A Recyclable Ru-Based Metathesis Catalyst

Jason S. Kingsbury, Joseph P. A. Harrity,[#] Peter J. Bonitatebus, Jr., and Amir H. Hoveyda*

Contribution from the Department of Chemistry, Merkert Chemistry Center, Boston College, Chestnut Hill, Massachusetts 02467

Received September 9, 1998

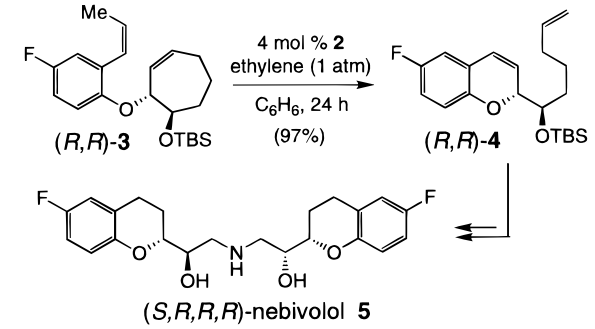
Abstract: A Ru carbene (**8**, Scheme 2) that contains an internal metal−oxygen chelate is an active metathesis catalyst and is readily obtained by the sequential treatment of $Cl_2Ru(PPh_3)_3$ with (2-isopropoxyphenyl)-diazomethane and PCy_3. This Ru-carbene complex offers excellent stability to air and moisture and can be recycled in high yield by silica gel column chromatography. The structures of this and related complexes have been unambiguously established by NMR and single-crystal X-ray diffraction studies.

Introduction

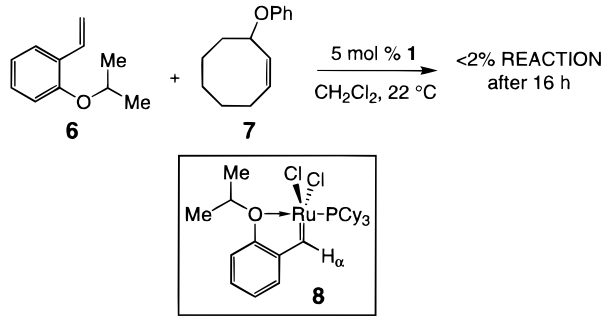
Metal-catalyzed olefin metathesis, as a result of the advent of well-defined Mo- and Ru-based catalysts,[1] continues to serve as the springboard for the development of a range of regio- and stereoselective processes. In this context, we have reported[2,3] a metal-catalyzed process that efficiently converts styrenyl cycloalkenyl ethers to 2-substituted chromenes in the presence of 4−10 mol % $(PCy_3)_2Cl_2Ru{=}CHPh$[4] (**1**) or the more active Mo-$(CHCMe_2Ph)(N(2,6\text{-}(i\text{-}Pr)_2C_6H_3))(OCMe(CF_3)_2)_2$ (**2**).[5] More recently, as depicted in Scheme 1 (**3** → **4**), we employed a Mo-catalyzed chromene synthesis to prepare optically pure 2-substituted chromanes in the first enantioselective total synthesis of the antihypertensive agent (*S*,*R*,*R*,*R*)-nebivolol (**5**).[6]

In the course of studies in connection with the mechanism of Ru-catalyzed styrenyl ether to chromene transformations,[3] we established that various catalytic metathesis reactions, such as ring-opening metathesis polymerization (ROMP) of **7**, are not as effectively catalyzed by **1** when **6** is also present in solution (Scheme 2). To account for this observation, we proposed the in situ formation of a Ru−chelate complex **8**, which is a less active catalyst (relative to **1**) in the presence of excess styrenyl terminal olefin (e.g., **6**). That is, we suggested that following the formation of **8**, the bidentate styrenyl ligand may sequester the transition metal and reduce the rate of subsequent propagation steps.

Scheme 1



Scheme 2



In this article we present the results of our more recent investigations with regard to the chemistry of complex **8**. Our data indicate that Ru complexes typified by **8** are active metathesis catalysts and offer an additional practical feature as well: These complexes can be readily recovered in high yield and reused in subsequent transformations. We also disclose an efficient synthesis scheme for the preparation of this class of Ru carbenes and present data that shed light on their reactivity and physical attributes.

Results and Discussion

Initial Synthesis of 8 and Determination of Its Structure. To gain support for the intermediacy of **8** in reactions such as that in Scheme 2, we set out to synthesize and isolate this metal carbene.[3] As shown in eq 1, when 2-isopropoxystyrene **6** is treated with 1 equiv of **1** (24 h), Ru−carbene complex **8** is

[#] Present address: Department of Chemistry, University of Sheffield, Sheffield, S3 7HF, United Kingdom.

(1) For recent reviews on olefin metathesis, see: (a) Schuster, M.; Blechert, S. *Angew. Chem., Int. Ed. Engl.* **1997**, *109*, 2036−2056. (b) Furstner, A. *Top. in Catal.* **1997**, *4*, 285−299. (c) Armstrong, S. K. *J. Chem. Soc., Perkin Trans. 1* **1998**, 371−388. (d) Grubbs, R. H.; Chang, S. *Tetrahedron* **1998**, *54*, 4413−4450.

(2) Harrity, J. P. A.; Visser, M. S.; Gleason, J. D.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1997**, *119*, 1488−1489.

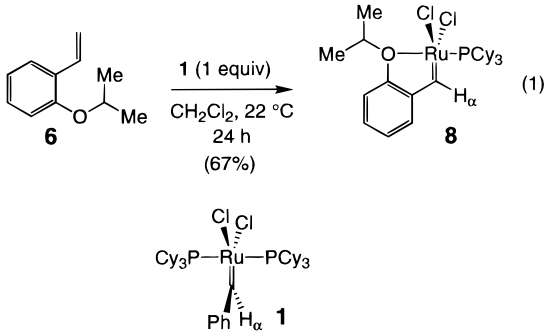
(3) Harrity, J. P. A.; La, D. S.; Cefalo, D. R.; Visser, M. S.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1998**, *120*, 2343−2351.

(4) (a) Schwab, P.; France, M. B.; Ziller, J. W.; Grubbs, R. H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2039−2041. (b) Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100−110.

(5) (a) Schrock, R. R.; Murdzek, J. S.; Bazan, G. C.; Robbins, J.; DiMare, M.; O'Regan, M. *J. Am. Chem. Soc.* **1990**, *112*, 3875−3886. (b) Bazan, G. C.; Schrock, R. R.; Cho, H.-N.; Gibson, V. C. *Macromolecules* **1991**, *24*, 4495−4502.

(6) Johannes, C. W.; Visser, M. S.; Weatherhead, G. S.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1998**, *120*, 8340−8347.

10.1021/ja983222u CCC: $18.00
Published on Web 01/15/1999



formed. Notably, ***8** is exceptionally robust and can be purified to homogeneity as a dark brown crystalline solid by simple silica gel column chromatography* (mp = 200−201 °C).

Circumstantial evidence for internal Ru−oxygen chelation was evident in its 400 MHz ^{1}H NMR and 100 MHz ^{13}C NMR spectra. Substantial shielding of the alkylidene proton (δH_α = 17.44 ppm) results in an upfield shift of ∼2.5 ppm relative to the parent complex (**1**).[4] The carbene carbon atom also resonates upfield (δC_α = 280.63 ppm) in comparison to that of **1** (δC_α = 294.72 ppm).[4] These findings are consistent with substitution of a tricyclohexylphosphine ligand by the aryl ether oxygen. Furthermore, whereas coupling between the phosphorus nucleus and the alkylidene proton is absent in **1** (P−Ru−C_α−H_α dihedral angle = 90°),[7] J_{PH} = 4.4 Hz in the case of **8**. This suggests that formation of the five-membered chelate is coincident with a 90° rotation about the carbon−metal double bond (compare H_α in **1** and **8**, eq 1).[8]

The proposed chelate structure was confirmed through single-crystal X-ray analysis (Figure 1) of the analogous naphthyl derivative **9**.[9] Accordingly, this organometallic complex carries a single monodentate phosphine and is characterized by distorted square pyramidal coordination about the metal center. Consistent with the aforementioned ^{1}H NMR analysis (400 MHz), the C_α−H_α bond lies in plane with the Ru−P and Ru−O bonds. The Ru−C_α bond length (1.84(1) Å) is close to that observed for the related Cl-substituted benzylidene complex $Cl_2Ru(=CH\text{-}p\text{-}C_6H_4Cl)(PCy_3)_2$ (1.839(3) Å),[4] but is significantly shorter than that in $(PCy_3)_2Cl_2Ru=CHCH=CPh_2$ (1.851(2) Å).[7a] These data indicate a stronger Ru=C bond for **9** compared to that of the latter diphenylvinyl carbene system. The Ru−O distance (2.257(7) Å) in **9** is typical for related Ru−O chelate complexes and suggests that the chelate linkage is reasonably strong.[10]

Alternative Syntheses of Ru-Carbene Complexes. Since the parent complex **1** is typically synthesized by the reaction of $Cl_2Ru(PPh_3)_3$ with phenyldiazomethane,[4] we judged that it would be more efficient to prepare **8** directly by a similar procedure where the corresponding *o*-alkoxyphenyldiazomethane is utilized. Moreover, synthesis of this class of Ru−carbene complexes with stoichiometric amounts of the relatively expensive **1**[11] would be somewhat impractical on a large scale.

