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Water-Soluble Ruthenium Alkylidenes: Synthesis, Characterization, and Application to Olefin Metathesis in Protic Solvents

David M. Lynn, Bernhard Mohr, Robert H. Grubbs,* Lawrence M. Henling, and Michael W. Day

Contribution from the Arnold and Mabel Beckman Laboratories of Chemical Synthesis, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125

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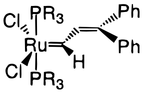
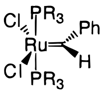
Abstract: Ruthenium alkylidenes **6** and **7** bearing cationically functionalized phosphine ligands are soluble and stable in protic solvents and initiate olefin metathesis reactions in methanol, water, and aqueous emulsions. NMR spectroscopy data and X-ray diffraction analyses of alkylidene **6** suggested that these new alkylidenes were structurally similar to previously reported complexes of the type $(PR_3)_2Cl_2Ru{=}CHR$, in which the alkylidene substituents lie in the Cl−Ru−Cl plane. The anionic chloride ligands of complexes **6** and **7** were found to undergo facile ligand exchange reactions with other anions in protic solution. Both alkylidenes initiate the ring-opening metathesis polymerization (ROMP) of strained, cyclic olefins in water. However, the propagating species in these reactions decompose prior to complete consumption of monomer. These complexes initiate the quantitative, living polymerization of functionalized monomers in water in the presence of a Brønsted acid. Both chain termination and chain transfer reactions were experimentally demonstrated to be absent on the time scale of these acid-activated polymerizations. Alkylidenes **6** and **7** react readily with acyclic olefins: alkylidene **6** reacted with *trans*-2-butene to yield a new ethylidene complex in either methanol or water, and the treatment of **6** with tri(ethylene glycol) methyl vinyl ether in water yielded water-soluble Fischer−carbene complex **16**.

Introduction

The introduction of well-defined, ruthenium-based alkylidene complexes such as **1** and **2** has significantly broadened the scope of the olefin metathesis reaction.[1,2] The exceptional functional group tolerances of these late-metal complexes offer several advantages: in addition to enabling the metathesis of highly functionalized olefins, substrates and solvents can be employed without the rigorous purification and drying normally required for the use of early metal alkylidenes. Importantly, the observation that **1** and **2** remained active toward metathesis in organic solvents in the presence of intentionally added water[2] introduced the opportunity to apply these complexes to olefin metathesis reactions in aqueous environments.



1a, R = Ph
1b, R = Cy



2a, R = Ph
2b, R = Cy

We recently reported the application of alkylidenes **1b** and **2b** to the living ring-opening metathesis polymerization (ROMP) of functionalized norbornene and 7-oxanorbornene monomers in aqueous emulsions and suspensions.[3] These polymerization reactions took place in the absence of chain termination and chain transfer reactions, and were useful in the synthesis of block copolymers by ROMP in aqueous environments. Kiessling *et al.* have extended the use of these biphasic systems to the polymerization of water-soluble, carbohydrate-functionalized monomers to yield new, biologically active glycopolymers.[4] The general application of complexes **1** and **2** to olefin metathesis in aqueous solution, however, has been limited by their insolubilities in protic solvents.

The ROMP of strained, cyclic olefins in aqueous solution initiated by ruthenium complexes [e.g. $RuCl_3{\cdot}xH_2O$ or $Ru(H_2O)_6$-tos$_2$, tos = *p*-toluenesulfonate] is well-known.[5] While these "classical" initiators are completely soluble in water, the lack of preformed alkylidene moieties in these pre-catalysts limits their practical usefulness. For example, initiation efficiency is

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[1] For details regarding the synthesis and applications of ruthenium benzylidene complexes, see: (a) Belderrain, T. R.; Grubbs, R. H. *Organometallics* **1997**, *16*, 4001. (b) Schwab, P. E.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100. (c) Schwab, P. E.; France, M. B.; Grubbs, R. H.; Ziller, J. W. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2039.

[2] For details regarding the synthesis and applications of vinyl-substituted alkylidenes, see: (a) Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1993**, *115*, 9858. (b) Nguyen, S. T.; Johnson, L. K.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 3974.

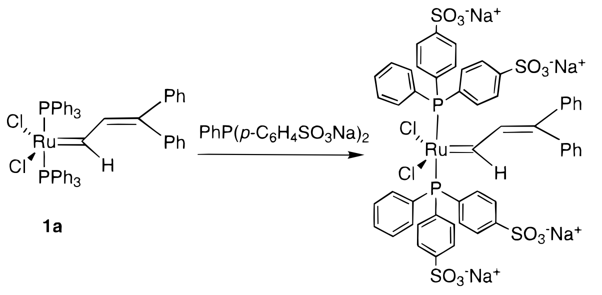
[3] Lynn, D. M.; Kanaoka, S.; Grubbs, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 784.

[4] For recent reports on the synthesis of new glycopolymers using alkylidene **2b** in aqueous environments, see: (a) Gordon, E. J.; Sanders, W. J.; Kiessling, L. L. *Nature* **1998**, *392*, 30. (b) Kanai, M.; Mortell, K. H.; Kiessling, L. L. *J. Am. Chem. Soc.* **1997**, *119*, 9931. (c) Manning, D. D.; Hu, X.; Beck, P.; Kiessling, L. L. *J. Am. Chem. Soc.* **1997**, *119*, 3161. (d) Manning, D. D.; Strong, L. E.; Hu, X.; Beck, P.; Kiessling, L. L. *Tetrahedron* **1997**, *53*, 11937. For reports on the synthesis of these polymers using ill-defined ruthenium initiators, see: Mortell, K. H.; Weatherman, R. V.; Kiessling, L. L. *J. Am. Chem. Soc.* **1996**, *118*, 2297 and references therein.

[5] For the application of "classical" ruthenium initiators to ROMP in aqueous media, see: (a) Hillmyer, M. A.; Lepetit, C.; McGrath, D. V.; Novak, B. M.; Grubbs, R. H. *Macromolecules* **1992**, *25*, 3345. (b) Feast, W. J.; Harrison, D. B. *J. Mol. Catal.* **1991**, *65*, 63. (c) Novak, B. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 7542. (d) Novak, B. M.; Grubbs, R H. *J. Am. Chem. Soc.* **1988**, *110*, 960.

10.1021/ja0003167 CCC: $19.00

poor and these initiators cannot be used to initiate living ROMP.[6] Furthermore, complexes such as $RuCl_3{\cdot}xH_2O$ and $Ru(H_2O)_6$-tos_2 do not initiate the metathesis of acyclic olefins, and thus cannot be applied to cross-metathesis[7] or ring-closing metathesis (RCM)[8] reactions in protic solvents. In an attempt to develop water-soluble derivatives of more active, well-defined alkylidenes, our group initially reported ruthenium alkylidene **3** bearing water-soluble triarylphosphine ligands.[9] This complex was synthesized *via* the exchange of the triphenylphosphine ligands in alkylidene **1a** with the commercially available PhP-(p-$C_6H_4SO_3Na)_2$ ligand (eq 1).



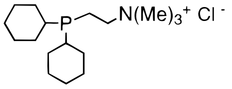
(1)

1a

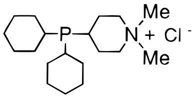
3

While alkylidene **3** was soluble in water, it did not initiate ROMP in aqueous solution. We attribute this lack of activity to the relatively small cone angle and poor electron-donating character of the coordinated triarylphosphine ligands. In general, the metathesis activities of alkylidenes of the type $(PR_3)_2Cl_2$-$Ru{=}CHR$ are maximized by the coordination of sterically bulky, electron-rich trialkylphosphines.[10] Tricyclohexylphosphine (PCy_3) has served as a model ligand for alkylidenes of this type, having the requisite combination of steric and electronic character necessary to produce stable, catalytically active alkylidenes soluble in organic solvents (such as **1b** and **2b**).

