Organometallics **1998,** *17,* 2758−2767

Synthesis and Investigation of Homo- and Heterobimetallic Ruthenium Olefin Metathesis Catalysts Exhibiting Increased Activities

Eric L. Dias and Robert H. Grubbs*

The Arnold and Mabel Beckman Laboratory of Chemical Synthesis, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125

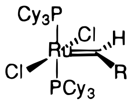
Received October 10, 1997

The previously reported ruthenium carbenes (PCy$_3$)$_2$Cl$_2$Ru=CHR (R = CHCPh$_2$ (**1a**), Ph (**1b**)) react with the bridged-chloride dimers [(*p*-cymene)RuCl$_2$]$_2$, [(*p*-cymene)OsCl$_2$]$_2$, and [(^{t}Bu$_2$Cp)RhCl$_2$]$_2$ to quantitatively form the bimetallic, bridged-chloride ruthenium carbenes **2a**,**b**, **4a**,**b**, and **6a**,**b** and 1 equiv of each corresponding piano-stool complex. In the ring-opening metathesis polymerization of 1,5-cyclooctadiene, catalyst activity was found to increase in the order M = Ru < Os < Rh for the ancillary metal centers, with all of the bimetallic catalysts having higher activities than **1a**,**b**. The kinetics of ROMP of the derivatized norbornene **9** were studied using catalyst **2a**, and the data support an associative mechanism of olefin metathesis, contrary to the mechanism of olefin metathesis proposed for the parent catalysts **1a**,**b**.

Introduction

The olefin metathesis reaction has found a wide variety of applications in both organic and polymer synthesis. Beginning with the simple ring-closing metathesis (RCM) of α,ω-dienes to cycloalkenes,[1] additional unsaturation in the form of alkynes[2] or cycloalkenes[3] can be incorporated in a substrate to make several different molecular geometries accessible. The ring-opening metathesis polymerization (ROMP) of cycloalkenes has also found several applications in the synthesis of internally and terminally functionalized polymers,[4] electroluminescent and conducting polymers,[5] and side chain liquid-crystalline polymers.[6] In conjunction with research in these areas, our group is also developing transition-metal alkylidene catalysts which are suitable for these applications.[7]

The ruthenium diphenylvinyl alkylidene (**1a**) was the first example of a well-defined, single-component ruthenium catalyst that is active for the metathesis of low-strain cyclic and acyclic olefins.[7c] The slow rate of initiation (relative to propagation) of **1a**, however, prompted the development of the ruthenium benzylidene **1b**.[7a,b] A comparison of these compounds showed that **1b** initiates metathesis significantly faster than **1a**, to the point where the rate of initiation is comparable to or faster than the rate of propagation. In addition, it was found that **1b** reacts with terminal olefins to produce new alkylidenes, such as **1c** and **1d**, that are easily isolated.[7a,b] However, because both **1a** and **1b** produce the same propagating species upon initiation, these types of modifications are limited in their ability to significantly alter overall catalyst activity.



1a: R = CHCPh$_2$
1b: R = Ph
1c: R = H
1d: R = Me

---

(1) For recent reviews, see: (a) Hashimi, A. S. K. *J. Prakt. Chem.* **1997**, *339*, 195−199. (b) Schmalz, H.-G. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1833−1836. (c) Grubbs, R. H.; Miller, S. J.; Fu, G. C. *Acc. Chem. Res.* **1995**, *28*, 446−552.

(2) (a) Kim, S.-H.; Zuercher, W. J.; Bowden, N. B.; Grubbs, R. H. *J. Org. Chem.* **1996**, *61*, 1073−1081. (b) Kim, S.-H.; Bowden, N.; Grubbs, R. H. *J. Am. Chem. Soc.* **1994**, *116*, 10801−10802.

(3) Zuercher, W. J.; Hashimoto, M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 6634−6640.

(4) (a) Maughon, B. R.; Grubbs, R. H. *Macromolecules* **1997**, *30*, 3459−3469. (b) Hillmyer, M. A.; Nguyen, S. T.; Grubbs, R. H. *Macromolecules* **1997**, *30*, 718−721. (c) Fraser, C.; Hillmyer, M. A.; Gutierrez, E.; Grubbs, R. H. *Macromolecules* **1995**, *28*, 7256−7261. (d) Hillmyer, M. A.; Laredo, W. R.; Grubbs, R. H. *Macromolecules* **1995**, *28*, 6311−6316. (e) Stumpf, A. W.; Saive, E.; Demonceau, A.; Noels, A. F. *J. Chem. Soc., Chem. Commun.* **1995**, 1127−1128.

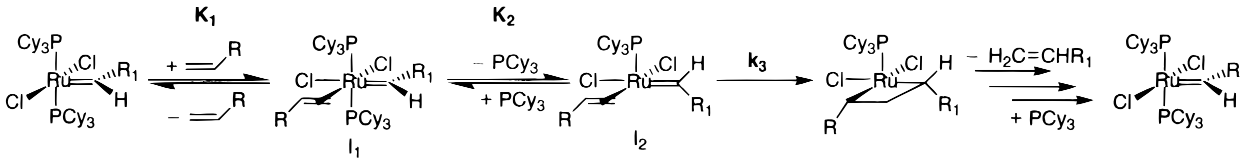
(5) For recent examples, see: (a) Wagaman, M. W.; Grubbs, R. H. *Synth. Met.* **1997**, *84*, 327−328. (b) Boyd, T. J.; Geerts, Y.; Lee, J. K.; Fogg, D. E.; Lavoie, G. G. et al. *Macromolecules* **1997**, *30*, 3553−3559. (c) Tasch, S.; Grapner, W.; Leising, G.; Pu, L.; Wagaman, M. W. et al. *Adv. Mater.* **1996**, *8*, 125. (c) Pu, L.; Wagaman, M. W.; Grubbs, R. H. *Macromolecules* **1996**, *29*, 1138−1143. (d) Schattenmann, F. J.; Schrock, R. R. *Macromolecules* **1996**, *29*, 8990−8991. (e) Baigent, D. R.; Friend, R. H.; Lee, J. K.; Schrock, R. R. *Synth. Met.* **1995**, *71*, 2171−2172. (f) Lee, J. K.; Schrock, R. R.; Baigent, D. R.; Friend, R. H. *Macromolecules* **1995**, *28*, 1966−1971.

(6) For recent examples, see: (a) Maughon, B. R.; Weck, M.; Mohr, B.; Grubbs, R. H. *Macromolecules* **1997**, *30*, 257−265. (b) Arehart, S. V.; Pugh, C. *J. Am. Chem. Soc.* **1997**, *119*, 3027−3037. (c) Pugh, C.; Liu, H.; Arehart, S. V.; Narayanan, R. *Macromol. Symp.* **1995**, *98*, 293−310. (d) Ungerank, M.; Winkler, B.; Eder, E.; Stelzer, F. *Macromol. Chem. Phys.* **1995**, *196*, 3623. (e) Pugh, C. *Macromol. Symp.* **1994**, *77*, 325.

(7) (a) Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100−110. (b) Schwab, P.; France, M. B.; Ziller, J. W.; Grubbs, R. H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2039−2041. (c) Nguyen, S. T.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 9858−9859. (d) Nguyen, S. T.; Johnson, L. K.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 3974−3975.

S0276-7333(97)00878-9 CCC: $15.00

Scheme 1



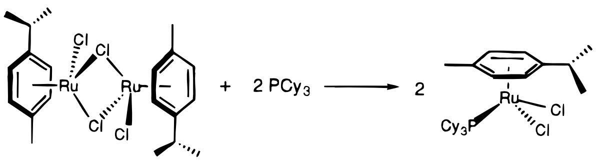
Several ruthenium vinyl alkylidenes containing different phosphines and halogens have been syntheszied, and it was found that the original catalysts **1a** and **1b** containing chlorides and tricyclohexylphosphines are the most active in the ring-closing metathesis of diethyl diallylmalonate.[8] Mechanistic studies indicate that, during metathesis, a phosphine reversibly dissociates from the ruthenium center. In accordance with this, it was found that addition of a phosphine scavenger, such as CuCl, activates these catalysts. Although faster turnover rates can be achieved in this manner, the catalyst lifetimes under these conditions are relatively short.[8]

This paper introduces a new class of well-defined, single-component ruthenium catalysts which are in some cases up to 80 times more active than the class of catalysts represented by **1a** and **1b**. These compounds are synthesized by a surprisingly general reaction that allows for several different derivatives to be prepared. In addition, the stability of these compounds is addressed, and a mechanism for olefin metathesis by these catalysts is proposed.

