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Reactions of Ruthenium Carbenes of the Type $(PPh_3)_2(X)_2Ru{=}CH{-}CH{=}CPh_2$ (X = Cl and CF_3COO) with Strained Acyclic Olefins and Functionalized Olefins

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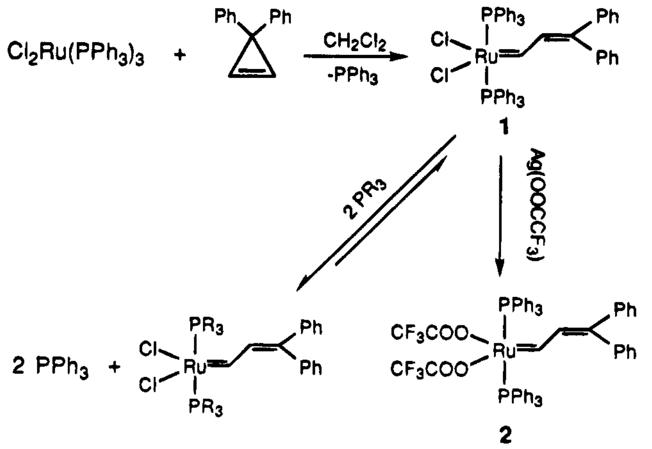
Abstract: Ruthenium carbene complexes of the type $(PPh_3)_2(X)_2Ru{=}CH{-}CH{=}CPh_2$ (**1**, X = Cl; **2**, X = CF_3COO) can react with strained acyclic olefins and functionalized olefins. Complex **1** reacts with methylenecyclopropane and methylenecyclobutane and their derivatives to generate new active ring-opening metathesis polymerization (ROMP) catalysts. The product from the reaction between **1** and ethyl vinyl ether decomposes through a bimolecular coupling pathway. Complex **2** reacts with functionalized terminal olefins, such as alkyl vinyl ether, enamine, and alkyl vinyl sulfide to give hetero-substituted carbene complexes. However, in the case of alkyl vinyl ether, the resulting alkoxymethylenecarbene complex decomposes to ruthenium carbonyl species at room temperature. Complex **2** can also isomerize allylic vinyl ether or alcohol. Aromatic amines can react with **2** by first coordinating *trans* to the carbene ligand; a fact which indicates that the potential coordination site for olefin metathesis may be *trans* to the carbene moiety. The reactivity pattern of **2** with functionalized vinyl olefins suggests that this reaction is best understood under the context of a Lewis acid/Lewis base interaction.

Introduction

Recently, we reported the synthesis of a new class of ruthenium(II) carbene complexes.[1] As shown in Scheme 1, ruthenium vinylcarbene complex **1** was obtained from the reaction of a ruthenium phosphine precursor with 3,3-diphenylcyclopropene.[1a−b] The bis(trifluoroacetate) (bis(TFA)) derivative **2** can then be synthesized from the direct metathesis between AgTFA and **1**.[1d] In contrast to the high oxidation state early transition metal alkylidene and metallacyclobutane complexes,[2] which have limited tolerance to acidic and polar functional groups, these new ruthenium vinylcarbene complexes possess a remarkable tolerance to many functional groups including protic species, such as water and HCl.[1b,c] Furthermore, complex **1** can catalyze the living ring-opening metathesis polymerization (ROMP) of strained cyclic olefins, such as norbornene,[1] bicyclo[3.2.0]hept-6-ene,[3a] and bicyclo[4.2.0]oct-7-ene.[3b] Although **1** and **2** do not react with unstrained olefins, this was the first time that a ruthenium carbene complex is observed to react directly with an olefin in a metathesis fashion, a fact which may be attributed to the electronic/coordinative unsaturation of the Ru^{II} centers in **1** and **2**.[4,5]

The exceptional stabilities of **1** and **2** toward a wide variety of functional groups suggest that the ruthenium−vinylcarbene bonds in these new ROMP catalysts are perhaps fairly nonpolarized, which would contribute to the inertness of this bond toward both electrophilic and nucleophilic attacks. To determine the effect of bond polarization in olefin metathesis reactions catalyzed by **1** and **2**, we carried out a systematic study where a series of substituted olefins was allowed to react with these catalysts. In addition to providing an in-depth understanding of the electronic nature of the ruthenium carbene bonds in **1** and **2**, this study should also shed some light into the reaction

Scheme 1. Formation of Ruthenium Vinylcarbene Complexes through the Ring Opening of 3,3-Diphenylcyclopropene



[®] Abstract published in *Advance ACS Abstracts,* April 15, 1995.

[1] (a) Gagne, M. R.; Grubbs, R. H. *Organometallics* **1992**, *11*, 3933−3935. (b) Nguyen, S. T.; Johnson, L. K.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 3974−3975. (c) Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1993**, *115*, 9858−9859. (d) Nguyen, S. T.; Grubbs, R. H. Unpublished results.

[2] (a) Grubbs, R. H.; Tumas, W. *Science* **1989**, *243*, 907−915 and references therein. (b) Schrock, R. R. *Acc. Chem. Res.* **1990**, *23*, 158−165 and references therein.

[3] (a) Wu, Z.; Benedicto, A. D.; Grubbs, R. H. *Macromolecules* **1993**, 26, 4975−4977. (b) Wu, Z. Ph.D Thesis, The California Institute of Technology, 1994.

[4] A wide variety of ruthenium carbene complexes are known in the literature, see: (a) Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, *22*, 59−128. (b) Bruce, M. *Chem. Rev.* **1991**, *91*, 197−257. (c) Wakatsuki, Y.; Yamazaki, H.; Kumegawa, N.; Satho, T.; Satoh, J. Y. *J. Am. Chem. Soc.* **1991**, *113*, 9604−9610. (d) Bohle, D. S.; Clark, G. R.; Rickard, C. E. F.; Roper, W. R.; Wright, L. J. *J. Organomet. Chem.* **1988**, *358*, 411−447. However, these do not exhibit metathesis activity in our hands and in the hands of others, see ref 1b.

[5] The combination of right oxidation state (Ru^{II}, neutral carbene fragment) and electronic/coordinative unsaturation (16-electron metal center/5-coordinate complex) is proposed to account for the enhanced olefin metathesis activity by **1** and its derivatives: Nguyen, S. T.; Grubbs, R. H. Manuscript in preparation.

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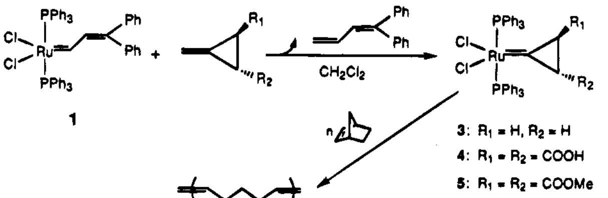
mechanisms of **1** and **2** in olefin metathesis[6] and allow the potentials of these catalysts in other synthetic applications to be explored.

Results and Discussion

Reaction of 1 with Methylenecyclopropane, Methylenecyclobutane, and Their Derivatives. Although catalyst **1** has been shown to be an active catalyst for the living ROMP of norbornene and other strained cyclic olefins,[1b,3a] it does not react with unstrained olefins. To determine if factors other than the release of ring-strain could drive the metathesis-type reactions, some acyclic olefins where the reactivity is enhanced by polarization or strain were allowed to react with **1**.

When **1** was treated with 1.1 equiv of methylenecyclopropane in CH_2Cl_2, a quantitative conversion of the starting material to complex **3** was observed by ^1H NMR spectroscopy (eq 1).



(1)

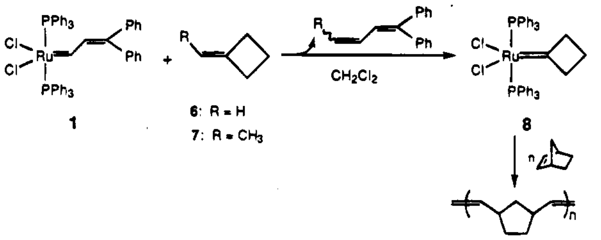
Complex **3** can also be isolated and characterized spectroscopically. Key to the structural assignment of **3** is a singlet at 0.66 ppm in the ^1H NMR spectrum due to the cyclopropyl protons and a signal at 306.5 ppm in the ^{13}C NMR spectrum due to the quarternary carbene carbon, which resonates further downfield than that of the vinylcarbene **1** (δC_α = 288.9 ppm).[1b] The ^{31}P NMR spectrum of **3** in CD_2Cl_2 exhibits a singlet at 29.95 ppm due to the presence of equivalent phosphine ligands. Complex **3** is a living catalyst for the polymerization of norbornene. For example, when 11 equiv of norbornene was added to a solution of **3** in CH_2Cl_2, a pseudo-quartet resonance corresponding to the propagating species of polynorbornene was observed at 17.6 ppm by ^1H NMR spectroscopy (~80% initiated), similar to that observed for the polynorbornene propagating species obtained from **1** and norbornene.[1b]

Other substituted methylenecyclopropanes also react with **1** to form the corresponding cyclopropylcarbene complexes. Reaction between **1** and 3-methylenecyclopropane-*trans*-1,2-dicarboxylic acid in THF proceeds slowly[7] to afford **4,** and treatment of **1** with 2 equiv of the corresponding dimethyl 3-methylenecyclopropane-*trans*-1,2-dicarboxylate[8] in CH_2Cl_2 results in a clean formation of **5** as observed by ^1H NMR spectroscopy (eq 1). In the ^1H NMR spectrum, characteristic singlet resonances of the cyclopropyl protons appear at 1.44 ppm for **4** and 1.79 ppm for **5**. The ^{31}P NMR spectra exhibit a singlet resonance at 29.60 ppm for **4** and 29.55 ppm for **5**.

