −30°C and the solvent sublimed off under vacuum after which the resulting green residue was dissolved in pentane, filtered through celite, and concentrated *in vacuo* to yield **2a** (54 mg, 77%) as a green powder. ^{1}H NMR (C_6D_6): δ 1.03 (s, 9H), 1.26 (br s, 20H), 1.38 (d, J = 3.9 Hz, 18H), 1.6–1.8 (m, 13H), 2.12 (br q, 9H), 5.32 (s, 1H), 5.99 (s, 1H), 7.24 (t, J = 9 Hz, 2H), 7.42 (t, J = 9 Hz, 1H), 8.46 (d, J = 9 Hz, 2H), 19.27 (d, J = 12 Hz, 1H). ^{13}C NMR (C_6D_6): δ 27.1, 29.0, 34.8, 41.5, 87.9, 90.8, 127.7, 128.7, 131.9, 154.1, 193.6, 195.2, 196.8, 199.0. ^{31}P NMR (C_6D_6): δ 39.12. HRMS (FAB+): calculated 838.4603, found 838.4617.

Preparation of 2.3: In a glovebox, **2.1** (50 mg, 0.061 mmol) and thallium (I) hexafluoroacetylacetonate (49 mg, 0.122 mmol) were dissolved in 3 ml of benzene and stirred at RT for 1 h. The reaction mixture was conc. and the resulting residue was dissolved in pentane and filtered after which CuCl (50 mg, 0.508 mmol) was added and the suspension stirred for 2 h. Finally, the solution was filtered and conc. to give **2.3** (40 mg, 74%) as a brown powder. ^{1}H NMR (C_6D_6): δ 0.94–2.02 (m, 33H), 5.95 (s, 1H), 6.57 (s, 1H), 7.19–7.28 (m, J = 3 Hz, 3H), 8.15 (d, J = 9 Hz, 2H), 18.91 (d, J = 12 Hz, 1H). ^{31}P NMR (C_6D_6): δ 42.3. HRMS (FAB+): Calculated 886.1594, found 886.1631.

Preparation of 2.4: In a glovebox, **2.1** (50 mg, 0.061 mmol) and thallium (I) acetylacetonate (36 mg, 0.120 mmol) were dissolved in 3 ml of benzene and stirred at RT for 2 h. The reaction was then worked up in a manner similar to catalyst **2.3**

above to yield **2.4** (29 mg, 81%) as a green powder. ^{1}H NMR (C_6D_6): δ 1.15–1.33 (m, 33H), 1.63 (s, 3H), 1.77 (s, 3H), 2.08 (s, 3H), 2.14 (s, 3H), 4.72 (s, 1H), 5.54 (s, 1H), 7.33 (t, J = 9 Hz, 2H), 7.44 (t, J = 9 Hz, 1H), 8.55 (d, J = 6 Hz, 2H), 19.32 (d, J = 12 Hz, 1H). ^{31}P NMR (C_6D_6): δ 38.92. HRMS (FAB+): Calculated 670.2725, found 670.2769.

Preparation of 2.5: In a glovebox, commercially available (PCy_3)Cl_2Ru(=CH-*o*-^{i}PrPh) (50 mg, 0.083 mmol) and 2,2,6,6-tetramethyl-3,5-heptanedionato thallium (46 mg, 0.118 mmol) were combined in a 20 ml vial and dissolved in 2 ml of benzene. The vial was sealed and heated to 60°C for 10 h after which it was cooled to RT, filtered and conc. to a greenish-brown powder (49 mg, 67%). ^{1}H NMR (C_6D_6): δ 1.09 (d, J = 6 Hz, 3H), 1.27 (m, 12H), 1.70 (br s, 18H), 1.78 (br s, 18H), 2.06 (br d, J = 9 hz, 3H), 2.13 (s, 3H), 2.18 (br s, 18H), 4.22 (q, J = 9 Hz, 1H), 4.75 (s, 1H), 5.59 (s, 1H), 6.62 (d, J = 9 Hz, 1H), 7.23 (t, J = 9 Hz, 1H), 7.54 (t, J = 9 Hz, 1H), 9.47 (d, J = 6 Hz, 1H), 19.95 (d, J = 15 Hz, 1H). ^{31}P NMR (C_6D_6): δ 40.53. HRMS (FAB+): Calculated 896.5022, found 896.5013.