Results and Discussion

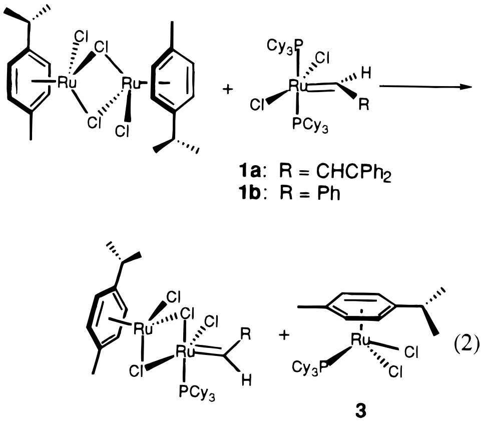
Synthesis of Bimetallic Ruthenium Alkylidenes. Previously, we proposed a mechanism for olefin metathesis by catalysts **1a** and **1b**.[8] The major pathway involves a preequilibrium for olefin binding and phosphine dissociation, followed by formation of a 14-electron metallacyclobutane, which is believed to be the rate-determing step. Subsequent breakdown of the metallacyclobutane and displacement of the product olefin by phosphine finish the catalytic cycle (Scheme 1). We have found that the equilibrium for olefin binding and phosphine dissociation is very poor, to the extent that even in the presence of a large excess of olefin, no free phosphine can be detected. (An exception to this is that during the ring-opening of cyclobutenes, free phosphine is sometimes observed due to the coordination of pendant olefins or functional groups.[4a,9]) Additionally, this preequilibrium makes the *effective* catalyst order approximately $^1/_2$, such that the rate of olefin metathesis depends on the square-root of the catalyst concentration. In the interest of designing a more active catalyst, we therefore reasoned that a compound containing only one phosphine and a hemilabile chelating ligand would make the rate equation first order in catalyst concentration and provide a group that dissociates more easily.

We have also reported the use of CuCl as a phosphine scavenger to increase catalyst activity.[8] Addition of CuCl to solutions of several catalysts containing different phosphines and halogens in the presence of an olefin substrate was found to increase the respective activities in all cases. Although CuCl is well-known to coordinate phosphines, the resulting CuCl·PR$_3$ complex is ill-defined and is believed to have an oligomeric structure in solution.[10] Furthermore, it is difficult to effectively add 1 equiv of CuCl because of its insolubility in most organic solvents. To further study this effect, we looked for compounds that would react quickly and cleanly with phosphines in a stoichiometric fashion. For example, the reaction of phosphines with transition-metal dimers containing bridging chloride ligands has been well established.[11] The reaction of tricyclohexylphosphine with [Ru(*p*-cymene)Cl$_2$]$_2$ is shown in eq 1.



(1)

Upon addition of 1 equiv of [Ru(*p*-cymene)Cl$_2$]$_2$ to a solution of either **1a** or **1b** in benzene at room temperature, the transformation shown in eq 2 proceeds cleanly and quantitatively, as determined by ^{1}H and ^{31}P NMR spectroscopy. While the [Ru(*p*-cymene)Cl$_2$]$_2$ dimer re-



1a: R = CHCPh$_2$
1b: R = Ph

(2)

2a: R = CHCPh$_2$
2b: R = Ph

3

acts with 1 equiv of phosphine to generate the three-legged piano-stool compound **3**, as expected, the remaining fragment chelates the ruthenium alkylidene *via* the bridging chloride ligands and, thus, serves to stabilize it toward decomposition.

These two products can be easily separated by washing the crude solids with benzene or a mixture of acetone and approximately 5−10% benzene. The alkylidene is isolated as either a yellow-orange (**2a**) or yellow-green

---

[8] Dias, E. L.; Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1997**, *119*, 3887−3897.

[9] Tallarico, J. A.; Bonitatebus, P. J.; Snapper, M. L. *J. Am. Chem. Soc.* **1997**, *119*, 7157−7158.

[10] (a) *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon: New York, 1987; Vol. 5. (b) *Advanced Inorganic Chemistry*; Cotton, F. A. Wilkinson, G., Eds.; Wiley: New York, 1988; 757−766.

[11] Bennett, M. A.; Smith, A. K. *J. Chem. Soc., Dalton Trans.* **1974**, 233.

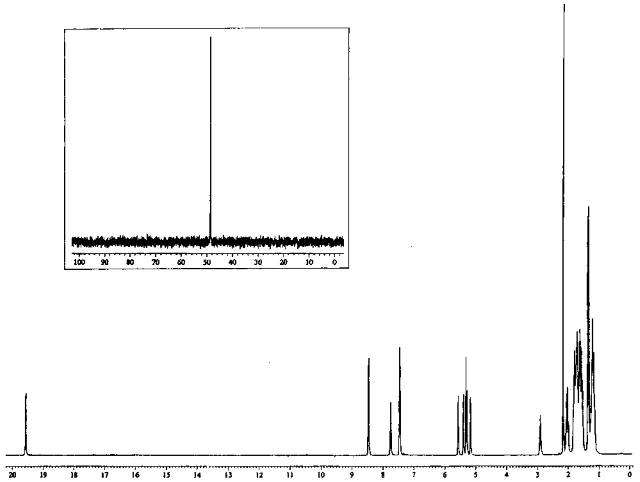
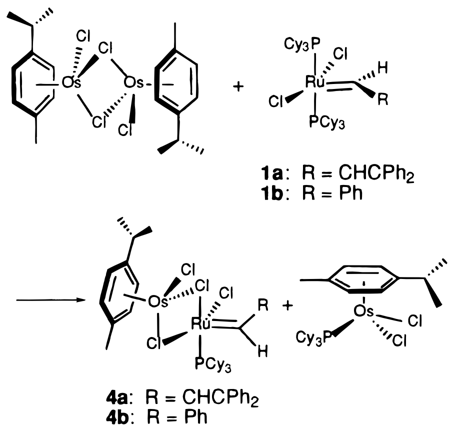


Figure 1. ^1H and ^{31}P (inset) NMR spectra of **2b** in CD_2Cl_2.

(**2b**) analytically pure solid in 60−65% yield and can be recrystallized from either dichloromethane/pentane or toluene/pentane if necessary. These bimetallic complexes are soluble in chlorinated solvents (dichloromethane, chloroform, chlorobenzene, *o*-dichlorobenzene) and sparingly soluble in aromatic solvents (benzene, toluene).

The bimetallic alkylidene products have been characterized by ^1H and ^{31}P NMR spectroscopy (Figure 1). The ^{31}P NMR spectrum of **2b** shows a single sharp peak at 48.68 ppm, and the ^1H NMR spectrum has several interesting features. The alkylidene H_α proton is coupled to the ^{31}P nucleus, indicating that the alkylidene moiety is coplanar with the Ru−P bond, contrary to what is observed for **1a** and **1b**. The four aromatic protons on the *p*-cymene ligand are inequivalent, resolved as four separate doublets. Likewise, the two methyl groups on the *p*-cymene ligand are inequivalent as well, resolved as two separate doublets. The *p*-cymene ligand is thus bound in an asymmetric environment, such that **2b** is chiral.

Reaction of $[Ru(benzene)Cl_2]_2$ with **1a** or **1b** produces the expected bimetallic alkylidenes only transiently, as detected by ^1H NMR spectroscopy, followed by decomposition to produce the corresponding alkylidene coupling products—1,1,6,6-tetraphenyl-1,3,5-hexatriene for **1a** and stilbene for **1b**. Likewise, bimolecular decomposition products are also observed upon reaction of the ruthenium methylidene (**1c**) or ethylidene (**1d**) with $[Ru(p\text{-cymene})Cl_2]_2$. In the particular case of the ruthenium methylidene (**1c**), a ruthenium−ethylene complex is observed in the ^1H NMR spectrum. Therefore, although the reaction in eq 2 proceeds for many ruthenium dimers and alkylidenes, the stability of the resulting products appears to depend dramatically upon the steric bulk of the ligand sphere. These results prompted us to explore the generality of this reaction and determine if this methodology can be extended to complexes of other transition metals.



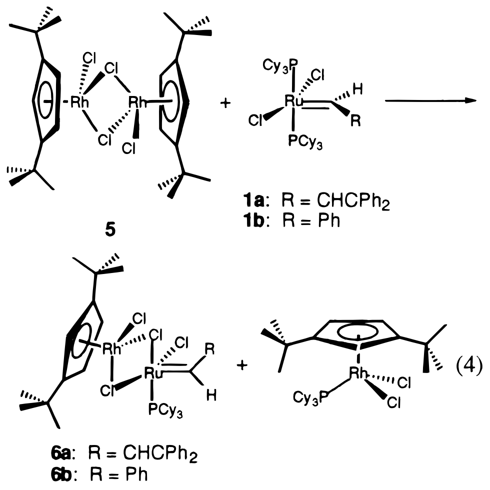
(3)

$[Os(p\text{-cymene})Cl_2]_2$ reacts with **1a** and **1b** in an analagous fashion (eq 3). The reaction proceeds cleanly and quantitatively to form the heterobimetallic osmium−ruthenium alkylidenes **4a** and **4b**. The products of this reaction are more difficult to separate than the products of the reaction with $[Ru(p\text{-cymene})Cl_2]_2$, due to the increased solubility of **4a** and **4b** in organic solvents. However, **4a** and **4b** can be isolated from the crude solids in moderate yield by preferential recrystallization from a mixture of toluene/pentane. The crystals can be washed with a benzene/pentane mixture to give a 40% isolated yield of analytically pure products. The vinylalkylidene **4a** is isolated as a yellow solid, and the benzylidene **4b** is isolated as a green solid. Their corresponding ^1H and ^{31}P NMR sprectra are similar to those for **2a** and **2b**, with only slight differences in chemical shifts.