Table 1. Selected Bond Lengths and Angles for **8**

	Bond Lengths (Å)		
Ru(1)–P(1)	2.386(1)	Ru(1)–P(2)	2.375(1)
Ru(1)–Cl(1)	2.370(1)	Ru(1)–Cl(2)	2.352(2)
Ru(1)–C(1)	1.830(4)	P(1)–C(5)	1.826(4)
P(1)–C(11)	1.837(4)	P(1)–C(17)	1.833(4)
P(2)–C(29)	1.843(4)	P(2)–C(35)	1.836(5)
	Bond Angles (deg)		
Ru(1)–C(1)–C(2)	133.8(4)	Ru(1)–C(1)–C(4)	134.6(4)
P(1)–Ru(1)–P(2)	170.9(1)	P(1)–Ru(1)–Cl(1)	90.4(1)
P(2)–Ru(1)–Cl(1)	87.4(1)	P(1)–Ru(1)–Cl(2)	88.9(1)
P(2)–Ru(1)–Cl(2)	88.7(1)	Cl(1)–Ru(1)–Cl(2)	150.4
P(1)–Ru(1)–C(1)	94.0(2)	P(2)–Ru(1)–C(1)	95.2(2)
Cl(1)–Ru(1)–C(1)	104.5(1)	Cl(2)–Ru(1)–C(1)	105.1(1)
Ru(1)–P(1)–C(5)	109.8(2)	Ru(1)–P(1)–C(11)	122.2(1)
C(5)–P(1)–C(11)	102.7(2)	Ru(1)–P(1)–C(17)	113.5(2)
C(5)–P(1)–C(17)	104.9(2)	C(11)–P(1)–C(17)	101.9(2)
Ru(1)–P(2)–C(23)	106.5(2)	Ru(1)–P(2)–C(29)	118.3(2)
C(23)–P(2)–C(29)	105.3(2)	Ru(1)–P(2)–C(35)	122.1(2)
C(23)–P(2)–C(35)	101.3(2)	C(29)–P(2)–C(35)	101.0(2)
C(2)–C(1)–C(4)	91.6(3)	C(1)–C(2)–C(3)	88.7(4)
C(2)–C(3)–C(4)	90.8(4)	C(1)–C(4)–C(3)	88.6(4)

Catalyst **1** also reacts with methylenecyclobutane **6** (eq 2). When a 0.01 M solution of **1** was treated with 2 equiv of methylenecyclobutane in CD_2Cl_2 at room temperature, the formation of complex **8** was observed by ^1H, ^{13}C, and ^{31}P NMR spectroscopies. Noteworthy is the ^{13}C resonance for the quarternary carbene carbon of **8** which appears at 344.5 ppm, even further downfield than that of **3**. Complex **8** can also be obtained from the reaction between **1** and a trisubstituted olefin ethylenecyclobutane **7** (eq 2). The acyclic metathesis of a trisubstituted olefin is quite unusual even with strongly electrophilic, high oxidation state alkylidene complexes.[9] Similar to **3**, **8** can be used to initiate a living ROMP of norbornene.



(2)

The structure of **8** was also confirmed by a single crystal X-ray analysis, and the important bond lengths and angles are listed in Table 1. The length of the ruthenium–carbon double bond (1.830(4) Å) is shorter than that (1.887(7) Å) of **1**,[1b] which indicates a relatively stronger bond for **8**. This increase in metal–carbon interaction, as compared to that in complex **1,** may result from the absence of the adjacent p-orbital in **8** to compete with the metal d_π-orbital for the same bonding p-orbital on the carbene carbon. The structure of **8** is a distorted trigonal bipyramid (Figure 1) with the two chlorides and the carbene carbon in the equatorial plane and the two phosphines in the axial positions, bent slightly away from the carbene carbon. The angles between phosphines and carbons are slightly larger than 90° (95.2(2)° and 94.0(2)°). The cyclobutane ring bisects the

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(6) For example, the following have been observed: (i) The increase in steric bulk of the phosphine ligand enhances the metathesis reactivity of **1** (ref 1c). (ii) The presence of excess phosphine slows down the rate of metathesis, and the rate of the reaction was greatly accelerated when one of the phosphines was removed by complexing with copper chloride. (a) Benedicto, A. D.; Grubbs, R. H. Unpublished results. (b) Dias, E. L.; Nguyen, S. T.; Grubbs, R. H. *Abstracts of Papers*, 207th National Meeting of the American Chemical Society, San Diego, CA; American Chemical Society: Washington, DC, 1994; INORG 141. These observations suggest that the phosphine dissociates during the reaction.

(7) The reaction is sluggish because catalyst **1** is only partially soluble in THF. However, due to the difficulty encountered while dissolving **4** in other solvents, such as benzene or CH_2Cl_2, THF is the only reasonable medium to solvate both **1** and **4**.

(8) Dimethyl 3-methylenecyclopropane-*trans*-1,2-dicarboxylate was synthesized from 3-methylenecyclopropane-*trans*-1,2-dicarboxylic acid and excess diazomethane. Diazomethane is generated from diazald (*N*-methyl-*N*-nitroso-*p*-toluenesulfonamide) and KOH–ethanol–H_2O (5 g:10 mL:8 mL) using a mini-Diazald apparatus purchased from the Aldrich Chemical Co.

(9) For example, the alkylidene complex $((CF_3)_2CH_3CO)_2(2,6\text{-}i\text{-}Pr_2\text{-}C_6H_4N)W(CH\text{-}t\text{-}Bu)$ does not react with 2-methyl-2-butene: Wu, Z.; Grubbs, R. H. Unpublished results. It should be noted, however, that the tandem metatheses of di- and trisubstituted olefins have been reported using $((CF_3)_2CH_3CO)_2(2,6\text{-}i\text{-}Pr_2\text{-}C_6H_4N)Mo(CH\text{-}t\text{-}Bu)$ in a ring-closing metathesis reaction, see: (a) Fu, G. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 5426–5427. (b) Fu, G. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 7324–7325.

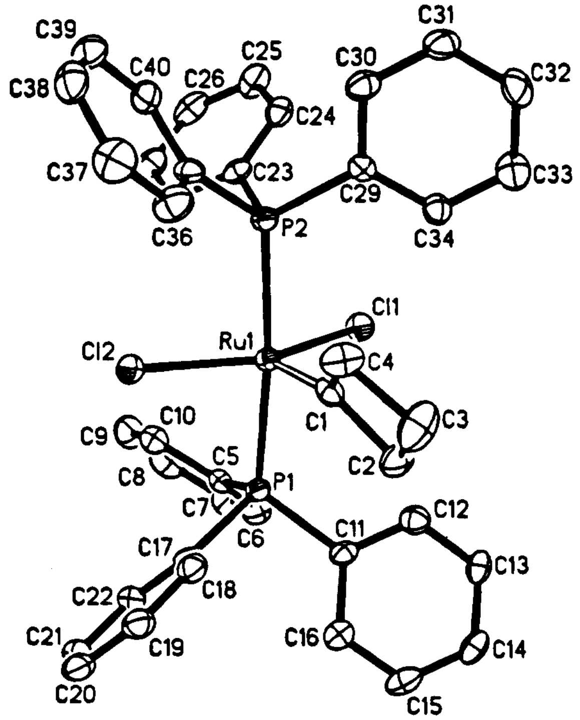
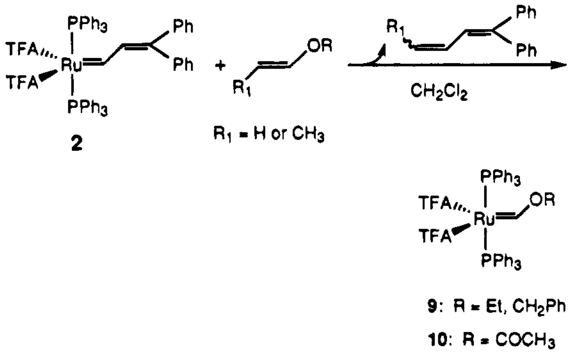


Figure 1. ORTEP plot of $Cl_2(PPh_3)_2Ru{=}C(CH_2)_3$ **8**. Thermal ellipsoid are drawn at the 50% probability level.

angle of P−Ru−Cl (the dihedral angel $Cl_1-Ru-C_1-C_4$ is −59.1(0.5)°). This may be a result of the crystal packing force and a tilting of the cyclobutyl ring away from the bulky triphenylphosphine ligands to minimize interactions of the methylene groups with the phenyls.[10] Also interesting is the large Cl−Ru−Cl angle in the structure of **8** (150.4°). From a steric point of view, the open coordination site for olefin binding may be *trans* to the carbene moiety, an unfavorable position for the formation of the metallacyclobutene intermediate in olefin metathesis.[11] Of course, other factors, such as electronic and ligand dissociation need to be taken into account before a final conclusion can be reached.

