The Organometallic Chemistry of Aqueous Ruthenium(II) with Functionalized Olefins: Complex Formation, Isomerization, and Metathesis Chain Transfer

Thesis by

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To my family

Mom, Dad, Martin, and MaryBeth

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ABSTRACT

The chemistry of aqueous $Ru^{II}(H_2O)_6(tos)_2$ (tos = *p*-toluene sulfonate) (**1**) with functionalized olefins has been investigated. Complexes of the type $(H_2O)_5Ru^{II}(olefin)(tos)_2$ are formed from **1** and monoolefins. Dienes such as diallyl ether and 1,5-hexadiene displace two aquo ligands from **1** to form chelate complexes of the type $(H_2O)_4Ru^{II}(olefin)_2(tos)_2$. Chelation of oxygen containing functionalities such as alcohols, ethers, and sulfonates has also been observed when the functional group is a specified distance from the olefin. Thus, 3-buten-1-ol, 3-butenyl methyl ether, and 2-propenesulfonate anion form chelate complexes $Ru^{II}(H_2O)_4(\eta^1(O):\eta^2(C,C')\text{-}HOCH_2CH_2CH{=}CH_2)(tos)_2$, $Ru^{II}(H_2O)_4(\eta^1(O):\eta^2(C,C')\text{-}CH_3OCH_2CH_2CH{=}CH_2)(tos)_2$, and $Ru^{II}(H_2O)_4(\eta^1(O):\eta^2(C,C')\text{-}OSO_2CH_2CH{=}CH_2)(tos)$, but allyl ethyl ether forms only the olefin complex $Ru^{II}(H_2O)_5(\eta^2(C,C')\text{-}CH_2{=}CHCH_2OCH_2CH_3)(tos)_2$. Carboxylic acid functionalities react irreversibly with **1** to form carboxylate complexes. 3-Pentenoic acid reacts with **1** yielding the bis(olefin)-bis(carboxylate) complex $Ru(H_2O)_2(\eta^1(O),\eta^2(C,C')\text{-}OCOCH_2CH{=}CHCH_3)_2$ which has been structurally characterized.

Olefin isomerization of allylic ethers and alcohols is catalyzed by **1** under mild conditions in aqueous solution to yield the corresponding carbonyl compounds. Non-allylic olefins are also isomerized, although homoallylic alcohols exhibit stability towards isomerization. An exclusive 1,3-hydrogen shift is observed in the **1**-catalyzed isomerization of allyl-*1,1-*d_2 alcohol to propionaldehyde-*1,3-*d_2 and allyl-*1,1-*d_2 methyl ether to 1-propenyl-*1,3-*d_2 methyl ether. The presence of crossover products from the isomerizations of mixtures of (a) allyl-*3-*^{13}C alcohol and allyl-*1,1-*d_2 alcohol and (b) allyl-*1,1-*d_2 methyl ether and allyl ethyl ether demonstrates that the isomerization of both ethers and alcohols occurs *via* intermolecular hydrogen shifts. A modified metal hydride addition-

elimination mechanism involving exclusive Markovnikov addition to the double bond directed by the oxygen functionality of the substrate has been proposed.

The acyclic terminal olefins 3-buten-1-ol and methyl acrylate are effective chain transfer agents in the ROMP the 7-oxanorbornene derivative 5,6-*exo*-bis(methoxymethyl)-7-oxabicyclo[2.2.1]hept-2-ene by **1**, providing the first example of acyclic olefin metathesis in this system. Oligomer samples with M_n as low as 2K have been prepared. End groups corresponding to the alkylidene moieties of the chain transfer agents have been identified in the ^1H and ^{13}C NMR of the oligomer mixtures. Connectivity has been established between these end groups and the polymer chain through two-dimensional ^1H NMR. Ring-opened monomer units end capped by the chain transfer agent have been identified by mass spectrometry techniques.

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CHAPTER 1.

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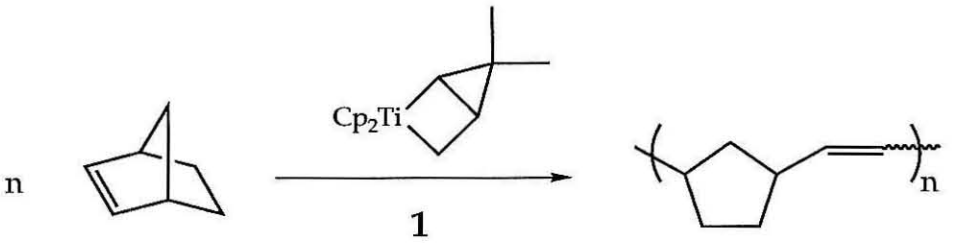
INTRODUCTION

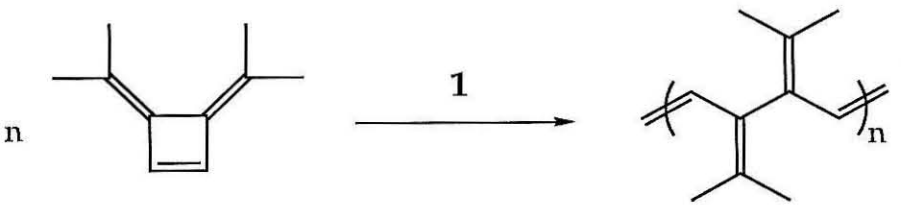
The technology of ROMP[1-3] has advanced considerably in recent years due to the preparation of discrete metal alkylidene and metallacyclobutane species[4] which are highly active catalysts for olefin metathesis.[5,6] These discrete, and often living, polymerization systems are powerful tools for the synthetic polymer chemist, having made possible the design of well-defined block copolymers, polymers with specific end groups, and polymers with polydispersity indices (PDI) approaching 1.

Discrete metathesis catalysts based on titanium have been utilized to prepare a number of new polymeric materials. Titanocyclobutane **1** is active for



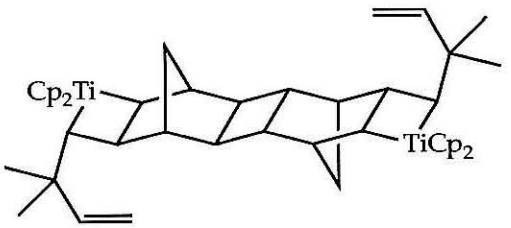
1

the living polymerization of norbornene and yields high molecular weight monodisperse polynorbornene.[7] Other strained cyclic olefins polymerized by **1** include 3,4-diisopropylidenecyclobutene **2**. The cross conjugated polymer **3** resulting from polymerization of **2** is conductive upon iodine doping.[8] The living characteristics of the polymerization system based on **1** allows for specific end capping of the polymer chain[9] and the preparation of well-defined block copolymers of norbornene with various other strained cyclic olefins.[10] Triblock



2 **3**

copolymers of the type ABA have been prepared by endcapping the living polymer chain with telechelic diketone polymers,[11] a reaction which takes advantage of the alkylidene transfer (Wittig) reactivity of transition metal alkylidenes. Alkylidene transfer has also been exploited in the preparation of aldehyde-endcapped polynorbornene. The aldehyde end group serves as an initiator for group transfer polymerization, resulting in polynorbornene-poly(silyl vinyl ether) block copolymers.[12] Di- and tetrafunctional initiators, such as **4**, containing two and four titanocyclobutane units have made possible the more efficient synthesis of ABA triblock copolymers and the preparation of ROMP star polymers.[13]



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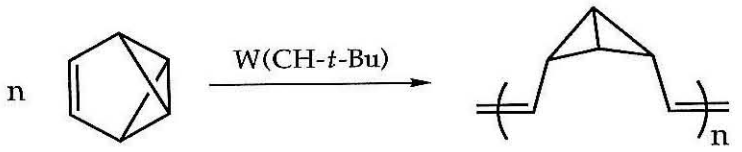
The highly active metathesis catalysts based on tungsten developed by Schrock[14-16] and Osborn[17, 18] allow the polymerization of both strained and unstrained cyclic olefins, yielding a number of polymeric materials with interesting properties. The highly strained monomer benzvalene **5** is polymerized to a thermally unstable, shock-sensitive polymer which can be



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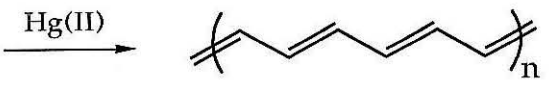
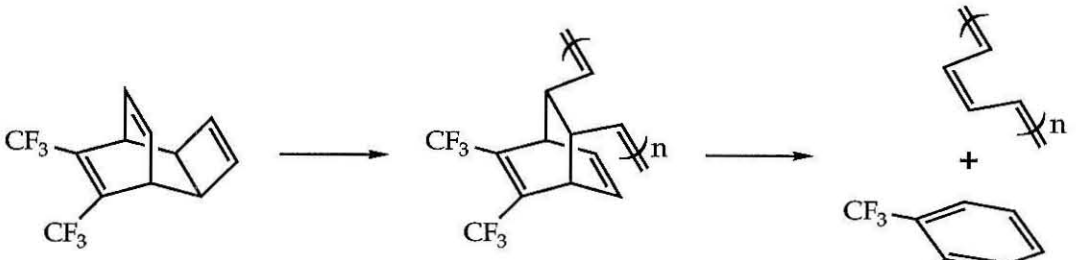
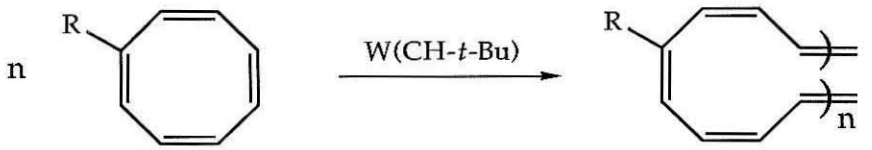


converted to polyacetylene by treatment with mercury salts.[19, 20] A precursor route to polyacetylene also has been developed by Feast. Polymerization of the tricyclic monomer **6**, followed by thermal extrusion of *o*-bis(trifluoromethyl)-



6

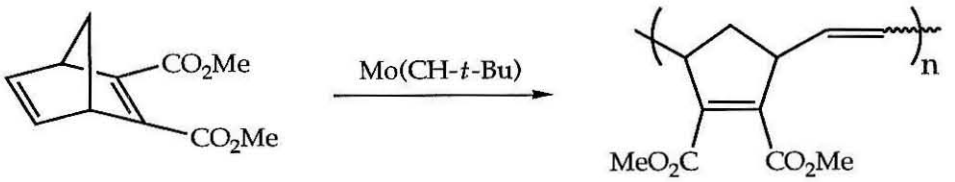
benzene leads to polyacetylene.[21] This technology has been exploited by Schrock in the preparation of a series of polyenes, containing up to 15 double bonds, and the synthesis of polynorbornene-polyacetylene-polynorbornene triblock copolymers.[22] Soluble derivatives of polyacetylene which are highly conjugated and retain the conducting properties of normal polyacetylene are obtained by the neat polymerization of monosubstituted cyclooctatetraenes.[23, 24] These materials have been utilized in the fabrication of solar cells[25] and for non-linear optical



studies.[26] Cyclobutene has been polymerized to fully linear, monodisperse polybutadiene by attenuating the relative rate of propagation versus initiation for W(CH-*t*-Bu)(NAr)(O-*t*-Bu) with added trimethylphosphine.[27] Hydrogenation affords monodisperse polyethylene. Recent advances in the synthesis of tungsten alkylidenes of the type $W(CHAr')(NAr)[OCCH_3(CF_3)_2]_2$ (Ar = 2,6-$Me_2C_6H_3$; Ar' = *o*-$MeOC_6H_4$) have made the preparation of other highly active

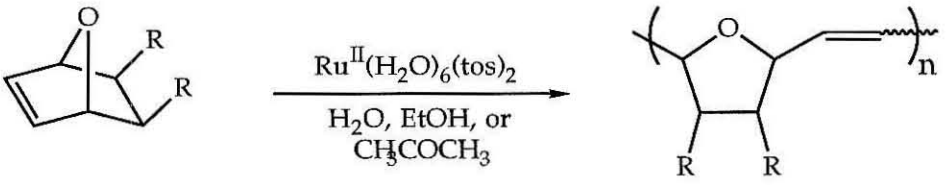
ROMP catalysts high yielding and from easily obtainable starting materials.[28]

Incorporation of functional groups within a polymer chain can have a dramatic influence on the material's mechanical, electrical and thermal properties.[29] Aside from the polymers obtained by end capping techniques,[11, 12, 30] however, almost all polymeric materials produced by ROMP are devoid of functional groups.[31] Indeed, the success of the well-defined ROMP catalysts based on titanium and tungsten is limited by their significant reactivity towards polar functional groups, particularly alcohols, ketones, aldehydes, and esters. While sometimes of synthetic utility,[32-34] this reactivity towards polar functional groups in all cases renders the metal complex inactive as a metathesis catalyst. The oxophilicity of the early transition metals in general also serves to deactivate classical catalyst systems in the presence of polar organic functionality. As a result, the metathesis of functionalized olefins is a goal that, for the most part, has eluded chemists. Some advances have been made in the classical catalyst arena. Unsaturated esters, nitriles, and halides are successfully metathesized by the binary catalyst $WCl_6/SnMe_4$[35] and the ternary catalyst $Re_2O_7/Al_2O_3/SnMe_4$.[35, 36] Among well-defined catalysts, metathesis of functionalized olefins also has met with limited success. The extreme reactivity of early transition metal alkylidene complexes with carbonyl compounds precludes their use for the metathesis of ketone and aldehyde containing olefins. Increased tolerance for ester functionalities, however, is exhibited by the molybdenum catalyst Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$[37, 38] over the tungsten



analogue.[39, 40] In addition, a well-defined rhenium alkylidene complex has been reported to slowly metathesize methyl oleate (methyl *cis*-octadecenoate).[41] Metathesis of protic functionalities, such as alcohols and carboxylic acids, has not been achieved.

In contrast, metathesis catalysts based on the transition metals of group VIII have shown a marked tolerance for functional groups. In fact, early studies on the chloride salts of iridium(III), ruthenium(III) and osmium(III) were actually carried out in alcoholic and even aqueous alcoholic solvents.[42-46] The tolerance of these catalysts for functional groups was demonstrated by the polymerization of alcohol and carboxylic acid substituted norbornenes by $IrCl_3$ in ethanol/benzene.[43] Advances made during the reinvestigation of these late metal systems by our group[47-49] identified the coordination complex $Ru^{II}(H_2O)_6(tos)_2$ (**1**) as a highly active catalyst for the polymerization of substituted norbornenes, 7-oxanorbornenes, and norbornadienes.[47, 49-51] This



R = -CH_2OH, -CH_2OCH_3, -CH_2OTMS, -CH_2COCH_3
-CO_2CH_3, -(COOCO)-, -(CON(Me)CO)-

ROMP system is stable to water, alcohols, and carbonyl compounds: polymerizations can be carried out in neat water, alcohol or acetone and yield high molecular-weight, low dispersity materials in near-quantitative yield. The stability of this, and other, group VIII metathesis catalysts to air and water, as well as their ability to metathesize olefins containing a host of different

functional groups, is a distinct advantage over the early transition metal catalysts which are extremely oxophilic and must be handled using standard Schlenk and drybox techniques.

However, **1**, and all other metathesis catalysts based on the transition metals of group VIII to date, is still an ill-defined system—it contains neither an alkylidene nor metallacyclobutane moieties, either of which is necessary for catalyzing metathesis. Although several methylidene complexes of ruthenium, osmium, and iridium have been prepared,[52-54] they display electrophilicity rather than the nucleophilicity[55-58] which characterizes the metathesis active alkylidenes of the early transition metals.[59] In addition, the mechanism of initiation—the pathway by which the precatalyst and monomer react to generate an alkylidene or metallacyclobutane—for these late transition metal catalysts is unknown. The elucidation of the actual structure of the initial catalytic species in ROMP catalyzed by **1**, therefore, is an immediate goal which would eventually lead to the *ab initio* synthesis of stable, metathesis-active alkylidene or metallacyclobutane species of the group VIII transition metals. In order to achieve this goal, we have explored the basic organometallic chemistry of **1** to gain knowledge of the organometallic transformations that this precatalyst is likely to undergo (Chapters 1 and 2). With this in hand, we have proposed a metathesis initiation mechanism for **1** based on the reactivity patterns we have observed (Chapter 3). We have also used the knowledge gained in the reactions of acyclic, functionalized olefins with **1** to select and implement certain acyclic olefins as chain transfer agents in ROMP of 7-oxanorbornenes, thus gaining further control over this polymerization system (Chapter 3).

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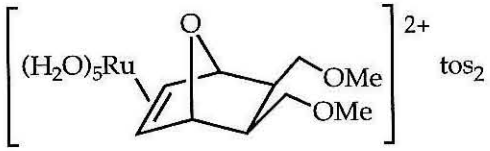
CHAPTER 1

Aqueous Ruthenium(II) Complexes of Functionalized Olefins

Introduction

We recently reported the development of a ring-opening metathesis polymerization (ROMP)[1-4] system based on low valent ruthenium complexes[5-7] that tolerates many organic functionalities known to deactivate early transition-metal metathesis catalysts. The coordination compound $Ru^{II}(H_2O)_6(tos)_2$ (tos = *p*-toluene sulfonate)[8, 9] **1** has demonstrated the greatest promise. This complex polymerizes a large variety of norbornene and 7-oxanorbornene derivatives to high polymer under mild reaction conditions (water or alcoholic solution, 55-70° C).[6, 7, 10, 11] During the course of the polymerization of 5,6-*exo*-bis(methoxy-methyl)-7-oxabicyclo[2.2.1]hept-2-ene **1** is converted to the mono-olefin adduct **2**, which can be observed by ^1H and ^{13}C NMR spectroscopy. This olefin complex is the first observed example of an organometallic complex formed from fully aqueous ruthenium(II) in water.



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Olefin complex **2** is currently our only glimpse into the initiation mechanism of aqueous ruthenium(II)-catalyzed ROMP. That it is involved in the transformation of the pre-catalyst **1** to a ruthenium alkylidene or metallacycle is only inferred, yet we believe this to be a reasonable assumption since the most likely interaction between an olefin substrate and a transition metal is coordination. Our knowledge of this system and further transformations it might undergo is limited, however, by the lack of organometallic chemistry involving aqueous ruthenium(II). In fact, relatively few studies on the

$Ru^{II}(H_2O)_6^{2+}/Ru^{II}(H_2O)_6^{3+}$ ion pair, the only example of a low spin t_{2g}^6–t_{2g}^5 redox couple, have been published,[12-18] and isolation of crystalline samples of a hexaaquoruthenium(II) ion was not achieved until 1982 when Bernhard, et al., reported the preparation of **1**.[9] In addition to electrochemical[19] and spectroscopic[20, 21] studies, **1** has been utilized in the preparation of coordination complexes of ruthenium(II). Its usefulness as a starting material for complexes of heterocyclic nitrogen donors,[22] phosphines,[23] and hydrides has been demonstrated, yet no organometallic complexes derived from aqueous ruthenium(II), aside from $[Ru^{II}(\eta^6\text{-}C_6H_6)(H_2O)_3]^{2+}$ prepared in ethanol from **1** and cyclohexadiene,[24] have been reported.[25]

In contrast, studies on the related ruthenium(II) ammine complexes are in abundance. The interaction of π-acceptor ligands—both nitrogen heterocycles[26-32] such as pyridines and pyrazines and unsaturated hydrocarbons[33-37] such as olefins and acetylenes—with the $(NH_3)_5Ru^{II}$ moiety has been extensively explored and is a classic example of metal to ligand π-back-bonding. The stability of the metal center towards oxidation in these complexes is increased by 0.6 to 1.4 V versus the parent hexaammineruthenium(II) ion.[38, 39] Another characteristic of this system is the presence of only one active site at the metal center. Under most common reaction conditions the pentaammine moiety is inert,[40, 41] and substitution at the sixth site is usually through displacement of the relatively labile aquo ligand. For example, Elliott and Shepherd reported the preparation of a number of pentaammineruthenium(II) complexes of dienes such as 1,3-butadiene, 1,4-pentadiene, and 1,5-hexadiene.[37] In no case did they observe the displacement of an ammine ligand by the pendant olefin.

The lability of the aqueous ruthenium(II) coordination sphere is, therefore, a distinguishing factor between the ammine and aquo systems. The water

exchange rates for **1** and $Ru^{III}(H_2O)_6(tos)_3$ are $(1.8 \pm 0.2) \times 10^{-2}$ s^{-1} and $(3.5 \pm 0.3) \times 10^{-6}$ s^{-1}, respectively, as measured by ^{17}O NMR.[42] Separate resonances for bound and free water are not seen in the ^1H NMR of **1**. As expected, displacement of all six aquo ligands is possible and this reactivity has been exploited in the preparation of the $Ru^{II}(C_5H_5N)_6^{2+}$ and $Ru^{II}(CH_3CN)_6^{2+}$ ions.[22, 42] A substrate which enters the coordination sphere of aqueous ruthenium(II) is therefore surrounded by labile ligands, and hence potentially active catalytic sites. We expect this to have important consequences for the olefin chemistry of the aqueous ruthenium(II) system.

Transition metal-olefin complexes are of fundamental importance in the field of organometallic chemistry. They are key intermediates in almost all catalytic processes involving olefinic substrates including hydrogenation,[43] hydroformylation,[44] hydrosilylation,[45-47] and hydrocyanation.[43, 48, 49] In fact, the first known transition metal organometallic complex, discovered in 1827, was Zeise's salt, an ethylene complex of platinum.[50] Since then, olefin complexes of all the members of the transition series except technetium have been prepared. Olefin-metal bonding is a classic example of transition metal-ligand multiple bonding. In the now widely accepted Dewar-Chatt-Duncanson bonding model,[51, 52] olefins simultaneously act as both σ-donors and π-acids (Figure 1). The filled olefin π-bonding molecular orbital overlaps with a vacant metal orbital of σ-symmetry (d_{z^2}) while a filled metal orbital of π-symmetry (d_{xz} or d_{yz}) back donates to the vacant olefin π^*-antibonding molecular orbital. This depopulation of the olefin π-bonding orbital and population of the olefin π^*-antibonding orbital results in the lengthening of the C=C bond upon coordination and serves to alter the hybridization of the olefin carbons towards an sp^3 configuration. This is evidenced by the positional distortion of the olefin substituents out of the plane

of the C=C bond.[53] Indeed, one extreme of this bonding model considers the olefin-metal bond much like a metallacyclopropane.[54] The relative strength of the two bonding components (σ and π) depends upon the oxidation state and charge on the metal, the substituents on the olefin, and the metal's ancillary ligands.[55] Therefore, qualitative information about the nature of the metal center can be obtained from the scope of different olefins which will successfully complex to a given metal center.

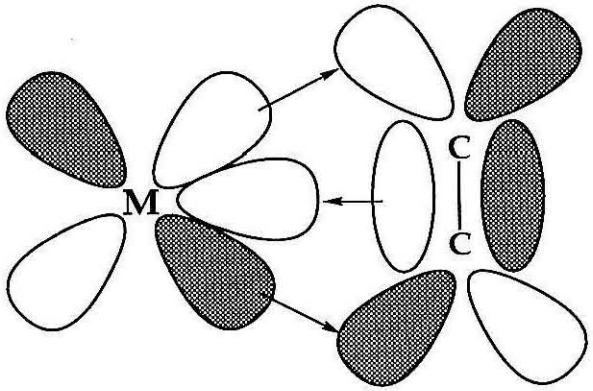


Figure 1. Bonding diagram for a transition metal-olefin bond. Arrows indicate flow of electron density. The filled olefin π-bonding orbital donates electron density to the empty metal orbital of σ-symmetry. The filled metal orbital of π-symmetry back donates to the vacant olefin π^*-antibonding molecular orbital.

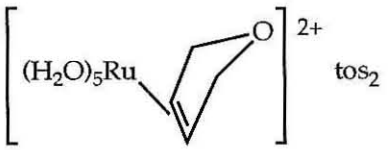
Given the fundamental nature of olefin complexes in organometallic chemistry and catalysis,[50] as well as the continuing emergence of water as an important solvent for catalytic chemistry,[56-60] we have explored the chemistry of aqueous ruthenium(II) with acyclic and monocyclic functionalized olefins in the hopes of gaining information on the basic reactivity patterns of ruthenium(II)

with olefins in aqueous media.[61] The olefin complexes prepared represent a link between classical coordination compounds and organoruthenium chemistry.[62] Our observations regarding the interaction between different pendant functionalities and the ruthenium(II) center have allowed us to predict and circumvent possible catalyst deactivating reactions which would interfere with the ROMP of functionalized monomers, thus further defining the scope of this ROMP system.

Results and Discussion

Olefin complexes of aqueous ruthenium(II) can be prepared by displacement of one or more aquo ligands from $Ru^{II}(H_2O)_6(tos)_2$ **1** at room temperature in aqueous solution. ^1H and ^{13}C NMR data for the complexes prepared are shown in Tables 1 and 2. Since most of the complexes could not be crystallized, the NMR integration ratio of bound olefin to tosylate counterion protons was taken as a measure of stoichiometry and has never exceeded one olefin per ruthenium(II) center with the exception of chelating olefins such as diallyl ether (vide infra). This ratio has been confirmed by elemental analysis of the complexes which could be crystallized. Other functional groups ligate to the ruthenium(II) center and, in the absence of X-ray structural data, we will present spectroscopic evidence in support of this.