The isoelectronic compounds $[Co(Cp^*)Cl_2]_2$, $[Rh(Cp^*)Cl_2]_2$, and $[Ir(Cp^*)Cl_2]_2$ (Cp* = pentamethylcyclopentadienyl) all react with **1a** and **1b** in a similar fashion; however, the heterobimetallic alkylidenes are not stable. The reactions of $[Co(Cp^*)Cl_2]_2$ and $[Rh(Cp^*)Cl_2]_2$ with **1b** are slower than the reactions in eqs 1 and 2—the alkylidene products initially build up to a steady-state concentration, followed by decomposition to produce the carbene coupling products described above. When the iridium dimer is used, the bimetallic alkylidene is formed very rapidly but decomposes with a half-life of approximately 30 min. These observations prompted the use of bulkier cyclopentadienyl ligands to stabilize the alkylidenes toward decomposition.

Lithium *tert*-butylcyclopentadienide (Li(^{t}BuCp)) reacts with $RhCl_3{\cdot}xH_2O$ in refluxing methanol to afford the dimer $[Rh(^tBuCp)Cl_2]_2$. $[Rh(^tBuCp)Cl_2]_2$ reacts rapidly with **1a** or **1b** to form the corresponding rhodium−ruthenium alkylidenes quantitatively, but these products decompose with a half-life of approximately 4 h at room temperature. Thus, while the bulkier, less electron-rich ^{t}BuCp ligand increases the rate of product formation, it affords only limited stability toward bimolecular decomposition.

Di-*tert*-butylcyclopentadiene ($^tBu_2CpH$) reacts with $RhCl_3{\cdot}xH_2O$ to afford the dimer $[Rh(^tBu_2Cp)Cl_2]_2$ (**5**), which can be recrystallized from ethanol to yield an analytically pure red solid. Reaction of $[Rh(^tBu_2Cp)Cl_2]_2$ with **1a** and **1b** proceeds cleanly and quantitatively to form the corresponding rhodium−ruthenium alkylidenes **6a** and **6b** (eq 4). The products of this reaction are easily separated by washing the crude solids with acetone to yield **6a** and **6b** as analytically pure yellow and red solids, respectively. The ^1H NMR spectrum indicates that the two *tert*-butyl groups on the cyclopentadiene ligand are equivalent, as are the two adjacent cyclopentadienyl protons. Otherwise, the ^1H and ^{31}P NMR spectra are similar to those for the other bimetallic alkylidenes. **6a** and **6b** decompose slowly in



5

1a: R = CHCPh$_2$
1b: R = Ph

6a: R = CHCPh$_2$
6b: R = Ph

(4)

solution at room temperature, having a half-life of approximately 1 day.

The following conclusions can be drawn from these results. First, the generality of the reaction to form bimetallic species extends to bridging chloride dimers of osmium, cobalt, rhodium, and iridium, as well as ruthenium. Second, there is a rigorous steric requirement imposed upon both the carbene moiety and the ligands bound to the ancillary metal center to prevent bimolecular decomposition of the bimetallic alkylidenes. Stability of the homobimetallic ruthenium alkylidenes increases as H $<$ Me $<$ Ph $\approx$ CHCPh$_2$ for the carbene substituents and benzene $<$ *p*-cymene for the arene ligands. The heterobimetallic rhodium–ruthenium alkylidenes show a similar trend: in order of increasing stability, Cp* $<$ ^{t}BuCp $<$ ^{t}Bu$_2$Cp. The rate of product formation (eq 4) increases in the order Cp* $<$ ^{t}BuCp $\approx$ ^{t}Bu$_2$Cp, which can be attributed to either the increased steric bulk or the decreased electron-donating ability of the *tert*-butyl-substituted ligands.

General Stability of Bimetallic Ruthenium Alkylidenes. The bimetallic compounds **2a**,**b**, **4a**,**b**, and **6a**,**b** are stable to air in the solid state. The ruthenium and osmium dimers **2a**,**b** and **4a**,**b** are also stable for days in a solution of dichloromethane under inert atmosphere. In a solution of chloroform under air, it was found that **2a** decomposed to produce 3,3-diphenyl propenal—the result of oxidation of the carbene fragment. (The ruthenium-containing products are unknown.) The bimetallic alkylidenes are also stable to water, as demonstrated by the addition of D$_2$O to solutions of the compounds in a mixture of 1:1 CD$_2$Cl$_2$/THF-d_8. Upon heating in CD$_2$Cl$_2$ or a mixture of CD$_2$Cl$_2$/C$_6$D$_6$, the alkylidenes decompose to produce the piano-stool compounds (cf. **3**) and the alkylidene coupling products.

Activities of Bimetallic Ruthenium Alkylidenes. The metathesis activities of the bimetallic catalysts were compared to those of the parent catalysts **1a** and **1b** for the ROMP of 1,5-cyclooctadiene (COD). COD was chosen as the substrate because the rates of polymerization were slow enough to be studied by ^{1}H NMR spectroscopy—it was found that the previously studied RCM of diethyl diallylmalonate was too fast to follow by NMR when the bimetallic catalysts were used.

The kinetics of the ROMP of COD by the **1a** and **1b** are complex, similar to what was previously observed for the RCM of diethyl diallylmalonate.[8] When the bimetallic catalysts are used, however, the kinetics are pseudo-first order with respect to COD (Figure 2). To compare the relative activities of the bimetallic catalysts to the parent catalysts, the kinetics of **1a** and **1b** were approximated by first-order curve fits such that (artificial) pseudo-first-order rate constants could be extracted, which in fact *overestimate* the rates of metathesis by these catalysts. The relative rate constants k_{rel} obtained in this manner are summarized in Table 1.

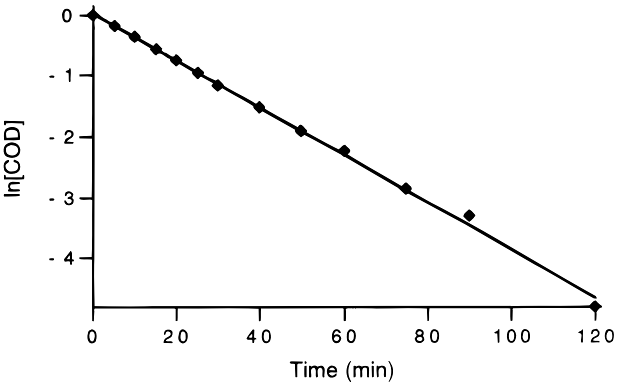
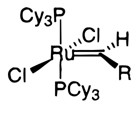
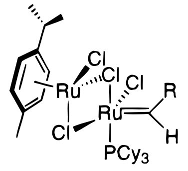
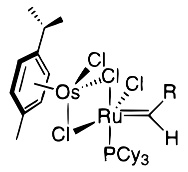
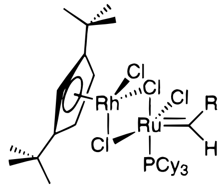


Figure 2. Log plot of [COD] vs time for catalyst **2b** in CD$_2$Cl$_2$ at 16 °C, where [COD]$_0$ = 0.730 M and [**2b**] = 3.25 mM. The filled diamonds are the data points, and the solid line is the best linear fit: slope = -0.0388 ± 0.0006, intercept = 0.0218 ± 0.0323, linear correlation coefficient = 0.999.