The observation that **1** is more reactive toward strained acyclic olefins can probably be attributed to the release of strain energy upon olefin coordination and metallacycle formation.[12] Other larger members of the methylenecycloalkane family such as methylenecyclopentane or methylenecyclohexane do not react with **1**, presumably due to the lack of double bond strain in these two substrates.[12]

Stoichiometric Metathesis of Vinyl Ethers and Vinyl Acetate by 1 and 2. Both terminal and internal vinyl ethers undergo a stoichiometric metathesis reaction with complex **1** or **2**. When a 0.01 M solution of **2** in CD_2Cl_2 was treated with 2 equiv of ethyl vinyl ether for several hours, a yellow solution resulted in which the stoichiometric formation of 1,1-diphenylbutadiene and a new ethoxy-substituted carbene species **9** was observed (eq 3). Characteristic of **9** is a triplet resonance in the ^1H NMR spectrum at 14.49 ppm (J_{HP} = 4.8 Hz) due to the carbene proton. The ^{13}C NMR spectrum exhibits a resonance for the alkoxy-substituted carbene carbon at 297.5 ppm. A single peak due to equivalent phosphine ligands was observed at 44.2 ppm in the ^{31}P NMR spectrum. Interestingly, **9** does not polymerize norbornene.



(3)

However, when complex **1** was treated with ethyl vinyl ether in a similar manner, only the organic product 1,1-diphenyl-1,3-butadiene was observed from the metathesis and no new carbene species were detected by ^1H NMR spectroscopy. The reaction was not complete even on prolonged heating. The ethoxycarbene species derived from **1** decomposed bimolecularly during the course of the reaction. The bimolecular nature of the decomposition[13] was suggested by an experiment in which a sealed NMR tube containing 0.02 M of **1** and 1.2 equiv of ethyl vinyl ether was left at room temperature for 48 h and the volatiles were collected by a vacuum transfer technique. A clean formation of 1,2-diethoxyethylene was observed by ^1H NMR spectroscopy in 50% yield relative to the starting material complex. The organometallic products from the decomposition were not identified. The observation that **2** tends to give more stable alkoxycarbene complexes than **1** in the reaction with alkyl vinyl ether suggests that, in contrast to the case of high oxidation state metal alkylidene complexes,[14] electron-withdrawing anionic ligands can better stabilize ruthenium(II) hetero-substituted carbenes.

Not surprisingly, cyclic vinyl ether also reacts with **2** in a stoichiometric fashion. The reaction of **2** with 2,3-dihydrofuran

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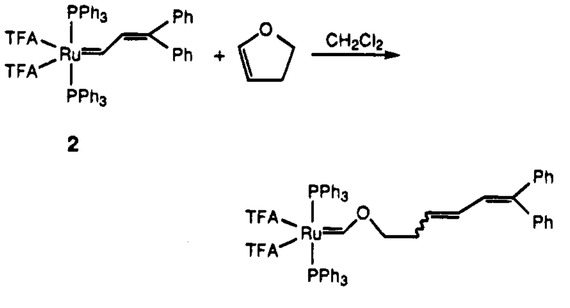
[10] It is interesting that this is the stable conformation of the carbene moiety. From a simple molecular orbital geometry picture, there is no available metal orbital to interact with the cyclobutylcarbene fragment in this solid-state orientation (i.e., bisecting the P−Ru−Cl angle); hence we suspect that this may be due to the crystal packing force and steric effects. Interestingly, in **1**, the plane that contains the vinylcarbene moiety is almost coplanar to the Ru−P bonds (the dihedral angle ($\angle P-Ru-C_1-C_2$) is 8.46°, calculated from the supplementary material of Nguyen, S. T.; Johnson, L. K.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 3974−3975), and in the bis(tricyclohexylphosphine) analog of **1**, $(Cl)_2(PCy_3)_2Ru(CHCHCPh_2)$, the plane that contains the vinylcarbene moiety is nearly perpendicular to the Ru−P bonds (the dihedral angle ($\angle P_3-Ru_2-C_{52}-C_{53}$) is −87.8° from the supplementary material of Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1993**, *115*, 9858−9859).

[11] The sterically preferred coordination site located *trans* to the carbene is apparent from a Chem3D three-dimensional space-filling drawings of **8** based on its crystal structure data. Coordination sites that are *trans* to the carbenes have also been observed in certain rhenium and tantalum alkylidene complexes. For detail discussions, see: (a) Wallace, K. C.; Davis, W. M.; Schrock, R. R. *Inorg. Chem.* **1990**, *29*, 1104−1106. (b) Murdzek, J. S.; Blum, L.; Schrock, R. R. *Organometallics 1988*, *7*, 436−441. (c) Schofield, M. H.; Schrock, R. R.; Park, L. Y. *Organometallics* **1991**, *10*, 1844−1851. (d) Flatt, B. T.; Grubbs, R. H.; Blanski, R. T.; Calabrese, J. C.; Feldman, J. *Organometallics* **1994**, *13*, 2728−2732.

[12] (a) Rappoport, A. *The Chemistry of Cyclopropyl Group*; Wiley: New York, 1987; Vol. 1. (b) For a detail evaluation of strain energy, see: Schleyer, P. v. R.; Williams, J. E.; Blanchard, K. R. *J. Am. Chem. Soc.* **1970**, *92*, 2377−2386. (c) The strain energies (SE's) for methylenecyclobutane, methylenecyclopropane, cyclobutane, and cyclopropane are 26.9, 40.9, 26.5, and 27.5 kcal/mol, respectively. The olefinic strains (OS's) for methylenecyclobutane and methylenecyclopropane are then estimated to be 0.4 and 13.4 kcal/mol, respectively. From these calculations, the transition states for the reactions in eqs 1 and 2 are stabilized by the release of the strain energy of the exocyclic double bond. The driving forces ($\Delta G°$) for eqs 1 and 2 were estimated (from heat of formation data) to be −33 and −14 kcal/mol respectively, assuming that the metal carbene bonds of **1** and **2** have similar energies.

[13] The general decomposition pathways for alkylidene complexes usually involve (i) rearrangement of alkylidenes to olefins (for Nb and Ta). (ii) rearrangement of metallacyclobutane to olefins via β-hydride elimination, and (iii) bimolecular coupling of alkylidenes to give olefins. For detail discussions, see: (a) Feldman, J.; Schrock, R. R. *Prog. Inorg. Chem.* **1991**, *39*, 1−74. (b) Vaughan, G. A.; Toreki, R.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1993**, *115*, 2980−2981.

leads to a ring-opened product, as shown in eq 4. Two 1:1 triplet resonances were observed at 14.49 ppm (J_{HP} = 5.0 Hz) and 14.55 ppm (J_{HP} = 4.9 Hz) corresponding to the carbene proton of **11**. There was, however, no further productive metathesis even on prolonged heating, and **11** does not catalyze the ROMP of norbornene.



2

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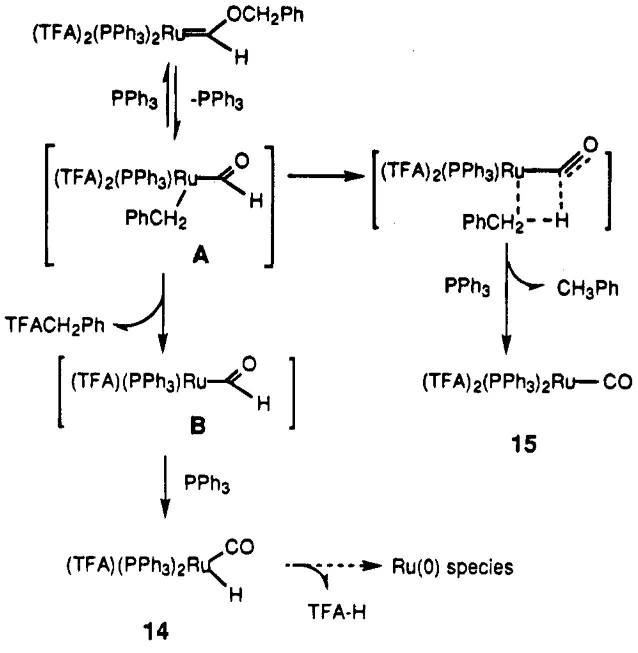
(4)

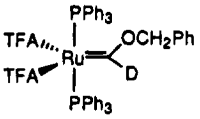
Complex **2** also reacts with vinyl acetate in a metathesis fashion though only stoichiometrically. When a 0.01 M solution of **2** in CD_2Cl_2 was treated with 1.5 equiv of vinyl acetate, a triplet resonance characteristic of a new carbene species was observed at 13.75 ppm (J_{HP} = 1.6 Hz) by ^1H NMR spectroscopy. However, the reaction of **2** with vinyl acetate was much slower than that with ethyl vinyl ether, presumably due to the lesser nucleophilicity of the former substrate. The resulting carbene decomposed during the reaction as indicated by the low intensity of the resulting carbene proton resonance and by the complex ^{31}P NMR spectrum.

The first stoichiometric metathesis reaction of transition metal carbene with vinyl ethers was reported in 1973 where $(CO)_5W{=}CPh_2$ was reacted with 1-phenylvinyl phenyl ether to produce the corresponding phenoxy-substituted tungsten(0) carbene and 1,1-diphenylethylene.[15] This reaction has been cited as providing the first model for the chain-propagation step in the olefin metathesis reaction.[16] Recently, Schrock and coworkers also reported the reaction of a rhenium(VII) alkylidene complex with vinyl ethers in which a stoichiometric metathesis is also observed to give the corresponding alkoxy-substituted rhenium(VII) alkylidene complex.[17] These workers also observed that the reaction rate between the parent rhenium(VII) alkylidene and terminal olefins increased as the nucleophilicity of the olefin increased, a fact that is consistent with our observation that vinyl acetate reacts slower with **2** than vinyl ether (*vide supra*). Unfortunately, no norbornene polymerization studies were reported for this alkoxy-substituted rhenium(VII) alkylidene to provide a direct comparison to our observations about the metathesis inertness of **9** and **11**.