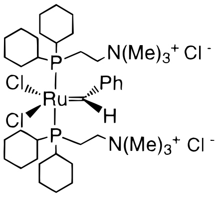
To overcome the lack of reactivity observed for alkylidene **3**, we designed water-soluble aliphatic phosphines **4** and **5**.[11] These ligands were designed to be similar to PCy_3, and an experimental determination of the steric and electronic parameters for these phosphines suggested that they were attractive ligands for the development of new water-soluble alkylidenes.[11] Complexes **6** and **7** formed from these complexes initiated olefin metathesis in water and methanol, and their activities as catalysts for living ROMP[12] and ring-closing metathesis (RCM)[13] were recently demonstrated. Herein, we provide a detailed characterization of the structures and properties of alkylidenes **6** and **7**, and describes in full the activities of these complexes toward the metathesis of cyclic and acyclic olefins in protic solvents.



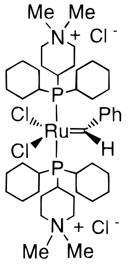
4a, X = Cl ⁻
4b, X = I ⁻



5a, X = Cl ⁻
5b, X = I ⁻



6



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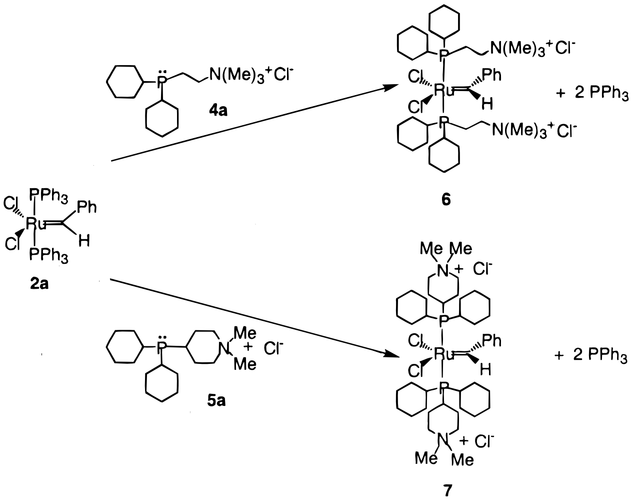
Results and Discussion

Our initial investigations into the development of water-soluble ruthenium alkylidenes were directed toward the synthesis of new phenyl-substituted alkylidenes (benzylidenes). Benzylidene complexes, such as **2b**, have been shown to be highly stable and initiate olefin metathesis reactions far more rapidly than otherwise equivalent vinyl-substituted alkylidenes (such as **1**).[2b] Ruthenium benzylidenes **6** and **7** were prepared in a single step by direct exchange of the triphenylphosphine ligands in alkylidene **2a** with phosphines **4a** and **5a** (Scheme 1), in analogy to the synthesis of alkylidene **2b**.[11] Alkylidenes **6** and **7** are soluble in protic, high-dielectric solvents such as water, methanol, and water/THF mixtures, and are completely insoluble in other common organic solvents including acetone, THF, and benzene. Complex **7** is additionally soluble in dichloromethane, but it decomposes rapidly (over a period of hours) in this solvent. Surprisingly, both complexes are also completely insoluble in Lewis acidic, Lewis basic, and Lewis neutral chloroaluminate–imidazolium ionic liquid melts.[14]

Scheme 1. Synthesis of Water-soluble Alkylidenes **6** and **7** via Direct Phosphine Exchange



Alkylidenes **6** and **7** are stable in methanol solution for over 3 weeks; however, significant decomposition is observed after

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[6] It has been estimated that fewer than 1% of the metal centers in these ill-defined initiators are converted to catalytically active alkylidenes.

[7] For recent references regarding ruthenium-catalyzed cross-metathesis, see: (a) O'Leary, D. J.; Blackwell, H. E.; Washenfelder, R. A.; Grubbs, R. H. *Tetrahedron Lett.* **1998**, *39*, 7427. (b) O'Leary, D. J.; Blackwell, H. E.; Washenfelder, R. A.; Miura, K.; Grubbs, R. H. *Tetrahedron Lett.* **1999**, *40*, 1091. (c) Brümmer, O.; Rückert, A.; Blechert, S. *Chem. Eur. J.* **1997**, *3*, 441.

[8] For recent reviews on RCM, see: (a) Grubbs, R. H.; Chang, S. *Tetrahedron* **1998**, *54*, 4413. (b) Grubbs, R. H.; Miller, S. J.; Fu, G. C. *Acc. Chem. Res.* **1995**, *28*, 446.

[9] Grubbs, R. H. In *Aqueous Organometallic Chemistry and Catalysis*; Horváth, I. T., Joó, F., Eds.; Kluwer Academic Publishers: The Netherlands, 1995; p 15.

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

[11] Mohr, B.; Lynn, D. M.; Grubbs, R. H. *Organometallics* **1996**, *15*, 4317.

[12] Lynn, D. M.; Mohr, B.; Grubbs, R. H. *J. Am. Chem. Soc.* **1998**, *120*, 1627.

[13] Kirkland, T. A.; Lynn, D. M.; Grubbs, R. H. *J. Org. Chem.* **1998**, *63*, 9904.

only 2 days in aqueous solution. The nature of this unexpectedly rapid decomposition in water is not known. Bimolecular decomposition to form stilbene (the organic fragment expected from a bimolecular coupling process) is not observed by ^{1}H NMR spectroscopy in solutions of decomposed **6** or **7**, suggesting that unique decomposition pathways may be accessible for these complexes in protic, high-dielectric solvents.

Alkylidenes **6** and **7** are highly air-sensitive in solution, and traces of adventitious oxygen result in rapid decomposition (within minutes) to a brilliant green solution. Solutions of these air-oxidized alkylidenes contain phosphine oxide as the single phosphorus-containing species, as determined by ^{31}P NMR.[15] This conversion to a green solution has been observed for structurally related ruthenium alkylidenes upon exposure to air in organic solution.[16] However, oxidative decomposition occurs much more slowly in these organic systems. Therefore, in contrast to the use of more oxidatively stable alkylidene **2b**, the solvents used to dissolve alkylidenes **6** and **7** must be rigorously degassed and all manipulations should be carried out using standard Schlenk techniques. Both alkylidenes **6** and **7** also decompose slowly under an atmosphere of air in the solid state, and should be stored and manipulated under an inert atmosphere.

Determination of Alkylidene Structure and Geometry. The NMR spectroscopic features of alkylidenes **6** and **7** are suggestive of the structures and geometries presented in Scheme 1, in which the disposition of the chloride ligands is *cis*, the two coordinated phosphine ligands are *trans*, and the alkylidene substituents lie in the Cl−Ru−Cl plane. These assignments have been made in analogy to the structures of parent alkylidene **2b** and other complexes of the type $(PR_3)_2Cl_2Ru{=}CHR$ bearing bulky trialkylphosphines.[1,2]

The ^{1}H NMR signals for the alkylidene protons in these complexes were observed as singlets. The lack of observable phosphorus−hydrogen coupling is consistent with a proposed Karplus-type relationship for P−H coupling constants in complexes of this type, in which a dihedral angle of 90° between the Ru−P and alkylidene C−H bonds is assumed to result in a near-zero P−H coupling constant.[1,2,10,16] This empirical relationship between the spatial orientation of alkylidene substituents and P−H coupling constants has been suggested for several related ruthenium alkylidene complexes based on correlations between NMR solution data and solid-state geometries determined from X-ray diffraction analyses.[17] For example, the alkylidene substituents in **1a** and **2a**, having triphenylphosphine ligands, lie in the P−Ru−P plane in the solid state and phosphorus coupling to the alkylidene proton is observed by ^{1}H NMR spectroscopy (J = 10−11 Hz).[1,2] The alkylidene substituents in **1b** and **2b**, however, lie in the Cl−Ru−Cl plane (orthogonal to the P−Ru−P plane) in the solid state, and the alkylidene proton resonances are observed as singlets.[1,2] The lack of observable P−H coupling for **6** and **7** suggests the geometries shown in Scheme 1, and is consistent with the coordination of electron-rich, sterically demanding phosphines. The ^{31}P NMR resonances of these complexes also appear as singlets, reflecting the equivalent, *trans*-disposition of the two coordinated phosphines. No evidence for the formation of analogous complexes having *cis*-phosphines was observed in any case.