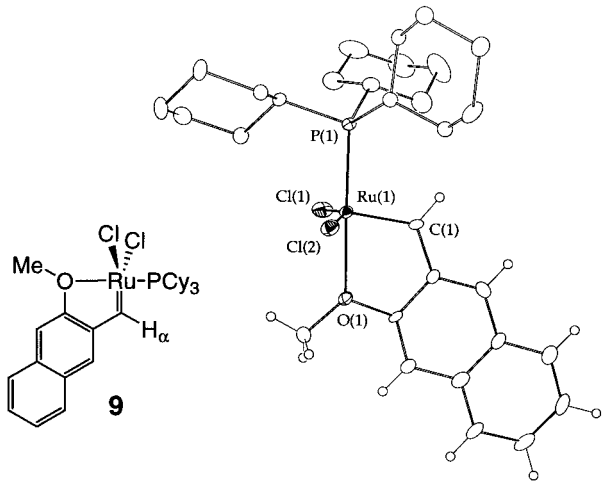


Figure 1. ORTEP diagram of $PCy_3Cl_2Ru(=CH\text{-}o\text{-}OMeC_{10}H_6)$ (**9**). Thermal ellipsoids are drawn at the 30% probability level. Selected bond distances [Å] and angles [deg]: Ru−C(1) 1.84(1), Ru−P 2.267(3), Ru−O 2.257(7), Ru−Cl(1) 2.333(3), Ru−Cl(2) 2.331(3); C(1)−Ru−P 99.4(3), C(1)−Ru−Cl(1) 99.0(3), C(1)−Ru−Cl(2) 104.6(3), P−Ru−Cl(1) 97.6(1), P−Ru−Cl(2) 90.88(10), C(1)−Ru−O 79.6(3), O−Ru−Cl(1) 85.7(2), O−Ru−Cl(2) 86.3(2), P−Ru−O 176.7(2), Cl(2)−Ru−Cl(1) 153.29(11).

As illustrated in Scheme 3, we opted to synthesize and examine the related methoxy carbene complex **12**, since the requisite **10** can be accessed from commercially available *o*-anisaldehyde (2-isopropoxybenzaldehyde is not commercially available).[12] This decision was based on the assumption that the methyl-substituted complex of Ru would behave analogous to the isopropoxy derivative **8** in terms of both stability and catalytic activity. Thus, we established that treatment of $Cl_2Ru(PPh_3)_3$[13] with **10** at −78 °C (CH_2Cl_2, 10 min) results in spontaneous evolution of N_2 to give bisphosphine Ru complex **11**, which is isolated as a bright yellow microcrystalline solid (98% yield). Successful transfer of the diazo carbene moiety to the metal is evident in the 400 MHz ^{1}H NMR spectrum of **11**; the alkylidene proton (H_α) signal appears as a doublet of

(7) Grubbs and co-workers have suggested that a version of the vicinal Karplus correlation may be applicable in these Ru-based systems for the P−Ru−C_α−H_α dihedral angle; see: (a) Nguyen, S. T.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 9858−9859. (b) Dias, E. L.; Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1997**, *119*, 3887−3897. In general, the magnitude of coupling between phosphine ligands and the α-proton of a carbene unit depends on their relative spatial orientation or geometry; see: (c) Klein, D. P.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 3079−3080.

(8) Recent mechanistic work by Grubbs indicates that this dynamic process is not energetically prohibitive. Carbene rotation is apparently the direct result of subtle variations made in the steric and/or electronic environments of a given Ru complex, implying that linear combinations of the two available π-bonding orbitals on Ru exist such that the metal−C double bond is not broken during the rotation process. For further discussion, see ref 7b.

(9) Single crystals of **9** from pentane at −20 °C; crystal size 0.1 × 0.05 × 0.05 mm; monoclinic; space group $P2_1/n$; a = 11.439(1) Å, b = 23.483(3) Å, c = 12.336(3) Å; β = 102.29(2)°; V = 3237.8(9) Å^3, D_{calcd} = 1.339 g/cm^3 for Z = 4; T = 183(2) K. In the solid state, the structure contained a disordered pentane unit that was modeled over two positions with 60:40 occupancy. Further details, including tables of crystallographic data, are available in the Supporting Information.

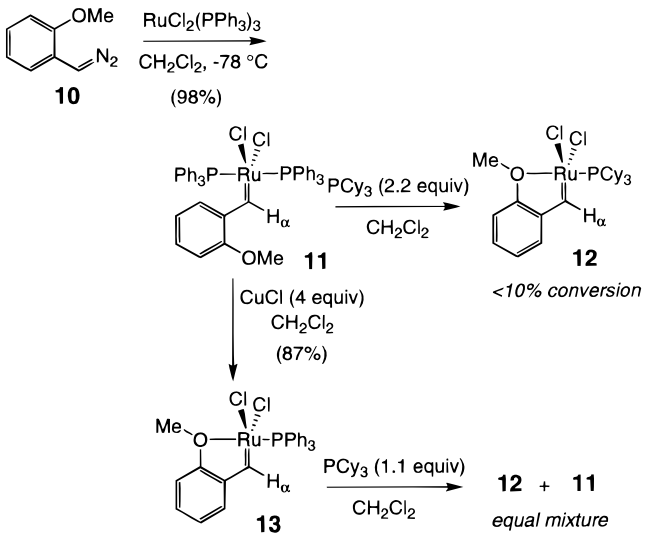
(10) For Ru−O chelate complexes with similar bond lengths, see: (a) Yang, H.; Alvarez-Gressier, M.; Lugan, N.; Mathieu, R. *Organometallics* **1997**, *16*, 1401−1409. (b) Lindner, E.; Mockel, A.; Mayer, H. A.; Fawzi, R. *Chem. Ber.* **1992**, *125*, 1363−1367. (c) Lindner, E.; Schober, U.; Fawzi, R.; Hiller, W.; Englert, U.; Wegner, P. *Chem. Ber.* **1987**, *120*, 1621−1628. (d) Jeffrey, J. C.; Rauchfuss, T. B. *Inorg. Chem.* **1979**, *18*, 2658−2666. For examples of stronger Ru−O chelation and the corresponding bond lengths, see: (e) Lindner, E.; Mockel, A.; Mayer, H. A.; Kuhbauch, H.; Fawzi, R.; Steimann, M. *Inorg. Chem.* **1993**, *32*, 1266−1271. For related alkylidene metal−oxygen chelate complexes of chromium, see: (f) Dotz, K. H.; Popall, M.; Muller, G. *J. Organomet. Chem.* **1987**, *334*, 57−75.

(11) $(PCy_3)_2Cl_2Ru=CHPh$ (**1**) is commercially available from Strem Chemicals, Inc., at $60/g.

(12) The aryldiazoalkane is available in a two-step, one-pot process (57% overall yield) from commercially available *o*-anisaldehyde, *p*-toluenesulfonylhydrazide, and 1,1,3,3-tetramethylguanidine. Treatment of the aldehyde with $TsNHNH_2$ in MeOH, followed by brief exposure to 1,1,3,3-tetramethylguanidine in the same vessel affords the diazo starting material (see the Experimental Section for details). For the use of tetramethylguanidine in the synthesis of *o*-substituted aryldiazoalkanes, see: Shankar, B. K. R.; Shechter, H. *Tetrahedron Lett.* **1982**, *23*, 2277−2280.

(13) Stephenson, T. A.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1966**, *28*, 945−956.

Scheme 3



doublets at 16.16 ppm (J_{PH} = 7.3, 6.8 Hz). The observed coupling implies that the dihedral angle between H_α and each ^{31}P nucleus is close to 0 or 180°.[7] Moreover, the phosphorus nuclei in **11** are chemically inequivalent, as judged by the 162 MHz ^{31}P NMR spectrum (two doublets at 34.25 and 56.65 ppm (J_{PP} = 38.1, 37.1 Hz, respectively)). The above data collectively suggest that the carbene unit is parallel to the P1−Ru−P2 axis.

The desired complex **12**, however, could not be readily accessed by phosphine exchange with **11**. All attempts were thwarted by low conversion (<30%, 400 MHz ^1H NMR analysis) even in the presence of a large excess of PCy_3 (up to 8 equiv). On the basis of the documented rate-enhancing effect of CuCl on Ru-catalyzed olefin metathesis,[14] we treated **11** with this phosphine scavenger to encourage PPh_3 dissociation and induce Ru−O chelation. Accordingly, in the presence of 4 equiv of CuCl, complete conversion of **11** to **13** is observed within 2 h (400 MHz ^1H NMR analysis). Formation of **13** can be monitored as the appearance of a new carbene proton (H_α) signal at δ 16.82 ppm (J_{PH} = 6.8 Hz). The multiplicity (doublet) of this resonance implies that the $C_\alpha-H_\alpha$ and Ru−P bonds are roughly coplanar in this complex. A sharp singlet at δ 61.33 ppm in the 162 MHz ^{31}P NMR spectrum of **13** corroborates the presence of a single phosphine ligand. Moreover, single-crystal X-ray analysis of **13** (Figure 2) confirms the structural assignment and reveals that this organometallic system crystallizes as dimeric entities containing bridging anionic chloride ligands.[15]

Selected bond lengths and angles for Ru complex **13** are provided in Table 1. The data indicate a distorted octahedral geometry about each metal center in the dimer. As suggested by the 400 MHz ^1H NMR data (see above), the carbene unit is parallel to the P−Ru−O axis. The Ru=C bond (1.861(3) Å) is shorter than that in $(PPh_3)_2Cl_2Ru{=}CHCH{=}CPh_2$ (1.887(7) Å)[16] but longer than the metal−carbene bond in $(PPh_3)_2Cl_2Ru{=}C(CH_2)_3$ (1.830(4) Å).[17] In addition, the Ru−O bond in **13** (2.284(2) Å) is longer and therefore likely weaker than that in **9** (2.257(7) Å).