Rearrangement of the Ruthenium(II) Alkoxycarbene Complex. When the ruthenium alkoxycarbene complex **9** was left at room temperature, the carbene resonance slowly disappeared and a hydride resonance was observed at −17.5 ppm by ^1H NMR spectroscopy. After several days at room temperature, slow disappearance of the hydride resonance was also observed. In order to examine the intermediates in this rearrangement, both deuterium- and ^{13}C-labeled complexes **12** and **13** were synthesized so that the reaction could be followed by ^2H and ^{13}C NMR spectroscopies.

Scheme 2. Two Possible Decomposition Pathways of Bis(trifluoroacetate)bis(triphenylphosphine)ruthenium Alkoxycarbenes





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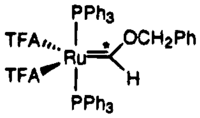

13

When a solution of **12** was left at room temperature for 12 h, we observed the formation of a ruthenium deuteride species (δ = −17.5 ppm (t), J_{PP} = 3 Hz) by ^2H NMR and a ruthenium carbonyl species by IR (ν_{CO} =1969.8 cm^{-1}) spectroscopy. Benzyl trifluoroacetate (*m/e* = 204) and $PhCH_2D$ (*m/e* = 92) were both identified by GC/MS.[18a] When **13** was left at room temperature for 24 h, ruthenium carbonyl resonances were observed at δ 205.1 (**14**, J_{CP} = 14 Hz), δ 204.8 (**15**, J_{CP} = 14 Hz), and δ 203−203.5 (multiplets) in the ^{13}C NMR spectrum. Two possible decomposition pathways consistent with these observations are shown in Scheme 2. The decomposition follows a path that is the reverse of the route for the synthesis of Fischer carbenes.[19] The first step involved a β-alkyl elimination to a ruthenium(IV) formyl intermediate **A**, which can rapidly eliminate benzyl trifluoroacetate to yield a ruthenium(II) formyl complex **B**, which further undergoes facile rearrangement to a ruthenium carbonyl complex **14** (Scheme 2, left pathway). Intermediate **A** can also undergo reductive elimination of toluene to form the carbonyl complex **15** (Scheme 2, right pathway).[18b]

Observation of the Isomerization of Allylic Ether and Allylic Alcohol. Novak and Grubbs have shown that the Werner-type complex $Ru(H_2O)_6(Tos)_2$ is an active catalyst for the ROMP of 7-oxonorbornene and its derivatives in polar or

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(14) The electron-withdrawing groups tend to destablize the high oxidation state metal alkylidene complex, see: (a) Feldman, J.; Davis, W. M.; Thomas, J. K.; Schrock, R. R. *Organometallics* **1990**, *9*, 2535−2548. (b) Robbins, J.; Bazan, G. C.; Murdzek, J. S.; O'Regan, M. B.; Schrock, R. R. *Organometallics* **1991**, *10*, 2902−2907.

(15) Casey, C. P.; Burkhardt, T. J. *J. Am. Chem. Soc.* **1973**, *95*, 5833−5834.

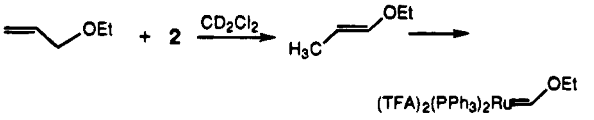
(16) Grubbs, R. H. *Prog. Inorg. Chem.* **1978**, *28*. 1−50.

(17) Toreki, R.; Vaughan, G. A.; Schrock, R. R. *J Am. Chem. Soc.* **1993**, *115*, 127−137.

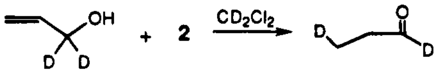
(18) (a) The final ratio of the benzyl trifluoroacetate and toluene generated from the decomposition is 8.5:1, indicating that the reductive elimination of benzyl trifluoroacetate proceeds much faster. For a review of transition metal formyl complexes, see: (b) Gladysz, J. A. *Adv. Organomet. Chem.* **1982**, *20*, 1−38. (c) Tam, W.; Lin, G. Y.; Gladysz, J. A. *Organometallics* **1982**, *1*, 525−529.

(19) Fischer, H. *The Synthesis of Carbene Complexes*; VCH: Deerfield Beach, FL, 1983.

aqueous media.[20] Recently, its catalytic activity in the isomerization of allylic ether or allylic alcohols in a protic solvent has been observed in which the formation of a ruthenium hydride species was implicated.[21] To test for the allylic isomerization activity of catalyst **2**, we examined the reactions of **2** with several allylic ethers and allylic alcohols (eqs 5−7). When a 0.01 M solution of **2** in CD_2Cl_2 was treated with 2 equiv of allyl ethyl ether for 4 h at 40 °C, all the starting olefins were isomerized to ethyl 1-propenyl ether and the metathesis product, ethoxycarbene complex, was also formed stoichiometrically as indicated by the resonance at 14.50 ppm in the ^1H NMR spectrum. Similarly, when a 0.01 M solution of **2** was treated with 20 equiv of 2,5-dihydrofuran in CD_2Cl_2 at room temperature overnight, 88% of the starting material was converted to 2,3-dihydrofuran. When a 0.01 M solution of complex **2** in CD_2Cl_2 was treated with 20 equiv of 1,1-dideuterioallyl alcohol at room temperature for 24 h, a clean formation of 1,3-dideuteriopropionaldehyde was observed (by NMR) in 67% conversion. In light of previous results with vinyl ether (Scheme 2), we assume that the isomerization activity is associated with ruthenium hydrides formed in decomposition side reactions during the normal metathesis sequence.



(5)



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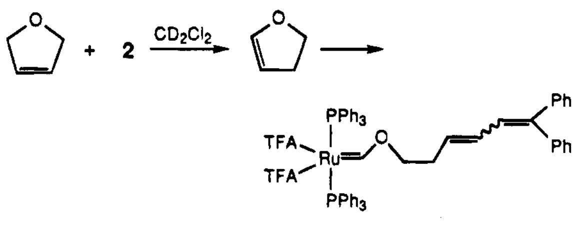

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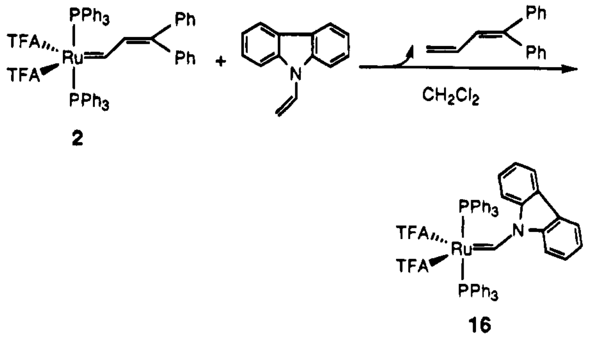
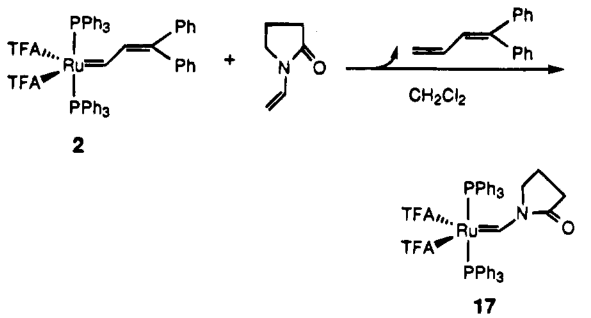
Reaction of Alkylamino-Substituted Terminal Olefins with Complex 2. Complex **2** react with 9-vinylcarbazole or 1-vinyl-2-pyrolidinone in CH_2Cl_2 to yield the corresponding nitrogen-substituted carbene species (eqs 8 and 9).[22] When a 0.015 M solution of **2** in CD_2Cl_2 was treated with 4 equiv of 9-vinylcarbazole for 48 h at 40 °C, a new triplet resonance was observed at 13.47 ppm (J_{HP} = 11.5 Hz) by ^1H NMR spectroscopy and 253.1 ppm (J_{CP} = 16 Hz) by ^{13}C NMR spectroscopy due to the carbene moiety of **16**. Compound **16** was isolated and further characterized spectroscopically. Similarly, 1-vinyl-2-pyrolidinone also react with **2** to yield the corresponding carbene species characterized by ^1H NMR spectroscopy (**17**, 14.33 ppm, t, J_{HP} = 1.80 Hz). However, these reactions proceed much slower than those of the corresponding reactions of alkyl vinyl ether and vinyl acetate with **2**, perhaps resulting from the lower electron-donating ability of the nitrogen caused by the extended electron delocalization onto the phenyl rings in vinylcarbazole and the conjugation with the carbonyl in vinylpyrolidinone. Similar to **9−11**, complexes **16** and **17** are not active in the ROMP of norbornene.