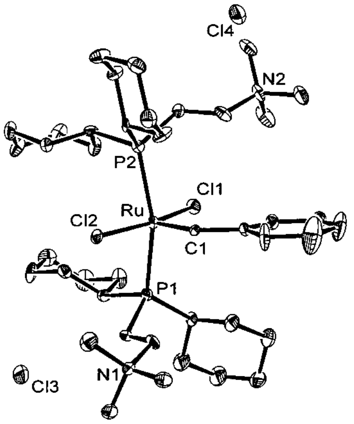

Figure 1. ORTEP drawing of alkylidene **6** (solvent molecules and hydrogen atoms omitted for clarity). Thermal ellipsoids are drawn at 50% probability.

Table 1. Selected Bond Lengths and Angles for Alkylidene **6**

Bond Lengths (Å)			
Ru−P1	2.384(2)	Ru−Cl1	2.393(2)
Ru−P2	2.393(2)	Ru−Cl2	2.399(2)
Ru−C1	1.816(7)		
Bond Angles (deg)			
C1−Ru−P1	99.5(2)	P1−Ru−P2	160.39(8)
C1−Ru−P2	99.8(2)	P1−Ru−Cl2	89.81(7)
C1−Ru−Cl1	103.6(2)	P2−Ru−Cl2	87.07(8)
C1−Ru−Cl2	88.1(2)	Cl1−Ru−P2	90.03(8)
P1−Ru−Cl1	89.11(8)	Cl1−Ru−Cl2	168.26(8)

A definitive determination of the structure of alkylidene **6** was made by X-ray diffraction analysis of a single crystal of this complex. Alkylidene **6** was recrystallized from a methanol/dichloromethane/diethyl ether solvent mixture to provide dark purple needles suitable for X-ray crystallographic analysis. An ORTEP diagram of the data from this analysis is shown in Figure 1. The coordination sphere around the ruthenium atom is distorted square pyramidal, with the phosphines and chloride ligands forming the base of the pyramid. Selected bond lengths and angles (Table 1) are consistent with those obtained for related complexes, such as **2b**.[1a,b] The alkylidene substituents are twisted 4.7° out of the Cl1−Ru−Cl2 plane (roughly orthogonal to the P1−Ru−P2 plane), revealing that the proposed NMR solution structure of this complex is retained in the solid state.

Synthesis of Related Alkylidenes. Cationic phosphines **4b** and **5b**, having iodide rather than chloride counterions, can also be employed in the synthesis of new alkylidene complexes *via* exchange with the triphenylphosphine ligands in alkylidene **2a**. It is noteworthy, however, that this particular phosphine exchange is concomitant with an anion metathesis reaction between the ammonium−iodide substituents on the phosphine and the ruthenium−chloride bonds in the alkylidene complexes. This exchange process is remarkably facile, and proceeds to

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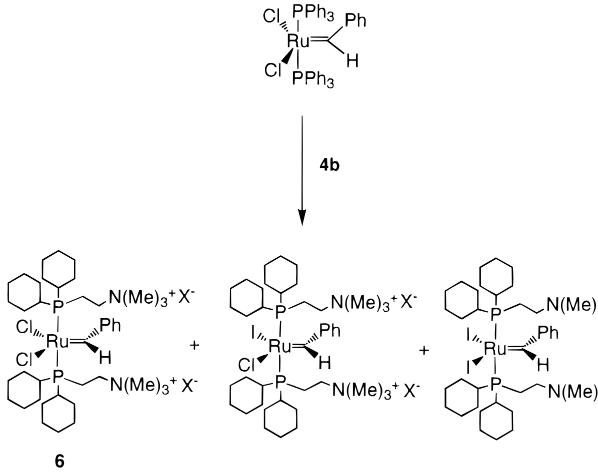
(14) For recent reports of organometallic chemistry and catalysis in ionic liquids, see: (a) Herrmann, W. A.; Bohm, V. P. W. *J. Organomet. Chem.* **1999**, *572*, 141. (b) Dullius, J. E. L.; Suarez, P. A. Z.; Einloft, S.; de Souza, R. F.; Dupont, J.; Fischer, J.; De Cian, A. *Organometallics* **1998**, *17*, 815. (c) Adams, C. J.; Earle, M. J.; Roberts, G.; Seddon, K. R. *Chem. Commun.* **1998**, 2097.

(15) The nature of the inorganic decomposition products is not known.

(16) Nguyen, S. T. Ph.D. Thesis, California Institute of Technology, 1995.

(17) This proposed relationship has been used to characterize the geometries of the alkylidene fragments in complexes of the type $(PR_3)_2Cl_2Ru{=}CHR$ based on NMR solution data correlated with solid-state geometries determined by X-ray diffraction (see refs 1, 2, and 10). While this relationship may prove useful, it does not appear to be completely general. A recent correlation of ^{1}H NMR P−H coupling constant data taken from a variety of published ruthenium alkylidenes with respect to the dihedral angles between the Ru−P and alkylidene C−H bonds in these complexes (determined by X-ray diffraction analysis) does not yield a sinusiodal Karplus-type relationship. Assignment of alkylidene geometries made strictly from NMR data, therefore, should be made with discretion. Sanford, M. S.; Matzger, A. J.; Grubbs, R. H. 1999. Unpublished results.

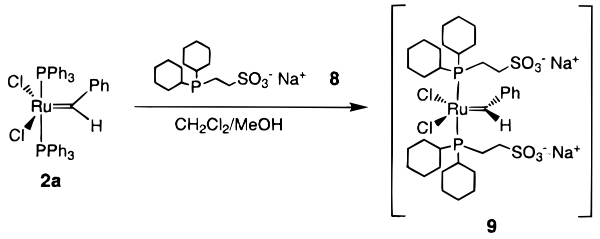
yield a mixture of dichloro, diiodo, and chloro/iodo mixed-halide alkylidene species (eq 2), as determined by ^1H NMR spectroscopy.



(2)

Chen *et al.* recently confirmed this observation by direct mass spectrometric observation of mixed-halide species following electrospray ionization of alkylidenes synthesized with phosphine **4b**.[18] As ruthenium alkylidenes of the type $(PR_3)_2X_2Ru{=}CHR$ bearing iodides as X-type ligands are generally less active than their dichloro-substituted counterparts in organic solvents,[10] iodide salts **4b** and **5b** were not investigated further as ligands for the synthesis of water-soluble, ruthenium alkylidene complexes. The facile nature of this anion exchange reaction should also be borne in mind with respect to the application of alkylidenes **6** and **7**, because substrate counterions and anion-containing additives such as emulsifiers could significantly alter the identity of the catalytic species in these reactions (as discussed below).