Preparation of 2.6: In a glovebox, (H_2IMes)(PCy_3)Cl_2Ru(=CHPh) (31 mg, 0.037 mmol) and 2,2,6,6-tetramethyl-3,5-heptanedionato thallium (27 mg, 0.069 mmol) were combined in a 20 mL scintillation vial and dissolved in 5 mL of benzene. The vial was sealed and heated to 60°C for ca. 1 h at which point the solution had turned green and a white precipitate had formed. After filtration through celite, CuCl (40 mg, 0.404 mmol) was added and the solution stirred for 2 h at RT. The solution was frozen at −30°C and the solvent sublimed off under vacuum after which the resulting green residue was dissolved in pentane, filtered through celite,

and concentrated *in vacuo* to yield **2.6** (24 mg, 80%) as a green crystalline solid. ^{1}H NMR (C_6D_6): δ 0.89 (s, 9H), 1.15 (s, 9H), 1.37 (s, 9H), 1.61 (br s, 9H), 1.86 (s, 3H), 1.99 (s, 3H), 2.06 (s, 3H), 2.59 (s, 3H), 2.62 (s, 3H), 2.66 (s, 3H), 3.45 (m, 4H), 6.03 (s, 1H), 6.37 (s, 1H), 6.781 (s, 2H), 6.86 (s, 2H), 7.04 (t, J = 6 Hz, 2H), 7.28 (t, J = 6 Hz, 1H), 8.14 (d, J = 7.5 Hz, 2H), 17.82 (s, 1H). ^{13}C NMR (C_6D_6): δ 18.7, 19.2, 20.2, 20.9, 21.4, 27.2, 28.5, 28.8, 29.6, 29.8, 31.0, 33.2, 41.2, 41.5, 41.9, 50.4, 51.9, 91.0, 129.0, 129.5, 130.0, 130.5, 131.0, 135.1, 137.1, 137.8, 138.2, 139.0, 140.6, 152.0, 197.2, 198.5, 222.4. HRMS (FAB+): calculated 864.4370, found 864.4397.

Preparation of 2.7: In a glovebox, (H_2IMes)Cl_2Ru(=CH-*o*-^{i}PrPh) (50 mg, 0.080 mmol) and 2,2,6,6-tetramethyl-3,5-heptanedionato thallium (62.4 mg, 0.159 mmol) were placed in a 20 ml vial and dissolved in 2 ml of benzene. The vial was sealed and heated to 60°C for 1.5 h. After cooling to room temperature, the reaction was worked up in a manner similar to that of **2.5** to give **2.7** (52 mg, 71%). ^{1}H NMR (C_6D_6): δ 0.68 (s, 18H), 1.21 (s, 18H), 1.34 (s, 18H), 1.94 (s, 3H), 2.63 (s, 3H), 3.30 (m, 4H), 3.94 (q, J = 6 Hz, 1H), 5.19 (s, 1H), 5.77 (s, 1H), 6.17 (d, J = 6 Hz, 1H), 6.52 (br s, 2H), 6.77 (br s, 3H), 7.20 (m, 1H), 9.72 (dd, J = 3 Hz, J = 6 Hz, 1H), 18.38 (s, 1H). HRMS (FAB+): Calculated 922.4798, found 922.4759.