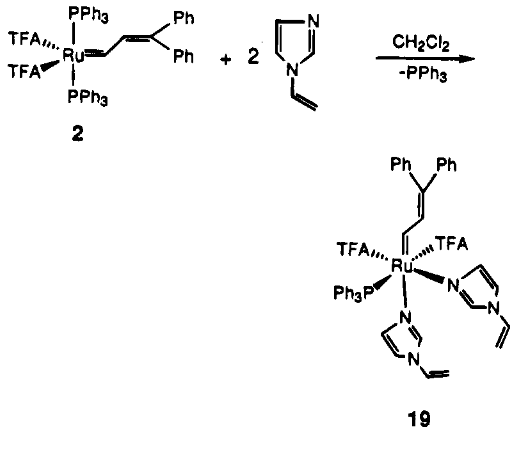


(8)



(9)

Complex **2** also reacts with 1-vinylimidazole. However, instead of the expected metathesis reaction sequence, we observed a double coordination of imidazole to the metal center in conjunction with the loss of one PPh_3 ligand to give complex **19** (eq 10). The structure of the complex **19** was supported by ^1H and ^{13}C NMR data and was further confirmed by both elemental analysis and high resolution mass spectrometry data. The formation of **19** appears to occur in a stepwise fashion. For example, when a 0.01 M solution of **2** in methylene chloride was treated with 2 equiv of vinylimidazole, new vinylcarbene resonances were observed immediately at δ 19.65 (H_α, q, J_{HP} = 10.9 Hz) and δ 8.43 (d, H_β, J_{HH} =13.0 Hz) by ^1H NMR spectroscopy. We observed a singlet resonance at δ 47.6 in the ^{31}P NMR spectrum and a singlet resonance at δ −75.5 in the ^{19}F NMR spectrum of this intermediate, consistent with two equivalent phosphines and two equivalent TFA groups, respectively. On the basis of these data, we propose that this intermediate is simply the vinylimidazole adduct of **2**, **18**, where the imidazole coordinates *trans* to the carbene (Scheme 3). After 24 h, 20 more equiv of vinylimidazole was added to this solution of **18** and a major new carbene species **19** was observed as a triplet at 18.50 ppm (J_{HP} = 12.8 Hz) and a doublet at 8.34 ppm (H_β, J_{HH} = 3.8 Hz). The coupling pattern of the proton



(10)

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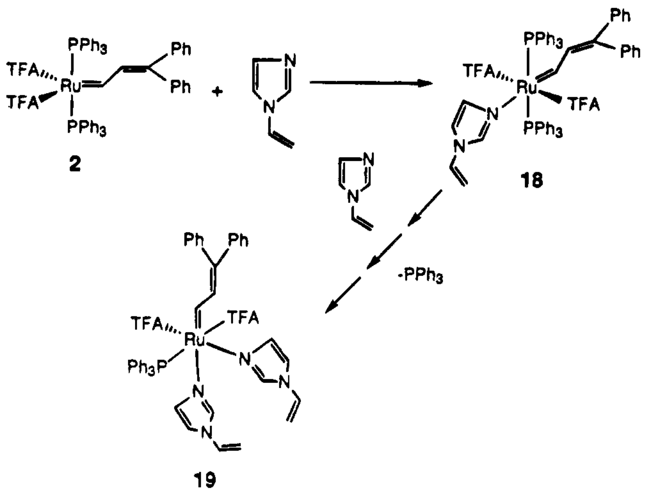
(20) (a) Ivin, K. J. *Olefin Metathesis*; Academic: New York, 1983. (b) Novak, B. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 960−961. (c) Novak, B. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 7542−7543.

(21) (a) McGrath, D. V.; Grubbs, R. H. *Organometallics* **1994**, *13*, 224−235. (b) Benedicto, A. D.; Grubbs, R. H. Unpublished results.

(22) Schrock and co-workers also reported the stoichiometric metathesis reaction of a rhenium(VII) neopentylidene complexes with 1-vinyl-2-pyrrolidinone, vinyl sulfide, and vinylferrocene to afford neohexene and the corresponding rhenium(VII) hetero-substituted alkylidene complexes, see ref 17.

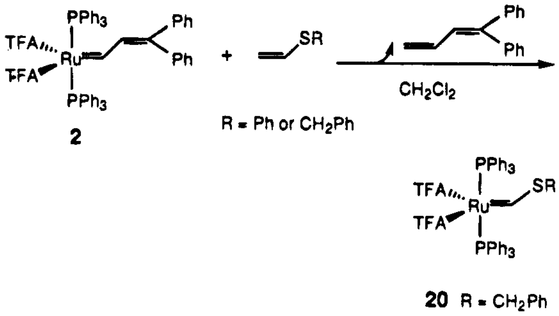
Scheme 3. Proposed Reaction Sequence for the Formation of the Monophosphine−bisimidazole complex **19**



spectrum indicated that only one phosphine was bound to the metal center, which was further supported by ^{31}P NMR data, which showed a singlet resonance at 41.7 ppm and a free phosphine signal at −4.9 ppm. The ^{13}C NMR data indicated that the phosphorus was *cis* to the carbene (J_{CP} = 13.8 Hz). The ^{19}F NMR spectrum showed two resonances at −75.20 and −75.98 ppm, consistent with two inequivalent TFA groups. Complex **19** can be isolated as a green solid although it does not catalyze the polymerization of norbornene.

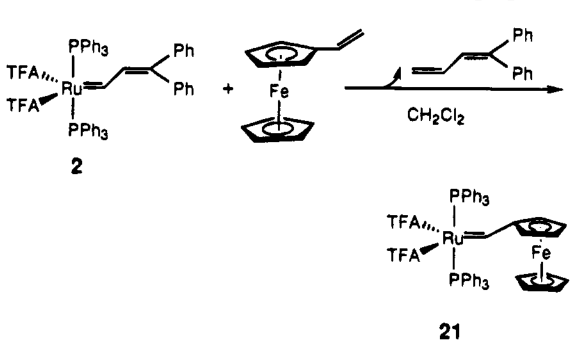
On the basis of the experimental data, we propose a reaction scheme for the formation of **19** from **2** and vinylimidazole (Scheme 3). The first step involves the coordination of base to the metal center *trans* to the carbene forming the octahedral complex **18**, which undergoes exchange of phosphine in the presence of excess imidazole to give product **19**. The finding that an aromatic amine displaces the phosphine ligand sheds some light on the mechanism of olefin metathesis by this type of ruthenium carbene complex. It is possible that an olefin reacts with **1** or **2** in a similar manner by first coordinating to the metal in the direction *trans* to the carbene and then losing one of the phosphines to generate the active metathesis species.[23]

Reaction of Complex 2 with Vinyl Sulfide. When a 0.01 M solution of **2** was treated with the commercially available phenyl vinyl sulfide at 40 °C for several hours, a new carbene resonance was observed at 16.3 ppm.[22] However, the reaction was sluggish and the conversion was low. Prolonged reaction time resulted in the slow conversion of the desired products to other species as shown by the appearance of multiple resonances in the carbene region. To determine if this lack of reactivity was related to the electron-withdrawing effect of the phenyl group, **2** was reacted with benzyl vinyl sulfide.[24] Indeed, this reaction occurs quite cleanly (eq 11) and is complete at room temperature in 24 h in the presence of excess benzyl vinyl sulfide. The resulting alkanethiol-substituted carbene complex **20** is stable at room temperature and is characterized by ^{1}H (δH_α = 17.43 ppm, t, J_{HP} = 3.7 Hz), ^{13}C (δC_α = 306.6 ppm), and ^{31}P (δP = 32.53 ppm) NMR spectroscopies as well as high-resolution mass spectrometry. Again, in contrast to **1** and **2**, complex **20** is inactive for catalyzing the ROMP of bicyclo-[3.2.0]hept-6-ene.



(11)

Reaction of Complex 2 with Other Functionalized Terminal Olefins. So far, the accumulated evidences indicated that the reactivity of **2** with vinyl-substituted olefins depends strongly on the vinyl substituents of the olefins and that electron-donating groups will tend to activate the adjacent double bond for the metathesis reaction with **2**. With this idea in mind, vinylferrocene, whose double bond is activated by the electron-rich Cp rings, and vinylsilane or vinylsiloxane, whose double bond is activated by the more electron-donating silicon atom, should react with **2** in a metathesis fashion.[22] This is indeed the case. When a 0.01 M solution of **2** in CD_2Cl_2 was reacted



(12)

with 2 equiv of vinylferrocene at 40 °C for 30 h, a 36% conversion of the product was observed by ^{1}H NMR spectroscopy (δ 18.9 ppm). Extended reaction time did not drive the reaction further, however. On the other hand, vinyltrimethylsilane or vinyltrimethylsiloxane reacted rapidly with **1** or **2** to give 1,1-diphenyl-1,3-butadiene, the initial organic product from the metathesis. However, the resulting carbenes decomposed to unidentified products.