In addition to alkylidenes **6** and **7**, we were interested in the synthesis of water-soluble alkylidene complexes bearing anionically functionalized phosphine ligands. Treatment of alkylidene **2a** with 2.2 equiv of sulfonated phosphine **8**[11] in a mixture of methanol and methylene chloride was not sufficient to achieve complete phosphine exchange. Instead, the reaction proceeded to generate a mixed-phosphine species, as determined by the presence of an A−B quartet in the ^{31}P NMR spectrum of the crude reaction mixture. However, treatment of **2a** with 4.0 equiv of **8** yielded a single new alkylidene species (**9**), as determined by NMR spectroscopy [^1H NMR: singlet, 20.66 ppm (alkylidene-H); ^{31}P NMR: singlet, 35.58 ppm] (eq 3). The observed downfield chemical shift of the alkylidene proton relative to complexes **6** and **7** is consistent with the coordination of more electron-rich phosphine **8**.[10] Alkylidene **9** was stable in the crude reaction mixture; however, repeated attempts to isolate this new species resulted in rapid decomposition.[19] The instability of this alkylidene was unfortunate, because previous analysis of the electronic character of anionic phosphine **8** ($\chi = -2.1$ cm^{-1})[11] suggested that alkylidene **9** would be very active water-soluble metathesis catalyst.



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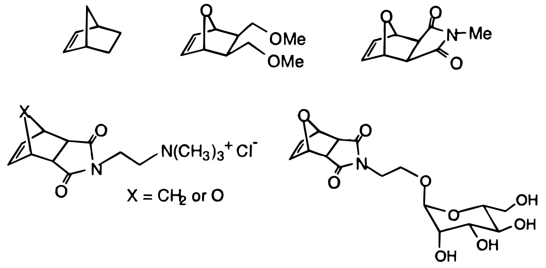
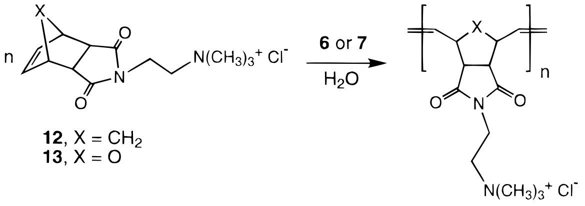


Figure 2. Selected norbornene and 7-oxanorbornene derivatives which will polymerize employing alkylidenes **6** and **7** in water, methanol, and aqueous emulsions.

Application of Alkylidenes 6 and 7 to ROMP in Aqueous Media. Initial experiments demonstrated that alkylidenes **6** and **7** served as efficient initiators for the ROMP of a variety of functionalized norbornenes and 7-oxanorbornene derivatives in water, methanol, and aqueous emulsions.[20] Figure 2 presents representative examples of monomers which can be polymerized employing these alkylidenes.

Initiation occurred rapidly and quantitatively in aqueous solution employing alkylidenes **6** and **7**. Initiation efficiency could be easily determined by the quantitative conversion of the initiating benzylidene species to broad upfield alkylidene resonances (≈19.2 ppm) in the ^1H NMR spectra of these reactions. The spectroscopic observation of propagating alkylidenes in these aqueous polymerizations was important, as propagating species have never been observed for aqueous ROMP initiated by “classical” ruthenium complexes. Furthermore, the direct observation of propagating species allowed the progress of the reactions to be monitored spectroscopically throughout the course of the reaction (as discussed below).

Although initiation occurred in a well-defined manner, the propagating species in the above reactions decomposed before polymerization was complete. For example, in the ROMP of water-soluble monomers **12** and **13** (eq 4), conversions ranging from 45−80% were observed under a variety of experimental conditions.[12,21] The color of these polymerization reactions progressed from light orange, a color indicative of the propagating alkylidene species, to a darker orange color, and a propagating alkylidene could no longer be observed by ^1H NMR spectroscopy. The polydispersity indices (PDIs) for the resulting polymers were broad (Figure 3, PDI ≈ 2.3), and the polymer molecular weights were lower than anticipated. Therefore,



(4)

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[18] Hinderling, C.; Adlhart, C.; Chen, P. *Angew. Chem., Int. Ed.* **1998**, *37*, 2685.

[19] The reasons for this rapid decomposition are not entirely clear. As relatively nonpolar solvents were employed in the workup of this complex, decomposition may have resulted from the intramolecular displacement of a chloride ligand by a sulfonate group. As ruthenium alkylidenes bearing alkoxy or carboxy X-type ligands are generally less stable than halide-substituted analogues, the formation of a six-membered chelate and the precipitation of NaCl could result in rapid alkylidene decomposition.

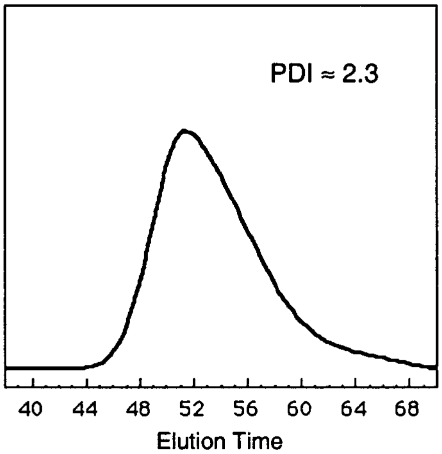
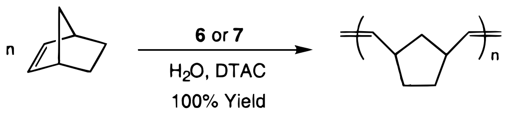


Figure 3. Aqueous GPC trace of poly-**13** initiated by alkylidene **6** in H_2O at 45 °C.

aqueous polymerizations initiated by alkylidenes **6** and **7** could not be considered living polymerizations.

A notable exception to the problems discussed above was the emulsion polymerization of norbornene initiated by alkylidenes **6** and **7** (eq 5, DTAC = dodecyltrimethylammonium chloride). In these cases, initiation was rapid and monomer was *quantitatively* consumed. Apparently, the reactivity of this unsubstituted monomer resulted in a rate of propagation that was sufficiently competitive with catalyst decomposition. The PDIs for polynorbornene produced in this system were as low as 1.18. However, the molecular weight distributions were sometimes bimodal, having small fractions of high molecular weight material observed as a small shoulder in the GPC traces of these samples.

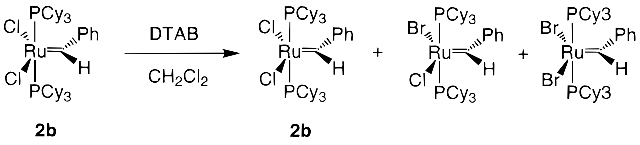


(5)

DTAC was employed as the emulsifier in the above reactions, rather than the corresponding bromide salt (DTAB) employed in previously reported experiments,[3] to avoid potential anionic ligand exchange reactions that could affect the structures and activities of alkylidenes **6** and **7**. We previously reported the living polymerization of strained, cyclic olefins in aqueous emulsions employing alkylidene **2b**.[3] Subsequent investigations into the effect of the emulsifier on the alkylidene **2b** in those reactions revealed that the bromide anion of DTAB underwent a facile exchange with the chloride ligands of the alkylidene, even in neat methylene chloride. For example, in the presence of 10 equiv of DTAB in methylene chloride, alkylidene **2b** is converted to a mixture of the dichloro, dibromo, and mixed-halide species, as determined by ^1H NMR spectroscopy (Scheme 2).

In view of the gross excess of DTAB used in the reported polymerization reactions (up to 500 equiv relative to catalyst), it is assumed that ligand substitution occurred rapidly during the reaction to yield a slower, dibromo-substituted catalytic species. Ruthenium alkylidene complexes of this type, having larger, less electronegative anionic ligands have been shown to be less active than the parent dichloro-substituted alkylidene **2b**. Therefore, future applications of aqueous emulsion-type polymerizations employing ruthenium alkylidenes should be conducted with this potential ligand exchange in mind. The use of dodecyltrimethylammonium chloride (DTAC), for example, should preserve the robust activities of alkylidenes **1** and **2**. It bears noting that while this ligand exchange process may yield a less active catalyst, the polymerization of monomers conducted in the presence of DTAB remains living.[3]

Scheme 2. Facile Scrambling of Anionic Cl− Ligands in **2b** in the Presence of Emulsifier



Living ROMP in Aqueous Solution Employing Alkylidenes 6 and 7. During previous work with "classical" ruthenium catalysts in water, it was discovered that initiation periods for these ill-defined complexes were shorter at lower pH, and that the catalysts decomposed rapidly in alkaline solution.[22] Consistent with these earlier observations, it was found that the presence of hydroxide ions in aqueous solutions of **6** and **7** also promoted the rapid decomposition of these well-defined alkylidenes. For example, the addition of 1 equiv of NaOD to alkylidene **6** in D_2O resulted in an instantaneous change in the color of the reaction solution from red/orange to dark orange. Further examination of this reaction *via* ^1H NMR spectroscopy suggested that NaOD reacted stoichiometrically with **6** to yield a new, nonalkylidene species which then underwent rapid decomposition to a mixture of products.