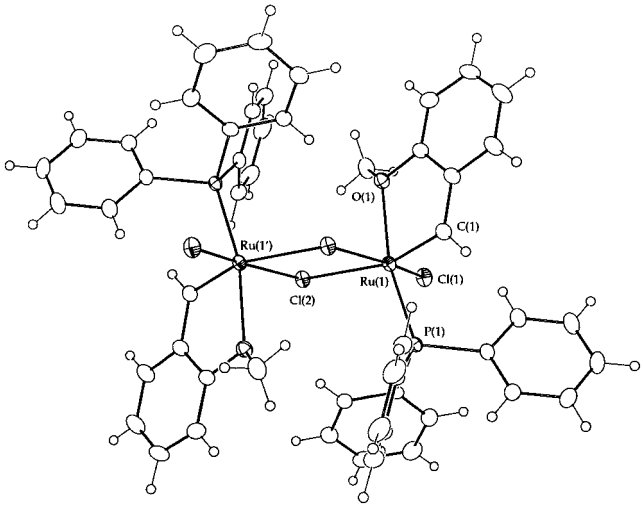


Figure 2. ORTEP diagram of $Cl_2Ru(=CH\text{-}o\text{-}OMeC_6H_4)PPh_3$ (**13**). Thermal ellipsoids are drawn at the 30% probability level.

Table 1. Selected Bond Lengths and Angles for $Cl_2Ru(=CH\text{-}o\text{-}OMeC_6H_4)PPh_3$ (**13**)

Bond Lengths (Å)			
Ru(1)−C(1)	1.861(3)	Ru(1)−Cl(1)	2.3555(8)
Ru(1)−P(1)	2.2432(9)	Ru(1)−Cl(2′)	2.3990(8)
Ru(1)−O(1)	2.284(2)	Ru(1)−Cl(2)	2.6394(8)
Bond Angles (deg)			
C(1)−Ru(1)−P(1)	91.48(10)	O(1)−Ru(1)−Cl(2′)	89.93(6)
C(1)−Ru(1)−O(1)	79.01(11)	Cl(1)−Ru(1)−Cl(2′)	163.81(3)
P(1)−Ru(1)−O(1)	167.16(6)	C(1)−Ru(1)−Cl(2)	162.00(11)
C(1)−Ru(1)−Cl(1)	102.66(9)	P(1)−Ru(1)−Cl(2)	104.45(3)
P(1)−Ru(1)−Cl(1)	88.90(3)	O(1)−Ru(1)−Cl(2)	86.35(6)
O(1)−Ru(1)−Cl(1)	84.85(6)	Cl(1)−Ru(1)−Cl(2)	86.22(3)
C(1)−Ru(1)−Cl(2′)	91.32(9)	Cl(2′)−Ru(1)−Cl(2)	78.15(3)
P(1)−Ru(1)−Cl(2′)	98.97(3)	Ru(1′)−Cl(2)−Ru(1)	101.85(3)

As illustrated in Scheme 3, as with complex **11**, phosphine exchange with **13** proved inefficient; treatment of **13** with 1 equiv of PCy_3 affords a 1:1 mixture of **12** and bisphosphine **11**. It is likely that upon exchange, the free PPh_3 in solution reacts with either **13** or the desired **12** to generate **11**. Subjection of **13** to 1 equiv of PPh_3 or treatment of **12** with 2 equiv of PPh_3 results in their complete conversion to **11** (400 MHz ^1H NMR analysis), indicating that Ru−carbene **11** is thermodynamically favored.[18]

In analogy to the related Ru-carbenes $(PPh_3)_2Cl_2Ru{=}CHCH{=}CPh_2$[16] and $(PPh_3)_2Cl_2Ru{=}CHPh$,[4] complexes **11** and **13** are inactive ring-closing metathesis (RCM) catalysts at 22 °C (<2% conversion after 24 h).[19] Furthermore, we quickly established that, contrary to our expectation, **12** is a less efficient metathesis catalyst than the isopropoxy derivative **8**. As an example, as shown in eq 2, in the RCM of 2-butenyl-(1-phenyl)allyl ether to give 2-phenyl-2,5-dihydrofuran (5 mol % **12**, CH_2Cl_2, 22 °C) reaction proceeds to only 38% conversion (400 MHz ^1H NMR analysis) within 24 h before the catalyst is lost to decomposi-

(14) CuCl is known to react with phosphines to make a marginally soluble, ill-defined complex; see: (a) Reference 7b. (b) Dias, E. L.; Grubbs, R. H. *Organometallics* **1998**, *17*, 2758−2767. (c) *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Permagon Press: New York, 1987; Vol. 5.

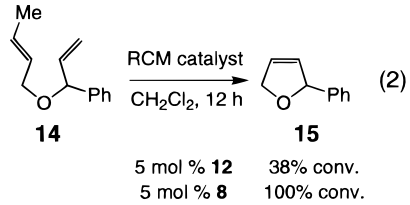
(15) Crystals suitable for X-ray analysis were obtained by slow diffusion of pentane into a concentrated CH_2Cl_2 solution at 22 °C. For experimental details and additional crystallographic data, see the Supporting Information.

(16) Nguyen, S. T.; Johnson, L. K.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 3974−3975.

(17) Wu, Z.; Nguyen, S. T.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1995**, *117*, 5503−5511.

(18) Variations in temperature and reaction time for the phosphine exchange afforded the same result. Because the reaction is nearly instantaneous, it is difficult to assess the identity of the kinetic product.

(19) The catalytic metathesis activity of **11** and **13** toward highly strained cyclic olefins such as norbornene, bicyclo[3.2.0]hept-6-ene, and *trans*-cyclooctene was not probed. For the metathesis activity of related triphenylphosphine-substituted Ru systems toward these substrates, see: (a) Reference 16. (b) Wu, Z.; Benedicto, A. D.; Grubbs, R. H. *Macromolecules* **1993**, *26*, 4975−4977.



tion.[20] In contrast, 100% conversion is observed in 12 h in the presence of 5 mol % **8** (CH_2Cl_2, 22 °C).

In a solution of undistilled chloroform under air, **12** slowly decomposes over a period of several weeks to produce *o*-anisaldehyde—the result of oxidation of the metal carbene. In the case of **8**, after two weeks in the same solvent under air, there is <2% decomposition as judged by the 400 MHz ^{1}H NMR spectrum. Additionally, we were unable to recover **12** in high yield after silica gel chromatography (in contrast to **8**); mass balances for **12** are variable, ranging from 0 to 65%.

It therefore appears that the variation from isopropoxy to methoxy chelating groups has a dramatic impact on the Ru ligand sphere. Differences in catalytic activity and stability of the methoxy (**12**) vs isopropoxy (**8**) Ru-carbene complexes likely arise from the relative steric bulk of these two substituents. If we assume that metathesis proceeds through a dissociative mechanism,[7b] the larger isopropoxy unit may facilitate dissociation of the oxygen atom from Ru during initiation. Moreover, the increased sterics in **8** might allow for more effective protection of the metal center from undesirable side reactions (e.g., carbene oxidation). In this context, a recent report has shown that the stablility of bimetallic, bridged-chloride Ru-carbene complexes can be critically dependent on the presence of steric bulk in the ligand environment surrounding the metal center.[14b] It is also tenable that the more Lewis basic isopropoxy group is a more robust ligating unit, offering enhanced electronic stability. Thus, in light of the attendant inefficiencies that accompanied the preparation of **12** and its catalytic metathesis activity, we returned our attention to the original isopropoxy styrene complex **8** and set out to examine a more efficient route for its synthesis.

As shown in Scheme 4, synthesis of **8** is realized through a two-step, single-pot procedure without any of the aforementioned complications encountered in our attempt to prepare **12**. Exposure of $Cl_2Ru(PPh_3)_3$[13] to aryldiazomethane **16** results in the formation of a *monophosphine* Ru-carbene **17**; <2% of the derived bisphosphine (analogous to **11**) is detected in the 400 MHz ^{1}H NMR spectrum of the unpurified reaction mixture. Moreover, treatment of **17** with 1 equiv of PPh_3 results in <10% conversion to the corresponding bisphosphine complex (as judged by 400 MHz ^{1}H NMR analysis). This finding further implicates the isopropyl aryl ether unit as an excellent Ru ligand. Complex **17** can be readily prepared by this route as a brick red solid residue in 90% yield after silica gel chromatography. An air-stable, microcrystalline solid (mp = 194−196 °C dec) is obtained from this residue by precipitation from CH_2Cl_2/pentane.