In water, excess 2,5-dihydrofuran reacts with **1** to give the mono-olefin adduct **3** (85% yield by NMR) which can be fully characterized by its ^1H and ^{13}C NMR spectra (Table 1). The NMR resonances of the complexed olefin exhibit upfield shifts of the olefinic protons (5.76 to 5.64 ppm), as well as the



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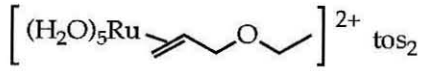
characteristic[37] olefinic carbon upfield shift of ca. 50 ppm (127.0 to 78.1 ppm), relative to those of free olefin. The side-on coordination of the olefin to the metal is indicated by the inequivalence of the allylic protons which now give rise to two doublets at 4.65 and 3.92 ppm (J = 11.0 Hz). NMR integration[63] and

elemental analysis[64] of the ditosylate salt support the formation of a mono-olefin complex. ROMP of 2,5-dihydrofuran is not observed.

A ruthenium(II) complex of allyl ethyl ether **4** can be prepared in a similar manner. Its ^1H NMR spectrum (Table 1) is characteristic of the spectra of allyl moieties bound to the Ru^{II} metal center. The olefin protons shift upfield, but



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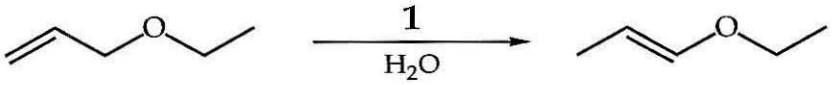
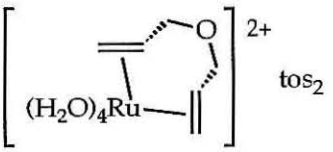
remain essentially unchanged in magnetic equivalence. The two allylic protons, however, are now diastereotopic and resonate at different chemical shifts. The shift difference can be quite dramatic in olefins which have other ligating moieties in addition to the olefin (vide infra). This diastereotopism induced by metal binding extends as far as the $-OCH_2CH_3$ protons which are no longer a simple quartet. In the ^{13}C NMR spectrum of **4**, the olefin carbons, as in **3**, shift upfield by ca. 50 ppm upon binding. The allylic carbon, however, experiences little shift perturbation. Although isolated **4** is stable in solution for days, **1** is observed to catalyze the isomerization of free allyl ethyl ether to 1-propenyl ethyl ether. Details of this reaction, as well as other olefin isomerizations, will be discussed in Chapter 2.

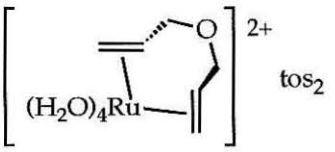


Bis(olefin) complexes of aqueous ruthenium(II) dication are most easily formed with chelating olefins such as diallyl ether. At room temperature in D_2O

diallyl ether and **1** react to form a mono-olefin complex, identified by its coordinated olefin protons at 5.34 (m), 4.91 (d), and 4.77 (d) ppm, which rapidly converts to a second product. Ten inequivalent protons of equal integration can be separated into two sets of five spins by two-dimensional ^{1}H-^{1}H correlation (COSY) NMR spectroscopy (Figure 2). Four olefinic resonances, as identified by their J_{CH} values of ~160 Hz, are observed in the ^{13}C NMR spectrum at chemical shifts upfield by 50 to 60 ppm relative to free diallyl ether. Recrystallization from aqueous 3.6 M *p*-toluenesulfonic acid solution yields canary yellow microcrystals which analyze as $Ru(H_2O)_4(C_6H_{10}O)(tos)_2$.[65] The ^{1}H NMR spectrum of this purified complex **5** reveals that the two sets of five protons are now of unequal intensity (ratio 1 : 1.6 :: isomer A : isomer B). Therefore, a mixture of two diallyl



5a



5b

ether complexes **5a** and **5b** with different solubilities, each having two-fold symmetry (mirror plane and C^2-axis), are formed in a 1 : 1 ratio from free olefin and ruthenium in solution. Heating either mixture to 65 °C in solution fails to change the ratio of the two complexes. An unequal mixture of the isomers can also be generated by preparing the complex from **3** in a displacement reaction (vide infra). This also gives the complexes in a 1.6 : 1 ratio, but with isomer A predominating. Full identification of both the ^{1}H and ^{13}C NMR resonances for each complex was made with the aid of a two dimensional ^{1}H-^{13}C shift correlation NMR spectrum (Figure 3).

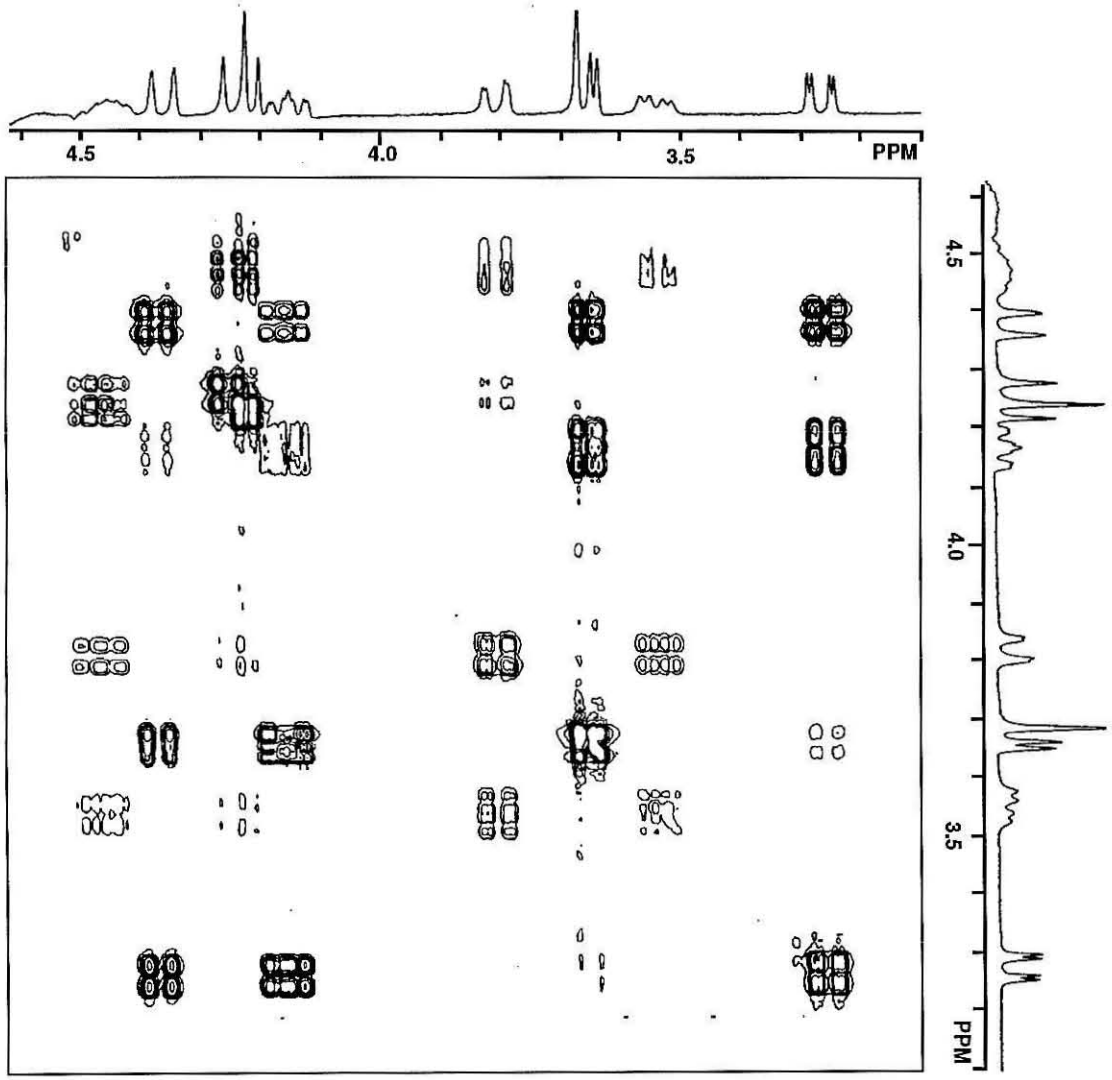


Figure 2. ^{1}H-^{1}H correlated COSY spectrum of Ru^{II}(diallyl ether)$(H_2O)_4(tos)_2$ (**5a, b**).

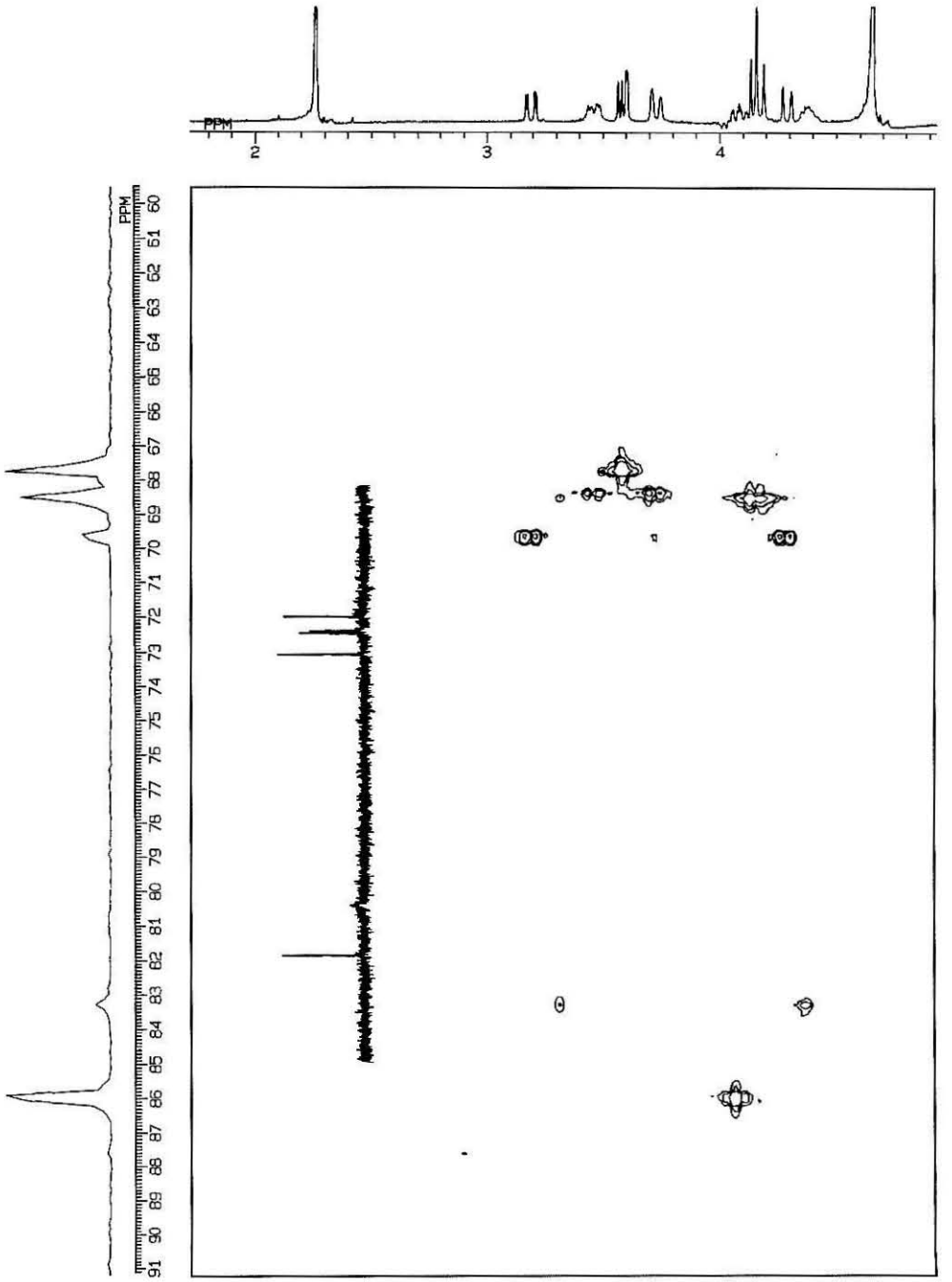
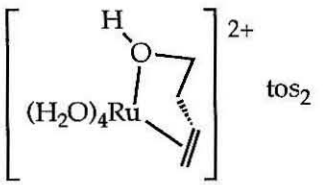


Figure 3. ^{13}C-^{1}H correlation spectrum of Ru^{II}(diallyl ether)$(H_2O)_4(tos)_2$ (**5a, b**). The side spectrum in the f_1 (^{13}C) dimension is projected data. A fully digitized spectrum of the corresponding region is inset.

Chelation of pendant oxygen functionalities has also been observed. For example, 3-buten-1-ol reacts with **1** in water to form the monoolefin complex **6**, which can be isolated by crystallization from concentrated aqueous *p*-toluene-sulfonic acid solution. The ^{13}C NMR spectrum shows the characteristic 50 ppm upfield shift for the olefinic carbons as well as a significant *downfield* shift (61.6 to 73.8 ppm) for the carbinol carbon, indicating proximity to the metal center through coordination of the alcohol oxygen to ruthenium.[66] The elemental analysis of this complex is consistent with $Ru^{II}(H_2O)_4(C_4H_8O)(tos)_2$.[67] The loss of two water molecules from the starting material futher supports a bidentate structure. The ^1H NMR spectrum was fully assigned with the aid of a two-dimensional ^1H-^1H shift correlation (COSY) NMR spectrum (Figure 4). The T_1 values for this complex indicate that the olefin protons relax an order of magnitude quicker when complexed to the metal center versus free in solution. Unlike with allyl ethyl ether, **1** does not catalyze olefin isomerization of 3-buten-1-ol. We attribute this to a chelation effect which will be discussed further in



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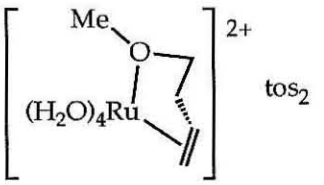


7

Chapter 2. Separate ligation of the two chelating moieties (olefin and alcohol) are not observed during the formation of **6** as in the formation of **5** (olefin and olefin). The methyl ether of 3-buten-1-ol (3-butenyl methyl ether) also forms a bi-dentate olefin complex **7** with ruthenium(II). The internal ether carbon ($-CH_2O-$) exhibits an analogous downfield shift (72.3 to 84.3 ppm) upon binding in the ^{13}C NMR spectrum (Table 1). Isomerization of 3-butenyl methyl ether is also

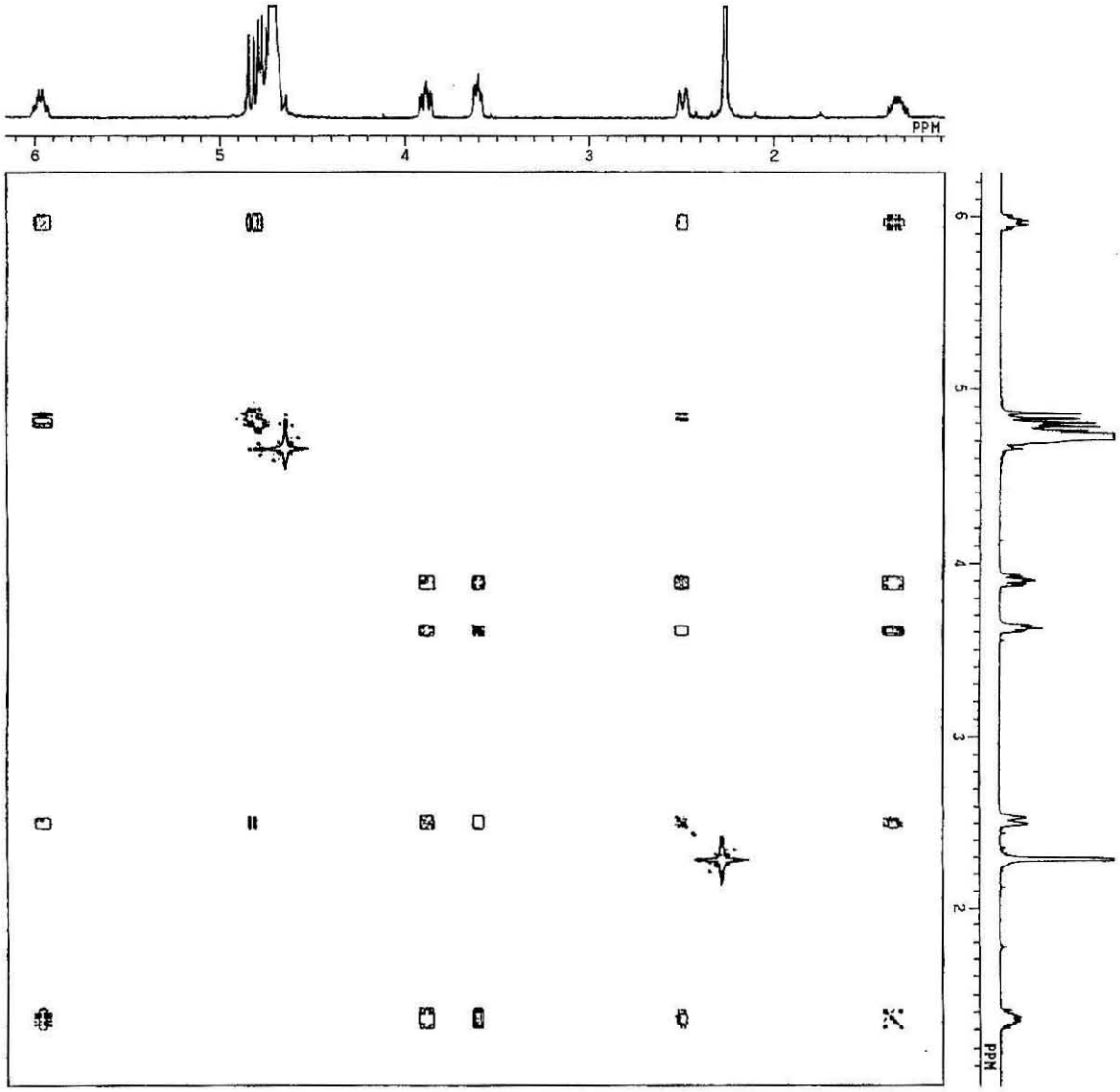
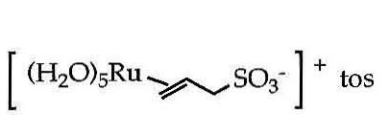


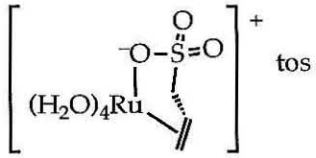
Figure 4. ^{1}H-^{1}H correlated COSY spectrum of Ru^{II}(3-buten-1-ol)$(H_2O)_4(tos)_2$ (**6**).

not observed.

Other oxygen functionalities, including carboxylic acids (vide infra) and sulfonates, also coordinate to the ruthenium center. Initially, sodium 2-propenesulfonate reacts with **1** in water to form a monodentate olefin complex **8a** (Table 1). Subsequently, sulfonate complexation is observed, as indicated in the ^{1}H NMR by the much more significant shift of the allylic protons relative to free ligand, to form chelating complex **8b** (Table 1). One proton shifts upfield by 0.9 ppm and the other moves downfield by 0.8 ppm. In the non-ligated sulfonate complex **8a** the resonances are shifted only 0.2 and 0.6 ppm upfield. An equilibrium ratio of **8a** to **8b** of approximately 8 : 1 is reached after one hour at 45 °C. Isolation of complexes **8** is precluded by their extreme solubility. Interestingly, the shift relative to free ligand for the allylic carbon in the ^{13}C NMR is neglible (+0.1 ppm), as is also observed for the allylic carbon of the 3-buten-1-ol complex (–0.1 ppm).



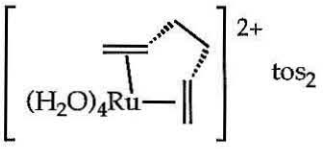
8a



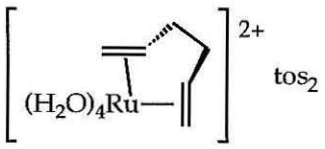
8b

Complexes of olefins which are only sparingly soluble in water are readily prepared in methanol. The reaction between 1,5-hexadiene and **1** in methanol yields a deep yellow solution after 12 h at room temperature. After removing methanol in vacuo and redissolving the yellow residue in D_2O an equal ratio of two isomeric 1,5-hexadiene complexes **9a** and **9b** (66% total yield) is observed in the ^{1}H NMR. Spectroscopic data for **9a** and **9b** support the formation of two different bidentate complexes of 1,5-hexadiene. Over the course of 48 h at room

temperature in D_2O these two complexes equilibrate to one isomer (**9a**) (Figure 5). We believe **9a** and **9b** to have different symmetrical orientations, one a C^2-axis and the other a mirror plane, of 1,5-hexadiene bridging two cis sites on the

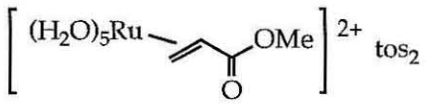


9a



9b

metal center similar to diallyl ether complexes **5a** and **5b**. A third complex **9c** is formed in relatively low yield but is as of yet unidentified. A possible structure is a binuclear ruthenium complex with a bridging 1,5-hexadiene ligand: $[Ru^{II}(H_2O)_5]_2(\eta^4$-1,5-hexadiene$)(tos)_2$. The connectivity of all three complexes has been confirmed in the two-dimensional ^1H-^1H shift correlation (COSY) NMR spectrum (Figure 6). Other olefins, such as 1,6-heptadiene, can likewise be rendered water soluble by coordination of a penta- or tetraaquo ruthenium(II) moiety. We have so far been unsuccessful in the preparation of aryl substituted olefin complexes of, for instance, 2-vinyl naphthalene and 4-biphenyl, by this or any other method. A methyl acrylate-ruthenium(II) complex **10** can be prepared in this manner (Table 1), but can be prepared with equal success in aqueous medium:



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The high water-solubility of all ruthenium(II)-olefin complexes studied, even those of water-insoluble olefins, hinders their crystallization from aqueous

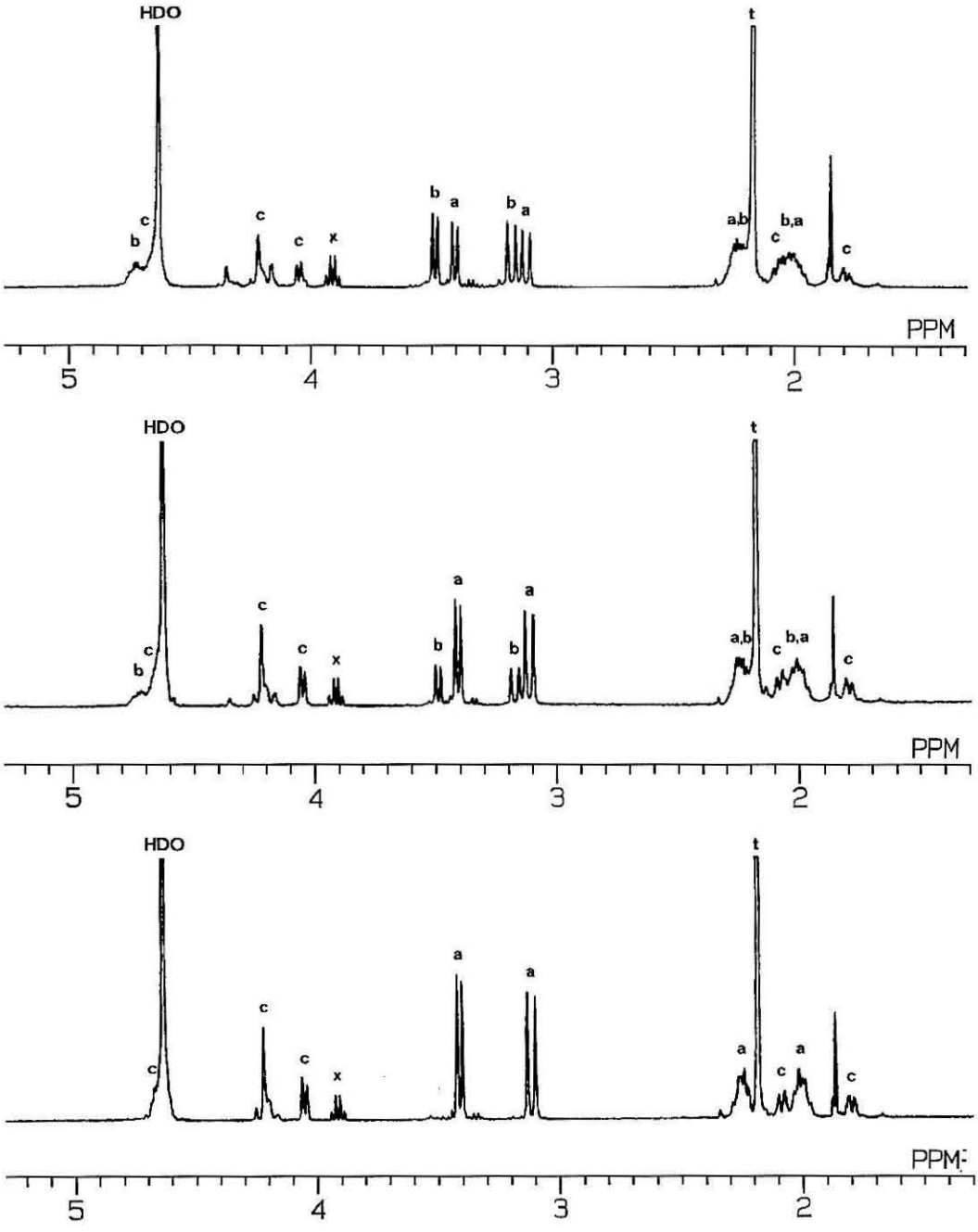


Figure 5. ^{1}H NMR (D_2O) spectrum of Ru^{II}(1,5-hexadiene)$(H_2O)_4(tos)_2$ (**9a**, **b**, **c**) at (from top) t = 0 h, t = 24 h, and t = 48 h (x = ether, t = tosylate).