The color change in the above reaction suggested that the catalyst deactivation observed during polymerizations employing alkylidenes **6** and **7** could potentially be due to the presence of hydroxide ions. As described above, the color of the reaction solutions in these polymerizations progressed from light orange to dark orange, concomitant with the decomposition of the propagating species. In an attempt to eliminate potential concentrations of hydroxide ions, we investigated the polymerization of monomers **12** and **13** in the presence of Brønsted acids. As described above, alkylidenes **6** and **7** undergo facile anionic ligand exchange reactions in aqueous solution. Because the activities of these catalysts could be directly influenced by these ligand exchange reactions, DCl was chosen as the Brønsted acid used in subsequent experiments to minimize the impact of this exchange processes.

It was found that monomers **12** and **13** could be *quantitatively* polymerized when small amounts of DCl (from 0.3 to 1.0 equiv relative to alkylidene complexes **6** or **7**) were added to the reaction mixture (eq 6). Additionally, the presence of acid was found to have a profound effect on polymerization rates: polymerizations were up to 10 times faster than those to which no acid had been added. Two propagating alkylidene species were observed by ^1H NMR spectroscopy at room temperature both *during* polymerization and *after* complete consumption of monomer (the nature of the two propagating species observed in these reactions will be discussed below). The PDIs of

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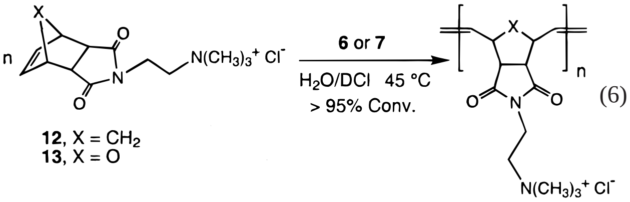
(20) Alkylidenes **6** and **7** were designed to initiate olefin metathesis in water and methanol. An additional and completely unexpected mode of reactivity, however, was discovered during the synthesis and isolation of these new complexes. Specifically, the alkylidene protons in complexes **6** and **7** were found to exchange rapidly and quantitatively with deuterons when they were dissolved in perdeuterated protic solvents such as D_2O and CD_3OD. The nature of this new reaction will be reported separately in a forthcoming contribution.

(21) These monomers were designed incorporating chloride counterions to alleviate potential anionic ligand exchange reactions which would alter the structure of the catalysts in these reactions.

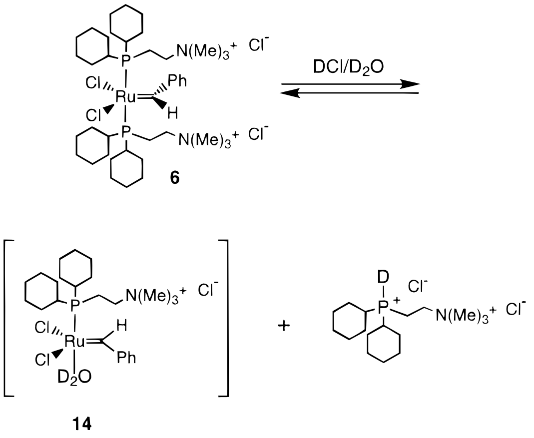
(22) Novak, B. M. Ph.D. Thesis, California Institute of Technology, 1989.



(6)

polymers produced in the presence of acid (Figure 4, PDI = 1.24) were considerably lower than the PDIs of polymers synthesized in the absence of acid (Figure 3, PDI ≈ 2.3). Finally, the injection of additional monomer into these completed polymerization reactions resulted in further quantitative polymerization, suggesting that these polymerizations could be living.

Spectroscopic Analysis of Activated Alkylidenes. To better understand the role of the acid in the above reactions, the reaction of DCl with alkylidene **6** was studied in the absence of monomer. The addition of 0.3 equiv of DCl to a solution of complex **6** in D_2O generated 0.3 equiv of a new alkylidene species (**14**, eq 7), identified *via* ^1H and ^{31}P NMR spectroscopy as a monophosphine derivative of **6**.



(7)

A resonance for the alkylidene proton of alkylidene **14** was observed in the ^1H NMR spectrum at 20.12 ppm (d, $J_{PH} = 12.0$ Hz), slightly downfield from that of alkylidene **6** (s, 19.76 ppm). Additionally, the resonances for the protons on the phenyl group were shifted approximately 0.1 ppm downfield. These data indicated that the added acid did not react irreversibly with the ruthenium−carbon bond, but rather reacted with **6** to yield a new alkylidene species. Examination of this reaction by ^{31}P NMR spectroscopy indicated that the acid protonated an equivalent of phosphine to yield a new alkylidene species and an equivalent of a phosphonium salt (eq 7). A resonance observed at 46.18 ppm in the ^{31}P NMR spectrum was assigned as alkylidene **14**. The structure of alkylidene **14** is assumed to be that shown in eq 7, in which the alkylidene substituents are perpendicular to the Cl−Ru−Cl plane, based on the observation of phosphorus coupling to the alkylidene proton in the ^1H NMR spectrum of this complex. We believe that this alkylidene geometry is consistent with a less sterically encumbered metal center.

A well-known reaction pathway for the decomposition of transition metal alkylidenes is bimolecular coupling to generate an internal olefin and a dimeric metal-containing species.[23] For ruthenium alkylidenes of the type $(PR_3)_2Cl_2Ru{=}CHR$, this type of bimolecular coupling is sterically discouraged by the two coordinated phosphine ligands which surround the alkylidene moiety. Considering this, it might be anticipated that a monophosphine complex, having a more sterically accessible metal center, would be predisposed to rapid bimolecular decomposition. Indeed, this has been observed for alkylidenes such as **1** and **2** in organic solution in the presence of phosphine scavengers such as $CuCl_2$.[10] Surprisingly, however, accelerated decomposition was not observed upon the protonation of phosphine in aqueous solution. In these aqueous systems, it is believed that the coordination of water molecules to the monophosphine species stabilizes the alkylidene and prevents bimolecular decomposition.

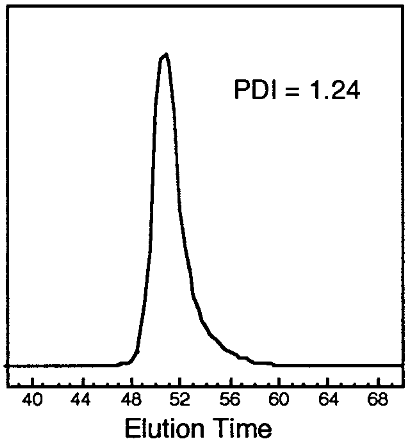


Figure 4. Aqueous GPC trace of poly-**12** initiated by alkylidene **6** in D_2O in the presence of 1.0 equiv of DCl at 45 °C ($M_n = 11500$, PDI = 1.24).