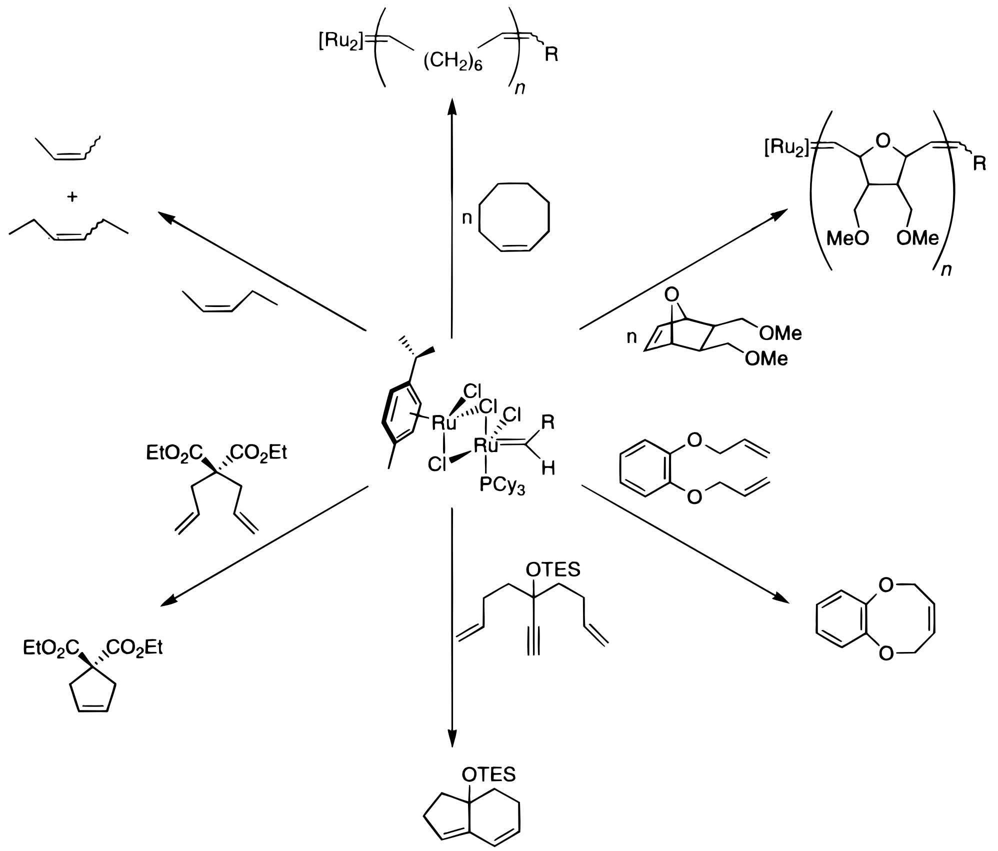
Table 1. Activities of Bimetallic Ruthenium Catalysts in the ROMP of 1,5-Cyclooctadiene

Structure	Compound	k_{rel}[a]
	**1a**: R = CHCPh$_2$	1
	1b: R = Ph	14
	**2a**: R = CHCPh$_2$	22
	2b: R = Ph	34
	**4a**: R = CHCPh$_2$	37
	4b: R = Ph	41
	**6a**: R = CHCPh$_2$	72
	6b: R = Ph	86

[a] Conditions: [catalyst] = 3.25 mM, [COD] = 0.73 M in CD$_2$Cl$_2$, temperature = 16.0 °C.

From Table 1, it is apparent that the activities of the bimetallic catalysts are substantially greater than those of the parent catalysts. The ruthenium catalysts **2a**,**b** exhibit rates approximately 20 times that of catalyst **1a**.

Scheme 2



When the analagous osmium catalysts **4a**,**b** are used, the reaction rate increases further—approximately 40 times that of **1a**. The rhodium-containing catalysts **6a**,**b**, however, show the most dramatic increase in catalyst activity by far, exhibiting relative rates that are *approximately 80 times* that of **1a**!

Comparing k_{rel} for **1a** and **1b** (Table 1), it is once again demonstrated that the vinyl alkylidene suffers from poorer initiation. Initiation is also found to be poorer for the vinyl alkylidenes **2a**, **4a**, and **6a** when compared to the benzylidenes **2b**, **4b**, and **6b** respectively; however, the differences in k_{rel} for the bimetallic catalysts are not nearly as large as that for **1a** and **1b**.

Reactivity of Bimetallic Ruthenium Alkylidenes. The bimetallic catalysts **2a**,**b**, **4a**,**b**, and **6a**,**b** perform all of the standard olefin metathesis reactions that are catalyzed by **1a,b** (Scheme 2). The RCM of diethyl diallylmalonate and the *ene*–*yne*–*ene* substrate proceed to quantitative conversion in less than 5 min at room temperature using 5 mol % of catalyst **2b**. The metathesis of *cis*-2-pentene (0.38 M in benzene) by **6b** (0.5 mol %) proceeds with an initial rate of 10 turnovers *per minute*, as compared with **1a** which exhibits a rate of 26 turnovers *per hour* under similar conditions.[7] Furthermore, because of their enhanced activities, it is often the case that much lower catalyst loadings can be used. For example, in the previously studied RCM of diallyl catechol to form the eight-membered cycloolefin[12] (Scheme 2), as little as 0.5 mol % of **2b** can be used with no decrease in the yield of cyclized product.

The bimetallic catalysts can also be used for reactions that proceed too slowly to make them feasible using catalysts **1a** and **1b**. For instance, when attempts are made to polymerize hexafluorodimethyl norbornadiene (**7**) or the alkyl-substituted benzobarrelene (**8**) with catalysts **1a**,**b**, the reactions proceed so slowly (on the order of days to weeks) at room temperature that catalyst decomposition becomes a problem. Furthermore, heating these reactions results in a faster rate of catalyst decomposition. When catalysts **2a**,**b**, or especially **6a**,**b**, are employed, the rate of polymerization is sufficient to make these reactions much more practical (Scheme 3). Even 2-butyne can be polymerized to an appreciable extent when catalyst **6a** or **6b** is used.

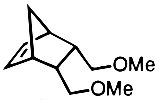
Mechanism of Olefin Metathesis by Bimetallic Ruthenium Alkylidenes. For the bimetallic catalysts discussed above, the structures and resulting activities suggest that the ancillary metal center may be acting as a hemilabile chelating group, such that the tricyclohexylphosphine may not dissociate during olefin metathesis. Furthermore, the pseudo-first-order kinetics observed for the ROMP of 1,5-cyclooctadiene by these catalysts also suggest a mechanism that is associative in nature.

During the activity studies summarized in Table 1, small deviations from first-order behavior were observed in a few cases. This can be attributed to bimolecular decomposition of the propagating species during the reaction, presumably due to the lack of steric bulk adjacent to the ruthenium metal center upon initiation with COD. It should be noted that even in these cases, the kinetics did not deviate far from ideal first-order behavior. However, to decrease such decomposition, substrate **9** was used in the following studies.

The polymerization of **9** with catalyst **2b** shows good pseudo-first-order kinetics with respect to substrate

---

[12] Miller, S. J.; Kim, S.-H.; Chen, Z.-R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1995**, *117*, 2108–2109.



9

concentration, as shown in Figure 3. A plot of k_{obs} vs catalyst concentration exhibits a linear relationship (Figure 4), and the plot of ln(k_{obs}) vs ln[Ru_2] (not shown) has a slope of 1, indicating that the rate expression is first order in catalyst concentration. Dependence of the rate upon phosphine concentration could not be tested because tricyclohexylphosphine slowly reacts with **2b** to produce **1b** and **3**. However, there is nothing in the kinetics to suggest that any phosphine dependence exists.

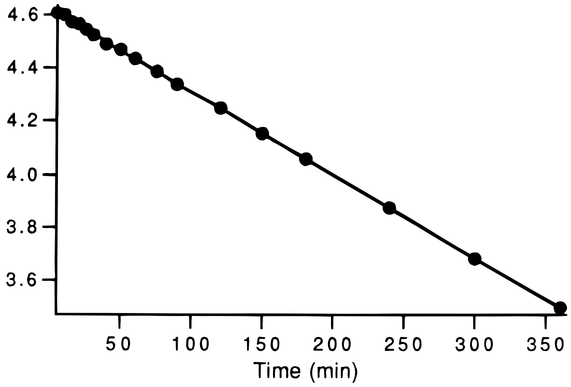


Figure 3. Plot of ln [**9**] vs time for catalyst **2a** in the polymerization of **9** in CD_2Cl_2 at 20 °C, where [**2a**] = 2.36 mM. The monomer concentration was expressed in terms of percentage remaining. The filled circles are the data points, and the solid line is the linear fit: slope = $(1.82 \pm 0.01) \times 10^{-3}$, intercept = 4.61 ± 0.01, linear correlation coefficient = 1.000.

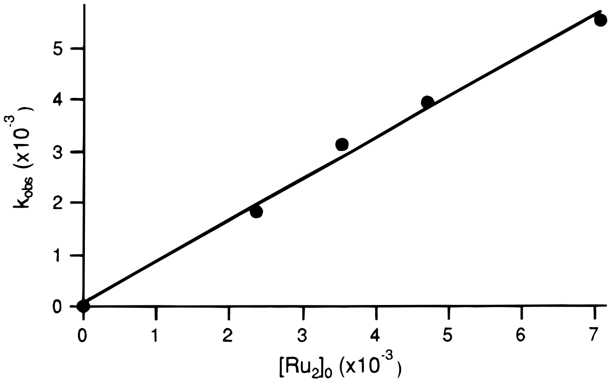
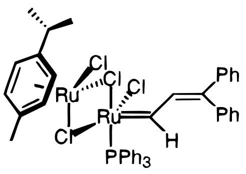


Figure 4. Plot of k_{obs} vs catalyst concentration for catalyst **2a** in the polymerization of **9** in CD_2Cl_2 at 20 °C. The filled circles are the data points, and the solid line is the linear fit: slope = 0.793 ± 0.040, intercept = $(8.07 \pm 16.9) \times 10^{-5}$, linear correlation coefficient = 0.996.