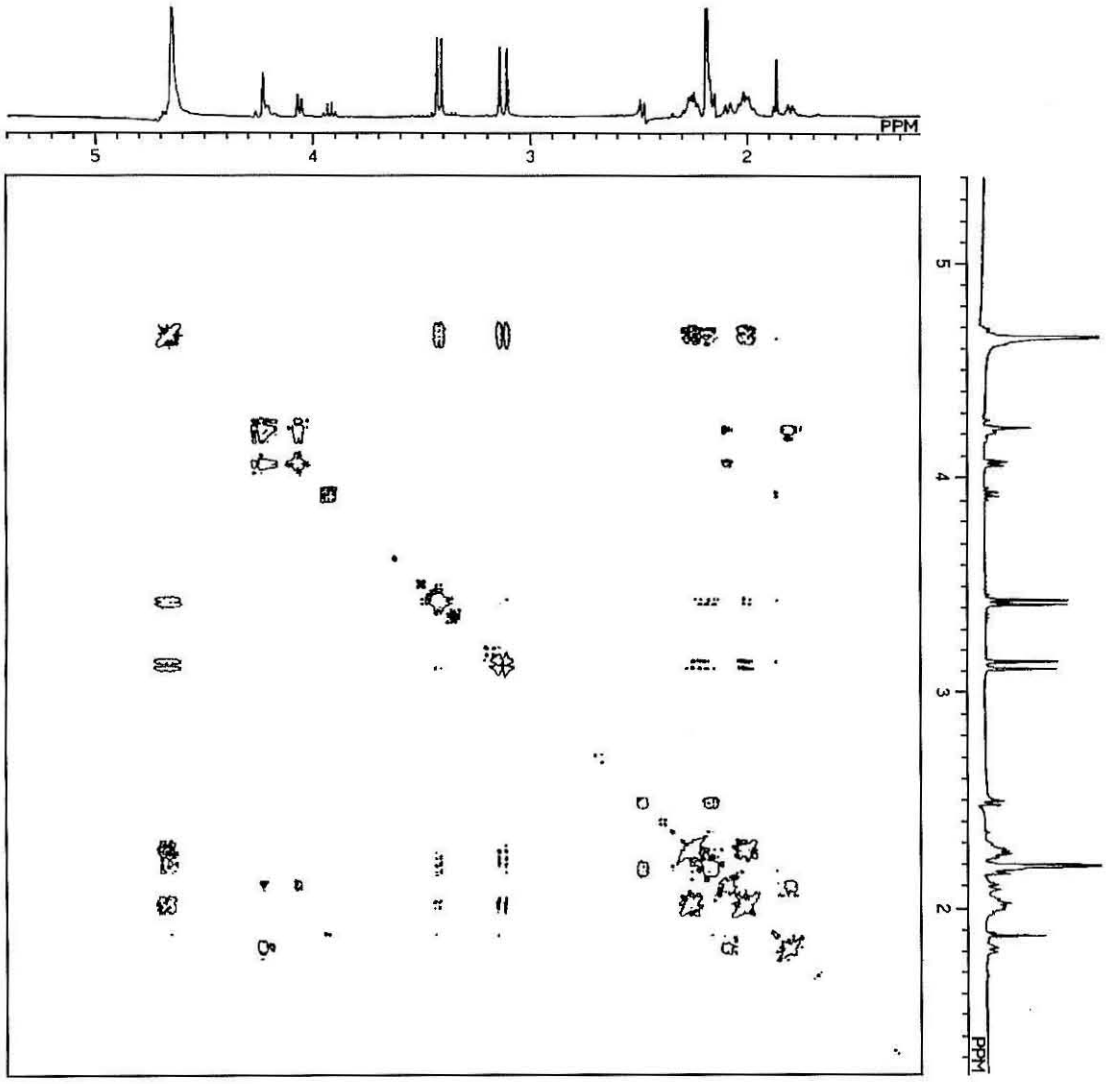


Figure 6. ^{1}H-^{1}H correlated COSY spectrum of Ru^{II}(1,5-hexadiene)$(H_2O)_4(tos)_2$ (**9a, b, c**).

Table 1. Spectroscopic Data of Ruthenium(II)-Olefin Complexes.

Olefin	^{1}H NMR[a]	^{13}C NMR[b]	Δδ (ppm)	Assignment
5,6-*exo*-bis(methoxy-methyl)-7-oxabicyclo-[2.2.1]hept-2-ene[c] (**2**)	δ 5.08 s	δ 84.6	–50.6	=CH–
	4.73 s	77.2	–3.0	>$CH_{bridgehead}$–
	3.44 m	71.5	–0.3	–CH_2O–
	3.26 s	58.9	0.5	–OCH_3
	2.54 m	42.6	3.1	>CH–
2,5-dihydrofuran (**3**)	δ 5.64 s	δ 78.1 J_{CH} = 172	–48.8	=CH–
	4.64 d J = 11.0	74.5 J_{CH} = 149	–1.5	–CH_2O–
	3.92 d J = 11.0			–CH_2O–
allyl ethyl ether (**4**)	δ 5.28 m	δ 76.8 J_{CH} = 158	–57.9	=CH–
	4.86 d J = 12.1	65.4 J_{CH} = 160	–53.6	=CH_2
	4.70 d J = 8.4			=CH_2
	3.81 m	75.0 J_{CH} = 145	2.7	=CHCH_2–
	3.49 m	67.4 J_{CH} = 145	0.4	–OCH_2CH_3
	1.02 t J = 7.1	15.0 J_{CH} = 127	0.2	–OCH_2CH_3
diallyl ether (**5a**)	δ 4.25 d J = 14.6	δ		–CH_2O–
	4.03 m	85.9 J_{CH} = 157	–48.4	=CH–
	3.53 d J = 9.8	67.5 J_{CH} = 162	–51.8	=CH_2
	3.53 d J = 13.2			=CH_2
	3.15 d J = 14.5	69.5 J_{CH} = 146	–2.2	–CH_2O–
diallyl ether (**5b**)	δ 4.33 br m	δ 83.2 J_{CH} = 155	–51.1	=CH–
	4.12 d J = 14.6	68.4 J_{CH} = 158	–50.9	=CH_2
	4.09 d J = 9.5			=CH_2
	3.69 d J = 13.7	68.3 J_{CH} = 148	–3.4	–CH_2O–
	3.42 dd J = 6.2, 14.8			–CH_2O–

Table 1. Continued.

Olefin	^{1}H NMR[a]	^{13}C NMR[b]	Δδ (ppm)	Assignment
3-buten-1-ol (6)	δ 5.89 m	δ 94.0 J_{CH} = 155	–42.5	=CH–
	4.75 d J = 10.5	67.3 J_{CH} = 161	–50.3	$=CH_2$
	4.71 d J = 8.1			$=CH_2$
	3.80 m, 3.53 m	73.8 J_{CH} = 147	12.2	$-CH_2OH$
	2.42 m, 1.28 m	36.6 J_{CH} = 123	0.1	$-CH_2CH_2OH$
3-butenyl methyl ether (7)	δ 5.89 m	δ 91.6 J_{CH} = 161	–44.8	=CH–
	4.89 d J = 8.1	67.8 J_{CH} = 160	–49.7	$=CH_2$
	4.84 d J = 12.1			$=CH_2$
	3.60 td J = 4.4, 8.8	84.3 J_{CH} = 148	12.0	$-CH_2O-$
	3.33 dt J = 5.1, 8.4			$-CH_2O-$
	3.18, s	64.1 J_{CH} = 147	5.7	$-OCH_3$
	2.30 m, 1.50 m	33.3 J_{CH} = 129	–0.6	$-CH_2CH_2O-$
2-propenesulfonate (8a)	δ 5.38 m	δ [d]		=CH–
	4.93 d J = 7.7			$=CH_2$
	4.82 d J = 8.1			$=CH_2$
	3.23 dd J = 3.0, 13.5			$-CH_2SO_3^-$
	2.78 dd J = 11.0, 13.6			$-CH_2SO_3^-$
2-propenesulfonate (8b)	δ 5.38 m	δ 70.4 J_{CH} = 164	–59.8	=CH–
	4.82 d J = 8.1	67.8 J_{CH} = 161	–60.8	$=CH_2$
	4.75 d J = 11.7			$=CH_2$
	4.25 dd J = 4.4, 13.6	56.4 J_{CH} = 136	0.1	$-CH_2SO_3^-$
	2.57 dd J = 13.6, 10.6			$-CH_2SO_3^-$

Table 1. Continued.

Olefin	^{1}H NMR[a]	^{13}C NMR[b]	Δδ (ppm)	Assignment
1,5-hexadiene (**9a**)	δ 4.66[e] m	δ 98.1 J_{CH} = 158		=CH–
	3.42 d J = 8.8	69.1 J_{CH} = 159		$=CH_2$
	3.13 d J = 12.9			$=CH_2$
	2.26 m	31.6 J_{CH} = 132		$-CH_2-$
	2.02 m			$-CH_2-$
1,5-hexadiene (**9b**)	δ 4.74 m	δ 99.7		=CH–
	3.51 d J = 8.8	69.9		$=CH_2$
	3.19 d J = 12.9			$=CH_2$
	2.13[e] m	31.6		$-CH_2-$
	2.07[e] m			$-CH_2-$
1,5-hexadiene (**9c**)	δ 4.07 d J = 7.5	δ 98.8 J_{CH} = 167		=CH–
	4.24 br s	70.2 J_{CH} = 161		$=CH_2$
	4.23 dd?			$=CH_2$
	2.19 d J = 9.0	27.7 J_{CH} = 132		$-CH_2-$
	1.80 d J = 9.0			$-CH_2-$
methyl acrylate (**10**)	δ	δ 180.4	10.4	>C=O
	5.77 d J = 11.5	72.0 J_{CH} = 163	–61.0	$=CH_2$
	5.34 dd J = 8.5, 11.7	68.6 J_{CH} = 166	–59.6	=CH–
	5.23 d J = 8.6			$=CH_2$
	3.52 s	53.2 J_{CH} = 148	0.3	–OMe
3-pentenoic acid (**11**)	δ 4.96 m	δ *f*		$=CHCH_2-$
	4.89 m			$CH_3CH=$
	3.46 dd J = 5.1, 17.2			$-CH_2CO_2H$
	2.15 dd J = 9.3, 17.2			$-CH_2CO_2H$
	1.32 d J = 5.7			$-CH_3$

Table 1. Continued.

Olefin	^{1}H NMR[a]	^{13}C NMR[b]	Δδ (ppm)	Assignment
3-butenoic acid (**13**)	δ 5.19 m	δ *f*		=CH–
	4.57 d *J* = 8.1			$=CH_2$
	4.39 d *J* = 11.7			$=CH_2$
	3.48 dd *J* = 5.5, 16.9			$-CH_2CO_2H$
	2.15 dd *J* = 9.5, 16.9			$-CH_2CO_2H$
(±)-3-cyclohexen-1-methanol	δ 5.62 d *J* = 9.2	δ 76.6 J_{CH} = 160	–52.0	=CH–
	5.53 m	75.6 J_{CH} = 161	–51.7	=CH–
	2.92 dd *J* = 2.2, 11.0			
	2.75 d *J* = 11.0			
	2.67 dd *J* = 5.1, 16.9			
	2.47 m			
	1.83 m			
	1.62 m 2H			
	1.39 m 2H			
N-methylmaleimide[g] (**17**)	δ	δ 174.2	–8.2	>C=O
	5.98 s	69.9	–65.3	=CH–
	2.56 s	24.0	0.1	$>NCH_3$
exo-*N*-methyl-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide[g] (**18exo**)	δ	δ 179.6	0.0	>C=O
	5.20 s	84.5	2.8	$>CH_{bridgehead}$
	5.09 s	76.6	–60.5	=CH–
	3.61 s	50.2	2.0	>CH–
	2.79 s	25.6	0.0	$>NCH_3$

Table 1. Continued.

Olefin	^{1}H NMR[a]	^{13}C NMR[b]	Δδ (ppm)	Assignment
endo-N-methyl-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide[g] (**18endo**)	δ 5.22 s 4.94 s 3.73 s 2.82 s	δ 179.1 82.9 73.4 49.1 25.5	0.2 3.0 –61.7 2.7 0.4	>C=O >$CH_{bridgehead}$ =CH– >CH– >NCH_3
endo-N-methylbicyclo[2.2.1]hept-5-ene-2,3-dicarboximide[g] (**19**)	δ 4.66 s 3.16 s 3.38 s 0.94 d J = 11.3 –0.33 d J = 11.3 2.75 s	δ 182.8 76.2 47.5 45.0 39.0 25.0	0.0 –58.9 0.8 –0.4 –13.7 0.3	>C=O =CH– >$CH_{bridgehead}$ >CH– >CH_2 >CH_2 >NCH_3
1-methyl-5,6-*exo*-bis(methoxymethyl)-7-oxabicyclo[2.2.1]hept-2-ene (**22**)	δ 5.23 d J = 5.5 4.61 s 5.02 d J = 5.5 3.57 dd J = 4.8, 9.5 3.46 dd J = 10.3, 6.2 3.40 dd J = 10.3, 6.2 3.33 t J = 9.8 3.21 s 3.17 s 2.58 td J = 4.4, 9.2 2.46 dt J = 6.2, 8.8 1.30 s	δ 92.9 84.6 J_{CH} = 175 81.4 J_{CH} = 172 79.8 J_{CH} = 176 72.0 J_{CH} = 145 70.2 J_{CH} = 143 58.9 J_{CH} = 142 58.6 J_{CH} = 142 45.3 J_{CH} = 134 44.3 J_{CH} = 136 14.9 J_{CH} = 127	4.1 –55.9 0.6 –56.2 –0.5 –0.6 0.1 0.1 3.2 2.8 –0.8	>CCH_3 =CH– >$CH_{bridgehead}$ =CH– –CH_2O– –CH_2O– –CH_2O– –CH_2O– –OCH_3 –OCH_3 >CH– >CH– >CCH_3

Table 1. Continued.

Olefin	^{1}H NMR[a]	^{13}C NMR[b]	Δδ (ppm)	Assignment
8-oxabicyclo[3.2.1]oct-6-ene-3-one (**25**)	δ 5.37 s	δ 212.8	0.2	>C=O
	4.68 d J = 4.9	78.8 J_{CH} = 178	–55.0	=CH–
	2.88 dd J = 5.1, 16.6	79.8 J_{CH} = 168	1.9	>CH–O
	2.72 d J = 16.8	47.2 J_{CH} = 132	0.5	–CH_2–
				–CH_2–
2,2,4,4-tetramethyl-8-oxabicyclo[3.2.1]oct-6-ene-3-one (**26**)	δ 5.57 s	δ [h]		=CH–
	4.13 s			>CH–O
	1.25 s			–$(CH_3)_2$
	1.12 s			–$(CH_3)_2$
5,6-*exo*-bis(carbomethoxy)tricyclo[2.2.2.2^{7,8}]deca-2,9-diene[i] (**28a**)	δ 6.36 m	δ [h]		H_a
	5.60 s			H_b
	3.46 s			-OMe
	3.10 br s			H_c
	2.89 s			H_d
	2.05 br s			H_e
5,6-*exo*-bis(carbomethoxy)tricyclo[2.2.2.2^{7,8}]deca-2,9-diene[i] (**28b**)	δ 4.70 m	δ [h]		H_a
	4.87 s			H_b
	3.45 s			-OMe
	3.02 br s			H_c
	3.08 s			H_d
	2.96 br s			H_e

[a] All ^{1}H NMR spectra also contain tosylate counterion resonances: δ 7.51, d, J= 8.3, H_{aryl} tos; 7.18, d, J= 8.3, H_{aryl} tos; 2.21, s, Me tos.

[b] All ^{13}C NMR spectra also contain tosylate counterion resonances: δ 143.3, 140.1, 130.2, 126.1, C_{aryl} tos; 21.3, Me tos.

[c] Novak, B. M., Ph. D. Thesis, California Institute of Technology, 1989.

[d] Spectrum not obtained due to the low concentration of this isomer.

Table 1. Continued.

[e] Resonance partially obscured.
[f] Spectrum not obtained due to instability of complex.
[g] C. LePetit, D. V. McGrath, R. H. Grubbs, unpublished data.
[h] Spectrum not obtained.
[i] Assignments made according to structure at right.

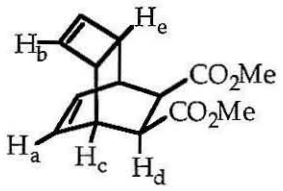


Table 2. Comparative J_{CH} Data of Ruthenium(II)-Olefin Complexes.

Olefin	^{13}C NMR		J_{CH}		Assignment
			Bound	Free	
2,5-dihydrofuran	δ	78.1	172	174	=CH–
(**3**)		74.5	149	150	$-CH_2O-$
allyl ethyl ether	δ	76.8	158	160	=CH–
(**4**)		65.4	160	157	$=CH_2$
		75.0	145	143	$=CHCH_2-$
		67.4	145	144	$-OCH_2CH_3$
		15.0	127	126	$-OCH_2CH_3$
diallyl ether	δ	85.9	157	160	=CH–
(**5a**)		67.5	162	160	$=CH_2$
		69.5	146	144	$-CH_2O-$
diallyl ether	δ	83.2	155	160	=CH–
(**5b**)		68.4	158	160	$=CH_2$
		68.3	148	144	$-CH_2O-$
3-buten-1-ol	δ	94.0	155	154	=CH–
(**6**)		67.3	161	155	$=CH_2$
		73.8	147	143	$-CH_2OH$
		36.6	123	123	$-CH_2CH_2OH$
3-butenyl methyl	δ	91.6	161	156	=CH–
ether		67.8	160	156	$=CH_2$
(**7**)		84.3	148	144	$-CH_2O-$
		64.1	147	142	$-OCH_3$
		33.3	129	127	$-CH_2CH_2O-$
2-propenesulfonate	δ	70.4	164	161	=CH–
(**8b**)		67.8	161	158	$=CH_2$
		56.4	136[c]	136	$-CH_2SO_3^-$
methyl acrylate	δ	180.4			>C=O
(**10**)		72.0	163	161	$=CH_2$
		68.6	166	162	=CH–
		53.2	148	148	–OMe
8-oxabicyclo[3.2.1]oct-	δ	212.8			>C=O
6-ene-3-one		78.8	178	176	=CH–
(**25**)		79.8	168	162	>CH–O
		47.2	132	132	$-CH_2-$

Table 2. Continued.

Olefin	^{13}C NMR	J_{CH}		Assignment
		Bound	Free	
1-methyl-5,6-*exo*-	δ 92.9			$>CCH_3$
bis(methoxymethyl)-7-	84.6	175	176	=CH–
oxabicyclo[2.2.1]hept-	81.4	172	169	$>CH_{bridgehead}$
2-ene	79.8	176	177	=CH–
(**22**)	72.0	145	144	$–CH_2O–$
	70.2	143	142	$–CH_2O–$
	58.9	142	142	$–OCH_3$
	58.6	142	142	$–OCH_3$
	45.3	134	138	>CH–
	44.3	136	137	>CH–
	14.9	127	128	$>CCH_3$

[a] All ^1H NMR spectra also contain tosylate counterion resonances: δ 7.51, d, J = 8.3, H_{aryl} tos; 7.18, d, J = 8.3, H_{aryl} tos; 2.21, s, Me tos.

[b] All ^{13}C NMR spectra also contain tosylate counterion resonances: δ 143.3, 140.1, 130.2, 126.1, C_{aryl} tos; 21.3, Me tos.

[c] Resonance partially obscured.

media. Limited success has been acheived with recrystallization from concentrated (3.6 M) aqueous *p*-toluenesulfonic acid solution. While the materials obtained were crystalline, their size precluded X-ray structural analysis. Interestingly, the only organic solvents in which the complexes have an appreciable solubility, methanol and ethanol, change the nature of the complexes as evidenced by the complex ^{1}H NMR spectra obtained in methanol-d_4. This change is reversible: removal of the solvent in vacuo and redissolution in D_2O yields the original ^{1}H NMR spectrum. We believe that reversible arene counterion coordination, most probably in an η^6 fashion, results in a number of isomeric complexes observed in the ^{1}H NMR in methanol. η^6-Arene complexes have been prepared from $Ru^{II}(H_2O)_6(tos)_2$ by dissolution in anhydrous alcoholic solvents.[25]

The olefin ligands in these complexes are quite non-labile, in contrast to the aquo ligands in $Ru^{II}(H_2O)_6(tos)_2$ **1**, $Ru^{III}(H_2O)_6(tos)_3$, and $Ru^{II}(\eta^6\text{-}C_6H_6)(H_2O)_3(tos)_2$.[24, 42] Olefin ligand exchange was not observed with **6** in the presence of free 3-buten-1-ol in aqueous solution at 50 °C as evidenced by the lack of broadening of the bound olefin resonances in the ^{1}H NMR. In addition, both **5** and **6** are stable at 65 °C in aqueous solution for periods of up to two hours.

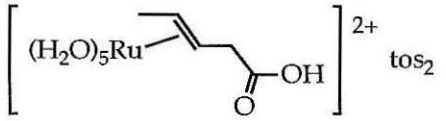
Although the olefin ligands are relatively non-labile, we were able to determine the relative binding constants of several different olefin ligands through a series of displacement reactions followed by ^{1}H NMR. In order of descending binding strength, the ligands can be classed as follows: diallyl ether > 3-buten-1-ol > sodium 2-propenesulfonate » methyl acrylate > 2,5-dihydrofuran > allyl ethyl ether > H_2O. Chelating olefins bind much more strongly to the metal center than non-chelating olefins. The order of binding affinities correlates

well with the reduction potentials (vide infra) for the various non-chelating olefins. For example, it is more difficult to oxidize the metal center in the methyl acrylate complex **10** versus the allyl ethyl ether complex **4**. This comparison of binding constant to reduction potential is valid for the non-chelating olefins since the olefin ligand in each complex is stabilizing a $(H_2O)_5Ru^{II}$ moiety. With the chelating olefins, however, the chelating moiety also affects the reduction potential of the metal center. The series of chelating olefins actually can be considered to be the effect of the chelating component (–OH, $–SO_3^-$, etc.) on the reduction potential of the $(H_2O)_4$(olefin)Ru^{II} moiety.

The lability of the ancillary aquo ligands in these complexes has not yet been determined, but would be of interest for comparison purposes with the ligand exchange rates of the $Ru^{II}(H_2O)_6^{2+}$, $Ru^{III}(H_2O)_6^{3+}$, and $Ru^{II}(\eta^6\text{-}C_6H_6)(H_2O)_3^{2+}$ cations. The aquo ligand exchange rate for the arene complex is 3 orders of magnitude faster than that for $Ru^{II}(H_2O)_6^{2+}$.[24] Based on simple backbonding arguments, however, the exchange rate for the arene complex should lie between those of $Ru^{II}(H_2O)_6^{2+}$ (1.8×10^{-2} s^{-1}) and $Ru^{III}(H_2O)_6^{3+}$ (3.5×10^{-6} s^{-1}).[42] This is also supported by the electrochemical data for these complexes which indicate that the Ru(II) center in $Ru^{II}(\eta^6\text{-}C_6H_6)(H_2O)_3^{2+}$ should behave as a Ru(III) center. Comparison of these different rates is somewhat difficult, however, since the activation parameters, notably ΔS^* and ΔV^*, indicate different exchange mechanisms for the different complexes.[24, 42] The activation entropies, ΔS^*, for water substitution on both $Ru^{II}(H_2O)_6^{2+}$ and $Ru^{II}(\eta^6\text{-}C_6H_6)(H_2O)_3^{2+}$ are positive, while $Ru^{III}(H_2O)_6^{3+}$ substitution has a significant negative activation entropy. A similar trend is seen for the activation volume ΔV^*. In general, ligand substitution on Ru(II) centers is through a type I dissociative mechanism, while that of Ru(III) is a type I_a associative pathway.[42] Kinetic data and activation

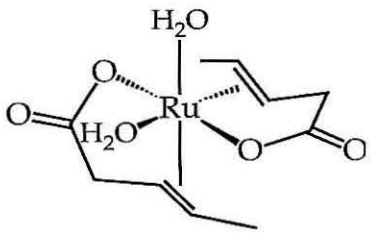
parameters for water exchange on the olefin complexes prepared here would therefore be useful for comparison with the other Ru^{II} ions.

Carboxylic Acids. Carboxylic acid functionalities react irreversibly with the ruthenium center. For example, 3-pentenoic acid reacts with **1** in water to form the monoolefin complex **11** (Table 1) which slowly reacts with excess 3-pentenoic acid to form a yellow crystalline precipitate **12**. This complex is only sparingly soluble in neutral water, but increasingly soluble at higher pH. The ^1H



11

NMR spectrum reveals a single seven spin system consistent with an intact 3-pentenoic acid moiety and the absence of any tosylate counterions (Table 3). This data and the elemental analysis of these crystals for $Ru(H_2O)_2(C_5H_7O_2)_2$[68] is consistent with a bis(olefin)-bis(carboxylate) structure having two-fold symmetry. The IR data (Table 3) indicates monodentate carboxylate ligands.[69] An X-ray structural analysis of **12** supports this structure (Figure 7, Table 4) and reveals the water ligands to be in a cis orientation. A non-crystallographic C_2-axis bisects the O(5)–Ru–O(6) angle. The Ru–OH_2 bond distances of 2.141(3) and



12

Table 3. Spectroscopic Data of Ruthenium(II)-Bis(Olefin)-Bis(Carboxylate) Complexes.