General Kinetics Experiment: In a glovebox, an NMR tube was charged with substrate **2.8** (14 mg), and **2.2** (2 mg, 5 mol %). C_6D_6 (0.1 M) was added and the NMR tube was capped with a rubber septum and removed from the glovebox. Acid was then injected as a solution in organic solvent (1 M HCl in Et_2O) after which the tube was inverted once to insure proper mixing and immediately placed into a ready NMR spectrometer. The ‘pad array’ function was used to monitor the

progress of the reaction until no further conversion was observed.

Ring-Closing Metathesis Procedure: In a glovebox, a quartz NMR tube was charged with substrate **2.18** (14 mg), **2.2** (2 mg, 5 mol %), and **2.10** (1.6 mg, 10 mol %). CD_2Cl_2 (0.1 M) was added and the NMR tube was capped with a rubber septum and irradiated for 1 h at RT after which the conversion was determined via ^1H NMR spectroscopy. The contents of the tube were emptied and concentrated before purifying the product by column chromatography on silica gel.

Ring-Opening Metathesis Polymerization: In a glovebox, a quartz NMR tube was charged with **2.18** (13 mg), **2.2** (2 mg, 5 mol %), and **2.10** (1.6 mg, 10 mol %). CD_2Cl_2 (0.1 M, relative to substrate, 0.5–0.75 ml) was added and the NMR tube was capped with a rubber septum and irradiated for the duration indicated in Table 2 at RT during which time the solution changed color from green to orange/brown. The contents of the NMR tube were emptied into a vial and the solvent was removed under reduced pressure, after which the residue was dissolved in a minimal amount of THF and precipitated into cold MeOH (poly-(cylcooctene)) or cold 1:1 Et_2O/Hexanes (polynorbornenes). The precipitate was then collected by filtration and dried under vacuum for several hours.

Trapping Experiment Procedure: In a glovebox, a 20 ml scintillation vial was charged with **2.2** (12.7 mg, 0.015 mmol) and **2.10** (9 mg, 0.030 mmol). The contents of the vial were dissolved in 0.75 ml of CD_2Cl_2 and loaded into a quartz NMR tube which was then capped with a rubber septum. β-methyl-*o*-isoprepoxystyrene, then **2.23** (53 mg, 0.3 mmol) was injected and the sample irradiated for 5 hours, after

which a ^{1}H NMR spectrum revealed the presence of catalyst **2.25**. The presence of **2.25** was also confirmed by ^{31}P NMR spectroscopy.

Preparation of 2.27: In a glovebox, a Schlenk was charged with $AgBF_4$ (12 mg, 0.030 mmol), a stirbar, and 4 ml of dry CH_2Cl_2. The Schlenk flask was removed from the glovebox and cooled to −78°C. After reaching this temperature, carbon monoxide was bubbled through the solution using a needle and **2.27** (21 mg, 0.027 mmol) was added in one portion as a solution in 1 ml of dry CH_2Cl_2. The solution immediately changed color from green to brown to yellow/orange within the span of about a minute. Once the solution had stopped changing color, the CO was turned off and the flask was opened to vacuum while warming to RT. Complex **2.27** was purified by column chromatography on TSI silica gel using 10% acetone in CH_2Cl_2 as the eluant. ^{1}H-NMR (CD_2Cl_2): δ 1.01 (br m, 18H), 1.62 (br m, 18H), 1.93 (s, 3H), 2.05 (s, 3H), 2.58 (s, 9H), 4.11 (m, 4H), 5.83 (s, 1H), 6.62 (s, 1H), 6.86 (s, 1H), 7.00 (s, 1H), 7.09 (s, 1H), 7.31 (s, 1H), 7.55 (s, 1H), 7.75 (t, J = 6 Hz, 1H), 8.35 (s, 1H), 15.75 (s, 1H). FT-IR: ν (cm^{-1}) = 2929.7, 2853.2, 2056.4, 1960.5, 1607.8, 1585.9, 1489.9, 1447.3, 1281.9, 1175.9, 1057.1. HRMS (FAB+): Calculated 841.3567, found 841.3566.

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