The addition of 1.0 equiv of DCl to alkylidene **2** yielded an equilibrium mixture of monophosphine and bisphosphine alkylidene species in a ratio of 1:2. The reasons for this nonstoichiometric protonation behavior are not fully understood, and both alkylidenes decomposed more rapidly under these conditions in the absence of monomer. In polymerization reactions conducted in the presence of 1.0 equiv of DCl, however, the propagating bisphosphine and monophosphine propagating species were *significantly* more stable than either initiating species **6** or **7**. For example, alkylidene **6** decomposes in aqueous solution over a period of days at room temperature. However, both the bisphosphine (**6**) and monophosphine (**14**) propagating species could be observed for over 3 months in polymerization reactions to which acid had been added. The addition of more than 1.0 equiv of DCl to **6** or **7** resulted in rapid decomposition.

Experimental Determination of Living Polymerizations. The results above suggested that the aqueous polymerizations carried out in the presence of acid could be living. To determine experimentally that a polymerization is living, propagation must be shown to take place in the absence of termination and chain transfer reactions.[24] To satisfy these criteria, an NMR-scale polymerization of monomer **12** was conducted in D_2O employing DCl (1.0 equiv relative to alkylidene), and the relative amount of propagating species was quantified *via* integration of the alkylidene protons relative to the aromatic protons of the polymer endgroups (eq 8).

As previously described, two propagating species, corresponding to bisphosphine alkylidene **6** and monophosphine alkylidene **14**, were observed for acid-activated polymerization

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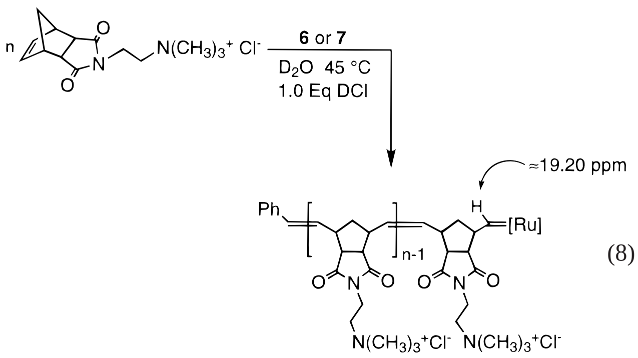
[23] (a) Ivin, K. J.; Mol, J. C. *Olefin Metathesis*; Academic Press: London, 1997. (b) Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis*, 2nd ed.; John Wiley & Sons: New York, 1992. (c) Schrock, R. R.; Sharp, P. R., *J. Am. Chem. Soc.* **1978**, *100*, 2389.

[24] For leading references on experimental criteria for the determination of living polymerizations, see: (a) Quirk, R. P.; Lee, B. *Polym. Inter.* **1992**, *27*, 359. (b) Matyjaszewski, K. *Macromolecules* **1993**, *26*, 1787.

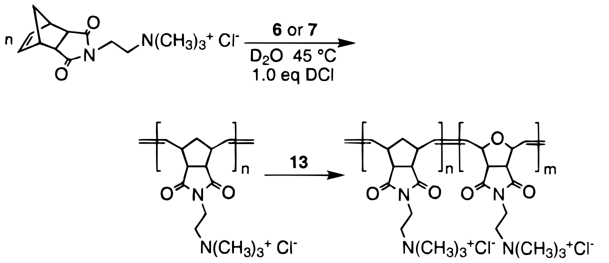


(8)

reactions initiated by alkylidene **6** at room temperature. The ^{1}H NMR resonances for these two alkylidenes coalesced at higher temperatures, however, indicating rapid equilibration *via* phosphine scrambling. Accordingly, the above NMR-scale experiment was carried out at 45 °C, as the resonances for the two propagating alkylidene species were observed as a single broad resonance at 19.2 ppm at this temperature.

After 15 min, the reaction was >95% complete and the relative integration of the alkylidene protons of the propagating species did not decrease either during the reaction or after all of the monomer had been consumed (data not shown).[12] In fact, the propagating species remained intact for an additional 15 min (at this temperature) in the absence of monomer before beginning to slowly decompose. Polymerization remained quantitative in experiments employing more than 1.0 equiv of acid; however, the propagating species were observed to steadily decompose over the course of the reactions. The stability of the propagating species for alkylidene **7** upon addition of acid was demonstrated in a similar manner.

A block copolymerization of monomers **12** and **13** was carried out *via* sequential monomer addition to further demonstrate the robust nature of the propagating species in the presence of 1.0 equiv of acid. After complete polymerization of monomer **12**, 20 equiv of monomer **13** were injected. Monomer **13** was completely consumed (eq 9), and the concentration of the propagating species remained constant both during and after the polymerization of the second block (as determined by ^{1}H NMR spectroscopy), providing further evidence for the living nature of these acid-activated polymerizations.



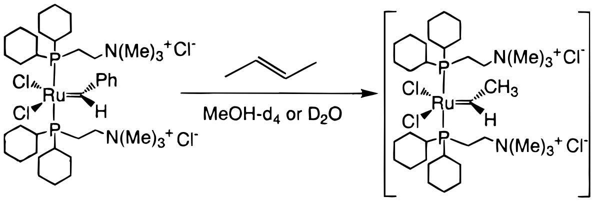
(9)

Within the limits of NMR sensitivity, the direct observation and quantification of the propagating alkylidenes in the above experiments demonstrated the absence of chain termination in these reactions. To demonstrate the absence of chain transfer in these reactions, the polymerization of monomer **12** was initiated by alkylidene **6** in the presence of 1.0 equiv of DCl, and the PDI of the resulting polymer was determined (by GPC) at various points in the reaction. Monomer **12** was polymerized quantitatively over a period of 20 min, and an aliquot of the reaction mixture was removed for analysis. The reaction was allowed to stand for an additional 20 min before polymerization was terminated. The PDI obtained for the initial aliquot was 1.24, and the PDI did not broaden upon standing. This experiment demonstrated the relative absence of chain transfer reactions on the time scale of the polymerization reaction.[25]

The equilibrium presented in eq 7 provides a convenient explanation for the rate enhancements, and thus the living nature, of the polymerizations described above. For alkylidene complexes of the type $(PR_3)_2Cl_2Ru{=}CHR$, olefin metathesis has been shown to proceed through a mechanism in which a phosphine dissociates from the metal center.[10] Rates of olefin metathesis in organic systems have been increased by the addition of phosphine scavengers, although the catalysts rapidly decompose under these conditions. In analogy to organic systems, protons appear to behave as phosphine scavengers in aqueous polymerizations employing alkylidenes **6** and **7**. Notably, the rate of olefin metathesis in these systems is increased *without* concomitant acceleration of catalyst decomposition. The difference in the rates of propagation and termination under acidic conditions allows for rapid, quantitative conversion of monomer in a living manner. Additionally, the presence of acid eliminates the potential for the generation of hydroxide ions, formed by the reaction of the basic phosphines with water, which would lead to catalyst decomposition.

Reactivity with Acyclic Olefins. The applications of "classical" ruthenium olefin metathesis initiators are generally limited to the ROMP of functionalized norbornenes and 7-oxanorbornenes.[5] These complexes lack preformed alkylidene moieties, and the presence of highly strained, cyclic olefins is required to generate the active species in the polymerization of those monomers. Thus, these complexes are not useful in initiating reactions with acyclic olefins and cannot be used to perform cross-metathesis reactions or ring-closing metathesis (RCM) reactions in aqueous solution or methanol.[26]

In contrast to "classical" ruthenium complexes, well-defined alkylidenes **6** and **7** react readily with terminal and internal acyclic olefins. For example, simply bubbling a stream of *trans*-2-butene through a solution of alkylidene **6** in either methanol or water resulted in quantitative conversion to a new ruthenium ethylidene complex (eq 10, determined by ^{1}H and ^{31}P NMR spectroscopy).