Olefin	IR (cm^{-1})	Assignment	^1H NMR	^{13}C NMR	Assignment
3-pentenoic acid	2495 w	ν(OH)	δ 4.28 m		CH_3CH=
(**12**)	2266 br m	ν(OH)	3.00 m		=$CH$$CH_2$–
					–$CH_aH_bCO_2$–
	1590 s	$\nu(OCO)_{asym}$	2.05 m		–$CH_aH_bCO_2$–
	1341 m	$\nu(OCO)_{sym}$	1.38 d J = 6.2		CH_3CH=
3-butenoic acid			δ	δ 191.6	>C=O
			3.72 d J = 12.2	79.6	=CH_2
			3.53 d J = 7.3		=CH_2
			2.95 m	76.7	=$CH$$CH_2$–
				41.0	–$CH_aH_bCO_2$–
			2.06 m		–$CH_aH_bCO_2$–

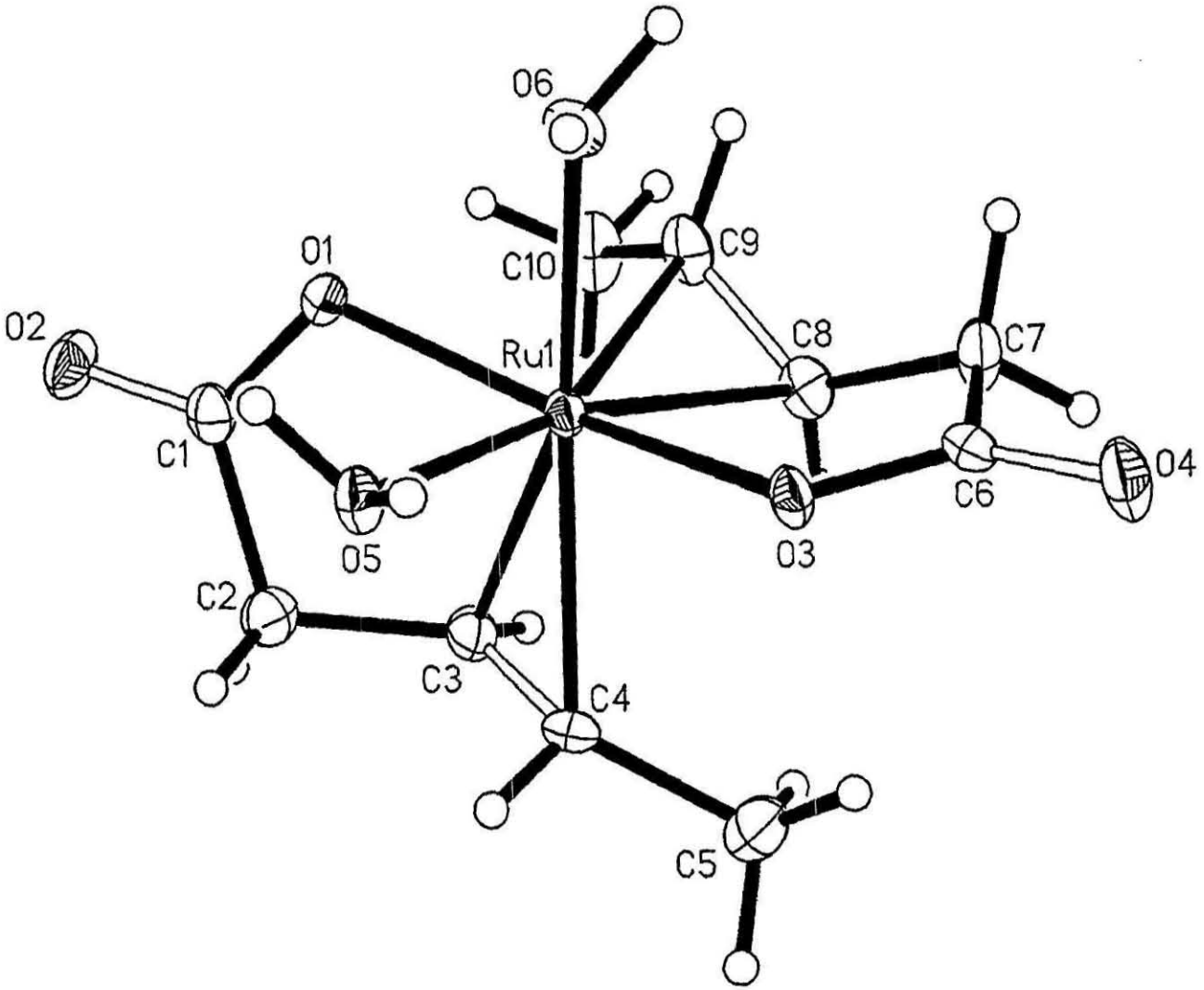


Figure 7. ORTEP diagram of $Ru(H_2O)_2(\eta^1\text{-}(O),\eta^2\text{-}(C,C')\text{-}OCOCH_2CH{=}CHCH_3)_2$ (**12**). For further information, see Appendix.

Table 4. Selected Bond Distances and Angles for **12**.

Bond Distances (Å)		Bond Angles (deg)		Bond Angles (deg)	
Ru-O(1)	2.080 (3)	O(5)-Ru-O(6)	83.3 (1)	O(6)-Ru-C(8)	100.8 (1)
Ru-O(3)	2.065 (3)	O(1)-Ru-O(5)	81.6 (1)	O(6)-Ru-C(9)	83.5 (1)
Ru-O(5)	2.141 (3)	O(1)-Ru-O(6)	83.1 (1)	O(1)-Ru-X1A[a]	93.7 (2)
Ru-O(6)	2.115 (3)	O(1)-Ru-O(3)	162.4 (1)	O(1)-Ru-X1B[b]	98.4 (2)
Ru-X1A[a]	2.088 (4)	O(3)-Ru-O(5)	85.3 (1)	O(3)-Ru-X1A[a]	97.5 (2)
Ru-X1B[b]	2.088 (4)	O(3)-Ru-O(6)	83.8 (1)	O(3)-Ru-X1B[b]	93.8 (2)
C(3)-C(4)	1.381 (6)	O(5)-Ru-C(3)	93.3 (1)	C(3)-C(4)-C(5)	124.0 (4)
C(8)-C(9)	1.381 (6)	O(5)-Ru-C(4)	82.4 (1)	C(8)-C(9)-C(10)	123.6 (4)

[a] X1A = center of C(3)-C(4) bond.

[b] X1B = center of C(8)-C(9) bond.

2.115(3) Å are typical for a Ru^{II} center.[9] The coordinated olefin bond distances, both 1.381(6) Å, are intermediate between a C–C single and double bond and are slightly longer than the coordinated olefin bond distance of 1.37(2) Å in Ru(1-5-η^5-C_8H_{11})(η^1(*O*),η^2-(*C*,*C'*)-$OCOCH_2CH{=}CH_2$)(PMe_3).[70] The J_{CH} coupling constant for the olefin protons could not be obtained due to the poor solubility of the complex in neutral water and its slow decomposition in media above pH 7. However, the dihedral angles between the planes defined by the two olefins and their substituents (Table 5, Figure 8) are indicative of substantial back bonding from the metal to the olefin.[53]

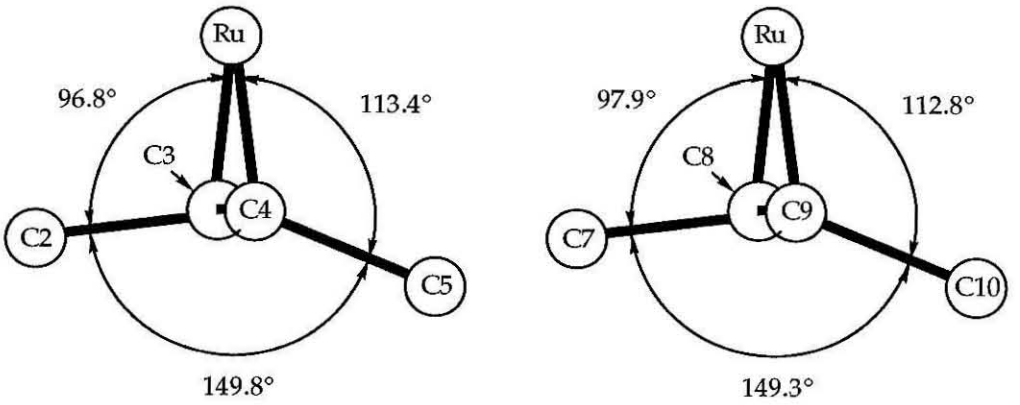


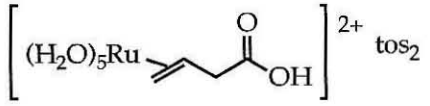
Figure 8. Illustration of the dihedral angles surrounding the olefin ligands of **12**. Planes are not explicitly illustrated. See Table 5.

The steric requirements of the terminal methyl group of 3-pentenoic acid are a significant factor in the selective formation of **12**. When this methyl group is removed less selective reactivity is observed. When 3-butenoic acid (vinylacetic acid) is allowed to react with **1** in D_2O at room temperature an olefin complex **13** forms in 60% observed yield over the course of 5 hours (Figure 9). After 5 days at room temperature or 1 hour at 45 °C, however, all resonances for

Table 5. Selected Dihedral Angles for **12**

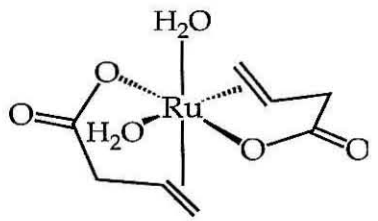
Dihedral Angles (deg)			
C(3)-Ru-C(4)	∠	C(2)-C(3)-C(4)	96.8
C(3)-Ru-C(4)	∠	C(3)-C(4)-C(5)	113.4
C(2)-C(3)-C(4)	∠	C(3)-C(4)-C(5)	149.8
C(8)-Ru-C(9)	∠	C(7)-C(8)-C(9)	97.9
C(8)-Ru-C(9)	∠	C(8)-C(9)-C(10)	112.8
C(7)-C(8)-C(9)	∠	C(8)-C(9)-C(10)	149.3
C(3)-Ru-C(4)	∠	C(8)-Ru-C(9)	88.1

13 are gone. A complex set of resonances is observed in the region from 2.0 to 4.3 ppm (Figure 9). This upfield shift is similar to that observed upon complexation to the metal of the second olefin moiety of diallyl ether (infra



13

supra) and, therefore, may be indicative of chelation of the carboxylic acid functionality. At this point the reaction mixture is washed with ether to remove excess starting material, pumped to dryness, and redissolved in D_2O. An additional 5 months at room temperature results in the somewhat simplified ^1H NMR spectrum shown in Figure 9. A two-dimensional ^1H-^1H shift correlation (COSY) NMR spectrum identifies the presence of four separate 5-spin systems (Figure 10). The retention of the five protons of the allyl moiety indicates that η^3-allyl complexes are not forming through allylic hydrogen abstraction.[71] Heating a freshly prepared solution of 3-butenoic acid and **1** in D_2O to 55 °C for 48 hours yields predominantly one of the 5-spin systems (3) from Figure 10. Analysis of the ^1H NMR spectrum (Table 3) leads us to believe that this complex is structurally analogous to **12** (structure **A**).



A

The nature of the different isomers observed during the reaction of 3-

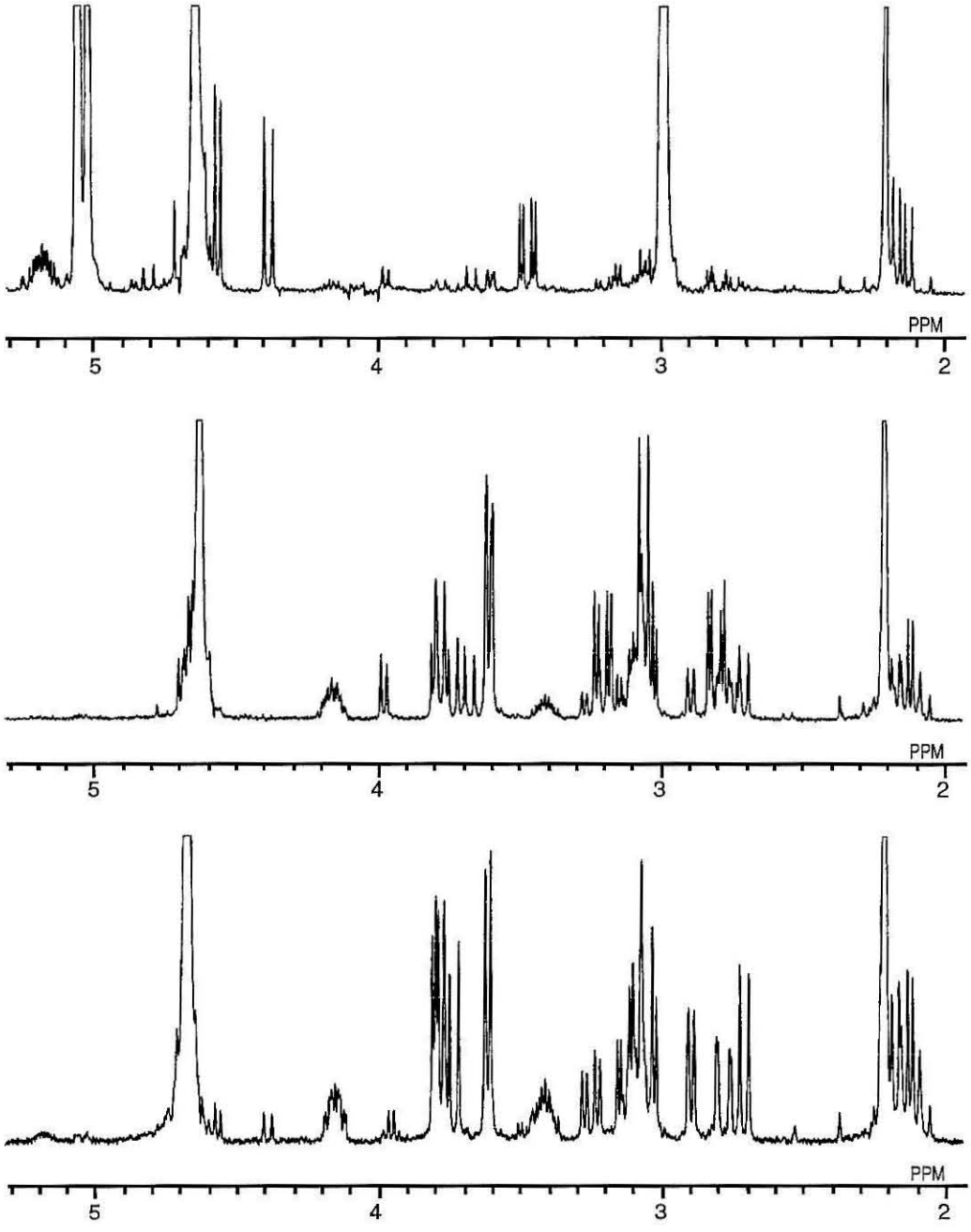


Figure 9. ^{1}H NMR (D_2O) spectra of the reaction between 3-butenoic acid and $Ru^{II}(H_2O)_6(tos)_2$ (**1**) after 5 hours (top), 5 days (middle), and 5 months (bottom) at room temperature.

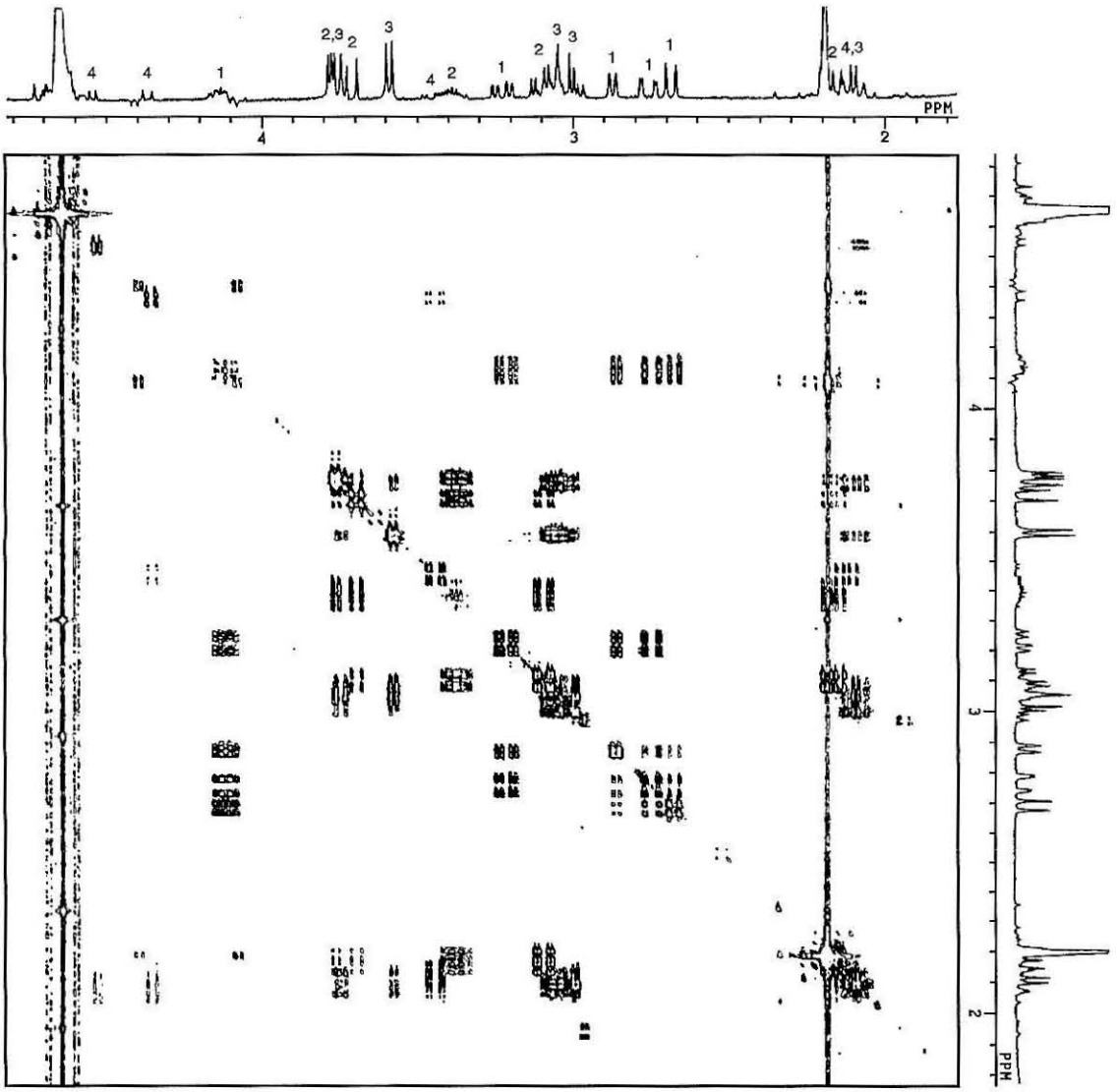
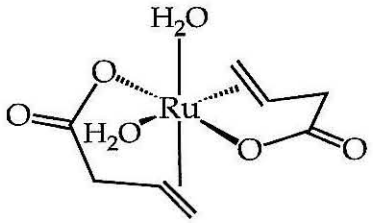
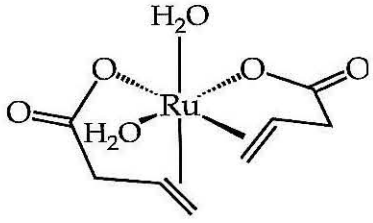


Figure 10. ^{1}H-^{1}H correlated COSY spectrum of the reaction between 3-butenoic acid and $Ru^{II}(H_2O)_6(tos)_2$ (**1**) in D_2O after 5 months at room temperature. The four spin systems (see text) are labelled.

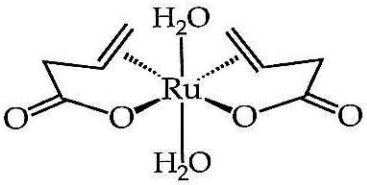
butenoic acid with **1** is presently unknown. While we believe that spin system 3 (Figure 10) is a bis(olefin)-bis(carboxylate) complex analogous to **12**, it is unclear whether the others are isomers of this bis(carboxylate)-bis(olefin) complex or olefin complexes with chelated carboxylic acid functionalities. Possible bis(carboxylate)-bis(olefin) complexes are structures **A-D**. Structure **A** is analogous to **12** and hence would give rise to spin system 3 from Figure 10. Structures **C** and **D** also have elements of symmetry (mirror plane and C^2-axis, respectively) and would therefore also give rise to 5-spin systems. Structure **B**, however, has no symmetry, and should give rise to a 10-spin ^{1}H NMR spectrum.



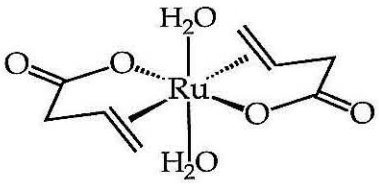
A



B



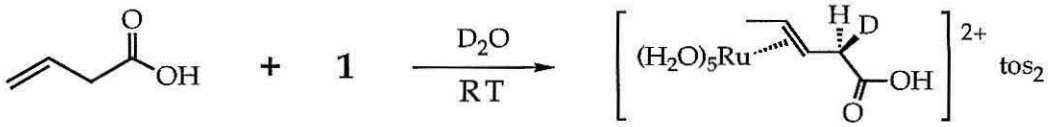
C



D

While the formation of these different isomers is plausible, we also have evidence which suggests the involvement of the carboxylic acid functionality with the metal prior to irreversible metal carboxylate formation. 2-Pentenoic acid reacts with **1** to form the ruthenium(II) complex of 3-pentenoic acid **11** (see

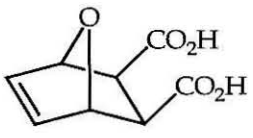
Chapter 2). When the reaction is carried out in D_2O, one of the diastereotopic hydrogens on C-2 is selectively deuterated as evidenced by the disappearance of the resonance at 2.15 ppm and the collapse of the doublet of doublets at 3.46 ppm to a doublet. As we shall see in Chapter 2, this selectivity is due to the directing



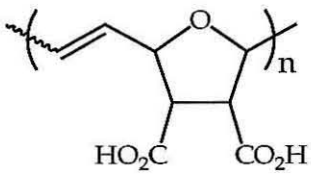
11-*d*

effects of the pendant functionality on the olefin, in this case the carboxylic acid group. Exactly how the carboxylic acid coordinates to the metal center, whether by direct donation or hydrogen bonding to an aquo ligand, is unknown. Irreversible carboxylate formation has not occurred at this point, however, but occurs eventually leading to the formation of **12**. It is possible, therefore, that the other spin systems in Figure 10 are carboxylic acid-chelated olefin complexes, but there is probably only one isomer of such a complex.

Irreversible carboxylate formation with ruthenium(II) centers as observed here is likely responsible for the deactivation of **1** and other ruthenium catalyst precursors in the attempted polymerization of the dicarboxylic acid monomer *exo*-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid **14** and its sodium salt.[5] Preparation of the poly(dicarboxylic acid) polymer **15** which would result from



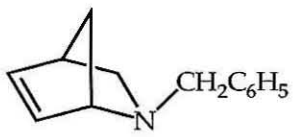
14



15

this monomer is possible through polymerization of the corresponding anhydride using either **1** (10-15% yield) or olefin complex **2** (>70% yield) as the catalyst.[5] Slow hydrolyzation of the anhydride functionality occurs during the course of the polymerization producing **15** and also resulting in catalyst deactivation which prevents high yields and catalyst recycling. By replacing the labile aquo ligands of **1** with much more substitutionally inert chloride ligands deactivation through carboxylate formation can be avoided. Near quantitative yields of **15** are obtained when the anhydride is polymerized with K_2RuCl_5 as the catalyst.[5]

Nitrogen Functionalities. Olefins do not compete successfully for the ruthenium(II) center in the presence of amines. When diallylmethylamine is added in excess to an aqueous solution of **1** the solution immediately turns dark brown. The ^1H NMR of this sample indicates preferential coordination of the amine moiety in a greater than 1 : 1 amine : Ru ratio. This is consistent with the relative substitutional labilities of amine, aquo, and olefin ligands for the ruthenium(II) center.[37, 40, 41, 62] Attempted protection of the amine lone pair by reaction with methyl iodide to form the non-basic ammonium salt diallyldimethylammonium iodide was not fully successful. Reaction of isolated

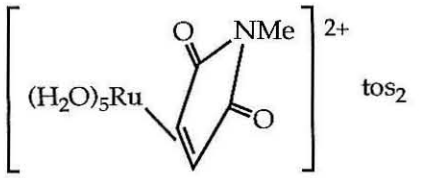


16

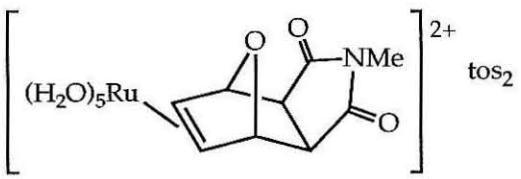
ammonium salt with **1** still resulted in a similar dark brown solution. Amine coordination to aqueous ruthenium(II) was prevented only in the presence of excess *p*-toluene sulfonic acid. When **1** is added to a solution of 2-benzyl-2-azabicyclo[2.2.1]hept-5-ene (N-benzyl-2-azanorbornene) **16** and 1.1 equivalents of

toluenesulfonic acid in D_2O the solution turns yellow after 5 min at 55 °C indicating the formation of a ruthenium(II) olefin complex rather than an amine complex.[72] Although polymerization of this monomer does not occur, we expect that polymerization of amines should be possible through a combination of protection (alkylation) and slight acidification of the solution.