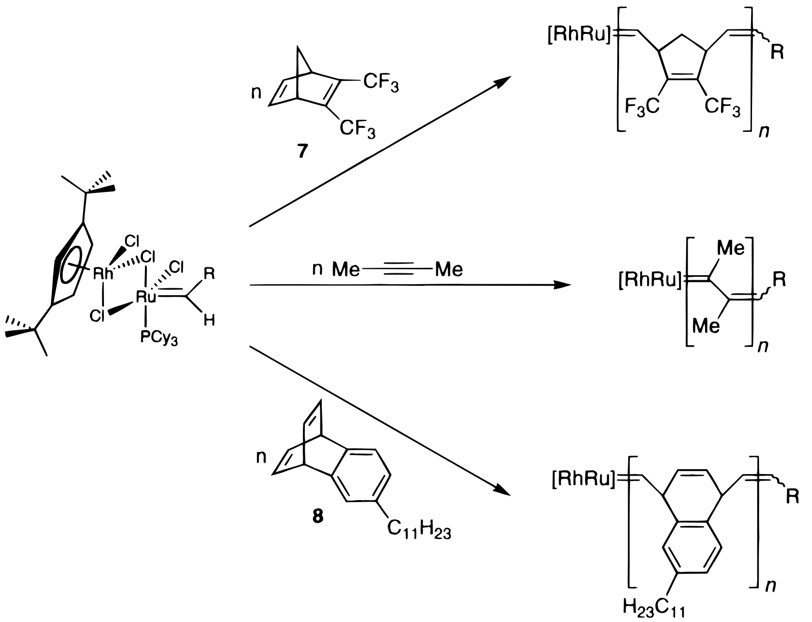
The resulting rate equation $-d[\mathbf{9}]/dt = k[\text{Catalyst}][\mathbf{9}]$ is consistent with an associative mechanism for olefin metathesis by these catalysts. This is supported experimentally by the fact that the compound **10**, employing a triphenylphosphine ligand, does *not* show activity for the metathesis of low ring-strain cyclic or acyclic olefins, similar to the triphenylphosphine analogues of **1a** and **1b**. If phosphine dissociation is required to produce the active catalytic species, as in the case of **1**, compounds **2a** and **10** would be expected to have similar reactivities.



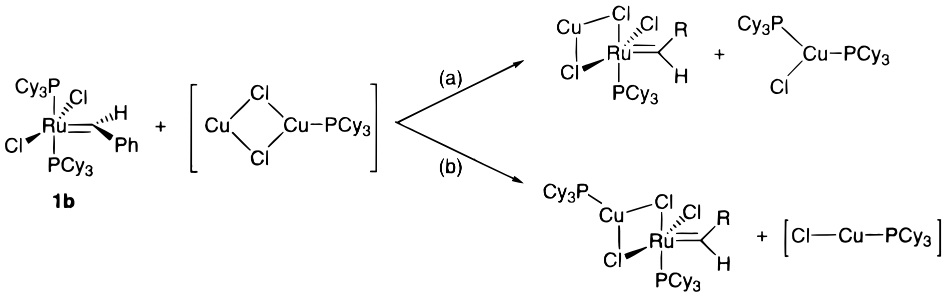
10

Explanation of Bimetallic Catalyst Activities. One source of the enhanced activity of the bimetallic catalysts is the associative mechanism of olefin metathesis. For the parent catalysts **1a**,**b**, dissociation of a phosphine ligand results in a rate expression that has an *effective* catalyst order of $^1/_2$. By introducing the second metal fragment as a chelating ligand, the absence of phosphine dissociation produces a rate

Scheme 3

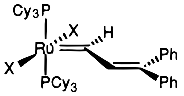


Scheme 4



expression that is first order in catalyst concentration. However, because there are substantial differences in the activities of the bimetallic catalysts as the ancillary metal center is varied, other effects must be present as well.

A possible explanation for the observed trend, Ru < Os < Rh in order of increasing activity, is that coordination of the second metal center to the bound chloride ligand (M···Cl–Ru) makes the chloride more electron withdrawing—similar effects have been observed by Estruelas et al. in bimetallic compounds containing bridging imidazolide and pyrazolide ligands.[13] Investigation of the relative metathesis activities of **1a** and its derivatives **11a** and **11b** indicate that more electron-withdrawing halogens produce more active catalysts, such that I < Br < Cl in order of increasing activity.[8]



1a: X = Cl
11a: X = Br
11b: X = I

While the higher oxidation state Rh(III) is expected to coordinate more strongly to the bound chloride than Ru(II) and Os(II), the difference between Ru(II) and Os(II) is less obvious. Because Ru(II) is more electronegative than Os(II), it might be expected to coordinate better to the bound chloride; however, because third-row transition metals generally form stronger bonds, the Os···Cl bond is expected to be stronger than the Ru···Cl bond.

It has been observed that the chemical shift of the carbene H_α proton correlates well with the relative electron-donating or -withdrawing ability of the halogens for catalyst such as **1a**, **11a**,**b**. For example, the chemical shift of the carbene H_α in **1a** is 19.07 ppm. The signal appears upfield at 18.88 ppm for **11a** and even further upfield at 18.54 ppm for **11b**. This trend is observed for other derivatives as well—more electron-withdrawing halogens shift the H_α resonance downfield.[8] From the ^{1}H NMR spectra of the bimetallic compounds, it is apparent that the chemical shifts for the osmium–ruthenium catalysts **4a**,**b** (18.60 and 19.62 ppm) are downfield of those for the corresponding ruthenium catalysts **2a**,**b** (18.55 and 19.58 ppm) while the chemical shifts for the rhodium–ruthenium catalysts **6a**,**b** are the furthest downfield (18.70 and 19.69 ppm). Following the trend observed for **1a** and **11a**,**b**, the electron-withdrawing ability of the chlorides in the bimetallic catalysts increases in the order Ru < Os < Rh, consistent with the observed activities.

Mechanism of CuCl Activation of 1a and 1b. Due to the observed tendency for **1a** and **1b** to form bimetallic complexes when one of the phosphines is removed from the metal center, the activation of **1a** and its derivatives by CuCl was examined in further detail. The $CuCl\cdot PR_3$ complex is ill-defined and oligomeric in solution—bridging of the chloride ligands leads to several types of higher-order structures.[10] It is therefore feasible that chloride-bridged complexes of copper and ruthenium may form as well.

A ^{1}H NMR study was conducted in which 5 equiv of CuCl was added to a solution of **1b** in CD_2Cl_2. After 20 min, two small doublets appeared in the carbene α-proton region of the spectrum at 19.18 and 19.72 ppm, upfield of the singlet for **1b** at 20.02 ppm. At this time, *cis*- and *trans*-stilbene were also observed, indicative of bimolecular decomposition. After 1 h, several minor peaks appeared between 19.60 and 20.00 ppm.

Because the carbene α-proton resonances for the bimetallic catalysts **2b**, **4b**, and **6b** all appear as doublets upfield of **1b** at 19.58, 19.62, and 19.69 ppm, respectively, it is believed that the peaks at 19.72 and 19.18 ppm correspond to bimetallic copper–ruthenium complexes. The appearance of two species can be explained by reaction of **1b** with dimeric copper compounds having the formula "$Cu_2Cl_2\cdot PCy_3$", which may form upon reaction of CuCl with PCy_3 (Scheme 4). The minor peaks that subsequently appear are most likely oligomeric species, which may form *via* path (a) in Scheme 4—the unsaturated copper center in the bimetallic alkylidene complex may accommodate other ligands (e.g., bridging chlorides). Due to the instability of these complexes, however, a more positive identification cannot be made at this time.

One-Pot Polymerization and Hydrogenation with 2b. It is well-documented that ruthenium dimers $[Ru(Ar)Cl_2]_2$ react with H_2 in the presence of triethylamine to form catalysts that hydrogenate olefins under mild conditions (1 atm of H_2, 30 °C).[14] Studies were undertaken to determine if catalysts such as **2a** and **2b** would show similar hydrogenation activities, such that ROMP polymers generated with these catalysts could be hydrogenated *in situ*.

---

(13) (a) Esteruelas, M. A.; Garcia, M. P.; Lopez, A. M.; Oro, L. A. *Organometallics* **1991**, *10*, 127–133. (b) Garcia, M. P.; Lopez, A. M.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A. *J. Chem. Soc., Dalton Trans.* **1990**, 3465–3472. (c) Garcia, M. P.; Lopez, A. M.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A. *J. Chem. Soc., Chem. Commun.* **1988**, 793–795. (d) Garcia, M. P.; Lopez, A. M.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A. *J. Organomet. Chem.* **1990**, *388*, 365–377.