6

(10)

The reaction of alkylidene **6** with ethylene in methanol or water did not yield the desired ruthenium methylidene complex. Several new resonances were observed in the far upfield region of the ^{1}H NMR spectrum (−15.9 ppm) and were assigned as ruthenium hydride species. Due to the rapid rate of this apparent decomposition reaction, a definitive determination of the

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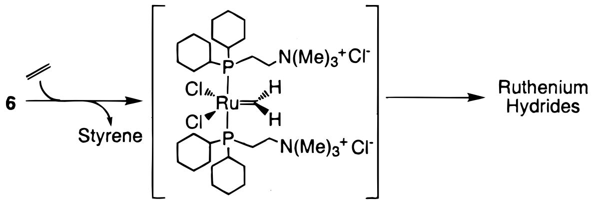
(25) Additionally, the ratio of trans to cis olefins in the backbone of the polymer (approximately 90% *trans*/10% *cis* as determined by ^{1}H NMR integration) remained constant over the entire reaction period, providing further evidence for the absence of chain transfer reactions in these systems.

(26) The propagating species in aqueous polymerizations initiated by "classical" ruthenium complexes do react with acyclic olefins under certain circumstances. For example, very high concentrations of *cis*-2-butene-1,4-diol or its dimethyl ether can be employed as chain transfer agents to obtain modest molecular weight control in aqueous systems (see ref 5b). In general, however, these complexes do not react with acyclic olefins and cannot be used for applications such as cross-metathesis or RCM in water or methanol.

decomposition pathway could not be made. However, the presence of styrene in the reaction mixture suggested that ethylene reacted first *via* metathesis with alkylidene **6** to produce a new methylidene species (**15**, eq 11), which then rapidly decomposed to ruthenium hydrides. These results support a recent report from our group in which ruthenium methylidenes were found to decompose by different mechanisms than ruthenium alkylidenes.[27]



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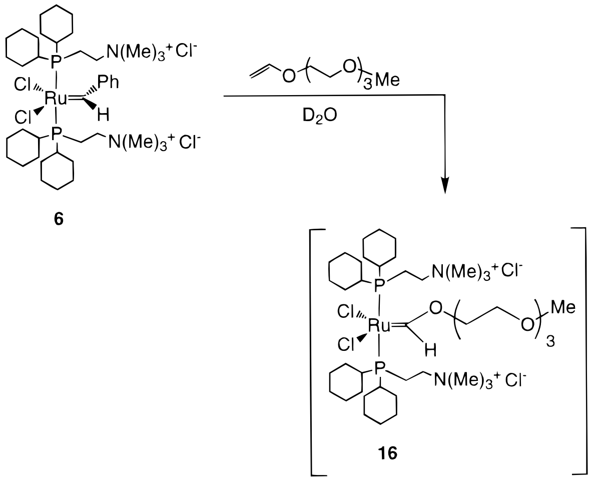
(11)

The results of this experiment carried unfortunate implications for the application of these alkylidenes to the cross-metathesis of acyclic olefins and the RCM of α,ω-dienes, because methylidene **15** would be the catalytically active species in these reactions. In fact, these alkylidenes did not promote the RCM of α,ω-dienes in methanol or water. However, diene substrates containing a terminal olefin and one nonterminal olefin were readily cyclized.[13] In the RCM of these substrates, metathesis occurred initially at the terminal olefin, the olefin substituent was transferred to the alkylidene upon cyclization, and the catalytically active species in those reactions were more stable, substituted alkylidenes. The instability of **15** also limited the application of **6** and **7** to the cross metathesis of acyclic terminal olefins. For example, the dimerization of 9-decene-1-ol in methanol using 1 mol % **7** proceeded to yield the desired product in 2% isolated yield.

Ruthenium alkylidenes have also been shown to react with vinyl ethers to yield metathesis-inactive Fischer-carbene complexes.[28] For example, ethyl vinyl ether reacts with ruthenium benzylidene **2b** to yield styrene and a new Fischer-carbene complex. Alkylidenes **6** and **7** react in an analogous manner with vinyl ethers in protic solvents: the treatment of alkylidene **6** with an excess of tri(ethylene glycol) methyl vinyl ether in aqueous solution yielded water-soluble Fischer-carbene complex **16** (eq 12), identified by the characteristic upfield resonance of the carbene proton (singlet, 14.34 ppm).[28] Ethyl vinyl ether has been used as an effective terminating reagent for living ROMP initiated by alkylidenes **1** and **2** in organic solvents.[29] Treatment of the aqueous living polymerization reactions shown in eq 6 with an excess of tri(ethylene glycol) methyl vinyl quantitatively terminated polymerization and endcapped the resulting polymers with a terminal methylene ($=CH_2$) group.



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16

(12)

Summary

Alkylidenes **6** and **7** are completely soluble in protic solvents and initiate olefin metathesis reactions in methanol, water, and aqueous emulsions. NMR spectroscopy data and X-ray diffraction analysis of alkylidene **6** suggested that these new alkylidenes were structurally similar to previously reported complexes of the type $(PR_3)_2Cl_2Ru{=}CHR$. The alkylidene substituents in these complexes lie in the Cl−Ru−Cl plane, as depicted in Scheme 1. This geometry is consistent with the coordination of electron-rich, sterically demanding phosphines **4a** and **5a**. The anionic chloride ligands of complexes **6** and **7** were found to undergo facile ligand exchange reactions with other anions in protic solution. These ligand exchange reactions can directly affect the structure and activities of **6** and **7**, and should be considered as important factors governing the design of substrate structure and general experimental conditions.

Both complexes **6** and **7** initiated the ROMP of a variety of functionalized norbornenes and 7-oxanorbornenes in methanol and water. However, the propagating species in these reactions were observed to decompose prior to complete consumption of monomer. Polymerization was rapid and quantitative in the presence of a Brønsted acid, and alkylidenes **6** and **7** were found to initiate the *living* polymerization of these monomers under acidic conditions. Both chain termination and chain transfer reactions were demonstrated to be absent on the time scale of the polymerizations, indicating that these polymerizations satisfied the fundamental criteria for living systems.

In contrast to "classical" ruthenium complexes, alkylidenes **6** and **7** also reacted readily with acyclic olefins. For example, these complexes reacted with tri(ethylene glycol) methyl vinyl ether in aqueous solution to yield water-soluble Fischer-carbene complex **16**. Initial studies revealed that the application of these complexes to the cross-metathesis of terminal olefins and the RCM of α,ω-dienes was limited by the stability of the catalytically active methylidene species **15** generated in these reactions. This limitation, however, could be overcome through the RCM of water-soluble diene substrates containing a terminal olefin and one internal olefin.[13] The methodology described above provides a solid framework for the application of olefin metathesis to the transformation of more structurally complex, water-soluble substrates, as well as the design of more robust aqueous metathesis catalysts.

Experimental Section

General Considerations. All manipulations involving free phosphines and ruthenium complexes were performed in a nitrogen-filled drybox or by using standard Schlenk techniques under an atmosphere of argon. Argon was purified by passage through columns of BASF R3-11 catalyst (Chemalog) and 4 Å molecular sieves (Linde). ^{1}H NMR (300.1 MHz) and ^{13}C NMR (75.49 MHz) spectra were recorded on a GE QE-300 spectrometer; ^{31}P NMR (161.9 MHz) spectra were recorded on a JEOL GX-400 spectrometer. All chemical shift values are given in ppm and are referenced with respect to residual protons in the solvent for proton spectra, or to phosphoric acid for phosphorus spectra. Gel permeation chromatographs were obtained using an Altex Model 110A

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[27] Ulman, M.; Grubbs, R. H. *J. Org. Chem.* **1999**, *64*, 7202.

[28] Wu, Z.; Nguyen, S. T.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1995**, *117*, 5503.

[29] For recent examples, see: (a) Reference 3. (b) Weck, M.; Schwab, P.; Grubbs, R. H. *Macromolecules* **1996**, *29*, 1789.

pump, a Rheodyne Model 7125 injector with a 100-μL injection loop, through an American Polymer Standards 10-μm mixed-bed column, and a Knauer differential refractometer; dichloromethane was used as the eluent at a flow rate of 1.0 mL/min. The molecular weights and polydispersities of the polymers are reported relative to monodisperse polystyrene standards.