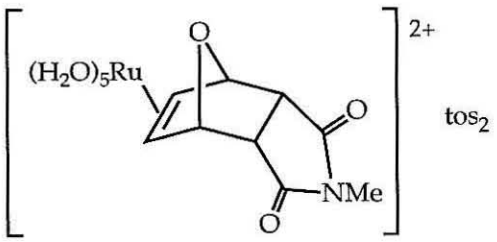
The lower basicity of the nitrogen atom in organic imides prevents them from interfering with olefin coordination to aqueous ruthenium(II). Complexes of *N*-methyl maleimide **17**, *exo*- and *endo*-*N*-methyl-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide **18endo** and**18exo**, and *endo*-*N*-methylbicyclo[2.2.1]hept-5-ene-2,3-dicarboximide **19** have been observed in solution and characterized as



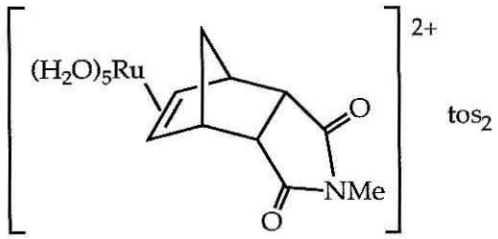
17



18exo



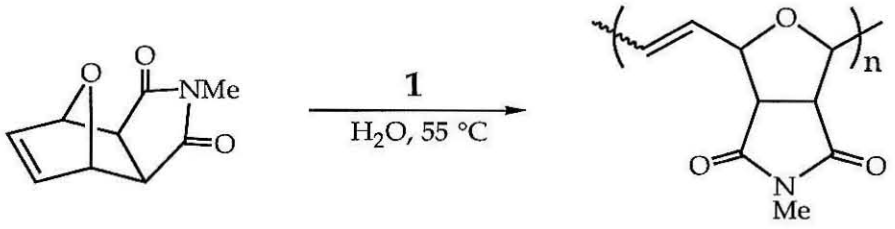
18endo



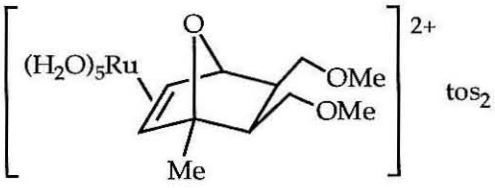
19

monolefin complexes by their ^1H and ^{13}C NMR spectra (Table 1).[10,73] We rule out nitrogen coordination based on the insignificant shift of the N-methyl carbon in the ^{13}C NMR spectra of all the imide complexes. Nitrogen coordination prior to stable olefin complex formation may be occurring as evidenced by an intense

violet color observed shortly after mixing the imide olefins in the aqueous ruthenium(II) solution. This violet color dissipates over time as the solution changes to the yellow color of the olefin complexes. More data is required, however, before we can conclude that this color is indicative of a kinetic nitrogen-coordinated ruthenium(II) complex. Imide containing bicyclic olefins are polymerized by **1** in high yield in degassed water.[11]

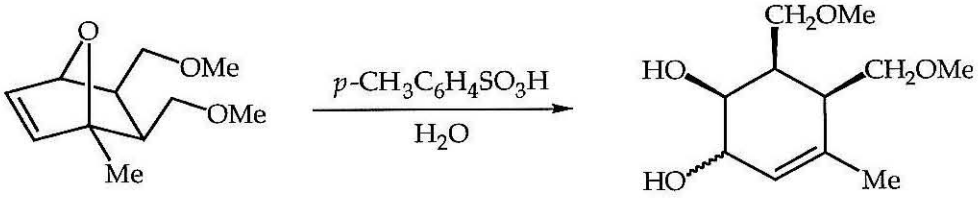


Bicyclic Olefins. To date **1** will ROMP only bicyclic olefins without benefit of added co-catalysts such as diazo initiators.[74] These bicyclics include norbornenes, 7-oxanorbornenes, and norbornadienes with a variety of pendant organic functionalities.[5, 10, 11, 75] There are, however, a number of bicyclic olefins which are not polymerized by **1** yet form stable olefin complexes. Undoubtedly the most intriguing of these is 1-methyl-5,6-*exo*-bis(methoxymethyl)-7-oxabicyclo[2.2.1]hept-2-ene **20**. Although this has the same carbon skeleton as our most active monomer,[5] 5,6-*exo*-bis(methoxymethyl)-7-oxabicyclo[2.2.1]hept-2-ene **21**, the methyl substituent on the bridgehead carbon prevents its polymerization. It forms an olefin complex **22** with ruthenium(II) in D_2O,



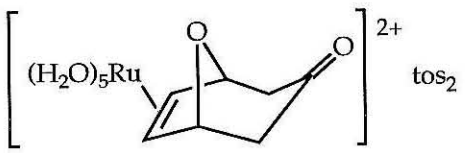
22

however, in high yield (98% by ^{1}H NMR). The olefin protons shift upfield by approximately 1.0 ppm and the *endo* protons on C-5 and C-6 shift *downfield* by approximately 0.7 ppm. The shift perturbations for all other protons are ≤ 0.1 ppm. All the spectral (Table 1) and electrochemical data (vide infra) for this complex are remarkably similar to that of the 5,6-*exo*-bis(methoxymethyl)-7-oxabicyclo[2.2.1]hept-2-ene ruthenium(II) complex **2**. The instability of the bridgehead-substituted monomer **20** in acidic media[76] may be responsible for its not polymerizing in the presence of **1**. When left at room temperature in dilute aqueous *p*-toluenesulfonic acid **20** decomposes, presumably to form a cyclohexenediol through hydrolysis of the 1,4 bridging epoxide. The ^{1}H NMR of the decomposition mixture is consistent with the structure shown.



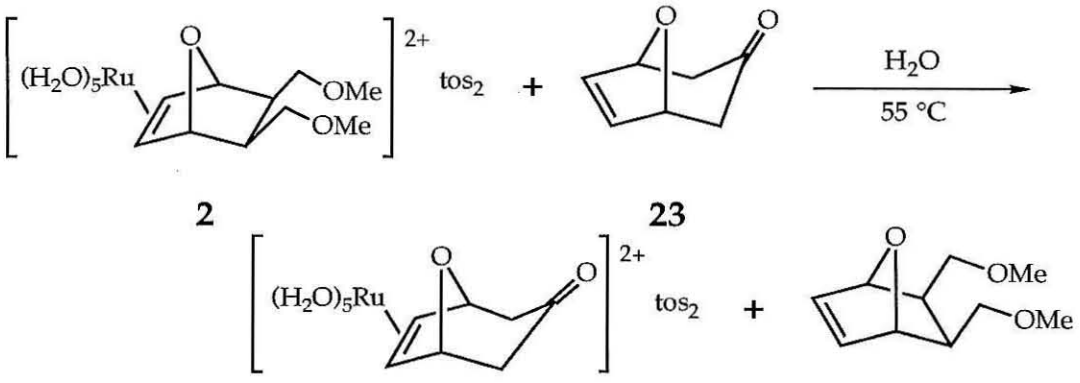
20

Equally perplexing in their reluctance to polymerize are the closely related olefins 8-oxabicyclo[3.2.1]oct-6-ene-3-one **23** and 2,2,4,4-tetramethyl-8-oxabicyclo[3.2.1]oct-6-ene-3-one **24**. Although not norbornene derivatives, the strain energy of these monomers is still relatively high.[77] When **23** is reacted with 10 mol % **1** in aqueous solution at 55 °C, however, only olefin complex **25** formation is observed (75% yield by ^{1}H NMR). No polymer is formed here or in



25

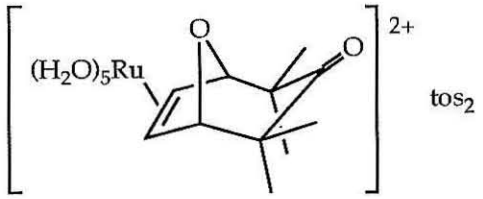
the presence or the more active catalyst[5] **2**. At 55 °C in water **23** reacts with **2** to yield ruthenium(II) olefin complex **25** and free oxanorbornene **21**. Olefin **24** also



2 **23**

25 **21**

reacts with **1** under similar conditions (aqueous solution, 55 °C) to form olefin complex **26** (75 % yield by ^{1}H NMR). The similar yield of olefin complexes **24** and **26** suggests a lack of steric interaction between the metal center and the methyl groups of **24**. This would be the case if the metal coordinates to the *exo* face of the bicyclic[3.2.1] olefins as shown. We believe *exo* coordination is also occurring with the bicyclic[2.2.1] olefins.

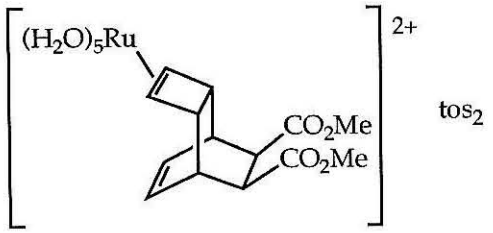


26

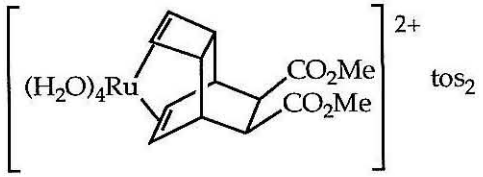
The coordination of the ruthenium(II) center to the *exo* face of the bicyclic[2.2.1] olefins as shown is supported by the large ^{1}H and ^{13}C shift perturbations experienced by both the protons and carbon of the methylene bridge (C-7) in complex **19**. The proton resonances shift upfield by 0.6 and 1.75

ppm and the carbon resonance shifts upfield by 13.7 ppm. In contrast, the methine carbons (C-2 and C-3) shift by less than 1 ppm in the ^{13}C NMR. Although the *endo* carboximide moiety may hinder ruthenium(II) coordination to the *endo* face of the olefin in this complex, we believe that the single carbon, or oxygen in the case of 7-oxa monomers, bridge is less sterically demanding than the two carbon bridge and thus facilitates metal coordination on this face of the olefin.

An intramolecular competition experiment was carried out between a cyclobutene and a cyclooctadiene moiety. Tricyclic diester 5,6-*exo*-bis(carbomethoxy)tri-cyclo[2.2.2.$2^{7,8}$]deca-2,9-diene **27** reacts with **1** at 55 °C in water to form olefin complexes **28a** and **28b** in an approximate 1 : 1 ratio (total yield 50%). Neither olefin polymerized in the presence of **1**. Cyclobutenes have been metathesis polymerized by ruthenium complexes.[78, 79]



28a

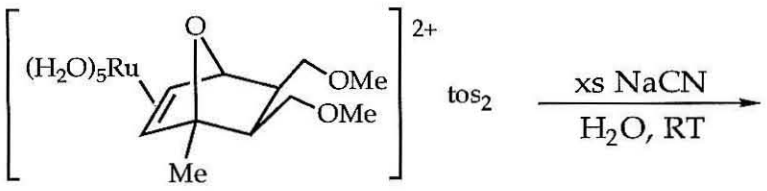


28b

Electrochemistry. All aqueous ruthenium(II) olefin complexes studied exhibit increased stabilization towards oxidation relative to the parent complex **1**.[80] Their formal reduction potentials, measured by cyclic voltammetry, are shown in Table 6. This stabilization, while not as large, is analogous to that observed for pentaammine ruthenium(II) olefin complexes[33-35, 37] and arises from the back donation of electron density from the metal d orbitals of π symmetry to the olefin π^* orbital according to the Dewar-Chatt-Duncanson model of the

transition metal-olefin bond.[51, 52] $E_{1/2}$ values for $(NH_3)_5RuL^{3+/2+}$ vary from 0.6 to 1.35 V more positive for L = olefin than L = NH_3 while we only see stabilizations of 0.18 to 0.89 V more positive for $(H_2O)_5RuL^{3+/2+}$ for L = olefin versus L = H_2O. Monodentate allyl ethyl ether is capable of raising the reduction potential of the pentaaquoruthenium(II) moiety 0.18 V over the parent hexaaquo ruthenium(II) complex, and electron withdrawing methyl acrylate raises the potential 0.74 V. This stabilization is greater than that provided by four pyridine ligands,[22] although this ignores the strong σ-donation provided by the pyridine nitrogen lone pair. The reduction potentials of the bicyclic olefin complexes are much larger, backdonation being more favorable for these strained carbon skeletons, than those of the acyclic monoolefin complexes. The oxidations, however, are not reversible, presumably due to fast loss of olefin on oxidation.

The back-bonding evident from the electrochemical data indicates that the bound olefins in these complexes may be subject to nucleophilic attack. Upon treatment with nucleophiles such as N_3^- and CN^-, however, complex **22** decomposes to free olefin **20** and ruthenium-nucleophile complexes.



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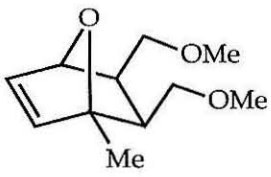

+ $Na_2[Ru(CN)_6]$

20

Table 6. Formal Redox Potentials of $Ru(H_2O)_nL^{3+/2+}$ (n = 4 or 5).

L	n	$E_{1/2}$, V vs NHE[a]
H_2O	5	+0.20[b]
allyl ethyl ether	5	+0.38
2,5-dihydrofuran	5	+0.83
methyl acrylate	5	+0.94
8-oxabicyclo[3.2.1]oct-6-ene-3-one	5	+1.24[c]
5,6-*exo*-bis(carbomethoxy) tricyclo[2.2.2.$2^{7,8}$]deca-2,9-diene	4,5	+1.30[c]
5,6-bis(methoxymethyl)-7-oxabicyclo[2.2.1]hept-2-ene	5	+1.33[c]
3-buten-1-ol	4	+0.62
sodium 2-propenesulfonate	4	+0.83
diallyl ether	4	large[d]
1,5-hexadiene	4	large[d]

[a] Glassy carbon working electrode, SSCE reference electrode, Pt wire auxiliary electrode, 0.1M $NaClO_4$, pH 2.
[b] Reference 17.
[c] E_p^{ox}, irreversible, measured at pH 7.
[d] exceeds limit of solvent window (+1.5 V).

Summary

Aqueous ruthenium(II) complexes of acyclic and monocyclic functionalized olefins have been prepared. Olefins, unlike amines, displace only one aquo ligand from the metal center to form monoolefin complexes of the $(H_2O)_5Ru^{II}$ moiety. Bis(olefin) complexes of aqueous ruthenium(II) dication may be formed, however, with chelating olefins such as diallyl ether. Functional groups of relatively low basicity, such as ethers, alcohols, esters, sulfonates, and imides, do not react irreversibly with the metal, but reversible chelation of pendant oxygen functionalities, such as alcohols, ethers, and sulfonates, has also been observed when the functional group is a specified distance from the olefin. Carboxylic acid functionalities, in contrast, react irreversibly with the ruthenium center leading to neutral bis(carboxylate complexes). Olefins do not compete successfully for the ruthenium(II) center in the presence of amines, yet the lower basicity of the nitrogen atom in organic imides prevents them from interfering with olefin coordination to aqueous ruthenium(II). A number of ruthenium(II) complexes of bicyclic olefins which are not polymerized in the presence of **1** have also been prepared. These complexes do not undergo rearrangement of the olefin ligand under polymerization conditions. All aqueous ruthenium(II) olefin complexes studied exhibit increased stabilization towards oxidation relative to the parent complex **1** consistent with the π-acidic nature of olefins when bound to transition metal centers.

Experimental

General Procedures. All manipulations involving air- and/or moisture-sensitive compounds were carried out using standard high vacuum or Schlenk techniques. Argon was purified by passage through columns of BASF RS-11 (Chemalog) and Linde 4Å molecular sieves. Solids were transferred and stored in a N_2-filled Vacuum Atmospheres glove box equipped with a MO-40-1 purification train, a DK-3E Dri-Kool conditioner, and a Dri-Cold Freezer.

Instrumentation. NMR spectra were recorded on a JEOL FX-90Q (89.6 MHz ^1H, 22.5 MHz ^{13}C), a JEOL GX-400 (399.65 MHz ^1H, 61.25 MHz ^2H, 100.40 MHz ^{13}C), a Varian XL-200 (200 MHz ^1H), Varian EM-390 (90 MHz ^1H) and a Bruker AM-500 (500.14 MHz ^1H, 76.78 MHz ^2H). Proton chemical shifts are referenced to internal residual solvent protons. Carbon chemical shifts are referenced to the carbon signal of the deuterated solvents. Deuterium chemical shifts are referenced to natural abundance deuterium in the solvent. Gas chromatography analyses were performed on a Shimadzu GC-Mini-2 flame-ionization instrument equipped with a 50 m capillary column and a Hewlett-Packard model 3390A integrator. Low-resolution mass spectrometry analyses were performed on a Hewlett-Packard model 5970 mass selective detector in conjunction with a Series 5890 GC equipped with a 15 m SE-30 capillary column or at the Southern California Mass Spectrometry Facility at the University of California, Riverside. Infrared spectra of solid complexes were recorded in Nujol mull on a Perkin-Elmer 1600 Series FT-IR. Elemental analysis was performed at the analytical facilities of the California Institute of Technology. Electrochemical measurements were performed on a Bio Analytical Systems Model 100 Electrochemical Analyzer or an EG&G Princeton Applied Research Model 173 Potentiostat/Galvanostat driven by an EG&G Princeton Applied Research Model

175 Universal Programmer utilizing a glassy carbon working electrode, a SSCE reference electrode, and a platinum wire auxiliary electrode in 0.1M aqueous $NaClO_4$ at pH 2 or pH 7.

Two-Dimensional ^1H-^1H Correlated NMR Spectra. The data were acquiredusing a JEOL GX-400 NMR spectrometer operating at 399.65 MHz proton frequency. The pulse sequence was 90°–t_1–90°–ACQTM–PD and the phases of the pulses and receiver were cycled to provide quadrature detection in f_1 and selection of "P-type" peaks. The ^1H 90° pulse width was measured on each individual sample by searching for the 180° null and was typically 8.0 μs on the 5mm ^1H probe. The f_2 spectral width was chosen at a minimum to accomodate all peaks in the one-dimensional spectrum and the pulse delay (PD) was minimally 1.0 s. One dummy scan was taken before each slice to eliminate non-equilibrium magnetization. A minimum of 8 transients of 1 K data points were collected for 256 increments of t_1. The data were apodized with a sine-bell window function and Fourier transformed in both dimensions. The absolute value spectrum was calculated and then symmetrized if necessary.

Two-Dimensional ^1H-^{13}C Correlated NMR Spectra. The data were acquiredusing a JEOL GX-400 NMR spectrometer operating at 399.65 MHz proton frequency and 100.40 MHz carbon frequency. The pulse sequence was taken from Bax[81] and the phases of the pulses and the receiver were cycled to provide quadrature detection in f_1. Broadband decoupling was applied during detection. The ^1H decoupler 90° and ^{13}C 90° pulse widths were measured on a sample of 1 : 1 :: chloroform : acetone-d_6 as described by Derome[82] and by searching for the 180° null, respectively, and were typically 41 and 10.5 μs, respectively, on the 5mm $^1H/^{13}C$ probe. The f_2 spectral width was 14000 Hz and the pulse delay (PD) was 1.4 s. The incrementation of t_1 provided an f_1 spectral

width of 2600 Hz. The fixed delays were optimized for J_{CH} = 150 Hz. One-hundred twenty-eight transients of 2 K data points were collected for 128 increments of t_1. The data were apodized in both dimensions with a sine-bell window function, Fourier transformed, and the absolute value spectrum calculated.

^{1}H-^{13}C INEPT Spectra. Coupling constants between proton and carbon nuclei were measured by INEPT[83] experiments performed on a JEOL GX-400 NMR spectrometer operating at 399.65 MHz proton frequency and 100.40 MHz carbon frequency. The ^{1}H decoupler 90° and ^{13}C 90° pulse widths were measured on a sample of 1 : 1 :: chloroform : acetone-d_6 as described by Derome[82] and by searching for the 180° null, respectively, and were typically 41 and 10.5 μs, respectively, on the 5mm ^{1}H/^{13}C probe. The fixed delays were set for J_{CH} = 150-155 Hz.

Materials. Benzene, diethyl ether, and tetrahydrofuran were distilled from sodium-benzophenone ketyl and methylene chloride was distilled from calcium hydride. Dried degassed solvents were stored under argon in dry glass vessels equipped with Teflon valve closures. Water was either house deionized or purchased from Aldrich (HPLC grade) and degassed prior to use. Chloroform-*d* and benzene-d_6 were purchsed from Cambridge Isotope Laboratories and used as received. Deuterium oxide was purchased from Aldrich or Cambridge Isotope Laboratories and degassed prior to use. 2,5-Dihydrofuran, allyl ethyl ether, diallyl ether, 1,5-hexadiene, and 1,6-heptadiene were purchased from Aldrich and stored degassed in dry glass vessels equipped with Teflon valve closures after distillation from calcium hydride under argon. 3-Buten-1-ol was purchased from Aldrich and purified by passage through reagent grade alumina before use. Methyl acrylate, 3-pentenoic acid, 3-butenoic

acid, 2-pentenoic acid, *N*-methylmaleimide, and (±)-3-cyclohexen-1-methanol were purchased from Aldrich and used as received. Diallylmethylamine was purchased from Pfaltz & Bauer and used as received. Sodium 2-propene-sulfonate was purchased from American Tokyo Casei and used as received. 3-Butenyl methyl ether was prepared from 3-buten-1-ol and methyl iodide in diethyl ether in the presence of an excess of sodium hydride and distilled at atmospheric pressure from the reaction mixture. Thin-layer chromatography (TLC) was performed on precoated TLC plates (silica gel 60 F-254, EM Reagents). Flash chromatography was performed by the method of Still et al.,[84] using silica gel 60 (230-400 mesh ATM, EM Reagents). Reagent grade petroleum ether (35-60 °C), methanol, diethyl ether, and ethyl acetate were used without futher purification. 5,6-*exo*-Bis(methoxymethyl)-7-oxabicyclo[2.2.1]hept-2-ene,[5] 8-oxabicyclo[3.2.1]oct-6-ene-3-one,[85] and 2,2,4,4-tetramethyl-8-oxabicyclo[3.2.1]oct-6-ene-3-one[85] were published by the literature procedures. 2-Benzyl-2-azabicyclo[2.2.1]hept-5-ene[86] and 5,6-*exo*-bis(carbomethoxy)tricyclo-[2.2.2.2^{7,8}]deca-2,9-diene were kindly supplied as gifts from E. J. Ginsburg of these laboratories. Maleimides *exo*- and *endo*-*N*-methyl-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide and *endo*-*N*-methylbicyclo[2.2.1]hept-5-ene-2,3-dicarboximide were prepared through standard Diels-Alder chemistry by C. LePetit of these laboratories. 1-Methyl-5,6-*exo*-bis(methoxymethyl)-7-oxabicyclo[2.2.1]hept-2-ene was kindly supplied as a gift from B. M. Novak of these laboratories. Paul Bernhard is gratefully acknowledged for initial samples of $Ru^{II}(H_2O)_6(tos)_2$[9] and for a modified procedure for its preparation prior to publication.[8] All samples of $Ru^{II}(H_2O)_6(tos)_2$ prepared in these laboratories were according to the literature procedure.[8]

Preparation of Aqueous Ruthenium(II) Olefin Complexes. To a schlenk

tube containing $Ru^{II}(H_2O)_6(tos)_2$ in water is added olefin (10 eq./Ru^{II}) and the pink solution is stirred under argon for 10-12 hours. The resulting yellow solution then extracted with ether to remove excess olefin and the solvent is removed in vacuo. In the case of volatile olefins (e.g., 2,5-dihydrofuran, allyl ethyl ether, diallyl ether) the solution is not extracted with ether before removal of solvent. The crude olefin complexes are rather pure, the only contaminant being small amounts of $Ru^{II}(H_2O)_6(tos)_2$. Recrystallization is possible by dissolving the complex in aqueous 1.8 M *p*-toluene sulfonic acid to 57 mM [Ru^{II}], concentrating the solution to half its original volume by rotory evaporation at 25-35 °C, and then cooling to 0 °C. The yellow crystals are collected on a medium sintered glass funnel, washed with ethyl acetate and diethyl ether to remove cocrystallized *p*-toluene sulfonic acid, and dried in vacuo.

Preparation of Aqueous Ruthenium(II) Olefin Complexes in Methanol. To a schlenk tube containing $Ru^{II}(H_2O)_6(tos)_2$ in methanol is added olefin (10 eq./Ru^{II}) and the pink solution is stirred under argon for 10-12 hours. To the resulting yellow solution is added an equivalent volume of water and the mixture is partitioned with petroleum ether. Repeated extraction with petroleum ether yields an aqueous solution of the desired olefin complex. Isolation follows the procedure outlined above.

$Ru(H_2O)_2(\eta^1\text{-}(O),\eta^2\text{-}(C,C')\text{-}OCOCH_2CH{=}CHCH_3)_2$ (12). A solution containing $Ru^{II}(H_2O)_6(tos)_2$ (250 mg, 0.45 mmol) and 3-pentenoic acid (450 mg, 4.5 mmol) in water (15 mL) was stirred at 55 °C under argon for 40 minutes. The solution was then allowed to cool to room temperature and stirred at room temperature for an additional 20 hours during which time a pale yellow precipitate formed. The product was collected on a medium sintered glass funnel, washed with water, and dried in vacuo (102 mg, 30 mmol, 67% yield).

The material obtained in this manner is pure by elemental analysis. X-ray quality crystals may be obtained by dissolving the powder in a minimum of dilute aqueous NaOH and neutralizing the solution with aqueous H_2SO_4. The crystals form over a period of weeks at room temperature and are isolated as above.

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(65) Anal. Calcd for $C_{20}H_{32}O_{11}RuS_2$: C, 39.15; H, 5.26. Found: C, 39.00; H, 5.19.

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Appendix

Crystal structure data for $Ru(H_2O)_2(\eta^1\text{-}(O),\eta^2\text{-}(C,C')\text{-}OCOCH_2CH{=}CHCH_3)_2$ (**12**) from the reaction of 3-pentenoic acid with $Ru^{II}(H_2O)_6(tos)_2$ (**1**).