(14) (a) Hinze, A. G. *Recl. Trav. Chim. Pays-Bas* **1973**, *92*, 542–552. (b) Iwata, R.; Ogata, I. *Tetrahedron* **1973**, *29*, 2753–2758. (c) Ogata, I.; Iwata, R.; Ikeda, Y. *Tetrahedron Lett.* **1970**, *34*, 3011–3014.

In preliminary experiments, 500 equiv of COD was polymerized with catalyst **2b** in benzene in a Fischer–Porter apparatus. After polymerization was complete, approximately 10 equiv of triethylamine was added to the solution. Heating the reaction to 50 °C under 30 psi of H_2 resulted in hydrogenation of the poly(butadiene) to polyethylene over 60 h, at which time the polymer became insoluble. It is estimated from the ^1H NMR spectrum that the resulting polyethylene contains <5% olefins, indicating an unoptimized yield of >90% for the hydrogenation reaction under what are relatively mild conditions.

Conclusions

A new strategy for synthesizing ruthenium-based olefin metathesis catalysts that exhibit a range of activities higher than those previously reported for ruthenium alkylidenes **1a** and **1b** has been developed. The reaction of 18-electron, chloride-bridged dimers of ruthenium, osmium, and rhodium with the ruthenium catalysts **1a** and **1b** proceeds cleanly and quantitavely to produce stable, bimetallic complexes that can be easily isolated. Although stoichiometric amounts of the corresponding piano-stool-type complexes are generated in these reactions, it should be emphasized that they do *not* affect catalyst activity and need not be separated for routine usage.

There are several indications that a sterically bulky environment is required to stabilize the bimetallic complexes. Bimolecular decomposition is observed for compounds containing alkylidene substituents that are smaller than the diphenylvinyl and phenyl moieties in **1a** and **1b**. While reaction of **1a** or **1b** with [Ru(*p*-cymene)Cl_2]$_2$ produces stable compounds **2a**,**b**, reaction with [Ru(benzene)Cl_2]$_2$ produces compounds that decompose rapidly. Further evidence for the steric requirement at the ancillary metal center is provided by the heterobimetallic rhodium–ruthenium complexes, from which it was determined that stability increases in the order Cp* < ^{t}BuCp < ^{t}Bu$_2$Cp.

The bimetallic catalysts exhibit relative rate constants for the ROMP of 1,5-cyclooctadiene that range from approximately 25 for the homobimetallic ruthenium catalysts to 80 for the heterobimetallic rhodium–ruthenium catalysts, with respect to parent catalyst **1a**. One possible explanation for the observed trend in activity, Ru < Os < Rh, is that coordination of the ancillary metal center to the ruthenium-bound chloride makes the chloride more electron withdrawing—an idea that is supported by spectroscopic evidence. Both kinetic and experimental studies support the hypothesis that these bimetallic catalysts operate *via* an associative mechanism of olefin metathesis—i.e., the bound tricyclohexylphosphine does not dissociate during the course of the reaction. With respect to the previously reported enhancement of the activity of catalyst **1a** by the addition of CuCl, there is spectroscopic evidence that at least two new bimetallic copper–ruthenium complexes are being generated in this system.

Preliminary experiments demonstrate that catalyst **2b** can also be used for the *in situ* hydrogenation of poly(butadiene) produced from the ROMP of 1,5-cyclooctadiene. The extension of this methodology to utilize the control over molecular weight and polydispersity provided by ROMP in the synthesis of polymers with saturated backbones is currently under investigation.

Experimental Section

All manipulations were performed using standard Schlenk techniques unless otherwise specified. Argon was purified by passage through columns of BASF R3-11 catalyst (Chemalog) and 4 Å molecular sieves (Linde). Solid organometallic compounds were transferred and stored in a nitrogen-filled Vacuum Atmospheres drybox. All ^1H and ^{31}P NMR spectra were recorded in CD_2Cl_2 on a JEOL JNM-GX400 (399.80 MHz ^1H). All NMR tubes and septa used were dried under vacuum and stored in a drybox.

All solvents were vacuum transferred from sodium benzophenone ketyl, except for chlorinated solvents (including CD_2Cl_2), which were vacuum transferred from CaH_2. All solvents were degassed by several freeze–pump–thaw cycles.

$(PCy_3)_2Cl_2Ru(CHCHCPh_2)$ (**1a**) and $(PCy_3)_2Cl_2Ru(CHPh)$ (**1b**) were synthesized from $Ru(PPh_3)_3Cl_2$ according to published procedures.[7] [[Os(*p*-cymene)Cl_2]$_2$,[15] [Co(Cp*)Cl_2]$_2$,[16] lithium *tert*-butylcyclopentadienide,[17] di-*tert*-butylcyclopentadiene,[18] and substrates **7**,[19] **8**,[5a] and **9**[20] were prepared according to literature procedures. [Ru(*p*-cymene)Cl_2]$_2$, [Ru(benzene)Cl_2]$_2$, [Rh(Cp*)Cl_2]$_2$, and [Ir(Cp*)Cl_2]$_2$ were purchased from Aldrich and used without further purification. $RhCl_3{\cdot}xH_2O$, purchased from Alfa (Johnson Matthey), consistently gave the best results.

Mass spectral analysis was performed at the Southern California Mass Spectrometry Facility at the University of California at Riverside and the Caltech Mass Spectrometry Facility. Elemental Analyses were performed by the Caltech Analytical Facility.

Synthesis of [(*p*-cymene)(Cl)Ru(*μ*-Cl)$_2$Ru(Cl)(PCy$_3$)(CHCHCPh$_2$) (2a). Inside the drybox, 1.0 g (1.08 mmol) of $(PCy_3)_2Cl_2Ru(CHCHCPh_2)$ (**1a**) and 0.660 g (1.08 mmol) of [(*p*-cymene)$RuCl_2$]$_2$ were weighed into a 100 mL Schlenk flask equipped with a stirbar and then dissolved in 60–70 mL of C_6H_6. The flask was capped with a rubber septum, removed from the drybox, placed under argon on the Schlenk line, and stirred for 3.5 h at 45 °C, during which time a yellow precipitate formed from the dark red-orange solution. The solvent was removed in vacuo, and the product was washed with a mixture of acetone (15 mL) and benzene (ca. 5 mL) to remove the [(*p*-cymene)Ru(Cl)$_2$(PCy$_3$)] byproduct and any unreacted starting materials. The solid product was isolated by cannula filtration, the washing procedure was repeated two more times, and the product was dried in vacuo, yielding 0.621 g (0.65 mmol, 60%) of a yellow-orange powder, which was isolated and stored inside of the drybox. Alternatively, the product can be isolated directly from the reaction mixture by cannula filtration and washed with benzene or acetone/benzene to give pure product in slightly lower yield. ^1H NMR: δ 18.55 (dd, 1 H, Ru=C*H*, $^3J_{HH} = 11$ Hz, $^3J_{HP} = 10$ Hz), 8.91 (d, 1 H, C*H*=CPh$_2$, $^3J_{HH} = 11$ Hz), 7.68 (d, 2 H, H_{ortho}, $^3J_{HH} = 7$ Hz), 7.54 (t, 1 H, H_{para}, $^3J_{HH} = 7$ Hz), 7.44 (t, 1 H, H_{para}, $^3J_{HH} = 7$ Hz), 7.32 (pseudo q, 4 H, H_{meta}, $^3J_{HH} = 7$ Hz), 7.23 (d, 2 H, H_{ortho}, $^3J_{HH} = 7$ Hz), 5.60 (d, 1 H, H_{cymene}, $^3J_{HH} = 6$ Hz), 5.51 (d, 1 H, H_{cymene}, $^3J_{HH} = 6$ Hz), 5.34 (d, 2 H, H_{cymene}, $^3J_{HH} = 6$ Hz), 2.95 (sept, 1 H, $H_{isopropyl}$, $^3J_{HH} = 6$ Hz), 2.29 (s, H_{methyl}, 3 H), 1.87 (app q, 3 H, $H_{cyclohexyl}$), 1.75–1.41(br m, 21 H, $H_{cyclohexyl}$), 1.37 (app t, 6 H, H_{methyl}, $^3J_{HH} = 6$ Hz), 1.33–1.00

---

[15] Cabeza, J. A.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1985**, 573–578.

[16] Koelle, U.; Fuss, B. *Chem. Ber.* **1984**, *117*, 743–752.

[17] Sullivan, M. F.; Little, W. F. *J. Organomet. Chem.* **1967**, *8*, 277.

[18] Venier, C. G.; Cassarly, E. W. *J. Am. Chem. Soc.* **1990**, *112*, 2808.

[19] Bazan, G. C.; Khosravi, E.; Schrock, R. R.; Feast, W. J.; Gibson, V. C. et al. *J. Am. Chem. Soc.* **1990**, *112*, 8378–87.