X-ray diffraction data from a single crystal of **17** confirmed the structural assignment (Figure 3).[15] The complex is a distorted trigonal bipyramid with the two chlorides and the carbene carbon atom in the equatorial plane and the phosphine and ether ligands in axial positions. The Cl(1)−Ru−Cl(2) angle (145.17(3)°) is smaller than the corresponding angle in the chloro-bridged dimer of **13** (163.81(3)°) but is similar to that in the related $(PPh_3)_2Cl_2Ru{=}C(CH_2)_3$ (150.4°).[17] The Ru−C_α bond length (1.837(3) Å) is shorter in **17** than in the dimeric **13** (1.861(3) Å). The Ru−O bond in **17** (2.309(2) Å) is longer than that in complex **13** (2.284(2) Å), perhaps reflecting the more severe steric repulsion that may exist in **17** due to the presence of the bulkier isopropoxy ligand.

(20) The instability of **12** in solution (relative to **8**) was confirmed by 400 MHz ^{1}H NMR.

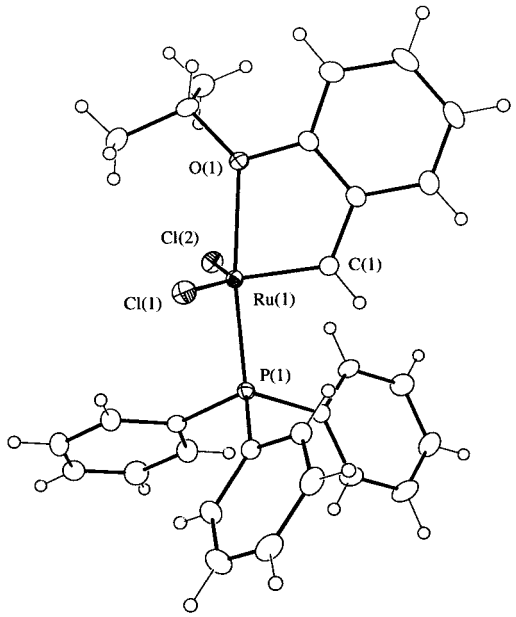
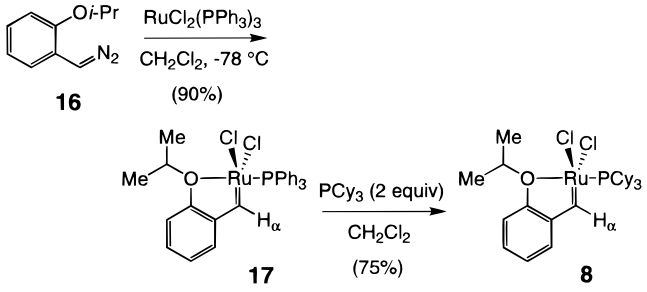


Figure 3. ORTEP diagram of $Cl_2Ru(=CH\text{-}o\text{-}O\text{-}i\text{-}PrC_6H_4)PPh_3$ (**17**). Thermal ellipsoids are drawn at the 30% probability level. Selected bond distances [Å] and angles [deg]: Ru−C(1) 1.837(3), Ru−P 2.2421(8), Ru−O 2.309(2), Ru−Cl(1) 2.3234(8), Ru−Cl(2) 2.3057(8); C(1)−Ru−P 93.28(10), C(1)−Ru−Cl(1) 106.99(9), C(1)−Ru−Cl(2) 106.99(9), P−Ru−Cl(1) 91.55(3), P−Ru−Cl(2) 93.93(3), C(1)−Ru−O 79.01(11), O−Ru−Cl(1) 90.81(5), Cl(2)−Ru−O 88.31(6), P−Ru−O 172.29(5), Cl(2)−Ru−Cl(1) 145.17(3).

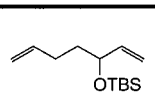
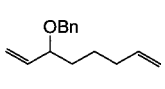
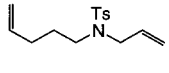
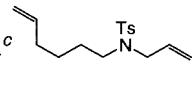
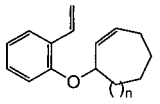
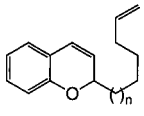
Scheme 4



Importantly, as illustrated in Scheme 4, the PPh_3 ligand in **17** is readily exchanged upon treatment with 2.0 equiv of PCy_3 to deliver the desired Ru−chelate complex **8** as a brown solid in 75% yield after silica gel chromatography. Large, needlelike crystals of **8** can be obtained by recrystallization from pentane at 22 °C. It deserves mention that the intermediate monophosphine **17** need not be isolated prior to the phosphine exchange; Ru-carbene **8** can be accessed in similar yield when PCy_3 is added shortly after exposure of $Cl_2Ru(PPh_3)_3$ to **16**.

Catalytic RCM with 8. With an efficient route for the preparation of **8** at hand, our focus turned to the potential of this complex as a RCM catalyst. As summarized in Table 2, **8** readily mediates the RCM of five-, six-, seven-, and eight-membered carbo- and heterocycles. It is noteworthy that *in each case the catalyst is recovered chromatographically in high yield after the reaction is complete. Complex **8** is recovered as a*

Table 2. Ring-Closing Metathesis of Acyclic Dienes Catalyzed by **8**[a]

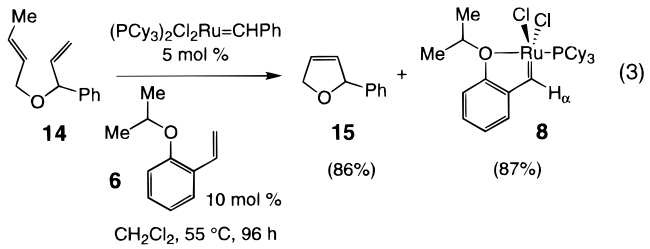
entry	substrate	product	time (h)	product yield (%)[b]	rec. catalyst yield (%)[b]
1	 **18**	 **19**	0.5	90	75
2	 **20**	 **21**	2.0	95	89
3[c]	 **22**	 **23**	1.0	99	88
4[c]	 **24**	 **25**	1.0	72	95
5	 **26**	 **27**	20	n=1 25 (69 dimer) n=2 42 (55 dimer)	82 72

[a] Conditions: 5 mol % **8**, CH_2Cl_2, 22 °C, Ar atm. [b] Isolated yields after silica gel chromatography. [c] Reaction performed in refluxing CH_2Cl_2.

homogeneous solid residue and maintains its catalytic activity in subsequent ring-closing metatheses upon the addition of new substrate.[21]

Catalyst Recycling. As depicted in Table 3, for transformations illustrated in entries 1, 3, and 4 of Table 2, recycled **8** was carried through *at least three additional* rounds of RCM. The data presented constitute typical results expected for a procedure that simply involves transfer of the recovered residue **8** to a new reaction vessel followed by the addition of substrate and solvent. It is noteworthy that when the present protocol is used, subsequent catalytic RCM processes suffer little in efficiency.

It is worth noting that a Ru-based initiator, such as **1**[4] or $(PCy_3)_2Cl_2Ru{=}CHCH{=}CPh_2$,[7a] may be purchased from commercial sources and recovered for subsequent use in the form of **8** by quenching the RCM reaction with **6**. Specifically, RCM of a diene substrate catalyzed by an alternative Ru-based catalyst (e.g., **1**) in the presence of 2-isopropoxystyrene (**6**) delivers complex **8** upon workup. As illustrated in eq 3, treatment of



(3)

diene ether **14** with 5 mol % **1**[4] and 10 mol % **6** affords 2-phenyl-2,5-dihydrofuran (**15**) as a light yellow oil and **8** as a brown solid in 86% and 87% isolated yields, respectively (after silica gel chromatography). This result attests to the stability of complex **8**, as the complex is recovered in 87% purified yield after 4 days in refluxing CH_2Cl_2. The reaction mixture changes color from deep purple to brown within 3 h, signifying the in situ formation of **8** (evident by 400 MHz ^{1}H NMR analysis). Since formation of **8** is accompanied by the release of PCy_3, the reaction rate likely suffers (96 h) due to the well-established inhibitory influence of excess phosphine.[7b] An alternative approach, which circumvents the incovenience of extended reaction times, is to add the styrene upon completion of catalytic RCM. Thus, ring-closing of **14** catalyzed by **1** (5 mol %) for 1 h at 55 °C, followed by the addition of 10 mol % **6** and 3 h of additional stirring at reflux delivers **15** and complex **8** in 87% and 80% yields, respectively, after silica gel chromatography.

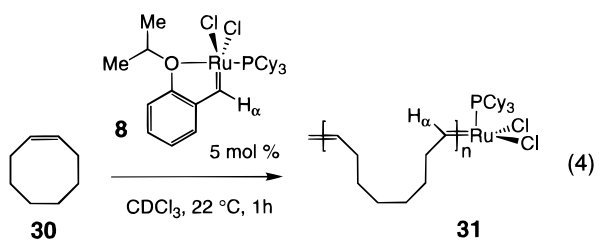
Several issues with regard to the results in Tables 2 and 3 merit further discussion:

(1) All product isolation work, including solvent removal following silica gel chromatography, was performed in air with undistilled, reagent-grade solvents—an inert atmosphere is *not* required to prevent decomposition of the catalyst. In the solid state, **8** is stable indefinitely in air. Furthermore, after one week in undistilled organic solvents in the presence of water, alcohol, and/or dilute acid (0.01 M HCl), no signs of decomposition (<2%) are evident according to 400 MHz ^{1}H NMR analysis.[22] Efficient cyclizations of the amides **22** and **24** at 55 °C (entries 3−4, Table 2) further attest to the thermal stability of the catalyst.