Formula: $C_{10}H_{18}O_6Ru$ Fw: 335.3

Color, habit: Yellow-gold plate Size: 0.08 x 0.26 x 0.32 mm

Temperature: 183 °K

Crystal System: Orthorhombic Space Group: $P2_12_12_1$ (No. 19)

a = 7.8085(12) Å D_{calcd}, g/cm^3 = 1.840

b = 8.0452(10) Å Z = 4

c = 19.2704(28) Å

Diffractometer: Siemens P3 (R3m/V System)

Radiation: MoKα (λ = 0.710730 Å) with oriented graphite monochrometer

Data Collected: $+h, +k, \pm l$ Scan Type: $\Theta - 2\Theta$

Scan Range: 1.2° plus Kα-separation Scan Speed: Fixed, 3.0° min^{-1} in ω

2Θ range: 4.0° to 50.0° μ(MoKα), mm^{-1} = 0.1.28

Reflections Collected: 2492 Independent Reflections: 1266

Reflections with $|F_o| > 2.0\sigma(|F_o|)$ Number of Variables: 156

Final R_F = 2.2%, R_{wF} = 2.7% Goodness of Fit: 1.04

Heavy Atom Coordinates (x 10^4) and Equivalent Isotropic Displacement Coefficients ($Å^2$ x 10^4)

	x	y	z	U(eq)
Ru(1)	1370.6(.4)	9250.6(.4)	1690.3(.1)	107(1)
O(1)	374(3)	11647(3)	1652(1)	144(8)
O(2)	-1682(4)	13278(4)	1232(2)	225(9)
O(3)	2121(4)	6938(3)	2041(1)	138(8)
O(4)	4248(4)	5163(4)	2193(2)	229(9)
O(5)	-892(4)	8842(3)	2295(1)	153(8)
O(6)	2386(4)	10079(4)	2647(1)	162(8)
C(1)	-921(5)	11935(5)	1255(2)	164(12)
C(2)	-1487(6)	10453(5)	822(2)	187(12)
C(3)	-29(5)	9265(6)	711(2)	170(11)
C(4)	2(6)	7638(5)	940(2)	177(12)
C(5)	951(7)	6251(6)	576(2)	263(14)
C(6)	3686(6)	6475(5)	1941(2)	154(11)
C(7)	4768(6)	7621(6)	1515(2)	196(12)
C(8)	3714(6)	8860(5)	1097(2)	171(11)
C(9)	3636(6)	10535(5)	1251(2)	178(11)
C(10)	3381(6)	11869(6)	712(2)	251(13)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

Interatomic Distances (Å) with Esd's

Ru(1)-O(1)	2.080(3)	Ru(1)-O(3)	2.065(3)
Ru(1)-O(5)	2.141(3)	Ru(1)-O(6)	2.115(3)
Ru(1)-C(3)	2.181(4)	Ru(1)-C(4)	2.217(4)
Ru(1)-C(8)	2.181(4)	Ru(1)-C(9)	2.217(4)
O(1)-C(1)	1.290(5)	O(2)-C(1)	1.234(5)
O(3)-C(6)	1.292(5)	O(4)-C(6)	1.242(5)
C(1)-C(2)	1.520(6)	C(2)-C(3)	1.503(6)
C(3)-C(4)	1.381(6)	C(4)-C(5)	1.512(6)
C(6)-C(7)	1.495(6)	C(7)-C(8)	1.523(6)
C(8)-C(9)	1.381(6)	C(9)-C(10)	1.506(6)

Interatomic Angles (Deg.) with Esd's

O(1)-Ru(1)-O(3)	162.4(1)	O(1)-Ru(1)-O(5)	81.6(1)
O(3)-Ru(1)-O(5)	85.3(1)	O(1)-Ru(1)-O(6)	83.1(1)
O(3)-Ru(1)-O(6)	83.8(1)	O(5)-Ru(1)-O(6)	83.3(1)
O(1)-Ru(1)-C(3)	77.1(1)	O(3)-Ru(1)-C(3)	115.5(1)
O(5)-Ru(1)-C(3)	93.3(1)	O(6)-Ru(1)-C(3)	160.2(1)
O(1)-Ru(1)-C(4)	109.8(1)	O(3)-Ru(1)-C(4)	79.8(1)
O(5)-Ru(1)-C(4)	82.4(1)	O(6)-Ru(1)-C(4)	159.0(1)
C(3)-Ru(1)-C(4)	36.6(2)	O(1)-Ru(1)-C(8)	115.4(1)
O(3)-Ru(1)-C(8)	78.7(1)	O(5)-Ru(1)-C(8)	162.8(1)
O(6)-Ru(1)-C(8)	100.8(1)	C(3)-Ru(1)-C(8)	88.1(2)
C(4)-Ru(1)-C(8)	88.7(2)	O(1)-Ru(1)-C(9)	81.5(1)
O(3)-Ru(1)-C(9)	108.6(1)	O(5)-Ru(1)-C(9)	159.7(1)
O(6)-Ru(1)-C(9)	83.5(1)	C(3)-Ru(1)-C(9)	93.8(2)
C(4)-Ru(1)-C(9)	114.1(2)	C(8)-Ru(1)-C(9)	36.6(2)

Ru(1)-O(1)-C(1)	118.7(2)	Ru(1)-O(3)-C(6)	118.6(2)
O(1)-C(1)-O(2)	123.7(4)	O(1)-C(1)-C(2)	114.4(3)
O(2)-C(1)-C(2)	121.8(4)	C(1)-C(2)-C(3)	110.9(4)
Ru(1)-C(3)-C(2)	105.0(3)	Ru(1)-C(3)-C(4)	73.1(2)
C(2)-C(3)-C(4)	124.8(4)	Ru(1)-C(4)-C(3)	70.3(2)
Ru(1)-C(4)-C(5)	119.9(3)	C(3)-C(4)-C(5)	124.0(4)
O(3)-C(6)-O(4)	121.4(4)	O(3)-C(6)-C(7)	116.0(4)
O(4)-C(6)-C(7)	122.6(4)	C(6)-C(7)-C(8)	112.9(4)
Ru(1)-C(8)-C(7)	105.7(3)	Ru(1)-C(8)-C(9)	73.1(3)
C(7)-C(8)-C(9)	123.3(4)	Ru(1)-C(9)-C(8)	70.3(3)
Ru(1)-C(9)-C(10)	119.4(3)	C(8)-C(9)-C(10)	123.6(4)

Anisotropic Displacement Coefficients ($Å^2 \times 10^4$)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ru(1)	89(2)	107(2)	126(2)	6(1)	7(1)	1(1)
O(1)	144(14)	135(13)	153(13)	26(11)	-7(13)	-26(12)
O(2)	266(19)	186(15)	224(15)	111(15)	-41(14)	-24(12)
O(3)	84(13)	149(13)	181(13)	14(13)	18(12)	19(12)
O(4)	125(15)	178(15)	382(18)	24(14)	-15(14)	96(14)
O(5)	128(14)	149(14)	184(13)	34(12)	8(12)	27(11)
O(6)	128(14)	192(14)	167(14)	-23(13)	-21(12)	4(12)
C(1)	141(21)	169(20)	183(21)	2(19)	32(17)	22(17)
C(2)	209(22)	169(20)	182(19)	22(21)	-29(18)	4(16)
C(3)	155(20)	203(20)	153(17)	25(22)	-25(17)	-31(20)
C(4)	150(21)	173(21)	208(20)	-19(19)	-64(19)	-57(18)
C(5)	289(27)	207(21)	293(22)	38(21)	-46(21)	-68(18)
C(6)	135(21)	158(19)	170(18)	-5(20)	-56(18)	-21(16)
C(7)	142(20)	182(20)	264(21)	57(18)	23(18)	26(18)
C(8)	134(19)	219(21)	158(18)	-11(19)	59(19)	18(16)
C(9)	106(18)	197(20)	232(19)	-5(22)	63(18)	70(17)
C(10)	232(25)	239(22)	283(22)	32(22)	81(20)	105(19)

The anisotropic displacement exponent takes the form:
$-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12})$

Hydrogen Atom Coordinates ($\times 10^4$) and Isotropic Displacement Coefficients ($Å^2 \times 10^4$)

	x	y	z	U
H(5A)	-763	8121	2648	600
H(5B)	-1181	9783	2518	600
H(6A)	1996	9489	3011	600
H(6B)	3490	10237	2765	600
H(2A)	-2411	9888	1051	600
H(2B)	-1899	10840	382	600
H(3A)	660	9481	308	600
H(4A)	-1094	7284	1111	600
H(5C)	145	5503	367	600
H(5D)	1688	6705	226	600
H(5E)	1646	5657	904	600
H(7A)	5535	8216	1815	600
H(7B)	5447	6969	1202	600
H(8A)	3552	8585	616	600
H(9A)	4447	10855	1600	600
H(10A)	4469	12306	567	600
H(10B)	2822	11405	313	600
H(10C)	2693	12745	904	600

Observed and Calculated Structure Factors for $Ru(H_2O)_2(\eta^1$-$(O),\eta^2$-(C,C')-$OCOCH_2CH{=}CHCH_3)_2$ (**12**)

h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s
2	0	0	140	135	5	3	9	0	276	282	7	5	7	1	141	135	7	1	6	2	592	589	9
4	0	0	1328	1290	4	1	0	1	1316	1269	1	6	7	1	530	519	5	2	6	2	481	476	4
6	0	0	403	402	5	2	0	1	76	67	5	0	8	1	560	585	4	3	6	2	330	327	5
8	0	0	743	742	6	3	0	1	1046	1015	2	1	8	1	437	450	4	4	6	2	495	484	4
1	1	0	1149	1111	2	4	0	1	84	71	10	2	8	1	183	178	5	5	6	2	609	599	4
2	1	0	962	930	3	5	0	1	71	85	7	3	8	1	441	434	11	6	6	2	361	367	6
3	1	0	97	95	5	6	0	1	201	199	6	4	8	1	301	299	5	7	6	2	197	193	13
4	1	0	679	660	4	7	0	1	450	465	8	5	8	1	200	187	10	0	7	2	848	881	5
5	1	0	899	883	4	8	0	1	80	64	11	0	9	1	152	168	5	1	7	2	320	329	4
6	1	0	341	345	6	9	0	1	128	155	26	1	9	1	408	414	5	2	7	2	75	73	8
7	1	0	88	106	15	0	1	1	452	472	16	2	9	1	311	313	5	3	7	2	360	363	4
8	1	0	58	65	21	1	1	1	1072	1039	3	3	9	1	157	146	6	4	7	2	624	622	8
9	1	0	758	766	7	2	1	1	988	958	3	0	0	2	1513	1618	3	5	7	2	391	390	7
0	2	0	716	741	3	3	1	1	158	187	3	1	0	2	1406	1361	4	6	7	2	281	284	15
1	2	0	858	864	3	4	1	1	191	196	7	2	0	2	267	264	3	0	8	2	158	163	5
2	2	0	377	362	3	5	1	1	535	517	3	3	0	2	920	889	3	1	8	2	337	335	4
3	2	0	983	972	4	6	1	1	456	457	9	4	0	2	459	463	3	2	8	2	285	286	6
4	2	0	762	759	4	7	1	1	348	343	14	5	0	2	707	696	3	3	8	2	187	188	15
5	2	0	363	352	5	8	1	1	410	410	5	6	0	2	163	167	7	4	8	2	230	232	5
6	2	0	52	5	19	9	1	1	245	238	12	7	0	2	111	119	6	5	8	2	355	361	5
7	2	0	714	730	6	0	2	1	722	748	12	8	0	2	245	242	8	0	9	2	264	260	5
8	2	0	383	386	7	1	2	1	203	212	6	9	0	2	672	677	8	1	9	2	342	349	5
9	2	0	1	6	–2	2	2	1	403	394	2	0	1	2	1655	1745	45	2	9	2	387	388	5
1	3	0	313	316	4	3	2	1	505	511	3	1	1	2	584	587	10	3	9	2	439	429	6
2	3	0	1083	1059	3	4	2	1	817	813	3	2	1	2	143	150	12	1	0	3	457	440	2
3	3	0	162	166	5	5	2	1	378	373	10	3	1	2	404	402	11	2	0	3	719	736	2
4	3	0	346	338	5	6	2	1	333	335	5	4	1	2	985	957	4	3	0	3	395	370	3
5	3	0	42	18	22	7	2	1	526	524	4	5	1	2	392	394	3	4	0	3	470	463	5
6	3	0	758	754	5	8	2	1	412	411	5	6	1	2	441	442	8	5	0	3	68	19	–272
7	3	0	351	350	7	9	2	1	231	238	8	7	1	2	274	271	5	6	0	3	521	522	4
8	3	0	518	519	7	0	3	1	701	732	9	8	1	2	539	551	6	7	0	3	94	94	7
0	4	0	341	344	4	1	3	1	763	760	2	9	1	2	430	433	6	8	0	3	424	413	5
1	4	0	1029	1007	4	2	3	1	326	317	3	0	2	2	675	689	18	9	0	3	112	31	–449
2	4	0	13	40	–27	3	3	1	674	651	3	1	2	2	803	791	2	0	1	3	779	823	11
3	4	0	517	515	5	4	3	1	564	564	3	2	2	2	786	770	2	1	1	3	1129	1106	7
4	4	0	691	666	5	5	3	1	864	857	3	3	2	2	855	822	6	2	1	3	667	638	4
5	4	0	332	325	6	6	3	1	76	77	8	4	2	2	412	410	3	3	1	3	844	844	11
6	4	0	101	102	10	7	3	1	189	186	6	5	2	2	776	764	3	4	1	3	402	408	3
7	4	0	464	464	7	8	3	1	329	333	5	6	2	2	685	679	4	5	1	3	499	505	3
8	4	0	160	154	9	0	4	1	1111	1149	10	7	2	2	353	357	5	6	1	3	224	217	4
1	5	0	473	468	4	1	4	1	845	820	3	8	2	2	308	302	6	7	1	3	590	583	4
2	5	0	817	803	4	2	4	1	217	220	3	9	2	2	206	203	7	8	1	3	331	330	5
3	5	0	377	384	5	3	4	1	197	201	4	0	3	2	112	119	8	9	1	3	64	59	15
4	5	0	161	154	7	4	4	1	664	653	3	1	3	2	1025	1013	7	0	2	3	145	157	3
5	5	0	542	534	5	5	4	1	514	513	4	2	3	2	558	544	13	1	2	3	532	534	2
6	5	0	591	595	6	6	4	1	218	220	19	3	3	2	704	692	7	2	2	3	647	651	2
7	5	0	176	171	10	7	4	1	76	74	9	4	3	2	342	347	5	3	2	3	426	425	3
0	6	0	521	540	5	8	4	1	408	405	5	5	3	2	370	370	10	4	2	3	363	354	3
1	6	0	209	212	6	0	5	1	449	457	3	6	3	2	422	419	4	5	2	3	743	737	6
2	6	0	115	118	7	1	5	1	395	398	3	7	3	2	563	560	7	6	2	3	556	551	9
3	6	0	165	164	7	2	5	1	444	428	6	8	3	2	305	323	8	7	2	3	255	262	5
4	6	0	635	628	6	3	5	1	540	534	3	0	4	2	44	18	10	8	2	3	294	291	5
5	6	0	93	87	12	4	5	1	337	336	18	1	4	2	682	666	3	9	2	3	435	430	6
6	6	0	409	396	7	5	5	1	259	252	12	2	4	2	1086	1057	3	0	3	3	1043	1093	33
7	6	0	293	293	8	6	5	1	427	430	5	3	4	2	583	573	3	1	3	3	303	289	3
1	7	0	539	534	5	7	5	1	245	243	5	4	4	2	445	439	5	2	3	3	346	330	3
2	7	0	151	153	7	0	6	1	62	68	10	5	4	2	278	287	4	3	3	3	278	283	5
3	7	0	584	577	6	1	6	1	461	460	5	6	4	2	476	475	10	4	3	3	1141	1115	3
4	7	0	146	142	8	2	6	1	454	444	11	7	4	2	273	274	12	5	3	3	81	74	12
5	7	0	673	680	6	3	6	1	569	553	8	8	4	2	397	398	5	6	3	3	288	278	5
6	7	0	61	7	20	4	6	1	204	204	6	0	5	2	707	705	6	7	3	3	68	76	11
0	8	0	556	563	6	5	6	1	362	370	5	1	5	2	710	688	4	8	3	3	487	488	5
1	8	0	263	263	6	6	6	1	375	388	8	2	5	2	506	501	3	0	4	3	162	155	3
2	8	0	177	194	8	7	6	1	516	509	5	3	5	2	525	516	3	1	4	3	984	969	9
3	8	0	183	172	8	0	7	1	396	408	5	4	5	2	496	486	4	2	4	3	356	337	5
4	8	0	505	496	6	1	7	1	298	302	4	5	5	2	345	339	4	3	4	3	387	390	3
5	8	0	1	61	–2	2	7	1	485	470	7	6	5	2	348	351	5	4	4	3	122	115	6
1	9	0	258	247	7	3	7	1	261	260	4	7	5	2	508	507	5	5	4	3	713	699	4
2	9	0	702	677	6	4	7	1	228	233	7	0	6	2	129	139	4	6	4	3	104	102	6

Observed and Calculated Structure Factors for $Ru(H_2O)_2(\eta^1$-$(O),\eta^2$-(C,C')-$OCOCH_2CH{=}CHCH_3)_2$ (12)

h	k	l	10Fo	10Fc	10s
7	4	3	65	61	13
8	4	3	158	161	9
0	5	3	834	849	21
1	5	3	390	385	10
2	5	3	82	89	7
3	5	3	672	669	3
4	5	3	458	444	5
5	5	3	93	100	18
6	5	3	236	243	5
7	5	3	413	402	5
0	6	3	82	78	9
1	6	3	148	149	5
2	6	3	836	821	3
3	6	3	246	235	5
4	6	3	357	351	8
5	6	3	283	283	5
6	6	3	690	686	4
7	6	3	44	53	21
0	7	3	279	288	6
1	7	3	342	338	9
2	7	3	128	127	6
3	7	3	617	621	7
4	7	3	126	123	6
5	7	3	268	265	6
6	7	3	115	115	8
0	8	3	46	30	14
1	8	3	357	372	12
2	8	3	601	602	4
3	8	3	318	325	5
4	8	3	121	119	18
0	9	3	435	452	5
1	9	3	215	214	5
2	9	3	149	158	6
0	0	4	1166	1255	7
1	0	4	1123	1107	2
2	0	4	295	280	3
3	0	4	680	661	3
4	0	4	694	666	3
5	0	4	703	689	3
6	0	4	603	609	4
7	0	4	1	27	−1
8	0	4	354	363	6
9	0	4	623	617	5
0	1	4	551	575	3
1	1	4	720	708	12
2	1	4	604	592	6
3	1	4	1156	1104	2
4	1	4	856	848	6
5	1	4	527	524	3
6	1	4	360	367	5
7	1	4	117	124	7
8	1	4	367	366	7
9	1	4	202	212	7
0	2	4	382	377	10
1	2	4	498	480	13
2	2	4	969	945	3
3	2	4	746	727	9
4	2	4	508	497	3
5	2	4	619	611	7
6	2	4	775	765	5
7	2	4	354	347	6
8	2	4	285	288	8
0	3	4	58	51	6
1	3	4	889	872	19
2	3	4	806	781	8
3	3	4	881	865	3
4	3	4	192	199	9
5	3	4	348	339	4
6	3	4	350	346	9
7	3	4	676	690	4
8	3	4	205	203	7
0	4	4	228	239	7
1	4	4	363	361	8
2	4	4	1011	999	6
3	4	4	178	181	4
4	4	4	263	255	4
5	4	4	327	324	5
6	4	4	391	382	4
7	4	4	300	301	10
8	4	4	284	293	6
0	5	4	925	926	24
1	5	4	521	520	3
2	5	4	430	414	3
3	5	4	692	684	3
4	5	4	559	557	6
5	5	4	344	343	8
6	5	4	244	236	5
7	5	4	482	480	13
0	6	4	479	485	9
1	6	4	523	514	14
2	6	4	98	87	7
3	6	4	307	315	15
4	6	4	203	193	13
5	6	4	612	598	4
6	6	4	149	145	10
7	6	4	168	176	21
0	7	4	578	581	16
1	7	4	296	297	4
2	7	4	214	202	11
3	7	4	106	77	17
4	7	4	667	651	5
5	7	4	258	263	5
6	7	4	167	162	6
0	8	4	433	450	7
1	8	4	470	474	4
2	8	4	322	323	10
3	8	4	239	235	5
4	8	4	331	323	12
0	9	4	196	216	8
1	9	4	379	391	5
2	9	4	229	232	10
1	0	5	434	427	3
2	0	5	1184	1157	2
3	0	5	942	924	3
4	0	5	580	569	3
5	0	5	273	285	4
6	0	5	422	408	10
7	0	5	532	523	4
8	0	5	347	348	5
9	0	5	142	151	7
0	1	5	815	857	2
1	1	5	1048	1038	6
2	1	5	1315	1289	15
3	1	5	737	732	3
4	1	5	568	558	3
5	1	5	643	626	12
6	1	5	563	564	4
7	1	5	378	386	5
8	1	5	338	341	10
9	1	5	204	193	14
0	2	5	777	806	16
1	2	5	256	270	14
2	2	5	556	542	7
3	2	5	222	234	12
4	2	5	771	766	3
5	2	5	503	505	3
6	2	5	541	539	4
7	2	5	299	300	5
8	2	5	424	421	9
0	3	5	702	732	17
1	3	5	613	629	6
2	3	5	301	282	3
3	3	5	369	363	4
4	3	5	601	594	7
5	3	5	637	625	4
6	3	5	276	275	9
7	3	5	244	250	14
8	3	5	310	316	5
0	4	5	795	814	31
1	4	5	545	534	10
2	4	5	166	163	8
3	4	5	259	267	7
4	4	5	654	646	6
5	4	5	316	327	4
6	4	5	109	109	7
7	4	5	288	295	11
8	4	5	359	361	6
0	5	5	303	318	11
1	5	5	427	435	3
2	5	5	601	610	7
3	5	5	465	453	4
4	5	5	362	361	6
5	5	5	263	248	10
6	5	5	369	370	6
7	5	5	185	186	15
0	6	5	295	307	9
1	6	5	153	160	5
2	6	5	423	423	4
3	6	5	613	608	4
4	6	5	147	149	6
5	6	5	349	337	5
6	6	5	402	403	11
0	7	5	261	270	7
1	7	5	68	78	15
2	7	5	508	508	4
3	7	5	371	380	14
4	7	5	243	238	7
5	7	5	132	127	17
6	7	5	400	394	5
0	8	5	262	273	8
1	8	5	434	439	7
2	8	5	506	509	4
3	8	5	420	421	8
4	8	5	253	257	6
0	9	5	322	319	5
1	9	5	374	377	10
2	9	5	259	256	5
0	0	6	535	561	2
1	0	6	528	522	2
2	0	6	32	4	−126
3	0	6	164	169	7
4	0	6	884	867	3
5	0	6	83	85	10
6	0	6	407	405	4
7	0	6	46	55	15
8	0	6	437	424	5
0	1	6	443	462	2
1	1	6	1034	1021	15
2	1	6	428	430	6
3	1	6	1025	989	9
4	1	6	182	177	4
5	1	6	741	727	5
6	1	6	456	453	4
7	1	6	126	139	10
8	1	6	28	32	22
0	2	6	214	240	3
1	2	6	590	588	4
2	2	6	127	122	5
3	2	6	1089	1048	4
4	2	6	693	694	7
5	2	6	434	422	4
6	2	6	305	315	4
7	2	6	603	603	9
8	2	6	335	348	12
0	3	6	154	143	6
1	3	6	187	184	4
2	3	6	1182	1170	5
3	3	6	134	140	8
4	3	6	155	169	4
5	3	6	439	430	4
6	3	6	641	633	6
7	3	6	92	85	9
8	3	6	347	356	6
0	4	6	479	476	10
1	4	6	825	820	8
2	4	6	140	144	10
3	4	6	882	859	6
4	4	6	108	117	6
5	4	6	247	243	16
6	4	6	118	122	9
7	4	6	645	641	4
8	4	6	237	248	6
0	5	6	314	321	8
1	5	6	675	665	14
2	5	6	653	646	3
3	5	6	288	279	4
4	5	6	141	138	6
5	5	6	459	456	4
6	5	6	403	409	5
7	5	6	194	193	6
0	6	6	698	707	24
1	6	6	197	197	9
2	6	6	320	324	4
3	6	6	269	282	16
4	6	6	701	692	4
5	6	6	112	121	7
6	6	6	167	181	6
0	7	6	91	92	6
1	7	6	611	605	6
2	7	6	231	238	5
3	7	6	289	281	11
4	7	6	85	69	22
5	7	6	606	598	5
0	8	6	595	609	5
1	8	6	266	269	14
2	8	6	109	109	7
3	8	6	287	285	5
4	8	6	433	429	10
0	9	6	105	116	7
1	9	6	259	264	5
2	9	6	512	510	7
1	0	7	645	657	3
2	0	7	669	659	3
3	0	7	816	805	11
4	0	7	74	66	12
5	0	7	338	346	6
6	0	7	338	345	4
7	0	7	622	619	4
8	0	7	191	201	10
0	1	7	381	395	2
1	1	7	421	432	10
2	1	7	1287	1251	2
3	1	7	361	367	12
4	1	7	207	210	12
5	1	7	332	333	8
6	1	7	765	748	7