[20] Lynn, D. M.; Kanaoka, S.; Grubbs, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 784–790.

(br m, $H_{cyclohexyl}$, 9 H). $^{31}P\{^1H\}$ NMR: δ 49.70 (s). FAB−HRMS: m/z calcd for $C_{43}H_{59}Cl_4PRu_2$ (M^+) 952.1155, found 952.1166.

Synthesis of [(*p*-cymene)(Cl)Ru(μ-Cl)$_2$Ru(Cl)(PCy$_3$)(CHPh) (2b). Inside the drybox, 0.700 g (0.85 mmol) of $(PCy_3)_2Cl_2Ru(CHPh)$ (**1b**) and 0.521 g (0.85 mmol) of [(*p*-cymene)RuCl$_2$]$_2$ were weighed into a 100 mL Schlenk flask equipped with a stirbar, and 50 mL of C_6H_6 was added. The flask was capped with a rubber septum, removed from the drybox, placed under argon on the Schlenk line, and stirred for 2 h at room temperature, during which time a yellow precipitate formed from the dark orange-brown solution. The solvent was removed in vacuo, and the product was washed with a mixture of acetone (30 mL) and benzene (ca. 1 mL) to remove the [(*p*-cymene)Ru(Cl)$_2$(PCy$_3$)] byproduct and any unreacted starting materials. The solid product was isolated by cannula filtration, the washing procedure was repeated two more times, and the product was dried in vacuo, yielding 0.621 g (0.46 mmol, 63%) of a yellow-green powder, which was isolated and stored inside of the drybox. Alternatively, the product can be isolated directly from the reaction mixture by cannula filtration and washed with benzene or acetone/benzene to give analytically pure product in slightly lower yield. ^1H NMR: δ 19.58 (d, 1 H, Ru=CH, $^3J_{HP} = 10$ Hz), 8.47 (d, 2 H, H_{ortho}, $^3J_{HH} = 7$ Hz), 7.76 (t, 1 H, H_{para}, $^3J_{HH} = 7$ Hz), 7.46 (t, 2 H, H_{meta}, $^3J_{HH} = 7$ Hz), 5.57 (d, 1 H, H_{cymene}, $^3J_{HH} = 6$ Hz), 5.41 (d, 1 H, H_{cymene}, $^3J_{HH} = 6$ Hz), 5.28 (d, 1 H, H_{cymene}, $^3J_{HH} = 6$ Hz), 5.17 (d, 1 H, H_{cymene}, $^3J_{HH} = 6$ Hz), 2.91 (sept, 1 H, $H_{isopropyl}$, $^3J_{HH} = 6$ Hz), 2.17 (s, H_{methyl}, 3 H), 2.04 (app q, 3 H, $H_{cyclohexyl}$), 1.80−1.55 (br m, 21 H, $H_{cyclohexyl}$), 1.37 (d, 3 H, H_{methyl}, $^3J_{HH} = 7$ Hz), 1.33 (d, 3 H, H_{methyl}, $^3J_{HH} = 6$ Hz), 1.27−1.15 (br m, $H_{cyclohexyl}$, 9 H). $^{31}P\{^1H\}$ NMR: δ 48.68 (s). Anal. Calcd for $C_{35}H_{53}Cl_4PRu_2$: C, 49.53; H, 6.29. Found: C, 49.42; H, 6.34.

Synthesis of [(*p*-cymene)(Cl)Os(μ-Cl)$_2$Ru(Cl)(PCy$_3$)(CHCHCPh$_2$) (4a). Inside the drybox, 100 mg (0.11 mmol) of $(PCy_3)_2Cl_2Ru(CHCHCPh_2)$ (**1a**) and 85 mg (0.11 mmol) of [(*p*-cymene)OsCl$_2$]$_2$ were weighed into a 10 mL Schlenk flask equipped with a stirbar and then dissolved in 5 mL of CH_2Cl_2. The flask was capped with a rubber septum, removed from the drybox, placed under argon on the Schlenk line, and stirred for 3 h at room temperature to yield a dark orange-brown solution. The solvent was removed in vacuo, the flask was placed in an ice/water bath, and the solids were washed with 2 × 5 mL of 0 °C toluene. The yellow solid was isolated from the orange filtrate by cannula filtration and washed with an additional 2 × 5 mL of 0 °C hexane to remove the residual toluene. The product obtained in this manner was dried in vacuo, yielding 37.5 mg (0.036 mmol, 33%) of a yellow powder, which was isolated and stored inside of the drybox. ^1H NMR: δ 18.60 (dd, 1 H, Ru=CH, $^3J_{HH} = 11$ Hz, $^3J_{HP} = 10$ Hz), 8.98 (d, 1 H, CH=CPh$_2$, $^3J_{HH} = 11$ Hz), 7.68 (d, 2 H, H_{ortho}, $^3J_{HH} = 7$ Hz), 7.54 (t, 1 H, H_{para}, $^3J_{HH} = 7$ Hz), 7.46 (t, 1 H, H_{para}, $^3J_{HH} = 7$ Hz), 7.34 (app q, 4 H, H_{meta}, $^3J_{HH} = 7$ Hz), 7.25 (d, 2 H, H_{ortho}, $^3J_{HH} = 7$ Hz), 6.18 (d, 1 H, H_{cymene}, $^3J_{HH} = 6$ Hz), 6.10 (1 H, H_{cymene}, $^3J_{HH} = 6$ Hz), 5.92 (app t, 2 H, H_{cymene}, $^3J_{HH} = 6$ Hz), 2.81 (sept, 1 H, $H_{isopropyl}$, $^3J_{HH} = 6$ Hz), 2.29 (s, 3 H, H_{methyl}), 1.91 (dt, 3 H, $H_{cyclohexyl}$), 1.71−1.43 (br m, 21 H, $H_{cyclohexyl}$), 1.35 (pseudo t, 6 H, H_{methyl}, $^3J_{HH} = 6$ Hz), 1.28−1.03 (br m, 9 H, $H_{cyclohexyl}$). $^{31}P\{^1H\}$ NMR: δ 51.30 (s).

Synthesis of [(*p*-cymene)(Cl)Os(μ-Cl)$_2$Ru(Cl)(PCy$_3$)(CHPh) (4b). Inside the drybox, 0.500 g (0.61 mmol) of $(PCy_3)_2Cl_2Ru(CHPh)$ (**1b**) and 0.480 g (0.61 mmol) of [(*p*-cymene)OsCl$_2$]$_2$ were weighed into a 50 mL Schlenk flask equipped with a stirbar, and 25 mL of C_6H_6 was added. The flask was capped with a rubber septum, removed from the drybox, placed under argon on the Schlenk line, and stirred for 2 h at room temperature to yield a dark green-brown solution. The solvent was removed in vacuo, and the product was dissolved in a minimum amount of toluene. Pentane was slowly added until a green solid began to precipitate, and the flask was stoppered and placed in the freezer at −10 °C overnight to selectively precipitate the product. The solid product was isolated by cannula filtration, and washed with a mixture of pentane/toluene (ca. 1 mL toluene in 20 mL pentane) and twice more with pentane (2 × 15 mL) to remove the residual toluene. The product was dried in vacuo, yielding 0.225 g (0.24 mmol, 40%) of a light green analytically pure powder, which was isolated and stored inside of the drybox. ^1H NMR: δ 19.62 (d, 1 H, Ru=CH, $^3J_{HP} = 10$ Hz), 8.47 (d, 2 H, H_{ortho}, $^3J_{HH} = 7$ Hz), 7.76 (t, 1 H, H_{para}, $^3J_{HH} = 7$ Hz), 7.48 (t, 2 H, H_{meta}, $^3J_{HH} = 7$ Hz), 6.12 (d, 1 H, H_{cymene}, $^3J_{HH} = 6$ Hz), 5.99 (d, 1 H, H_{cymene}, $^3J_{HH} = 6$ Hz), 5.85 (d, 1 H, H_{cymene}, $^3J_{HH} = 6$ Hz), 5.73 (d, 1 H, H_{cymene}, $^3J_{HH} = 6$ Hz), 2.75 (sept, 1 H, $H_{isopropyl}$, $^3J_{HH} = 6$ Hz), 2.16 (s, H_{methyl}, 3 H), 2.08 (app q, 3 H, $H_{cyclohexyl}$), 1.85−1.56 (br m, 21 H, $H_{cyclohexyl}$), 1.33 (app t, 6 H, H_{methyl}, $^3J_{HH} = 6$ Hz), 1.27−1.16 (br m, $H_{cyclohexyl}$, 9 H). $^{31}P\{^1H\}$ NMR: δ 51.57 (s). Anal. Calcd for $C_{35}H_{53}Cl_4POsRu$: C, 44.82; H, 5.70. Found: C, 44.80; H, 5.93.