Throughout this study, we found that complex **2**, with more electron-withdrawing trifluoroacetate ligand, has higher reactivities than **1** toward functionalized olefins. This observation, together with the reactivity profiles of **2** toward α-hetero-substituted olefins, suggests a simple Lewis acid/Lewis base model for the reaction between the ruthenium(II) vinylcarbene center and different hetero-substituted terminal olefins. By making the metal center more electrophilic, the metal−carbene bond becomes more Lewis acidic and its reactivity toward Lewis-basic, electron-rich olefins is enhanced. This simple model can account for the quantitative formation of Ru=C(H)-ER (E = O, S, NR) from the reaction of Ru=CH−CH=CPh_2 and CH_2=C(H)ER and the inaccessibility of the reverse reaction (i.e., formation of Ru=CH−CH=CPh_2 from Ru=C(H)ER and CH_2=CH−CH=CPh_2 is not observed). Furthermore, it may explain the inactivities of **1** and **2** in the Wittig-type olefination of organic carbonyls: the Ru=C bonds in these complexes do not possess the correct bond polarization required for this reaction to occur (Scheme 4).

Conclusion

In summary, the reactions of functionalized acyclic olefins with **1** and **2** have revealed that these complexes are active in

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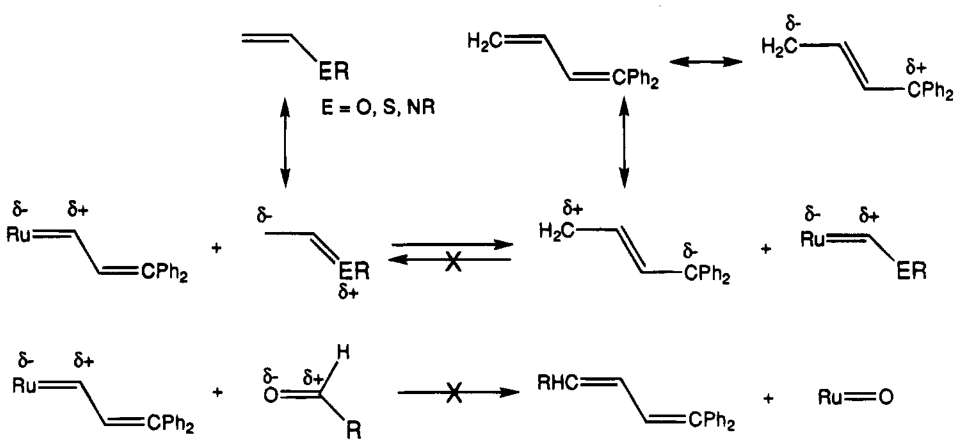
[23] Recent work in our group has indicated that the active species in this system may indeed be a monophosphine complex: Dias, E. L.; Grubbs, R. H. Unpublished results. See also ref 6.

[24] (a) Negishi, E. I. *Organometallics in Organic Synthesis*; Wiley: New York, 1980; pp 243−248. (b) Ellison, R. A.; Woessner, W. D.; Williams, C. C. *J. Org. Chem.* **1972**, *37*, 2757−2759. (c) Trost, B. M.; Salzmann, T. N. *J. Org. Chem.* **1975**, *40*, 148−150.

Scheme 4. Lewis Acid/Lewis Base Model for the Reactivity of **1** and **2** toward Functionalized Substrates



the stoichiometric metathesis of strained acyclic olefins and functionalized olefins. The reactions with strained acyclic olefins are probably favored kinetically by the release of the strain energy of the exocyclic double bonds upon olefin coordination. The α-alkoxy-substituted carbene complexes of type **1** undergo a bimolecular decomposition, while the α-alkoxy-substituted carbene complexes of type **2** decompose through a β-alkyl elimination with the formation of ruthenium carbonyl species as a driving force for the reaction. Reactions of **2** with Lewis basic aromatic amines reveal that the phosphine is labile and the Lewis base initially coordinates *trans* to the carbene. Although the hetero-substituted ruthenium(II) carbene complexes reported herein are themselves not active catalysts in ROMP or catalytic metathesis of other olefins, they constitute a new type of α-substituted ruthenium(II) carbene complexes which may have synthetic applications in organic and organometallic chemistries.[9ab,25] Furthermore, they provide evidences that the substituents on the carbene ligand control the olefin metathesis activity of 16-electron, 5-coordinate Ru^{II} carbene complexes: α-heteroatom substituents will significantly reduce the ROMP activities of the Ru^{II} carbene complexes relative to ordinary carbon substituents.

Experimental Section

General Procedures. All manipulations of air- and/or moisture-sensitive compounds were carried out using standard Schlenk or vacuum-line techniques or in a N_2-filled drybox. Argon was purified by passage through a column of BASF RS-11 (Chemlog) and Linde 4 Å molecular sieves. NMR spectra were recorded on a JEOL GX-400 MHz (399.65 MHz, ^1H; 100.4 MHz, ^{13}C; 61.25 MHz, ^2H; 161.85 MHz, ^{31}P; 375.98 MHz, ^{19}F) spectrometer or on a QE Plus-300 MHz (300.1 MHz, ^1H; 75.33 MHz, ^{13}C) spectrometer. The chemical shifts of the phosphorus and fluorine resonances were determined relative to the phosphoric acid and trichlorofluoromethane standards, respectively. Infrared spectra were recorded using a Perkin-Elmer 1600 series FT-IR spectrometer. Gas chromatography was carried out using a Hewlett-Packard HP 5890 Series II gas chromatograph equipped with 30 mm SE-30 (OV-1) capillary column and a HP 3396 Series II integrator. Elemental analysis was performed by the Oneida Research Corp. microanalysis group. Low-resolution mass spectroscopy analyses were obtained using a Hewlett-Packard model 5970 mass selective detector coupled to a Series 5890 GC equipped with a 15 mm capillary column and a Hewlett-Packard model 3390A integrator. High-resolution FAB mass spectrometry analyses were carried out at the Mass Spectrometry Facility at the University of California, Riverside.

Materials. Catalysts **1** and **2** were synthesized according to the published procedures.[1b,d] Methylenecyclobutane and methylenecyclopropane were distilled from lithium aluminum hydride. CH_2Cl_2 and DMSO were distilled from CaH_2. All the other common solvents used were distilled from sodium benzylphenone ketyl. All other olefinic materials were either dried and distilled or degassed before use. Deuterated compounds were purchased from Cambridge Isotope Lab. All other commercially available compounds were purchased from the Aldrich Chemical Co.

Preparation of the Carbene Dichlorobis(triphenylphosphine)-ruthenium Cyclopropylidene 3. Inside a drybox, complex **1** (102 mg, 0.138 mmol) was dissolved in CH_2Cl_2 (5 mL) inside a 50 mL Schlenk flask equipped with a magnetic stirbar. The flask was brought out of the drybox and connected to a vacuum line. Next, methylenecyclopropane (46.6 mg, 0.86 mmol) was condensed into the Schlenk flask at 77 K. The reaction mixture was then allowed to warm up to room temperature and stirred for 3 h, during which time the color of the solution changed from dark green to red. The reaction mixture was then concentrated, and pentane was added dropwise to precipitate a red powder. The supernatant was removed with a cannula filter, and the residue was washed with pentane (2 × 5 mL) and dried *in vacuo*. Yield = 49 mg, 57%. ^1H NMR (300 MHz, CD_2Cl_2): δ 7.52 (m, 12H), 7.46 (m, 6H), 7.38 (m, 12H), 0.622 (s, 4H, cyclopropyl β-proton). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 306.5 (pseudo-quartet, J_{CP} = 13.8, 15.8 Hz), 134.9 (t, J_{CP} = 5.9 Hz), 132.4 (t, J_{CP} = 20.7 Hz, C_{ipso}), 130.4, 128.5 (t, J_{CP} = 3.9, 4.9 Hz), 31.6 (t, J_{CP} = 6.7 Hz, cyclopropyl CH_2). ^{31}P NMR (161.85 MHz, CD_2Cl_2): δ 29.95.

Preparation of the Carbene Dichlorobis(triphenylphosphine)-ruthenium Cyclobutylidene 8. Inside an N_2-filled glovebox, complex **1** (105.7 mg, 0.1189 mmol) was weighed into a 50 mL Schlenk flask equipped with a magnetic stirbar and dissolved in methylene chloride (5 mL). Next, methylenecyclobutane (55 μL, 0.6 mmol) was added to this solution via a gas-tight syringe. The flask was capped with a rubber septum and brought out of the drybox. The solution was stirred at 30 °C for 0.5 h and then at room temperature for 4.5 h. All the volatiles were then removed under vacuum, and the residue was dissolved in a minimal amount of CH_2Cl_2 followed by dropwise addition of pentane to precipitate a red powder. The supernatant was removed with a cannula filter, and the solid was washed twice with pentane and dried *in vacuo*. yield = 60 mg, 62%. ^1H NMR (CD_2Cl_2): δ 7.55 (m, 12H, Ph), 7.46 (m, 6H, Ph), 7.39 (m, 12H, Ph), 2.66 (t, J_{HH} = 7.42 Hz, cyclobutyl γ-proton), 2.31 (q, J_{HH} = 7.42 Hz, cyclobutyl β-proton). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 344.49 (t, J_{CP} = 10.5 Hz, C_α), 135.06 (t, J_{CP} = 5.56, 5.42 Hz), 132.08 (t, J_{CP} = 20.3 Hz), 130.38, 128.42 (t, J_{CP} = 4.36 Hz), 68.09 (t, J_{CP} = 7.32 Hz, cyclobutyl C_β), 18.44 (cyclobutyl C_γ). ^{31}P NMR (161.85 MHz, CD_2Cl_2): δ 30.1.