(2) As the data in Table 3 illustrate, when RCM reactions are carried out at elevated temperatures, higher yields of the recovered catalyst can be obtained. It is plausible that the increased temperature facilitates the reformation of the more robust alkoxy styrenyl Ru−chelate after all the starting material has been consumed (for further discussion, see below).

General Mechanism. A plausible mechanistic scenario can be proposed that accounts for RCM activity and subsequent recovery of **8**. Scheme 5 illustrates the initiation and propagation steps that are likely operative (**18** → **19** is used as the prototype). Thus, formation of Ru-carbene **28** from the reaction of **8** and **18** results in the release of styrene **6**. Subsequent conversion of **28** to RCM product **19** through the derived metallacyclobutane intermediate releases monophosphine Ru−methylidene **29** to complete the initiation stage. With an excess of the diene substrate present, the highly reactive **29** enters the propagation cycle to promote additional product formation (concomitant with the release of ethylene). Upon complete consumption of **18**, methylidene complex **29** encounters the initially released **6** to regenerate **8** (termination of the catalytic cycle).

Kinetic Studies with Ru Complexes 1 and 8. The influence of internal chelation on the initiation and propagation rates of **8** relative to the parent benzylidene complex **1** was probed by monitoring the ROMP of *cis*-cyclooctene (**30**) (eq 4).[23] Pseudo-

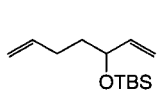
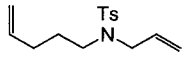
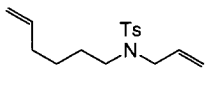
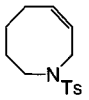


(4)

first-order rate constants for initiation (consumption of **8**) and propagation (formation of **31**) were measured by integration of the H_α resonances of carbenes **8** and **31** and the olefinic proton

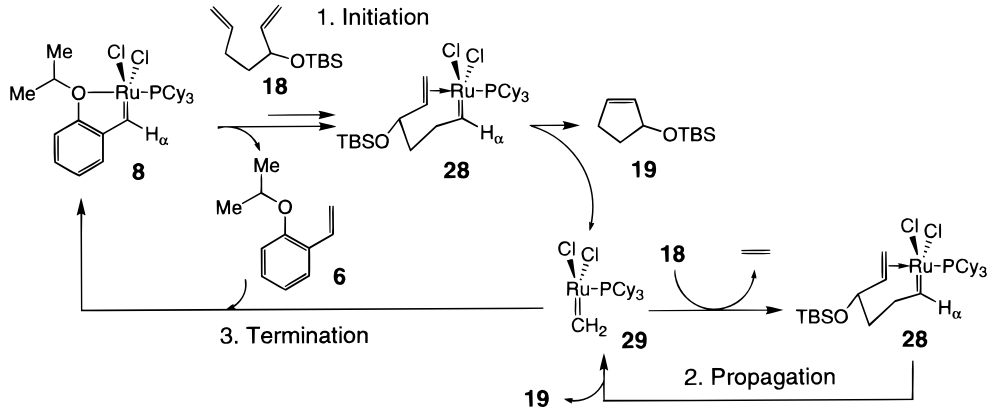
(21) The recovered residue is identical to recrystallized (pentane, 22 °C) **8** by 400 MHz ^{1}H NMR, 100 MHz ^{13}C NMR, and elemental analysis (Anal. Calcd for $C_{28}H_{45}Cl_2OPRu$ residue: C, 55.99; H, 7.55. Found: C, 56.36; H, 7.72).

Table 3. Utility of Recycled Ru Complex **8** in Catalyzing RCM[a]

entry	substrate	product	cycle	product[b] yield (%)	rec. catalyst[b] yield (%) at 22 °C	rec. catalyst[b] yield (%) at 55 °C
1[c]	 **18**	 **19**	1	77	73	88
			2	71	80	86
			3	85	74	90
2	 **22**	 **23**	1	>98	68	98
			2	>98	74	95
			3	>98	70	>98
3	 **24**	 **25**	1	72	-	>98
			2	64	-	86
			3	67	-	94

[a] Conditions: 5 mol % **8**, CH_2Cl_2, 22 °C or 55 °C, Ar atm. [b] Isolated yields after silica gel chromatography. [c] Isolated yields for **19** are variable due to product volatility.

Scheme 5



signals of **30** and **31**, respectively (400 MHz ^{1}H NMR analysis).[4b] These ^{1}H NMR experiments indicate that **8** initiates approximately 30 times slower and propagates nearly four times faster than **1**.[24] The enhanced propagation activity of **8** lends support to the intermediacy of *mono*phosphine complex **29** (Scheme 5) and is consistent with the known rate-retarding effects of excess phosphine in Ru-catalyzed metathesis reactions.[7b] The slower rate of initiation may be due to the less facile dissociation of the smaller isopropyl aryl ether ligand (relative to PCy_3) from the sterically congested metal center. Moreover, reassociation of the alkoxy unit to the transition metal center should be rate-inhibiting and more favored on entropic grounds (alkoxy styrene is bound to the transition metal at two sites).

Conclusions

The synthesis and structural characterization of a metathesis-active Ru carbene (**8**) containing an internal oxygen chelate is disclosed. The complex is an extremely robust catalyst and represents a practical addition to the growing family of well-defined, single-component precatalysts that initiate olefin metathesis. With its appreciable activity and unique stability, Ru complex **8** may find use in the large-scale preparation of a variety of organic substrates. The catalyst is recyclable[25] and can be recovered after the reaction through simple chromatography. As such, to the best of our knowledge, **8** represents the first recyclable metal-based system that catalyzes an efficient *homogeneous* olefin metathesis reaction with no detectable loss of activity upon reuse.

Further application of this class of RCM catalysts, particularly in relation to enantioselective catalysis,[26] is in progress and will be the subject of future reports from these laboratories.

Experimental Procedures

General. Infrared (IR) spectra were recorded on a Perkin-Elmer 781 spectrophotometer, ν_{max} in cm^{-1}. Bands are characterized as broad (br),

(22) For an early account of the striking functional-group tolerance of $(PCy_3)_2Cl_2Ru{=}CHCH{=}CPh_2$ and the insensitivity of the catalyst to oxygen, moisture, and adventitious impurities during its reactions, see: Fu, G. C.; Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1993**, *115*, 9856−9857.

(23) Tallarico, J. A.; Bonitatebus, P. J., Jr.; Snapper, M. L. *J. Am. Chem. Soc.* **1997**, *119*, 7157−7158.

(24) For catalyst **8**, the propagating carbene proton signal is never detectable by NMR under the given reaction conditions. It is plausible that the highly active monophosphine propagating species is short-lived on the NMR time scale. The consumption of **8** was thus monitored relative to ferrocene as an internal standard (see Experimental Section for further details). Furthermore, a plot of −ln [**8**] vs time generated a curve with exponential and not linear character, suggesting that the kinetics are not first order in Ru. These numbers only represent an approximation of the relative activity profiles for **1** and **8**.

(25) Other recyclable metathesis catalyst systems have been recently reported. In a recent study, Grubbs and Nguyen prepared a series of polystyrene−divinylbenzene (PS-DVB)-supported Ru−vinylcarbene complexes and their metathesis activities were explored. Unfortunately, recovery and reuse of the catalysts led to small losses in activity (20% after each cycle), suggesting that the complexes experience a finite lifetime when bound to the polymer support. Moreover, reaction rates with the polymer-supported carbenes were orders of magnitude lower than that of their homogeneous analogues. See: Nguyen, S. T.; Grubbs, R. H. *J. Organomet. Chem.* **1995**, *497*, 195−200.

(26) For recent studies on asymmetric ring-closing metathesis (ARCM), see: (a) Alexander, J. B.; La, D. S.; Cefalo, D. R.; Hoveyda, A. H.; Schrock, R. R. *J. Am. Chem. Soc.* **1998**, *120*, 4041−4042 and references therein. (b) La, D. S.; Alexander, J. B.; Cefalo, D. R.; Graf, D. D.; Hoveyda, A. H.; Schrock, R. R. *J. Am. Chem. Soc.* **1998**, *120*, 9720−9721.

strong (s), medium (m), and weak (w). ^{1}H NMR spectra were recorded on a Varian GN-400 (400 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CHCl_3$: δ 7.26 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz), integration, and assignment. ^{13}C NMR spectra were recorded on a Varian GN-400 (100 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent as the internal reference ($CHCl_3$: δ 77.0 ppm). ^{31}P NMR spectra were recorded on a Varian GN-400 (162 MHz) spectrometer with complete proton decoupling. The chemical shifts of the phosphorus resonances were determined relative to phosphoric acid as the external standard (H_3PO_4: δ 0.0 ppm). High-resolution mass spectra were obtained at the Mass Spectrometry Facility of the University of Illinois (Urbana-Champaign, IL). Elemental microanalyses were performed by Robertson Microlit Laboratories (Madison, NJ).