Observed and Calculated Structure Factors for $Ru(H_2O)_2(\eta^1$-$(O),\eta^2$-(C,C')-$OCOCH_2CH{=}CHCH_3)_2$ (**12**)

h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s
7	1	7	208	210	11	4	1	8	473	483	3	5	1	9	83	78	8	5	1	10	191	187	9
8	1	7	380	391	5	5	1	8	481	472	6	6	1	9	240	238	6	6	1	10	491	488	6
0	2	7	284	320	4	6	1	8	161	175	5	7	1	9	759	764	10	7	1	10	323	339	5
1	2	7	835	826	11	7	1	8	267	280	13	8	1	9	239	240	6	8	1	10	389	391	5
2	2	7	570	547	4	8	1	8	300	312	9	0	2	9	112	104	9	0	2	10	324	337	3
3	2	7	589	579	8	0	2	8	252	270	3	1	2	9	701	720	7	1	2	10	272	290	3
4	2	7	602	593	3	1	2	8	691	685	3	2	2	9	763	758	7	2	2	10	956	956	3
5	2	7	309	307	4	2	2	8	798	795	3	3	2	9	437	425	8	3	2	10	341	349	13
6	2	7	249	242	5	3	2	8	336	338	15	4	2	9	164	165	5	4	2	10	362	369	4
7	2	7	512	518	4	4	2	8	445	436	5	5	2	9	706	685	4	5	2	10	273	278	4
8	2	7	372	363	5	5	2	8	495	493	4	6	2	9	342	351	4	6	2	10	586	586	5
0	3	7	119	131	4	6	2	8	528	528	4	7	2	9	212	223	6	7	2	10	211	226	10
1	3	7	842	844	6	7	2	8	455	466	5	8	2	9	204	174	17	8	2	10	314	310	17
2	3	7	339	327	9	8	2	8	149	162	7	0	3	9	914	951	5	0	3	10	223	228	4
3	3	7	548	559	5	0	3	8	185	190	12	1	3	9	276	281	6	1	3	10	500	501	9
4	3	7	454	442	5	1	3	8	775	778	12	2	3	9	174	168	4	2	3	10	444	447	8
5	3	7	684	675	7	2	3	8	703	695	7	3	3	9	274	278	4	3	3	10	561	552	3
6	3	7	178	177	7	3	3	8	651	653	3	4	3	9	724	722	4	4	3	10	185	190	5
7	3	7	240	249	14	4	3	8	234	221	6	5	3	9	225	222	6	5	3	10	200	192	5
8	3	7	176	183	6	5	3	8	249	251	10	6	3	9	429	428	4	6	3	10	305	316	9
0	4	7	1207	1235	35	6	3	8	450	447	9	7	3	9	129	130	8	7	3	10	558	565	5
1	4	7	305	303	11	7	3	8	616	606	4	8	3	9	501	512	5	0	4	10	129	129	5
2	4	7	238	236	4	8	3	8	131	138	8	0	4	9	341	347	3	1	4	10	433	441	17
3	4	7	265	269	8	0	4	8	342	340	7	1	4	9	702	700	9	2	4	10	700	691	5
4	4	7	702	688	4	1	4	8	386	384	5	2	4	9	482	477	6	3	4	10	438	432	11
5	4	7	165	159	11	2	4	8	733	720	4	3	4	9	667	660	4	4	4	10	66	76	8
6	4	7	395	395	6	3	4	8	469	469	11	4	4	9	124	46	−496	5	4	10	242	255	13
7	4	7	207	220	6	4	4	8	105	86	17	5	4	9	589	588	4	6	4	10	518	511	4
0	5	7	439	433	14	5	4	8	111	108	15	6	4	9	280	281	5	7	4	10	337	334	5
1	5	7	519	518	9	6	4	8	485	487	9	7	4	9	173	173	15	0	5	10	155	159	5
2	5	7	670	668	6	7	4	8	303	298	7	0	5	9	673	684	8	1	5	10	419	429	4
3	5	7	308	304	5	0	5	8	109	116	5	1	5	9	445	439	4	2	5	10	104	100	6
4	5	7	406	397	8	1	5	8	517	509	10	2	5	9	175	168	5	3	5	10	200	203	5
5	5	7	426	426	4	2	5	8	435	420	4	3	5	9	420	417	4	4	5	10	400	403	4
6	5	7	394	389	5	3	5	8	459	453	4	4	5	9	494	490	7	5	5	10	278	285	5
7	5	7	198	203	6	4	5	8	468	469	10	5	5	9	286	286	5	6	5	10	241	235	10
0	6	7	484	499	14	5	5	8	319	318	5	6	5	9	255	262	8	0	6	10	280	277	4
1	6	7	398	394	12	6	5	8	373	368	6	7	5	9	509	496	6	1	6	10	344	335	5
2	6	7	221	231	4	7	5	8	234	227	6	0	6	9	29	52	−116	2	6	10	110	107	12
3	6	7	785	774	4	0	6	8	450	459	13	1	6	9	383	379	4	3	6	10	386	382	4
4	6	7	428	429	4	1	6	8	471	483	4	2	6	9	633	626	4	4	6	10	337	349	9
5	6	7	293	294	5	2	6	8	132	120	12	3	6	9	159	156	12	5	6	10	452	448	7
6	6	7	241	242	5	3	6	8	394	386	7	4	6	9	303	292	7	6	6	10	125	111	8
0	7	7	148	147	5	4	6	8	309	318	15	5	6	9	218	211	5	0	7	10	596	587	10
1	7	7	181	190	9	5	6	8	483	481	13	6	6	9	601	603	5	1	7	10	180	182	5
2	7	7	634	637	4	6	6	8	162	155	10	0	7	9	112	105	7	2	7	10	109	123	16
3	7	7	381	395	10	0	7	8	456	449	7	1	7	9	461	462	7	3	7	10	124	124	12
4	7	7	192	201	6	1	7	8	385	391	13	2	7	9	47	40	−188	4	7	10	522	518	8
5	7	7	203	203	6	2	7	8	250	249	5	3	7	9	588	572	4	0	8	10	153	135	6
0	8	7	349	352	5	3	7	8	273	275	12	4	7	9	1	45	−1	1	8	10	342	342	10
1	8	7	394	395	4	4	7	8	534	525	6	5	7	9	274	280	5	2	8	10	328	334	5
2	8	7	133	129	11	5	7	8	332	332	5	0	8	9	113	116	6	3	8	10	308	303	6
3	8	7	323	326	12	0	8	8	360	360	7	1	8	9	267	257	5	1	0	11	753	768	5
4	8	7	300	305	9	1	8	8	326	334	9	2	8	9	392	391	6	2	0	11	879	873	3
0	9	7	185	191	6	2	8	8	420	420	4	3	8	9	195	197	6	3	0	11	470	477	4
1	9	7	326	330	5	3	8	8	331	323	5	0	0	10	342	355	3	4	0	11	86	3	−343
0	0	8	644	695	4	1	0	9	121	126	10	1	0	10	1074	1084	3	5	0	11	450	448	4
1	0	8	817	830	3	2	0	9	1766	1732	8	2	0	10	164	164	4	6	0	11	277	278	5
2	0	8	60	50	7	3	0	9	108	104	5	3	0	10	534	536	3	7	0	11	585	603	4
3	0	8	582	573	5	4	0	9	28	26	15	4	0	10	177	179	4	8	0	11	106	125	15
4	0	8	411	418	6	5	0	9	210	214	5	5	0	10	592	592	7	0	1	11	297	353	19
5	0	8	491	495	4	6	0	9	770	767	4	6	0	10	1	7	−1	1	1	11	370	388	14
6	0	8	356	363	4	7	0	9	177	185	6	7	0	10	150	146	7	2	1	11	602	614	4
7	0	8	104	106	7	8	0	9	272	282	10	8	0	10	134	143	7	3	1	11	585	579	3
8	0	8	292	289	10	0	1	9	289	325	12	0	1	10	1201	1247	3	4	1	11	321	321	5
0	1	8	1043	1084	2	1	1	9	597	623	3	1	1	10	564	569	6	5	1	11	200	205	14
1	1	8	148	154	11	2	1	9	192	200	4	2	1	10	235	244	4	6	1	11	452	455	6
2	1	8	346	345	7	3	1	9	842	845	3	3	1	10	475	481	5	7	1	11	499	503	5
3	1	8	688	679	3	4	1	9	504	503	3	4	1	10	463	467	6	8	1	11	294	287	7

Observed and Calculated Structure Factors for $Ru(H_2O)_2(\eta^1$-$(O),\eta^2$-(C,C')-$OCOCH_2CH{=}CHCH_3)_2$ (**12**)

h	k	l	10Fo	10Fc	10s
0	2	11	555	557	6
1	2	11	774	793	11
2	2	11	381	391	3
3	2	11	609	615	4
4	2	11	420	411	8
5	2	11	429	430	4
6	2	11	297	294	5
7	2	11	325	324	5
0	3	11	379	401	13
1	3	11	612	621	8
2	3	11	226	219	4
3	3	11	306	322	11
4	3	11	510	501	4
5	3	11	581	570	4
6	3	11	332	341	5
7	3	11	164	148	20
0	4	11	686	712	3
1	4	11	578	580	4
2	4	11	143	144	5
3	4	11	457	455	4
4	4	11	512	516	4
5	4	11	403	409	4
6	4	11	360	365	7
7	4	11	223	231	9
0	5	11	321	330	4
1	5	11	537	552	6
2	5	11	452	440	11
3	5	11	420	417	12
4	5	11	291	285	10
5	5	11	457	455	5
6	5	11	407	412	5
0	6	11	314	315	5
1	6	11	329	335	7
2	6	11	381	381	11
3	6	11	582	575	4
4	6	11	182	172	10
5	6	11	244	235	11
0	7	11	43	41	–172
1	7	11	342	340	5
2	7	11	561	560	9
3	7	11	290	285	5
4	7	11	142	150	9
0	8	11	355	359	8
1	8	11	253	254	11
2	8	11	316	302	16
0	0	12	803	850	3
1	0	12	325	319	8
2	0	12	111	106	6
3	0	12	14	29	–56
4	0	12	504	493	4
5	0	12	165	157	14
6	0	12	444	439	8
7	0	12	178	180	6
0	1	12	208	210	4
1	1	12	644	662	4
2	1	12	278	274	4
3	1	12	424	430	4
4	1	12	138	153	15
5	1	12	416	415	12
6	1	12	443	441	9
7	1	12	161	166	7
0	2	12	605	624	3
1	2	12	452	452	6
2	2	12	415	404	4
3	2	12	558	543	4
4	2	12	483	467	7
5	2	12	257	256	19
6	2	12	170	176	6
7	2	12	388	387	13
0	3	12	338	348	4
1	3	12	183	193	14
2	3	12	908	901	14
3	3	12	197	199	14
4	3	12	243	234	6
5	3	12	111	113	11
6	3	12	549	544	9
7	3	12	104	61	–415
0	4	12	175	175	5
1	4	12	494	503	4
2	4	12	144	145	8
3	4	12	503	498	14
4	4	12	208	211	6
5	4	12	188	192	6
6	4	12	72	58	11
0	5	12	46	25	14
1	5	12	361	357	4
2	5	12	589	591	11
3	5	12	256	247	4
4	5	12	199	204	5
5	5	12	518	519	6
6	5	12	324	318	14
0	6	12	775	775	4
1	6	12	143	142	7
2	6	12	125	127	6
3	6	12	185	187	6
4	6	12	596	581	9
5	6	12	147	141	7
0	7	12	1	6	–1
1	7	12	436	434	6
2	7	12	186	178	16
3	7	12	243	247	6
4	7	12	175	181	6
0	8	12	395	398	5
1	8	12	382	376	5
1	0	13	679	706	9
2	0	13	315	309	4
3	0	13	528	533	4
4	0	13	102	101	7
5	0	13	246	241	5
6	0	13	351	354	8
7	0	13	666	662	8
0	1	13	154	162	6
1	1	13	462	476	4
2	1	13	753	771	6
3	1	13	270	278	4
4	1	13	195	198	6
5	1	13	416	423	4
6	1	13	500	486	4
7	1	13	242	249	7
0	2	13	746	774	4
1	2	13	403	410	4
2	2	13	178	187	16
3	2	13	624	608	6
4	2	13	685	681	4
5	2	13	384	384	4
6	2	13	157	182	12
7	2	13	203	204	6
0	3	13	326	340	8
1	3	13	673	693	6
2	3	13	27	49	22
3	3	13	381	383	4
4	3	13	256	256	13
5	3	13	662	647	4
6	3	13	169	185	19
7	3	13	182	190	7
0	4	13	667	679	4
1	4	13	159	174	13
2	4	13	206	196	5
3	4	13	244	246	4
4	4	13	668	658	7
5	4	13	217	217	10
6	4	13	260	254	6
0	5	13	331	334	4
1	5	13	506	500	4
2	5	13	471	469	9
3	5	13	335	330	5
4	5	13	98	101	10
5	5	13	430	426	5
0	6	13	263	258	5
1	6	13	395	398	4
2	6	13	148	143	6
3	6	13	535	535	4
4	6	13	176	173	14
0	7	13	107	98	18
1	7	13	164	171	13
2	7	13	597	599	5
3	7	13	176	188	6
0	0	14	412	418	4
1	0	14	266	262	4
2	0	14	134	144	5
3	0	14	408	406	4
4	0	14	524	517	10
5	0	14	398	400	4
6	0	14	173	181	9
7	0	14	79	85	9
0	1	14	682	696	5
1	1	14	588	600	3
2	1	14	147	137	20
3	1	14	490	482	4
4	1	14	577	571	4
5	1	14	395	400	4
6	1	14	305	304	7
7	1	14	278	274	12
0	2	14	315	313	7
1	2	14	203	201	7
2	2	14	476	472	5
3	2	14	420	426	4
4	2	14	379	384	4
5	2	14	328	324	5
6	2	14	335	331	6
7	2	14	235	239	7
0	3	14	360	364	4
1	3	14	358	358	4
2	3	14	474	478	5
3	3	14	470	456	4
4	3	14	196	209	5
5	3	14	223	213	7
6	3	14	301	302	11
0	4	14	255	259	5
1	4	14	291	297	4
2	4	14	533	532	4
3	4	14	468	465	13
4	4	14	185	198	6
5	4	14	218	226	6
6	4	14	370	378	6
0	5	14	421	416	4
1	5	14	285	293	5
2	5	14	363	364	11
3	5	14	239	243	5
4	5	14	385	388	7
5	5	14	342	348	8
0	6	14	397	386	8
1	6	14	369	366	11
2	6	14	221	227	5
3	6	14	179	177	6
4	6	14	442	432	5
0	7	14	391	394	5
1	7	14	301	297	8
2	7	14	153	152	7
1	0	15	126	127	5
2	0	15	853	846	3
3	0	15	105	95	7
4	0	15	205	209	5
5	0	15	73	83	11
6	0	15	609	610	4
7	0	15	89	4	–358
0	1	15	382	413	7
1	1	15	576	578	9
2	1	15	110	130	13
3	1	15	628	625	7
4	1	15	453	456	4
5	1	15	318	333	5
6	1	15	181	166	14
0	2	15	151	160	5
1	2	15	616	628	6
2	2	15	385	385	4
3	2	15	205	208	5
4	2	15	204	216	5
5	2	15	648	651	10
6	2	15	342	349	5
0	3	15	759	753	7
1	3	15	128	133	6
2	3	15	240	238	10
3	3	15	139	144	13
4	3	15	737	732	4
5	3	15	188	204	6
6	3	15	150	147	15
0	4	15	140	149	5
1	4	15	435	428	4
2	4	15	176	182	5
3	4	15	443	433	8
4	4	15	215	206	6
5	4	15	451	443	5
0	5	15	606	591	7
1	5	15	290	286	5
2	5	15	76	77	10
3	5	15	358	356	5
4	5	15	380	379	6
5	5	15	311	318	5
0	6	15	136	100	28
1	6	15	199	203	6
2	6	15	456	453	19
3	6	15	87	58	–349
0	7	15	130	123	16
1	7	15	319	316	11
0	0	16	163	168	5
1	0	16	391	399	6
2	0	16	130	142	9
3	0	16	513	522	4
4	0	16	79	21	–318
5	0	16	659	652	18
6	0	16	19	39	–26
0	1	16	663	653	5
1	1	16	172	181	5
2	1	16	76	91	9
3	1	16	244	247	5
4	1	16	663	662	4
5	1	16	249	247	6
6	1	16	222	236	5
0	2	16	132	134	12
1	2	16	372	381	4
2	2	16	371	371	5
3	2	16	256	262	11
4	2	16	361	366	5
5	2	16	495	486	10
6	2	16	294	297	5

Observed and Calculated Structure Factors for $Ru(H_2O)_2(\eta^1$-$(O),\eta^2$-(C,C')-$OCOCH_2CH{=}CHCH_3)_2$ (**12**)

h	k	l	10Fo	10Fc	10s
0	3	16	145	161	5
1	3	16	450	447	6
2	3	16	184	180	5
3	3	16	681	683	4
4	3	16	162	170	5
5	3	16	279	280	5
6	3	16	154	148	7
0	4	16	105	109	7
1	4	16	256	252	5
2	4	16	612	605	5
3	4	16	179	186	6
4	4	16	125	121	7
5	4	16	88	70	-352
0	5	16	532	519	4
1	5	16	352	352	8
2	5	16	180	177	5
3	5	16	373	372	9
4	5	16	467	459	14
0	6	16	239	239	5
1	6	16	527	511	13
2	6	16	259	267	5
3	6	16	175	174	6
1	0	17	352	349	4
2	0	17	371	366	6
3	0	17	413	422	6
4	0	17	58	32	14
5	0	17	196	203	7
6	0	17	367	361	5
0	1	17	1	59	-1
1	1	17	281	283	6
2	1	17	505	500	4
3	1	17	251	237	5
4	1	17	318	320	5
5	1	17	265	274	11
6	1	17	283	278	9
0	2	17	502	504	4
1	2	17	293	286	4
2	2	17	371	365	4
3	2	17	302	307	7
4	2	17	562	576	4
5	2	17	333	324	5
0	3	17	764	740	4
1	3	17	375	382	4
2	3	17	171	171	5
3	3	17	271	266	7
4	3	17	377	383	5
5	3	17	379	378	5
0	4	17	417	419	9
1	4	17	324	323	7
2	4	17	126	129	8
3	4	17	217	224	9
4	4	17	427	417	5
0	5	17	326	321	5
1	5	17	351	353	5
2	5	17	220	215	7
3	5	17	329	328	7
0	6	17	132	121	7
1	6	17	252	234	6
2	6	17	393	398	5
0	0	18	809	797	4
1	0	18	96	58	-384
2	0	18	1	29	-1
3	0	18	84	98	21
4	0	18	608	610	4
5	0	18	296	297	7
0	1	18	241	243	7
1	1	18	539	530	4
2	1	18	247	254	5
3	1	18	273	268	5
4	1	18	241	244	6
5	1	18	554	556	6
0	2	18	456	437	8
1	2	18	271	270	5
2	2	18	178	176	8
3	2	18	458	462	8
4	2	18	312	333	5
5	2	18	190	191	6
0	3	18	29	37	-114
1	3	18	244	243	5
2	3	18	559	556	4
3	3	18	152	146	7
4	3	18	187	195	12
0	4	18	312	302	5
1	4	18	480	474	4
2	4	18	117	122	11
3	4	18	457	446	5
4	4	18	216	212	7
0	5	18	155	149	6
1	5	18	306	299	17
2	5	18	324	319	9
3	5	18	244	242	5
1	0	19	533	528	9
2	0	19	366	363	5
3	0	19	453	449	5
4	0	19	38	75	20
5	0	19	258	262	6
0	1	19	210	218	6
1	1	19	164	163	6
2	1	19	507	508	4
3	1	19	164	159	7
4	1	19	204	202	5
5	1	19	256	265	6
0	2	19	592	590	12
1	2	19	213	215	5
2	2	19	146	145	6
3	2	19	265	266	5
4	2	19	485	487	9
0	3	19	78	92	12
1	3	19	435	442	5
2	3	19	175	183	6
3	3	19	276	280	5
4	3	19	250	251	6
0	4	19	590	583	5
1	4	19	280	282	5
2	4	19	95	93	27
3	4	19	173	180	6
0	5	19	164	153	7
1	5	19	297	288	9
0	0	20	668	637	12
1	0	20	524	515	11
2	0	20	61	40	13
3	0	20	270	269	5
4	0	20	513	513	5
0	1	20	448	432	7
1	1	20	384	365	5
2	1	20	299	306	5
3	1	20	256	272	7
4	1	20	259	262	5
0	2	20	430	410	9
1	2	20	422	419	5
2	2	20	217	212	9
3	2	20	364	371	18
4	2	20	173	175	7
0	3	20	1	36	-1
1	3	20	304	293	6
2	3	20	411	410	14
3	3	20	271	271	7
0	4	20	151	155	10
1	4	20	351	328	5
2	4	20	367	373	5
1	0	21	202	215	20
2	0	21	498	484	6
3	0	21	191	191	7
0	1	21	1	43	-1
1	1	21	380	365	6
2	1	21	161	163	7
3	1	21	296	286	5
0	2	21	194	197	6
1	2	21	326	317	5
2	2	21	307	304	5
3	2	21	315	309	17
0	3	21	622	587	10
1	3	21	138	126	9
2	3	21	53	18	-212
0	0	22	209	201	6
1	0	22	386	374	14
2	0	22	52	26	15
0	1	22	658	629	5
1	1	22	155	151	23
2	1	22	147	128	11
0	2	22	57	17	-226
1	2	22	350	329	5

CHAPTER 2

On the Mechanism of Aqueous Ruthenium(II)-Catalyzed Olefin Isomerization

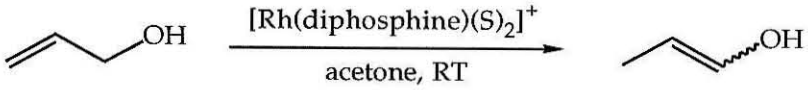
Introduction

The studies detailed in Chapter 1 revealed that the coordination complex $Ru^{II}(H_2O)_6(tos)_2$ (tos = *p*-toluenesulfonate) **1**[1, 2] is an efficient catalyst for the isomerization of olefins. Although olefin isomerization[3] is an important transformation in a number of transition-metal-catalyzed reactions such as hydrozirconation,[4, 5] hydroformylation,[6-12] hydrosilylation[13-15] and hydrocyanation,[16-18] none of these processes involve water as a solvent. Indeed, to the best of our knowledge, this study is the first example of fully aqueous metal catalysis. The lack of data regarding organometallic transformations catalyzed by **1** has led us to probe the mechanism of olefin isomerization in this system. By determining which fundamental transformations are taking place, we can better predict a plausible pathway for initiation of the active metathesis catalyst formed by this species. The extent of this reaction as well as experiments designed to elucidate the mechanism of this transformation are reported in this chapter.

Isomerization Systems. A large amount of the mechanistic work reported in the literature on the olefin isomerization reaction, some of which will be detailed later, has centered on strictly hydrocarbon substrates such as 1-butene, 1-pentene, and 3-phenyl-1-propene. However, olefin isomerization has seen its widest application in the isomerization of functionalized substrates.

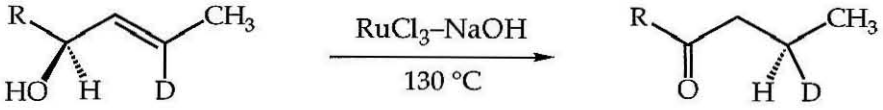
Allylic alcohols are isomerized to saturated aldehydes or ketones via an intermediate enol by a number of catalysts based on molybdenum,[19] iron,[20, 21] ruthenium,[22-25] cobalt,[26] rhodium,[22-30] iridium,[27-32] and platinum.[33-35] The enol is almost never observed, yet in a recent paper, Bergens and Bosnitch[30] reported the generation of enols—of surprising stability—in acetone solution from the corresponding allylic alcohols employing $[Rh(diphosphine)(solvent)_2]^+$ (diphos-

phine = 1,2-(diphenylphosphino)-ethane (DIPHOS) or 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP)) (eq 1). Some of the systems reported previously



(1)

can produce aldehydes and ketones from allylic alcohols in sufficient yields to be synthetically useful.[21, 23, 28] Only limited success has been seen with asymmetric isomerizations, however. A mixture of $RuCl_3$-NaOH has been used to isomerize chiral secondary allylic alcohols to optically active ketones[24] (eq 2), but chirality transfers were only ca. 40%. Allyl ethers are not isomerizable in this system.