X-ray Data Collection, Structure Determination, and Refinement for $Cl_2(PPh_3)_2Ru(C(CH_2)_3)$ (8). X-ray quality crystal of **8** may be obtained by slow diffusion of pentane into a CH_2Cl_2 solution of the complex. A red-orange crystal of approximate dimensions 0.17 x 0.26

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[25] (a) Schubert, U. *Advances in Metal Carbene Chemistry*; Kluwer Academic Publishers: Boston, MA, 1988. (b) Fu, G. C.; Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1993**, *115*, 9856–9857. (c) Kim, S.-H.; Bowden, N. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **1994**, *116*, 10801–10802. (d) Miller, S. J.; Kim, S. H.; Chen, Z.; Grubbs, R. H. *J. Am. Chem. Soc.*, **1995**, *117*, 2108–2109. (e) Morken, J. P.; Didiuk, M. T.; Visser, M. S.; Hoveyda, A. M. *J. Am. Chem. Soc.* **1994**, *116*, 3123–3124. (f) Borer, B. C.; Deerenberg, S.; Bieraugel, H.; Pandit, U. K. *Tetrahedron Lett.* **1994**, *35*, 3191–3194.

× 0.32 mm was oil-mounted on a glass fiber and transferred to the Siemens P3 automated four-circle diffractometer that was equipped with a modified LT-2 low-temperature system. The determination of Laue symmetry, crystal class, unit cell parameters, and the crystal's orientation matrix were carried out by previously described methods similar to those of Churchill.[26] Low-temperature (158 K) intensity data were collected via a $\theta-2\theta$ scan technique with Mo Kα radiation.

All 5376 data were corrected for absorption and for Lorentz and polarization effects and placed on an approximately absolute scale. Any reflection with $I(\text{net}) < 0$ was assigned the value $|F_o| = 0$. The systematic absences observed were $0k0$ for $k = 2n + 1$ and $h0l$ for $l = 2n + 1$; the diffraction symmetry was $2/m$. The centrosymmetric monoclinic space group $P2_1/n$, a nonstandard setting of $P2_1/c$ [C^5_{2h}; no. 14], is therefore uniquely defined.

All crystallographic calculations were carried out using either the UCI modified version of the UCLA Crystallographic Computing Package[27] or the SHELXTL PLUS program set.[28] The analytical scattering factors for neutral atoms were used through the analysis;[29a] both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion were included.[29b] The quantity minimized during least-squares analysis was $\sum w(|F_o| - |F_c|)^2$ where $w^{-1} = \sigma^2(|F_o|) + 0.0004(|F_o|)^2$.

The structure was solved by direct methods and refined by full-matrix least-squares techniques. Hydrogen atoms were included using a riding model with $d(\text{C}-\text{H}) = 0.96$ Å and $U(\text{iso}) = 0.08$ Å. There was one molecule of dichloromethane present in the asymmetric unit. Refinement of positional and thermal parameters led to convergence with $R_F = 4.0\%$, $R_{wF} = 4.4\%$, and GOF = 1.33 for 433 variables refined against those 4197 data with $|F_o| > 3.0\sigma(|F_o|)$. A final difference-Fourier synthesis showed no significant features, $\varrho(\text{max}) = 0.77$ e Å^{-3}.

Preparation of Ethylenecyclobutane (7). In the drybox, ethylenetriphenylphosphorane (4.15 g, 14.3 mmol) was weighed into a 100 mL three-necked round-bottom flask. The flask was capped with a rubber septum and brought out of the box; then dry DMSO (25 mL) was added. Cyclobutanone (1.06 mL, 14.2 mmol) was degassed and dissolved in DMSO (3 mL), which was added into the phosphorane dropwise via a cannula in 20 min, during which the color of the solution started to turn orange and a precipitate formed. (The precipitate redissolved as the reaction continued.) After addition, the mixture was stirred at room temperature for 0.5 h. All the volatiles were then vacuum-transferred into a flask equipped with a Teflon valve. The compound collected was washed with deionized water and dried over $MgSO_4$ before being vacuum-transferred onto NaH. Pure product (690 mg, 59%) was obtained after distillation from NaH. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 5.06−5.09 (m, 1H, *C*H=*C*H), 2.59−2.65 (m, 4H, β-*C*H_2), 1.92 (quintet, 2H, γ-*C*H_2), 1.45−1.53 (m, 3H, *C*H_3).

General Procedure for NMR Tube Reactions. In the drybox, complex **1** or **2** was weighed into an NMR tube and dissolved into 0.5∼0.6 mL of CD_2Cl_2. The tube was capped with a rubber septum, and a calculated amount of olefins was added via a gas-tight syringe. The tube was then shaken vigorously and brought out of the drybox. The tube was either left standing at room temperature or put into a preheated oil bath at the desired temperature. The reaction was monitored by ^{1}H NMR spectroscopy at different time intervals.

Synthesis of Benzyl Formate-*d*. Deuterated sodium formate (0.88 g, 12.7 mmol), benzyl bromide (1.51 mL, 12.7 mmol), and HMPA (13 mL) were added together in a 25 mL round-bottom flask. The mixture was stirred at room temperature for 60 h. The content of the flask was then poured into deionized H_2O (100 mL). The organic phase was separated off, and the aqueous phase was extracted several times with ether. The ether solution was successively washed with deionized H_2O and saturated aqueous NaCl and dried over $MgSO_4$. Evaporation of solvent yielded a yellow oil which was then subjected to purification by flash chromatography on silica gel using pentane−ether (100:3) as the eluent. A colorless oil (1.72 g, 87%) was obtained after the removal of solvent. ^{1}H NMR (300 MHz, C_6D_6): δ 7.2−7.3 (m, 5H, Ph), 5.1 (s, 2H, CH_2).

Synthesis of Benzyl Formate-^{13}*C*. ^{13}C-Enriched formic acid (>99%), benzene (10 mL), DBU (1.61 mL, 10.5 mmol), and benzyl bromide (1.38 mL, 11.6 mmol) were successively added into a 25 mL round-bottom flask equipped with a magnetic stirbar. The mixture was heated to 80 °C and refluxed at this temperature for 2 h, and the reaction was monitored by TLC. The reaction mixture was then cooled to room temperature and poured into H_2O (100 mL). The organic layer was separated, and the aqueous phase was extracted several times with ether. The ether solution was successively washed with deionized H_2O and saturated aqueous NaCl and dried over $MgSO_4$. Evaporation of the solvent yielded a yellow oil which was then subjected to purification by flash chromatography on silica gel using pentane−ether (100:3) as the eluent. A colorless oil (1.2 g, 82.3%) was obtained after the removal of solvent. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.15 (d, 1H, J_{HC} = 226.2 Hz), 7.30−7.39 (m, 5H), 5.21 (d, 2H, J_{HC} = 3.3 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.8 (COO), 129.8, 129.4, 128.5, 128.3, 65.7 (d, J_{CH} = 2.2 Hz, CH_2).

Preparation of Vinyl-*1*-d_1 Benzyl Ether. In the drybox, Tebbe reagent (4.3 g, 15.1 mmol) was weighed into a 100 mL round-bottom flask and dissolved in CH_2Cl_2 (24 mL). The flask was capped with a rubber septum and brought out of the drybox. In another 100 mL round-bottom flask equipped with a magnetic stirbar, benzyl-*d* formate was dissolved in a mixed solvent of CH_2Cl_2−THF (18 mL:6 mL) containing pyridine (100 μL). Both flasks were cooled to −40 °C. Tebbe reagent was added into the ester solution via cannula over a 0.5 h period. After the addition was complete, the flask was warmed to room temperature and stirred for another 0.5 h, then was cooled back down to −10 °C. A 15% NaOH solution (5 mL) was added to quench the reaction, and the mixture was filtered through a pad of Celite to remove the solid. The filtrate was concentrated and stirred rapidly while pentane (200 mL) was added. The resulting mixture was filtered again through a pad of Celite, and the filtrate was passed through a neutral alumina column using pentane as an eluent. Evaporation of the solvent yielded a yellow oil (1.02 g, 61%) which was determined to be pure by ^{1}H NMR. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.4 (m, 5H, Ph), 4.8 (s, 2H, CH_2), 4.32 (m, 1H), 4.10 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.3 (CH(OBn), J_{CD} = 27.7 Hz), 136.8, 128.4, 127.8, 127.5, 87.0 (olefinic CH_2), 69.9 (OCH_2Ph).

Synthesis of Vinyl-α-^{13}*C* Benzyl Ether. A procedure similar to that used for the preparation of the deuterium-labeled compound gave a yellow oil (0.66 g, 56%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.3−7.38 (m, 5H, Ph), 6.88 (dd, 0.5H, J_{HC} = 181.9 Hz), 6.27 (dd, 0.5H, J_{HC} = 181.9 Hz), 4.77 (d, 2H, J_{HD} = 3.1 Hz, CH_2), 4.27−4.34 (m, 1H, CH_2), 4.07−4.11 (m, 1H, CH_2). ^{13}C (75 MHz, $CDCl_3$): δ 151.6, 136.8, 128.5, 127.9, 127.5, 87.3 (d, J_{CC} = 78.8 Hz, olefinic CH_2), 70.1 (OCH_2Ph).