Unless otherwise noted, all reactions were conducted in oven- (135 °C) and flame-dried glassware with standard Schlenk or vacuum-line techniques under an inert atmosphere of dry argon. In most instances, solid organometallic compounds were recovered and stored in a drybox under an atmosphere of Ar. Tetrahydrofuran and diethyl ether were distilled from sodium metal/benzophenone ketyl. Dichloromethane, pentane, and hexanes were distilled from calcium hydride. $RuCl_2(PPh_3)_3$[13] and $(PCy_3)_2Cl_2Ru{=}CHPh$[4] were prepared according to literature procedures. The following chemicals were obtained from commercial sources and used without further purification: *p*-toluenesulfonylhydrazide, 2-iodopropane, 2-methoxybenzaldehyde, tricyclohexylphosphine, triphenylphosphine, 1,1,3,3-tetramethylguanidine, and copper(I) chloride.

All silica gel column chromatography was driven with compressed air and performed with silica gel 60 (230−400 mesh; pH (10% suspension) 6.5−7; surface area 500 m^2/g; pore volume 0.75 mL/g) obtained from TSI Chemical Co. (Cambridge, MA). In the purification of reaction products **19**, **21**, **23**, **25**, and **27** (Tables 2 and 3), a hexanes/CH_2Cl_2 solvent mixture was selected to allow for facile separation of the catalyst and cycloolefin. Ru-carbene **8** is quite polar, and therefore the ring-closing reaction products eluted before the catalyst for all substrates examined in this study. Since all reactions are catalytic in **8** (5 mol %), detecting the presence of catalyst in highly dilute chromatography fractions by TLC proves tedious and is unnecessary. The complex forms a brown-colored solution in organic solvents, and thus the progress of the chromatography can instead be monitored visually (brown band on column), and the presence of catalyst in fractions of eluant is evident by simple visual inspection.

2-Methoxybenzaldehyde *p*-Toluenesulfonhydrazone. A suspension of *p*-toluenesulfonyl hydrazide (3.02 g, 16.2 mmol) in methanol (15 mL) was treated rapidly with *o*-anisaldehyde (2.22 g, 16.3 mmol, 1.0 equiv) with stirring. The hydrazide and aldehyde were observed to enter solution rapidly; within 10 min a white crystalline solid precipitated. The reaction mixture was cooled to 0 °C to ensure complete precipitation. The supernatant was removed subsequently by cannula filtration and the solid was washed thoroughly with ice-cold methanol (2 × 10 mL). Drying in vacuo afforded the desired product as a white solid (4.89 g, 16.1 mmol, 99%). IR (KBr): 3188 (s), 3069 (w), 3006 (w), 2974 (w), 2943 (w), 1608 (m), 1597 (m), 1488 (m), 1466 (m), 1435 (s), 1358 (s), 1332 (s), 1255 (s), 1168 (s), 1048 (s), 948 (s), 837 (m), 813 (m), 757 (s), 704 (m), 669 (s), 602 (m), 575 (s), 544 (s), 509 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (s, 1H, CH═N), 8.08−7.80 (br, 1H, C═NNH), 7.87 (d, J = 7.8 Hz, 2H, aromatic H), 7.82 (dd, J = 7.8, 1.5 Hz, 1H, aromatic H), 7.36−7.30 (m, 1H, aromatic CH), 7.29 (d, J = 8.3 Hz, 2H, aromatic H), 6.94 (dd, J = 7.8, 7.3 Hz, 1H, aromatic H), 6.85 (d, J = 8.8 Hz, 1H, aromatic H), 3.79 (s, 3H, OCH_3), 2.39 (s, 3H, $ArCH_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.99, 144.56, 144.13, 135.33, 132.03, 129.62, 127.95, 126.87, 121.42, 120.81, 110.94, 55.50, 21.56. HRMS Calcd for $C_{15}H_{16}N_2O_3S$: 304.0882. Found: 304.0882. Anal. Calcd for $C_{15}H_{16}N_2O_3S$: C, 59.19; H, 5.30; N, 9.20. Found: C, 59.12; H, 5.11; N, 9.27.

$Cl_2Ru(=CH\text{-}o\text{-}OMeC_6H_4)(PPh_3)_2$ (11). 2-Methoxybenzaldehyde tosylhydrazone (1.14 g, 3.75 mmol) was treated with 1,1,3,3-tetramethylguanidine (5.0 mL, 40 mmol, 10.6 equiv) in a 25 mL round-bottom flask. The reaction mixture was heated for 30 min at 55 °C, during which time the hydrazone slowly dissolved in the base, forming a viscous, deep-red solution. If the reaction mixture became cloudy at any point during heating, distilled water was added dropwise until the red color was restored. After 30 min, 15 mL of distilled water was added, and the mixture was transferred to a separatory funnel. The aryldiazoalkane **10** was extracted with pentane (3 × 25 mL), and the combined organic layers were washed with saturated sodium bicarbonate (3 × 100 mL) and sodium chloride (3 × 100 mL) solutions. The organic layers were dried over $MgSO_4$ and concentrated in vacuo to afford (2-methoxyphenyl)diazomethane (**10**) as a red oil (325 mg, 2.19 mmol, 58%). The diazo product was promptly cooled to −78 °C under Ar to prevent thermal decomposition. At this point, $Cl_2Ru(PPh_3)_3$ (1.05 g, 1.10 mmol) was dissolved in CH_2Cl_2 (10 mL) and the mixture was cooled to −78 °C, after which it was treated, by cannula, with an ice-cold pentane (6 mL) solution of **10** (325 mg, 2.19 mmol, 2.0 equiv). Addition of the carbene source caused a color change from purple-brown to green-brown, and slight gas evolution was observed. After 5 min, the reaction mixture was slowly concentrated under vacuum. The resulting green solid residue was dissolved in 2 mL of CH_2Cl_2, and 60 mL of pentane was added to cause precipitation of a yellow solid. The brown mother liquor was removed with a cannula filter and the solid was washed twice with 30 mL portions of pentane. The remaining yellow microcrystalline solid was dried under vacuum and recovered in the drybox to afford 880 mg of complex **11** (1.08 mmol, 98%). IR (KBr): 3056 (w), 2936 (w), 2905 (w), 1589 (m), 1573 (w), 1481 (m), 1459 (w), 1433 (s), 1239 (w), 1188 (w), 1157 (w), 1091 (m), 999 (w), 862 (w), 746 (m), 696 (s), 536 (s), 521 (s), 502 (w). ^{1}H NMR (400 MHz, $CDCl_3$): δ 16.16 (dd, J_{PH} = 7.3, 6.8 Hz, 1H, Ru═CH), 7.66 (dd, J = 8.3, 7.3 Hz, 1H, aromatic H), 7.62−6.90 (m, 32H, aromatic H and $P(C_6H_5)_3$), 6.79 (d, J = 8.3 Hz, 1 H, aromatic H), 3.80 (s, 3H, OCH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 300.25, 160.47, 143.14, 134.85 (d, J_{PC} = 8.8 Hz), 133.24, 129.88, 127.64 (d, J_{PC} = 36.1 Hz), 125.99, 123.30, 113.52, 55.25. ^{31}P NMR (162 MHz, $CDCl_3$): δ 56.65 (d, J_{PP} = 37.1 Hz, $P(C_6H_5)_3$), 34.25 (d, J_{PP} = 38.1 Hz, $P'(C_6H_5)_3$). HRMS Calcd for $C_{44}H_{38}Cl_2OP_2Ru$: 816.0818. Found: 816.0824. Anal. Calcd for $C_{44}H_{38}Cl_2OP_2Ru$: C, 64.17; H, 4.69. Found: C, 64.44; H, 4.82.

$Cl_2Ru(=CH\text{-}o\text{-}OMeC_6H_4)PPh_3$ (13). Inside a drybox, 500 mg (0.612 mmol) of **11** and 250 mg (2.52 mmol, 4.1 equiv) of CuCl were weighed into a 10 mL round-bottom flask. The flask was capped with a rubber septum, removed from the drybox, charged with 5 mL of CH_2Cl_2, and stirred for 2 h under Ar at 22 °C. Volatile solvents were removed in vacuo and the resulting residue was passed through a short column of silica gel (CH_2Cl_2). The progress of silica gel chromatography was monitored visually, as the product rapidly eluted as a red-orange band. The silica gel column was washed with a 10:1 CH_2Cl_2:CH_3OH solution, and this fraction was concentrated and checked by 400 MHz ^{1}H NMR analysis for residual product (minor amounts of **13** could adhere to the Lewis basic silica media during chromatography). If necessary, a second chromatographic separation was effected to recover additional product. This process was repeated until no alkylidene signal could be detected in the ^{1}H NMR spectrum of the methanolic rinse fraction. Pooling of fractions and removal of volatiles in vacuo delivered the desired product as a homogeneous, dark green solid residue. An air-stable microcrystalline solid could be obtained from this residue by precipitation from 1:30 CH_2Cl_2:pentane (295 mg, 0.532 mmol, 87%). IR (KBr): 3056 (w), 2999 (w), 2949 (w), 2842 (w), 1589 (m), 1573 (m), 1477 (m), 1457 (m), 1431 (s), 1240 (m), 1225 (m), 1186 (m), 1094 (s), 1003 (s), 754 (s), 695 (s), 534 (s).^{1}H NMR (400 MHz, $CDCl_3$): δ 16.82 (d, J_{PH} = 6.8 Hz, 1H, Ru═CH), 7.65 (dd, J = 8.3, 7.3 Hz, 1H, aromatic H), 7.58−7.32 (m, 16H, aromatic H and $P(C_6H_5)_3$), 7.21 (d, J = 8.3 Hz, 1H, aromatic H), 7.14 (dd, J = 7.3, 7.3 Hz, 1H, aromatic H), 4.43 (s, 3H, OCH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 279.76, 156.84, 142.99, 134.32 (d, J_{PC} = 9.8 Hz), 131.88, 131.34, 130.83, 130.49, 128.62 (d, J_{PC} = 9.8 Hz), 123.18 (d, J_{PC} = 132.8 Hz), 112.19, 58.80. ^{31}P NMR (162 MHz, $CDCl_3$): δ 61.33 (s, $P(C_6H_5)_3$). HRMS Calcd for $C_{26}H_{23}Cl_2OPRu$: 553.9907. Found: 553.9908.