Synthesis of [(^{t}Bu$_2$Cp)RhCl$_2$]$_2$ (5). $RhCl_3 \cdot xH_2O$ ($x \approx 3$) (0.500 g, 1.90 mmol) was weighed into a 50 mL Schlenk flask, which was evacuated and filled with argon. A 25 mL amount of degassed methanol was added, followed by 0.500 g (2.8 mmol) of di-*tert*-butyl cyclopentadiene. The flask was fitted with a reflux condenser with a bubbler outlet and purged with argon for 15 min. The argon flow was adjusted to one bubble every 2−3 s, and the reaction was heated to reflux for 36 h. The reaction was allowed to cool to room temperature, the reflux condenser was replaced with a stopper, and the solvent was removed in vacuo. The solids were scraped out onto a Buchner funnel and washed liberally with hexanes until the washings were colorless. The resulting red solid was recrystallized from boiling ethanol, yielding 0.250 g (0.71 mmol, 37%) of a red crystalline solid. ^1H NMR: δ 5.62 (s, 2 H), 5.36 (s, 1 H), 1.33 (s, 18 H). FAB−HRMS: m/z calcd for $C_{26}H_{42}Cl_3Rh_2$ ($M - Cl^+$) 665.0467, found 665.0467.

Synthesis of [(^{t}Bu$_2$Cp)(Cl)Rh(μ-Cl)$_2$Ru(Cl)(PCy$_3$)(CHCHCPh$_2$) (6a). Inside the drybox, 66 mg (0.071 mmol) of $(PCy_3)_2Cl_2Ru(CHCHCPh_2)$ (**1a**) and 50 mg (0.071 mmol) of [(^{t}Bu$_2$Cp)RhCl$_2$]$_2$ were weighed into a 10 mL Schlenk flask equipped with a stirbar and then dissolved in 5 mL of CH_2Cl_2. The flask was capped with a rubber septum, removed from the drybox, placed under argon on the Schlenk line, and stirred for 5 h at room temperature to produce a red-orange solution. The solvent was removed in vacuo, and the product was washed with acetone (3 × 5 mL) to remove the (^{t}Bu$_2$Cp)RhCl$_2$(PCy$_3$) byproduct and any unreacted starting materials. The product was isolated by cannula filtration and dried in vacuo to yield 10 mg (0.010, 15%) of a yellow powder. ^1H NMR: δ 18.70 (dd, 1 H, Ru=CH, $^3J_{HH} = 11$ Hz, $^3J_{HP} = 10$ Hz), 9.01 (d, 1 H, CH=CPh$_2$, $^3J_{HH} = 11$ Hz), 7.70 (d, 2 H, H_{ortho}, $^3J_{HH} = 7$ Hz), 7.53 (t, 1 H, H_{para}, $^3J_{HH} = 7$ Hz), 7.45 (t, 1 H, H_{para}, $^3J_{HH} = 7$ Hz), 7.35 (t, 2 H, H_{meta}, $^3J_{HH} = 7$ Hz), 7.31 (t, 2 H, H_{meta}, $^3J_{HH} = 7$ Hz), 7.26 (d, 2 H, H_{ortho}, $^3J_{HH} = 7$ Hz), 5.51 (s, 1 H, H_{Cp}), 5.48 (s, 2 H, H_{Cp}), 1.91 (app q, 3 H, $H_{cyclohexyl}$), 1.71−1.43 (br m, 21 H, $H_{cyclohexyl}$), 1.42 (s, 18 H, $H_{tert-butyl}$), 1.30−1.03 (br m, 9 H, $H_{cyclohexyl}$). $^{31}P\{^1H\}$ NMR: δ 49.03 (s).

Synthesis of [(^{t}Bu$_2$Cp)(Cl)Rh(μ-Cl)$_2$Ru(Cl)(PCy$_3$)(CHPh) (6b). Inside the drybox, 173 mg (0.21 mmol) of $(PCy_3)_2Cl_2Ru(CHPh)$ (**1b**) and 150 mg (0.21 mmol) of [(^{t}Bu$_2$Cp)RhCl$_2$]$_2$ were weighed into a 25 mL Schlenk flask equipped with a stirbar and then dissolved in 10 mL of CH_2Cl_2. The flask was capped with a rubber septum, removed from the drybox, placed under argon on the Schlenk line, and stirred for 30 min at room temperature to produce a red-orange solution. The solvent was removed in vacuo, and the product was washed with acetone (3 × 10 mL) to remove the (^{t}Bu$_2$Cp)RhCl$_2$(PCy$_3$) byproduct and any unreacted starting materials. The product was isolated by cannula filtration and dried in vacuo to yield 100 mg (0.11 mmol, 53%) of analytically pure red-orange powder. ^1H NMR: δ 19.69 (d, 1 H, Ru=CH, $^3J_{HP} = 10$ Hz), 8.52 (d, 2 H, H_{ortho}, $^3J_{HH} = 7$ Hz), 7.76 (t, 1 H, H_{para}, $^3J_{HH} = 7$ Hz), 7.46 (t, 2 H, H_{meta}, $^3J_{HH} = 7$ Hz), 5.45 (s, 1 H, H_{Cp}), 5.30 (s, 2 H, H_{Cp}), 2.08 (app q, 3 H, $H_{cyclohexyl}$), 1.83−1.62 (br m, 21 H, $H_{cyclohexyl}$), 1.37 (s, 18 H, $H_{tert-butyl}$), 1.27−1.18 (br m, $H_{cyclohexyl}$, 9 H). ^{31}P-{^{1}H} NMR: δ 47.75 (s). Anal. Calcd for $C_{38}H_{60}Cl_4PRhRu$: C, 51.07; H, 6.77. Found: C, 50.80; H, 6.74.

Ring-Opening Metathesis Polymerizations of 1,5-Cyclooctadiene and 9. Reactions for kinetic studies were performed in screw-cap NMR tubes available from Wilmad, sealed with septum-fitted screw caps. Polymer formation and diene disappearance were measured against a blank (no catalyst) solution of either COD or **9** as an external standard.

(1) Relative Catalyst Activity Experiments. A 10X stock solution of each catalyst **2a**,**b**, **4a**,**b**, and **6a**,**b** was made by dissolving 0.0162 mmol of catalyst in 5 mL of CD_2Cl_2. Inside the drybox, 50 μL of the catalyst solution was diluted with 405 μL of CD_2Cl_2 in a screw-top NMR tube. The NMR tube was then capped with a septum-fitted screw cap and removed from the drybox. A sample of COD was prepared in the drybox in a vial and capped with a septum-fitted screw cap.

The NMR probe was equilibrated to 16.0 °C (ambient temperature), and 45 μL of COD was injected via syringe immediately before the sample was placed in the probe. The final concentrations were [catalyst] = 3.25 mM, [COD] = 0.73 M. Ratio of [COD]/[catalyst] = 225/1.

(2) Catalyst Dependence Experiments. A catalyst stock solution was made by dissolving 25 mg (0.0295 mmol) of **2b** in 0.5 mL or CD_2Cl_2. Inside the drybox, 20, 30, 40, and 50 μL of catalyst stock solution were syringed into a screw-cap NMR tube and diluted with CD_2Cl_2 to bring the volume to 480 μL. The NMR tube was capped with a septum-fitted screw cap and removed from the drybox. A sample of **9** was prepared in the drybox in a vial and capped with a septum-fitted screw cap.

The NMR probe was equilibrated to 20.0 °C (ambient temperature in summer), and 20 μL of **9** was injected via syringe immediately before the sample was placed in the probe. The final concentrations of catalyst were 2.36, 3.54, 4.72, and 5.90 mM.

One-Pot Polymerization/Hydrogenation. Inside the drybox, 30 mg (0.035 mmol) of **2b** was weighed into a Fischer−Porter bottle w/stirbar and dissolved in approximately 20 mL of benzene. A 2 g amount (18.5 mmol, 530 equiv) of COD was added to the solution, which subsequently turned orange. The bottle was fitted with a regulator top, sealed, and removed from the drybox. The polymerization was stirred for 5 h at room temperature, after which a hydrogen inlet was fitted to the apparatus. Under flowing H_2, approximately 50 μL of NEt_3 (10 equiv) was added via syringe, and the apparatus was placed in an oil bath preheated to 50 °C and pressured up to 30 psi of H_2. After 24 h, an additional 10 mL of benzene was added via syringe under flowing H_2 to dilute the solution, which was pale yellow in color. After 60 h, the polymer became insoluble and the solution became a thick gel. The apparatus was removed from the oil bath and quickly opened, and toluene was added to losen the gel. The resulting mixture was poured into stirring methanol to precipitate the polymer as a fluffy white solid, which was collected by filtration and dried in vacuo, yielding 1.65 g of poly(ethylene).

Acknowledgment. Financial support has been provided by Rohm and Haas and the National Institute of Health.

OM9708788