Synthesis of $(TFA)_2(PPh_3)_2Ru(^{13}CHOCH_2Ph)$ (13). In the drybox, complex **2** (90.4 mg, 0.086 mmol) was weighed into a 50 mL Schlenk flask equipped with a magnetic stirbar and dissolved in CH_2Cl_2 (10 mL). ^{13}C-Labeled benzyl vinyl ether (40 μL, 0.29 mmol) was added. The flask was capped with a rubber septum and brought out of the drybox. The solution was stirred at room temperature for 2 h until the color of the solution turned to yellow. All the volatiles were removed under vacuum, and the residue was washed twice with cold pentane; then the supernatant was carefully removed via a cannula filter. The remaining solid was dried under vacuum to give a yellow powder. Yield = 60 mg, 65%. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 14.81 (t, J_{HP} = 4.26 Hz, Ru=*C*H), 14.29 (t, J_{HP} = 4.34, Ru=CH), 4.44 (s, CH_2). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 297.46 (t, J_{CP} = 11.2 Hz, J_{CH} = 158 Hz, Ru=C), 163 (J_{CP} = 37.14 Hz, CO_2CF_3), 112.9 (quartet, J_{CF} = 288.6 Hz, CF_3), 84.1 (d, J_{CC} = 3.8 Hz, CH_2). ^{31}P NMR (161.85 MHz, CD_2Cl_2): δ 35.5 (d, J_{CP} = 11.1 Hz).

Synthesis of $(TFA)_2(PPh_3)_2Ru(CDOCH_2Ph)$ (12). A procedure similar to that used for the synthesis of the ^{13}C-labeled compound was employed here. ^{2}H NMR (61.25 MHz, CD_2Cl_2): δ 14.58.

Reaction of 2 with 2,3-Dihydrofuran. In the drybox, **2** (6.6 mg, 6.3 × 10^{-3} mmol) and 2,3-dihydrofuran (1.0 μL, 0.013 mmol) were added into a 5 mm J-Young valve NMR tube containing CD_2Cl_2. The mixture was heated at 40 °C for 15 min, and a bright yellow solution resulted. The NMR spectrum was then recorded. ^{1}H NMR (300 MHz,

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CD_2Cl_2): δ 14.49 (t, J_{HP} = 4.96 Hz, $Ru{=}CH$), 14.55 (t, J_{HP} = 4.9 Hz, $Ru{=}CH$), 6.7 (d, 1H, J_{HH} = 10.74 Hz, CH), 6.24 (dd, 1H, J_{HH} = 11.23 and 14.92 Hz, CH), 5.84 (pseudo-quartet, 1H, CH), 4.37 (t, 2H, J_{HH} = 6.6 Hz, OCH_2), 2.51 (pseudo-quartet, 2H, CH_2). ^{31}P NMR (161.85 MHz, CD_2Cl_2): δ 44.17.

Synthesis of $(TFA)_2(PPh_3)_2Ru(CHN(C_{12}H_8))$ (16). In a drybox, complex **2** (50 mg, 0.048 mmol) and 9-vinylcarbazole (18.8 mg, 0.096 mmol) were weighed into a small flask equipped with a Teflon valve and a magnetic stirbar and dissolved in CH_2Cl_2 (5 mL). The reaction mixture was then stirred at 40−50 °C for 38 h, and a clear reddish-brown solution resulted. All the volatiles were removed under high vacuum. The residue was redissolved into a minimum amount of CH_2Cl_2, and the mixture was cooled down to −78 °C. Next, pentane was added dropwise to the CH_2Cl_2 solution under rapid stirring to generate a fine precipitate. The supernatant was removed via a cannula filter. The remaining solid was washed twice with pentane and dried *in vacuo* to give a yellow powder. Yield = 40 mg, 80%. ^1H NMR (300 MHz, CD_2Cl_2): δ 13.51 (t, 1H, J_{HP} = 11.5 Hz, $Ru{=}CH$). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 253.11 (t, J_{CP} = 16 Hz). ^{31}P NMR (161.85 MHz, CD_2Cl_2): δ 50.41. Anal. Calcd for $C_{53}H_{39}F_6NO_4P_2Ru$: C, 61.75; H, 3.813; N, 1.36. Found: C, 61.57; H, 3.87; N, 1.04. FAB-HRMS: *m*/*z* calcd for $C_{51}H_{38}F_3NO_2P_2Ru$ (M^+ − TFA) 917.1373. found 917.1321.

Synthesis of $(TFA)_2(PPh_3)_2Ru(CHNCOCH_2CH_2CH_2)$ (17). A procedure similar to that used for the synthesis of compound **16** was used in the synthesis of **17**. The mixture was stirred at 40−50 °C for 72 h, and the product (33 mg, 66%) was isolated in a similar manner. ^1H NMR (300MHz, CD_2Cl_2): δ 14.33 (t, 1H, J_{HP} = 1.80 Hz). ^{31}P NMR (161.85 MHz, CD_2Cl_2): δ 34.17.

Synthesis of $(TFA)(PPh_3)Ru(vinylimidazole)_2Ru(CHCHCPh_2)$ (19). Inside the dry box, **2** (97.1 mg, 0.093 mmol) was weighed into a small Schlenk flask equipped with a magnetic stirbar and dissolved in CH_2Cl_2 (5 mL). Vinylimidazole (10.2 μL, 0.113 mmol) was added to the flask via a gas-tight syringe. The flask was then capped with a rubber septum and brought out of the drybox. The mixture was stirred at 40 °C for 7 h, and all the volatiles were removed under high vacuum. The residue was redissolved in a minimum amount of benzene, and the product was precipitated out by dropwise addition of pentane. The supernatant was removed with a cannula, and the product was further purified by redissolving in a minimum amount of CH_2Cl_2 and cooling to −78 °C. Ether was then added dropwise to the solution to precipitate a green powder which was dried *in vacuo*. Yield = 60 mg, 57%. ^1H NMR (300 MHz, CD_2Cl_2): δ 18.5 (t, 1H, J_{HP} = 12.83 Hz, $Ru{=}CH$), 8.34 (d, 1H, J_{HH} = 3.76 Hz, $Ru{=}CH{-}CH$). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 321.59 (d, J_{CP} = 13.83 Hz, J_{CH} = 141.4 Hz, $Ru{=}CH$). ^{31}P NMR (161.85 MHz, CD_2Cl_2): δ 41.7. Anal. Calcd for $C_{47}H_{39}N_4O_4F_6PRu$: C, 58.2; H, 4.05; N, 5.78. Found: C, 58.5; H, 4.52; N, 6.24. FAB-HRMS: *m*/*z* calcd for $C_{45}H_{39}F_3N_4O_2PRu$ (M^+ − TFA) 857.1806, found 857.1815.

Preparation of Benzyl Vinyl Sulfide. Benzyl disulfide (6.19 g, 24.6 mmol) was dissolved in THF (30 mL) in a 250 mL round-bottom flask equipped with a magnetic stirbar and degassed for 19 min with a stream of argon. Vinylmagnesium bromide (60 mL, 0.1 M solution in THF) was added to the above solution slowly with a syringe. The mixture was stirred at room temperature for 5 h. The progress of the reaction was monitored by TLC. The reaction was quenched by the addition of 15% aqueous NaOH solution at 0 °C, and the mixture was then filtered through a pad of Celite. THF was evaporated, and the residue was extracted with ether. The ether extract was then washed with 15% aqueous NaOH solution and dried over Na_2SO_4. Evaporation of the solvent yielded a yellow oil which was distilled in a Kugelrohr distillation apparatus to give a colorless oil (2.4 g, 65%). ^1H NMR (300 MHz, CD_2Cl_2): δ 7.26−7.36 (m, 5H, Ph), 6.39 (dd, 1H, J_{HH} = 10.2, 16.8 Hz), 5.12−5.2 (m, 2H), 3.92 (s, 2H, CH_2).

Synthesis of $(TFA)_2(PPh_3)_2Ru(CHSCH_2Ph)$ (20). In the drybox, **2** (87.6 mg, 0.084 mmol) was weighed into a small Schlenk flask equipped with a magnetic stirbar and dissolved in CH_2Cl_2 (5 mL). Benzyl vinyl sulfide (40 μL, 0.27 mmol) was added, and the Schlenk flask was capped with a rubber septum and brought out of the drybox. The mixture was stirred at room temperature for 48 h, and the resulting reddish-brown solution was dried under vacuum. The residue was dissolved in a minimum amount of CH_2Cl_2, and the flask was cooled down to −78 °C. Pentane was added dropwise via a cannula to rapidly precipitate a red powder which was washed twice with cold pentane and dried *in vacuo*. Yield = 40 mg, 48%. ^1H NMR (300 MHz, CD_2Cl_2): δ 17.43 (t, 1H, J_{HP} = 3.91 and 3.41 Hz, $Ru{=}CH$), 3.7 (s, 2H, CH_2). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 306.6 (t, J_{CP} = 10.99 and 8.31 Hz, J_{CH} = 152.9 Hz, $Ru{=}CH$), 47.06 (SCH_2). ^{31}P NMR (161.85 MHz, CD_2Cl_2): δ 32.53. Anal. Calcd for $C_{47}H_{38}O_4F_6P_2SRu$: C, 57.85; H, 3.92. Found: C, 58.31; H, 3.75. FAB-HRMS: *m*/*z* calcd for $C_{46}H_{38}F_3O_2P_2SRu$ (M^+ − TFA) 875.1063, found 875.1074.

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Supplementary Material Available: Table of experimental data, thermal ellipsoid drawings of **8**, and tables of anisotropic displacement coefficients, atomic coordinates, interatomic distances and angles, and torsion angles (17 pages); listing of structure factors (11 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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