$RuCl_2(=CH\text{-}o\text{-}OMeC_6H_4)PCy_3$ (12). In the drybox, **13** (40.0 mg, 0.0721 mmol) and tricyclohexylphosphine (23.0 mg, 0.082 mmol, 1.1 equiv) were combined in a 5 mL round-bottom flask. The flask was removed from the drybox and CH_2Cl_2 (2 mL) was added at −78 °C.

After the mixture was stirred at room temperature for 30 min, 400 MHz ^{1}H NMR analysis revealed a 1:1 mixture of metal complexes **11** and **12** by integration of the corresponding carbene proton (H_α) signals. The reaction mixture was concentrated under reduced pressure and loaded onto a short column of silica. Elution with CH_2Cl_2 afforded **12** as a green-brown solid residue. In analogy to the purification of complex **13**, the column was washed with a 10:1 CH_2Cl_2:CH_3OH solution to determine if any product had adhered to the silica gel during the flash. Yield = 13.6 mg, 0.0238 mmol, 33%. IR (KBr): 2926 (s), 2850 (s), 1592 (w), 1574 (w), 1476 (m), 1459 (m), 1446 (m), 1294 (w), 1239 (w), 1226 (w), 1111 (w), 1011 (m), 849 (w), 746 (m), 731 (w), 515 (w). ^{1}H NMR (400 MHz, $CDCl_3$): δ 17.36 (d, J_{PH} = 4.7 Hz, 1H, Ru=CH), 7.67−7.60 (m, 2H, aromatic H), 7.14−7.09 (m, 2H, aromatic H), 4.31 (s, 3H, OCH_3), 2.36−0.84 (m, 33H, $P(C_6H_{11})_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 277.70, 155.01, 143.36, 129.99, 123.71, 122.26, 112.01, 58.16, 35.33 (d, J_{PC} = 24.4 Hz), 29.73, 27.45, (d, J_{PC} = 10.8 Hz), 25.94. ^{31}P NMR (162 MHz, $CDCl_3$): δ 61.17 (s, $P(C_6H_{11})_3$). Anal. Calcd for $C_{26}H_{41}Cl_2OPRu$: C, 54.54; H, 7.22. Found: C, 54.29; H, 7.06.

2-Isopropoxybenzaldehyde *p*-Toluenesulfonhydrazone. A mixture of sodium metal (1.16 g, 50.4 mmol, 2.1 equiv) in ethanol (50 mL) was charged dropwise with 2.60 mL (24.4 mmol) of salicylaldehyde in a 100 mL round-bottom flask; the sodium salt of the phenoxide ion quickly precipitated as a yellow solid. The reaction flask was subsequently charged with 2-iodopropane (5.0 mL, 50 mmol, 2.1 equiv) and equipped with a reflux condenser. The mixture was heated at reflux for 5−6 h, forming a clear, gold-colored solution; at this time, the reaction was quenched with 10 mL of a saturated solution of sodium chloride. Basic (1 M NaOH) aqueous extraction with methylene chloride and removal of volatiles in vacuo afforded a yellow oil that was purified by silica gel chromatography to yield 3.20 g (19.5 mmol, 80%) of a light yellow oil. IR (NaCl): 2979 (m), 2935 (w), 2860 (w), 2760 (w), 1686 (s), 1600 (s), 1243 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.50 (d, J = 0.9 Hz, 1H, HC=O), 7.83 (dd, J = 7.9, 1.8 Hz, 1H, aromatic H), 7.51 (ddd, J = 8.4, 7.3, 1.8 Hz, 1H, aromatic H), 6.99 (m, 2H, aromatic H), 4.68 (septet, J = 6.0 Hz, 1H, $(CH_3)_2CHO$), 1.40 (d, J = 6.0 Hz, 6H, $(CH_3)_2CHO$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.14, 160.57, 135.70, 128.24, 125.69, 120.35, 113.96, 71.05, 21.94. HRMS Calcd for $C_{10}H_{12}O_2$: 164.0837. Found: 164.0840. Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.15; H, 7.37. Found: C, 72.90; H, 7.31. 2-Isopropoxybenzaldehyde (890 mg, 5.42 mmol, 1.1 equiv) and *p*-toluenesulfonyl hydrazide (900 mg, 4.83 mmol) were used to prepare this hydrazone in analogy to 2-methoxybenzaldehyde *p*-toluenesulfonhydrazone as a bright white crystalline solid (1.58 g, 4.75 mmol, 98%). If the product failed to crash out of the reaction mixture upon dissolution of the reactants, seed crystals of authentic product were added to induce precipitation. IR (NaCl): 3200 (b), 2980 (w), 2930 (w), 1598 (m), 1484 (m), 1457 (m), 1363 (s), 1325 (m), 1295 (w), 1248 (w), 1167 (s), 1118 (w), 1094 (w), 1043 (w), 947 (w), 668 (m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (s, 1H, CH=N), 7.98 (s, 1H, C=NNH), 7.88 (m, 2H, aromatic H), 7.82 (m, 1H, aromatic CH), 7.31−7.26 (m, 3H, aromatic H), 6.90 (dd, J = 7.5, 7.7 Hz, 1H, aromatic H), 6.85 (d, J = 8.4 Hz, 1H, aromatic H), 4.53 (septet, J = 6.0 Hz, 1H, $OCH(CH_3)_2$), 2.39 (s, 3H, $ArCH_3$), 1.29 (d, J = 6.2 Hz, $OCH(CH_3)_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.51, 144.65, 144.14, 135.47, 131.73, 129.66, 128.00, 126.83, 122.55, 120.63, 113.58, 70.82, 21.89, 21.45. HRMS Calcd for $C_{17}H_{20}N_2O_3S$: 332.1195. Found: 332.1196. Anal. Calcd for $C_{17}H_{20}N_2O_3S$: C, 61.42; H, 6.06; N, 8.43. Found: C, 61.23; H, 6.11; N, 8.54.

Cl_2Ru(=CH-*o*-O-*i*-PrC_6H_4)PPh_3 (17). Starting from 2-isopropoxybenzaldehyde tosylhydrazone (1.57 g, 4.72 mmol) and 1,1′,3,3′-tetramethylguanidine (6.5 mL, 52 mmol, 11 equiv), a procedure identical to that used for the synthesis of 2-methoxydiazomethane was employed to obtain the diazo precursor **16**; the diazo compound was isolated as a red oil (503 mg, 2.85 mmol, 60%). An ice-cold pentane solution of **16** (503 mg, 2.85 mmol, 2.0 equiv) was transferred by cannula directly into a CH_2Cl_2 solution of $RuCl_2(PPh_3)_3$ (1.37 g, 1.43 mmol) at −78 °C. A color change from purple-brown to deep red ensued along with a spontaneous evolution of N_2. After 5 min the solvent was removed in vacuo and the resulting red-brown residue was purified by silica gel flash chromatography (CH_2Cl_2). As in the purification of **13**, the chromatography protocol was repeated if necessary until no product was detectable (400 MHz ^{1}H NMR analysis) in the methanolic rinse fraction. Evaporation of the solvent provided the product **17** as an analytically pure brick red solid residue (750 mg, 1.29 mmol, 90%). This complex was obtained as a microcrystalline red powder (mp 194−196 °C dec) by dissolving the purified residue in 5 mL of CH_2Cl_2 and precipitating with pentane (150 mL). IR (KBr): 3056 (w), 2980 (w), 2924 (w), 1587 (m), 1474 (m), 1434 (s), 1114 (m), 1096 (s), 928 (m), 694 (s), 538 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 16.76 (d, J_{PH} = 6.4 Hz, 1H, Ru=CH), 7.65−7.53 (m, 9H, $P(C_6H_5)_3$), 7.52−7.47 (m, 2H, aromatic H), 7.46−7.39 (m, 6H, $P(C_6H_5)_3$), 7.20 (d, J = 8.3 Hz, 1H, aromatic H), 7.11 (dd, J = 7.8, 7.3 Hz, 1H, aromatic H), 5.43 (m, 1H, $OCH(CH_3)_2$), 1.89 (d, J = 6.4 Hz, 6H, $OCH(CH_3)_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 278.16, 154.59, 143.27, 134.12 (d, J_{PC} = 9.8 Hz), 131.67, 131.13, 130.78 (d, J_{PC} = 2.0 Hz), 130.16, 128.58 (d, J_{PC} = 10.7 Hz), 122.80 (d, J_{PC} = 16.6 Hz), 113.56, 76.35, 21.86. ^{31}P NMR (162 MHz, $CDCl_3$): δ 61.11 (s, PPh_3). HRMS Calcd for $C_{28}H_{27}Cl_2OPRu$: 582.0220. Found: 582.0220. Anal. Calcd for $C_{28}H_{27}Cl_2OPRu$: C, 57.74; H, 4.67. Found: C, 57.50; H, 4.72.