Materials. Dichloromethane, tetrahydrofuran, and pentane were purified by passage through solvent purification columns containing activated alumina. Deionized water and methanol used for the polymerizations were degassed by purging with argon and then stirring under vacuum prior to use. Phosphines **4** and **5**,[11] alkylidenes **6** and **7**,[11] alkylidene **2a**,[1] and monomers **12** and **13**[12] were prepared as previously reported. DCl/D_2O solutions were purchased from Cambridge Isotopes, Inc. and were serially diluted under an inert atmosphere prior to use. All other reagents were reagent grade and used without further purification.

X-ray Diffraction Study of Alkylidene 6.[30] A concentrated solution of alkylidene **6** (0.020 g) in methanol (50 μL) was diluted with methylene chloride (1.5 mL). Dark purple needles of **6** were obtained by slow diffusion of a layer of diethyl ether (1.0 mL) into this solution at room temperature. The crystals fragmented severely upon removal from the mother liquor, and were coated immediately with degassed Paratone oil.

A dichroic purple/orange crystal fragment of the size 0.41 × 0.33 × 0.07 mm^3 was selected, oil-mounted on a glass fiber, and transferred to a CAD-4 diffractometer. 21 914 reflections were collected, 10 474 of which were independent [$R_{\text{int}} = 0.051$; $\text{GOF}_{\text{merge}} = 1.00$]. Data were collected at 85 K with Mo Kα radiation (wavelength = 0.71073 Å). The range of θ used for data collection was 1.57° to 24.97°. The absorption coefficient was 0.886 mm^{-1} and data were not corrected for absorption. Three check reflections were measured every 75 min, with a variance of −1.5%. The crystal system was determined to be monoclinic, and the selected space group ($P2_1/n$) led to successful refinement. Unit cell parameters: $a = 13.958(6)$ Å, $b = 25.919(11)$ Å, $c = 16.819(5)$ Å, $\beta = 101.45(3)°$, $Z = 4$.

The structure was solved with SHELXS-97[31] using the Patterson (primary) and difference Fourier map (secondary) methods. The crystal contained several disordered solvent molecules, modeled as six molecules of dichloromethane with partial occupancies which altogether add to 3.8 full occupancy molecules [empirical formula $C_{41}H_{58}N_2P_2Cl_4Ru\cdot3.8(CH_2Cl_2)$; formula weight 1217.61 (883.78·333.82)]. Hydrogens were placed at geometrically calculated sites. The structure was refined on F^2 against all reflections using SHELXL-97[32] by the full-matrix least-squares method. The goodness-of-fit on F^2 was found to be 2.306. The final R indices [$I > 2\sigma(I)$] were $R(F^2) = 0.0897$ and $R(wF^2) = 0.1518$.

General Polymerization Procedure. In a nitrogen-filled drybox, monomer was added to a septum-capped vial equipped with a Teflon-coated stirbar. Catalyst was added to second a vial and capped with a rubber septum. Outside the drybox, water or methanol was added to each vial *via* a gastight syringe, and the polymerization was initiated by adding the catalyst solution to the vial containing the monomer. Polymerizations were terminated either by adding an excess of ethyl vinyl ether or by removing solvent under vacuum prior to analysis.

General Polymerization Procedure for NMR-Scale Experiments. In a typical experiment, monomer was weighed into an NMR tube and the tube was capped with a rubber septum. Alkylidene was weighed into a vial, and the vial was capped with a rubber septum. Outside the drybox, monomer was dissolved in 250 μL of rigorously degassed D_2O delivered *via* syringe. The pierced septum was wrapped with Parafilm and lowered into the NMR probe (preheated at 45 °C) for 2 min to allow the solution to reach thermal equilibrium. Alkylidene was quickly dissolved in a rigorously degassed solution of DCl in D_2O (0.022 M, a volume containing 1.0 equiv of DCl relative to alkylidene used). The NMR tube was ejected from the probe, the alkylidene solution was injected *via* syringe, and the NMR tube was shaken vigorously and immediately lowered back into the NMR probe for data collection. Alternatively, monomer was dissolved in a degassed solution of DCl in D_2O (a volume and molarity containing 1.0 equiv of DCl relative to the amount of alkylidene to be used) and alkylidene was dissolved in degassed D_2O. The alkylidene solution was then added to the acidic monomer solution *via* syringe.

Emulsion Polymerization of Norbornene. In a nitrogen-filled drybox, norbornene (65.0 mg, 0.690 mmol) and dodecyltrimethylammonium chloride (550 mg) were added to a 10 mL screw-necked pressure flask equipped with a magnetic stirbar, and the flask was sealed with a Teflon needle valve. Alkylidene **6** (5.0 mg, 0.0055 mmol) was weighed into a 1 dram vial, and the vial was capped with a rubber septum. Outside the drybox, water (3 mL) was added to the flask containing monomer and emulsifier *via* syringe under an argon purge, and the mixture was stirred at room temperature until it became an optically clear microemulsion. Occasionally, mild heat was applied to expedite this process. Alkylidene **6** was dissolved in water (1 mL) and the resulting red/orange solution was added to the monomer emulsion *via* syringe under an argon purge. An immediate color change from orange/red to pale yellow was observed upon addition of the catalyst solution to the monomer emulsion. The flask was resealed with a Teflon needle valve, and the reaction was allowed to stir at room temperature. After 10 min, the flask was opened to air, and the contents were precipitated into methanol (750 mL) to yield polynorbornene (65 mg) as a fluffy white solid.

General Procedure for Reaction with Acyclic Olefins. A solution of alkylidene **6** (10 mg, 0.11 mmol) in CD_3OD (0.5 mL) was placed in a NMR tube capped with a rubber septum. This solution was heated to 45 °C and purged with *trans*-2-butene, resulting in a rapid color change from purple to orange. The reaction was monitored by ^1H NMR spectroscopy after 15 min. The reaction proceeded to yield a new alkylidene resonance at 19.29 ppm. Styrene was also observed in the reaction mixture. Analysis of the reaction mixture *via* ^{31}P NMR spectroscopy revealed a new alkylidene species, observed as a singlet at 33.3 ppm. Evaporation of solvent from the reaction mixture yielded the crude ethylidene complex as an orange powder.

Reaction of Alkylidene 6 with Tri(ethylene glycol) Methyl Vinyl Ether. Alkylidene **6** (10 mg, 0.011 mmol) was dissolved in D_2O (0.250 mL). Tri(ethylene glycol) methyl vinyl ether (25 mg, 0.131 mmol, 12 equiv relative to **6**) was dissolved in D_2O (0.250 mL), and the two solutions were mixed. Upon mixing, the color of the reaction mixture changed from red/orange to light orange. This solution was placed in an NMR tube, and the tube was capped with a rubber septum. The reaction mixture was kept at room temperature, and the progress of the reaction was monitored *via* ^1H NMR spectroscopy. The resulting Fischer-carbene complex was observed as a singlet at 14.34 ppm.

Acknowledgment. The authors wish to thank Professor Laura Kiessling, Kathy Mortell, Ross Weatherman, and Laura Strong for providing several carbohydrate-functionalized water-soluble monomers. Aqueous GPC measurements were made by Dr. Rudolf Bruessau at BASF AG Ludwigshafen. This work was supported by the NSF.

Supporting Information Available: Additional details of the X-ray structural determination for alkylidene **6**, including details of the data collection and structural refinement, atomic coordinates, bond lengths and angles, thermal displacement parameters, and hydrogen atomic coordinates (PDF). This material is available free of charge *via* the Internet at http://pubs.acs.org.

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[30] Crystallographic data (excluding structure factors) for the structure of alkylidene **6** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC121704. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033. E-mail: deposit@ccdc.cam.ac.uk).

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