Cl_2Ru(=CH-*o*-O-*i*-PrC_6H_4)PCy_3 (8). Starting with **17** (375 mg, 0.644 mmol) and tricyclohexylphosphine (360 mg, 1.28 mmol, 2.0 equiv) in CH_2Cl_2 (6.5 mL) at −78 °C, **8** was obtained in analogy to **12** as a dark brown solid residue after silica gel column chromatography (CH_2Cl_2) (292 mg, 0.486 mmol, 75%). Chromatography was monitored visually, as the product was observed to rapidly elute as a dark brown band. As in the purification of **13**, the chromatography procedure was repeated if necessary until no product was detectable in the methanolic rinse fraction (400 MHz ^{1}H NMR analysis). All product fractions were then pooled, concentrated, and chromatographed once with 3:1 hexane:CH_2Cl_2. Large needlelike crystals (mp = 200−201 °C) of **8** were obtained by dissolving the solid residue in pentane at 30−35 °C and slowly cooling to 22 °C. The crystals were cooled to −20 °C for 24 h to complete the recrystallization. All attempts to recrystallize complex **8** prior to purification by chromatography were unsuccessful. IR (KBr): 2932 (s), 2849 (s), 1589 (m), 1473 (m), 1450 (m), 1375 (w), 1296 (m), 1216 (m), 1114 (s), 1098 (m), 934 (m), 744 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 17.44 (d, J_{PH} = 4.4 Hz, 1H, Ru=CH), 7.67 (ddd, J = 7.3, 1.5, 1.0 Hz, 1H, aromatic H), 7.61 (ddd, J = 8.3, 7.3, 1.0 Hz, 1H, aromatic H), 7.10−7.04 (m, 2H, aromatic H), 5.28 (m, 1H, $OCH(CH_3)_2$), 2.37−1.20 (m, 33H, $P(C_6H_{11})_3$), 1.80 (d, J = 5.9 Hz, 6H, $OCH(CH_3)_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 280.63, 153.15, 144.22, 129.89, 123.06, 122.71, 113.52, 75.52, 35.41 (d, J_{PC} = 10.7 Hz), 29.85, 27.49 (d, J_{PC} = 24.4 Hz), 26.01, 21.81. ^{31}P NMR (162 MHz, $CDCl_3$): δ 59.17 (s, PCy_3). HRMS Calcd for $C_{28}H_{45}Cl_2O_3PRu$: 597.1644 (^{99}Ru isotope peak). Found: 597.1648. Anal. Calcd for $C_{28}H_{45}Cl_2O_3PRu$: C, 55.99; H, 7.55. Found: C, 56.27; H, 7.75.

One-Pot Synthesis of Cl_2Ru(=CH-*o*-O-*i*-PrC_6H_4)PCy_3 (8). A solution of $RuCl_2(PPh_3)_3$ (825 g, 0.860 mmol) in CH_2Cl_2 (10.0 mL) was treated at −78 °C with an ice-cold solution of **16** (300 mg, 1.70 mmol, 2.0 equiv) in pentane (5 mL). The resulting mixture was stirred for 5−10 min at −78 °C, at which point a solution of PCy_3 (490 mg, 1.75 mmol, 2.0 equiv) in CH_2Cl_2 (5 mL) was added via cannula. The cooling bath was removed and the mixture was allowed to warm to 22 °C and stirred for 30 min. Removal of volatiles in vacuo afforded a dark brown solid residue that was purified as above by passage through a plug of silica gel (CH_2Cl_2) to afford 390 mg of the desired product (0.649 mmol, 76%).

Cl_2Ru(=CH-*o*-$OMeC_{10}H_6$)PCy_3 (9). A 5 mL round-bottom flask was charged with Cl_2Ru(=CHPh)$(PCy_3)_2$ (85.0 mg, 0.103 mmol, 1.1 equiv), 2-methoxy-3-ethenylnaphthalene (17.0 mg, 0.0923 mmol), and CH_2Cl_2 (1 mL). The resulting mixture was stirred for 22 h at 22 °C, after which the volatiles were removed in vacuo. The resulting solid residue was purified by silica gel chromatography to afford **9** as a brown solid (30.0 mg, 0.0482 mmol, 52%), which was then dissolved in pentane at 22 °C and recrystallized at −20 °C (mp = 195−196 °C (dec). ^{1}H NMR (400 MHz, $CDCl_3$): δ 17.52 (d, J_{PH} = 4.4 Hz, 1H, Ru=CH), 8.19 (s, 1H, aromatic H), 8.03 (d, J = 8.4 Hz, 1H, aromatic H), 7.72 (d, J = 7.6 Hz, 1H, aromatic H), 7.65 (dd, J = 8.0, 6.8 Hz, 1H, aromatic H), 7.39 (ddd, J = 7.6, 6.8, 0.8 Hz, 1H, aromatic CH), 7.33 (s, 1H, aromatic H), 4.39 (s, 3H, OCH_3), 2.38−0.86 (m, 33H, $P(C_6H_{11})_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 269.20, 152.71, 144.04, 133.81, 130.74, 129.29, 128.05, 127.52, 125.99, 120.19, 107.52, 58.31,

35.45 (d, J_{PC} = 24.9 Hz), 29.86, 27.56 (d, J_{PC} = 10.9 Hz), 26.05. HRMS Calcd for $C_{30}H_{43}Cl_2OPRu$: 622.1472. Found: 622.1471.

Representative Experimental Procedure for RCM Catalyzed by 8. Tosyl amide **22** (106 mg, 0.379 mmol) and **8** (12.4 mg, 0.0206 mmol, 0.054 equiv) were weighed into a 10 mL round-bottom flask in air. The flask was equipped with a reflux condenser, evacuated, and filled with an atmosphere of argon (vacuum−argon flush cycle was repeated three times). The vessel was charged with CH_2Cl_2 (7.6 mL, 0.05 M) and submerged in an oil bath preheated to 55 °C. The reaction was stirred for 1 h at 55 °C, at which point TLC analysis indicated completion of the reaction. Removal of the solvent in vacuo afforded a dark brown oil that was purified by silica gel chromatography (3:2 hexanes:CH_2Cl_2), affording **23** as a white solid (94.1 mg, 0.374 mmol, 99%) and **8** as a brown solid (11.8 mg, 0.0196 mmol, 95%). The recovered catalyst was transferred directly into a clean flask for a subsequent RCM.

Kinetic Studies Involving ROMP of Cyclooctene with 1 and 8 as Catalysts. Complex **1** or **8** (0.108 mmol, 0.05 equiv) was weighed into a small vial containing recrystallized ferrocene (0.108 mmol, 0.05 equiv); $CDCl_3$ (0.4 mL) was used to quantitatively transfer the contents of the vial to an NMR tube. The mixture was treated with distilled *cis*-cyclooctene (0.212 mmol, 1.0 equiv) in 0.4 mL of $CDCl_3$. A 400 MHz ^{1}H NMR timing sequence was commenced immediately, collecting 20 aquisition arrays within 40 min. The integrals in each spectrum were standardized relative to ferrocene. For catalyst **1**, the initiation rate constant (k_i) was determined by integration of the H_α resonances of the initiating (20.0 ppm) and propagating carbene (19.3 ppm) species. The initiation rate constant for **8** was measured by monitoring the decrease of catalyst concentration (δH_α = 17.4 ppm) vs the internal standard.[24] The propagation rate constants (k_p) were determined by integration of the olefinic proton resonances of the substrate (5.6 ppm) and the polymer (5.4 ppm). Representative kinetic plots for catalyst **8** are included in the Supporting Information.

Acknowledgment. J.S.K. acknowledges the National Science Foundation for a predoctoral fellowship (1998−2001) and the Department of Education for a GAANN fellowship (1997−1998). The National Institutes of Health (GM-47480) and the National Science Foundation (CHE-9632278) are acknowledged for support of this research. In addition, we thank the NIH (1S10RR09008) for the Siemens SMART X-ray crystallography instrumentation grant. We are grateful to Dr. John A. Tallarico for helpful discussions.

Supporting Information Available: Tables of crystallographic experimental details, atomic coordinates and isotropic displacement parameters, interatomic bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates and isotropic displacement parameters, and kinetic plots for the ROMP of cyclooctene catalyzed by Ru−carbene **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

JA983222U