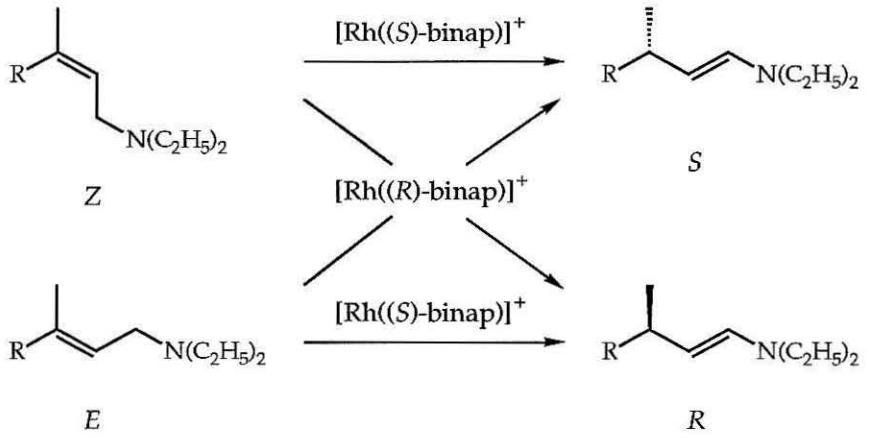
(2)

Allylic ethers are isomerized to enol ethers by complexes of molybdenum,[19] iron,[36, 37] rhodium,[29, 38] iridium,[31] palladium,[39] and platinum.[34, 35] In particular, rhodium[40-43] and iridium[44] complexes are used as deprotecting agents for allyl ethers which often serve as protecting groups in carbohydrate chemistry.[40, 43, 45, 46] The allyl ether is isomerized to a 1-propenyl ether which can be hydrolyzed under acidic conditions[38] or cleaved by treatment with mercuric oxide.[46] This deprotection exhibits reasonable selectivity as allyl ethers can be isomerized in the presence of other protecting groups such as the "prenyl" group (3-methyl-2-butenyl).[43]

Transition-metal catalysts have been reported to isomerize various other functionalized olefins including, but not limited to, allylic acetates,[47] allylic siloxanes,[48] and N-allylamides and -imides.[49] 3-Pentenenitrile is kinetically isomerized[16] to 4-pentenenitrile, an intermediate in the industrial synthesis of

adiponitrile, by $HNi[P(OR)_3]_4^+$ (R = alkyl or aryl).[50, 51] Allylamines are isomerized asymmetrically by $[Rh(binap)S_2]^+$ (binap = 2,2'-bis(diphenyl-phosphino)-1,1'-binaphthyl; S = solvent or other coordinative molecule) in what is by far the most successful asymmetric isomerization system developed to date.[52-55] Enantiomeric eneamines of both senses can be generated depending on the chirality of the BINAP ligand (Scheme 1). Enantiomeric excesses are ≥ 90% in all cases. This system is also active for the isomerization of allylic alcohols and ethers, but with only moderate optical yields (≈ 40–50%).[29]

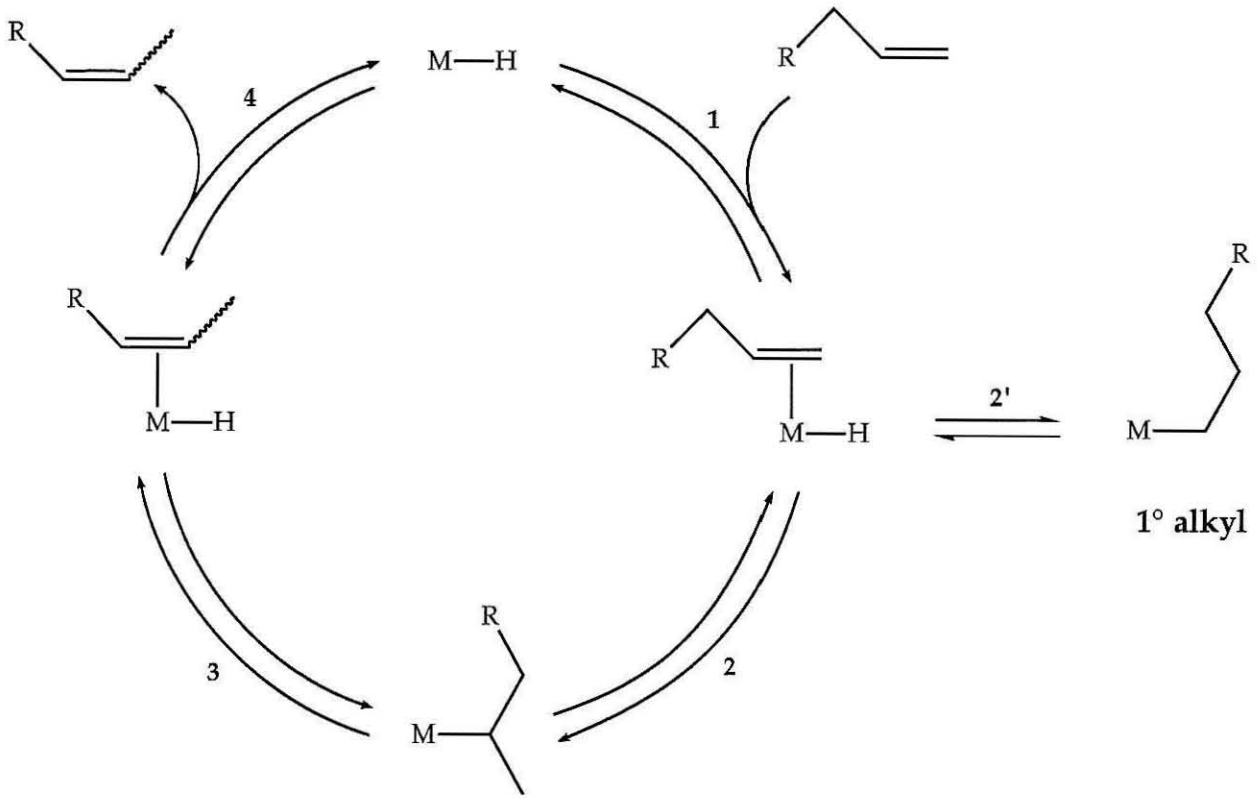
Scheme 1. Asymmetric Isomerization of Allylamines.[56]



Mechanism. The two established pathways for transition-metal-catalyzed olefin isomerization are the π-allyl metal hydride and the metal hydride addition-elimination mechanisms.[57, 58] These mechanisms include fundamental steps such as ligand association and dissociation, olefin insertion, β-elimination, and allylic hydride abstraction.

The metal hydride addition-elimination mechanism (Scheme 2) is the more prevalent pathway for transition metal-catalyzed isomerizations and has been established for catalysts based on cobalt, rhodium, iridium, and nickel.

Scheme 2. Metal Hydride Olefin Isomerization Mechanism.



In this mechanism, free olefin coordinates to a kinetically long-lived metal hydride species. Subsequent insertion into the metal-hydride bond yields a metal alkyl. Formation of a secondary metal alkyl followed by β-elimination yields isomerized olefin and regenerates the initial metal hydride. Non-productive cycling of the olefin through formation and β-elimination from a primary metal alkyl generally occurs to a great extent since formation of the primary alkyl is thermodynamically favored. If all steps are truly reversible, eventual equilibration to a thermodynamic ratio of olefins is observed. Certain modifications have been placed on this generic mechanism to fit observed data for individual systems.

A number of these modifications arise from data obtained when the isomerizations are carried out in the presence of protic sources. Deuterium incorporation, or lack thereof, into the substrate from deuterated solvents or cocatalysts can give some idea of the relative rates of the individual steps in the catalytic cycle. Tolman reported that the isomerization of 1-butene to a mixture of 2-butenes with $Ni[P(OEt)_3]_4$ in CH_3OD initiated by D_2SO_4 occurs with a high ratio of isomerization to deuteration (170 : 1).[51] This led the author to conclude that the nickel hydride catalyst responsible for isomerization preferentially reacts with substrate rather than excess phosphite ligand, which leads to hydride-solvent exchange. Cramer and Lindsey studied the isomerization of 1-butene with soluble rhodium catalysts activated by HCl in methanol solution.[59-61] In contrast to Tolman's system, deuterated medium (i. e., DCl in CH_3OD) yields a ratio of deuterium incorporation to isomerization of approximately 1 : 1. Throughout the course of the reaction almost all the deuterium is present in unisomerized $CH_2=CDCH_2CH_3$, although some $CH_3CH=CDCH_3$ and $CH_2DCH=CHCH_3$ are also detected. These and other observations are

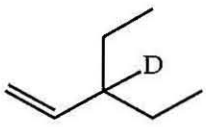
interpreted by the authors as (a) the reaction of initial rhodium-deuteride with 1-butene leads to deuterated 1-butene (i.e., a non-productive olefin insertion/elimination (Scheme 2, step 2') which is detectable through deuterium incorporation at the C-2 position) and (b) the resulting rhodium hydride formed from this initial isomerization persists, continuing to isomerize non-productively (Scheme 2, step 2'), until productive isomerization yields 2-butene, whereupon the rhodium hydride is reduced through loss of a proton. The reason for preferential reduction of the 2-butene complex is unclear, but is explained as either slower displacement of coordinated 2-butene by free olefin or greater stability of rhodium-hydride when coordinated to 1-butene.

The ratio of non-productive (step 2') to productive (step 2) insertion is indicative of the relative rates of Markovnikov versus anti-Markovnikov addition of the metal hydride across the olefinic bond and is determined by examining the position of the deuterium label in the products after isomerization. From the ratio of $CH_2DCH{=}CHCH_3$ versus other deuterated butenes in the isomerization of 1-butene by DCl-activated rhodium catalysts, Cramer estimated the rates of Markovnikov : anti-Markovnikov addition to be approximately 1 : 15.[59] This ratio seems consistent with the thermodynamics of metal alkyls, although conflicting results have been reported for other systems. For example, both Hendrix and von Rosenberg[62] and Taylor and Orchin[8] reported isomerization product compositions from the $HCo(CO)_4$-catalyzed isomerization of deuterated olefins to be consistent with a 65-70% preference for Markovnikov metal hydride addition.

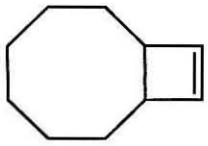
The formation of the initial metal hydride in Scheme 2 varies from system to system and is often unknown. While many isomerization catalysts that act through the metal hydride addition-elimination mechanism are stable, isolable

metal hydrides (e.g., $HCo(CO)_4$, $RhH(CO)(PPh_3)_3$, $IrH(CO)(PPh_3)_3$, $RuHCl(PPh_3)_3$), many are not (e.g., $RhCl_3$, $RhCl(PPh_3)_3$, $Ni[P(OEt)_3]_4$). A number of pathways are known for the generation of the initial metal hydrides with the latter catalysts.[63] These include reaction with protic sources (as in both Tolman's[51] and Cramer and Lindsey's[59-61] systems), hydrogen,[31] alcohols, and the olefin substrate itself.

The π-allyl hydride mechanism (Scheme 3) is the less commonly observed pathway for olefin isomerization. In this mechanism, free olefin coordinates to a transition metal fragment that does not have a hydride ligand. Oxidative addition of an activated allylic C—H bond to the metal yields a π-allyl metal hydride. Transfer of the coordinated hydride to the opposite end of the allyl group yields isomerized olefin. Casey and Cyr,[64] in a study that presented clear evidence in favor of the π-allyl hydride mechanism for the $Fe_3(CO)_{12}$-catalyzed isomerization of 3-ethyl-1-pentene-3-d_1 **2** conclude that the equilibria leading to isomerization (steps 2 and 3) are fast relative to decomplexation of bound olefin (step 4). They based these conclusions on observations regarding deuterium label scrambling in recovered starting material and the relative rates of



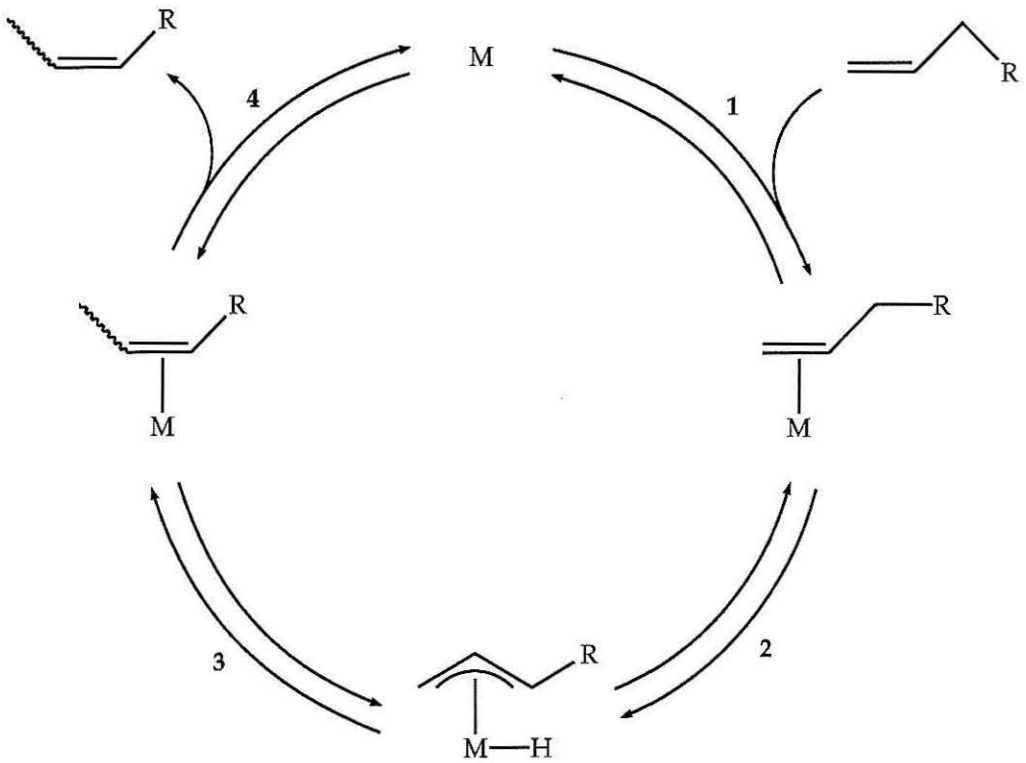
2



3

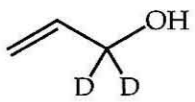
isomerization versus deuterium label scrambling within the product. The generality of their conclusions is unknown, but, a similar effect was seen by Barborak et al. in the isomerization of bicyclo[6.2.0]dec-9-ene **3**.[65] Again, if all steps are truly reversible, eventual equilibration to a thermodynamic ratio of olefins is observed.

Scheme 3. Allyl Hydride Olefin Isomerization Mechanism.

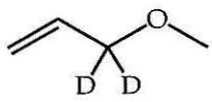


Mechanistic Studies. While both mechanisms yield the same product—a thermodynamic mixture of olefins—two differences make them distinguishable through labelling studies. First, the π-allyl hydride mechanism is a formal 1,3 hydrogen shift in the sense that a hydrogen in the allylic position undergoes a metal-mediated transfer to a terminal position (in an α-olefin). The metal hydride addition-elimination mechanism, however, can involve a 1,2 hydrogen shift through formation of a primary metal alkyl and β-elimination of a different hydrogen. Readdition of the metal hydride to the olefin to yield a secondary metal alkyl followed by appropriate β-elimination completes the 1,2 shift. These shifts become distinguishable through isotopic labelling of the individual hydrogen atoms in the substrate. Second, the π-allyl hydride mechanism is intramolecular: a single substrate molecule is rearranged by the metal and released as product. The metal hydride addition-elimination mechanism, however, is intermolecular: hydrogen atoms from one substrate molecule are transferred to the catalyst and then to another substrate molecule. As we shall see in our studies on the aqueous ruthenium(II) system, the intra/intermolecularity of the process is the ultimate distinguishing feature between the two mechanisms.

A useful substrate for probing the nature of the hydrogen shift in olefin isomerization is allyl-*1,1-d*$_2$ alcohol **4**[30, 66] as well as the corresponding methyl ether **5**.[31, 67] Isomerization of allyl-*1,1-d*$_2$ alcohol via the π-allyl metal hydride mechanism should yield exclusively propionaldehyde-*1,3-d*$_2$, while a mixture of



4



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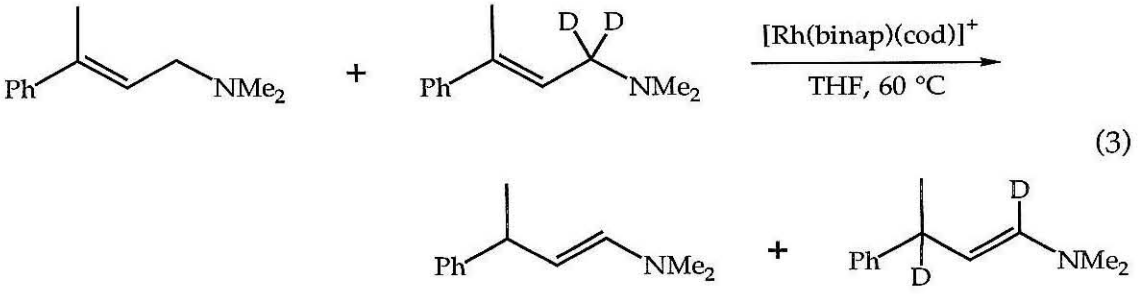
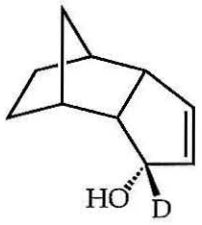
deuterated propionaldehydes with deuterium washed into the C-2 position should be obtained through competitive non-productive olefin insertion (Scheme 2, step 2' with Ru–D) if the metal hydride mechanism is operative. This particular labelling study is common and is often taken by itself as convincing evidence for the π-allyl hydride mechanism.[30, 31, 66] Baudry et al. cited an observed 1,3-shift in the isomerization of allyl-*1,1-d*$_2$ methyl ether to 1-propenyl-*1,3-d*$_2$ methyl ether as evidence for the π-allyl metal hydride mechanism even though the catalyst, [Ir(η^4-1,5-cyclooctadiene)(PCy_3)(C_5H_5N)]PF_6, was activated by hydrogen.[31] In addition, Hendrix et al.[66] observed propionaldehyde-*1,3-d*$_2$ as the product of the $Fe(CO)_5$-catalyzed isomerization of allyl-*1,1-d*$_2$ alcohol and reasoned that exclusive Markovnikov addition of an iron hydride was unlikely, since formation of a primary metal alkyl is thermodynamically favored over formation of a secondary metal alkyl, and thus could not be responsible for the exclusive 1,3-shift. Indeed, while predominant Markovnikov addition has been observed in some metal-hydride-catalyzed olefin isomerization systems,[8, 62] anti-Markovnikov addition is always a competing pathway.

Tests for intra/intermolecularity are less common and are based on mass spectrometry or ^2H NMR data. Tani et al. reported obtaining GC-MS data consistent with an intramolecular process in the isomerization of a mixture of non-labelled and labelled identical allylamines by [Rh(binap)(η^4-1,5-cycloocta-diene)]$^+$ (eq 3).[29] No mono-deuterated enamine was detected. Strauss and



(3)

Ford[68] reported a crossover experiment that supported the previous results of Hendrix et al. on the $Fe(CO)_5$-catalyzed isomerization of allylic alcohols.[66, 69] Their crossover experiment, however, utilized two vastly different substrates, the tricyclic alcohol **6** and cyclohex-2-enol, and they did not indicate whether the



6

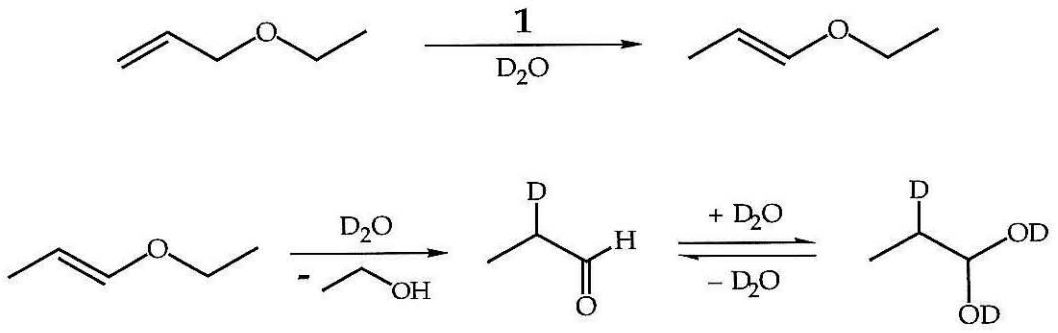
reaction was monitored at low conversion in order to rule out preferential reactivity of either substrate. Casey and Cyr,[64] in their study of the $Fe_3(CO)_{12}$-catalyzed isomerization of **2**, also utilized different substrates in a crossover experiment, but the difference in this case was small. They observed negligible crossover (< 1%) between **2** and an excess of 3-methyl-1-butene after isomerization was carried to 55% and 89% conversion, respectively.

The studies detailed below seek to determine the nature of the isomerization mechanism for the aqueous ruthenium(II)-catalyzed isomerization of allylic alcohols and ethers through similar labelling experiments. In determining which fundamental organometallic transformations aqueous ruthenium(II) undergoes, we will be better equipped to predict a mechanism of initiation for the active metathesis catalyst formed from **1**.

Results

When the reaction of allyl ethyl ether and **1** (10 mol %) in D_2O is followed by ^1H NMR, four organic products are observed in addition to the starting material and Ru^{II}(allyl ethyl ether)$(D_2O)_5(tos)_2$[70] (see Chapter 1). After complete consumption of the starting material the organic products can be extracted into C_6D_6 and analyzed by ^1H NMR. In this organic solvent, however, only three products are observed. These products can be isolated by preparative gas chromatography and identified as *trans*-1-propenyl ethyl ether ($J_{CH=CH}$ = 13 Hz), propionaldehyde-2-*d* and ethyl alcohol. The fourth product observed in aqueous medium is the hydrate of propionaldehyde-2-*d*. *cis*-1-Propenyl ethyl ether is not observed at any time during the course of the reaction. The formation of these products are consistent with the reaction pathway shown in Scheme 4. Aqueous

Scheme 4. Isomerization of Allyl Ethyl Ether by $Ru^{II}(H_2O)_6(tos)_2$.

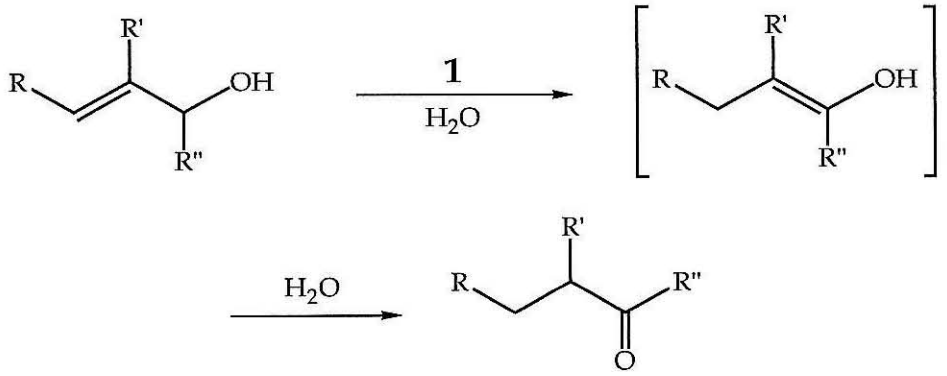


ruthenium(II) catalyzes the isomerization of allyl ethyl ether to *trans*-1-propenyl ethyl ether which then undergoes acid-catalyzed hydrolysis[71, 72] to ethanol and propionaldehyde-2-*d*. With substrate to catalyst ratio of 10 : 1 the conversion to aldehyde is complete in 4-5 hours at 45 °C. The appearance and disappearance of the products in the ^1H NMR are consistent with the pathway shown in Scheme 4. The olefin complex Ru^{II}(allyl ethyl ether)$(D_2O)_5(tos)_2$ can be isolated by

removing the volatiles of the reaction in vacuo. This complex is stable for up to one week at room temperature in D_2O solution.

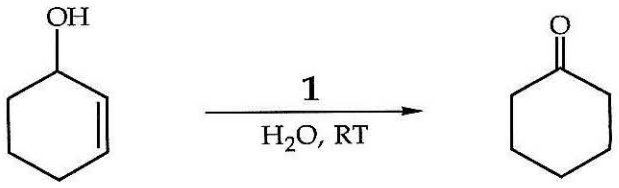
Allylic alcohols also undergo isomerization in the presence of **1** and the reaction is quite general (Scheme 5). Greater than 90% conversion to the isomeric aldehyde is observed by ^1H NMR in all cases. Oxidation products are also observed in some instances. In the case of crotyl alcohol (2-buten-1-ol), ca. 5%

Scheme 5. Isomerization of Allylic Alcohols by $Ru^{II}(H_2O)_6(tos)_2$.



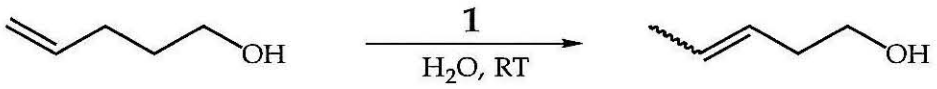
R, R' = H; R" = H, Me, Et
R = Me; R', R" = H
R, R" = H; R' = Me

crotonaldehyde is observed in the product mixture by ^1H NMR and ca. 18% of the ruthenium is present as a crotonaldehyde complex. In the case of (±)-3-buten-2-ol ca. 33% of the ruthenium is present as a complex with methyl vinyl ketone after total consumption of starting material. Small but detectable amounts of free methyl vinyl ketone are observed during the course of the reaction. Cyclic olefins are also isomerized (eq 4).



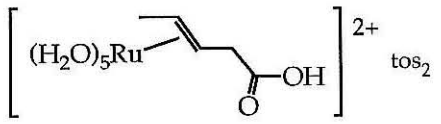
(4)

Note that the isomerization reaction is not restricted to olefins with activated allylic hydrogens. Although isomerization of 3-buten-1-ol is not observed as mentioned in Chapter 1, isomerization of 4-penten-1-ol to a mixture of *cis*- and *trans*-3-penten-1-ol proceeds in high yield (eq 5). Isomerization stops at this stage and does not continue along the hydrocarbon chain to yield valeraldehyde.



(5)

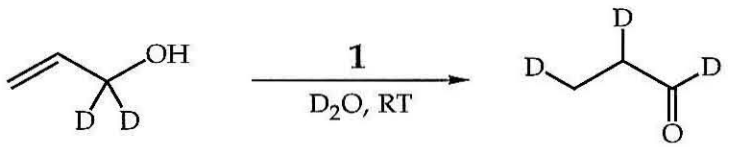
Isomerization of a substrate olefin moiety to a specified distance from a pendant oxygen-containing functional group is also observed for unsaturated carboxylic acids. 2-Pentenoic acid reacts with **1** to yield the olefin complex of 3-pentenoic acid **7**.[70] Catalytic production of free 3-pentenoic acid is not observed.



7

When the reaction is carried out in D_2O, one of the diastereotopic hydrogens on C-2 is selectively deuterated during isomerization as evidenced by the disappearance of the resonance at 2.15 ppm and the collapse of the doublet of doublets at 3.46 ppm to a doublet. The position of the deuterated site with respect to the metal (endo/exo) was not determined. Eventual formation of the bis(olefin)-bis(carboxylate) complex $Ru(H_2O)_2(\eta^1\text{-}(O),\eta^2\text{-}(C,C')\text{-}OCOCH_2CH{=}CHCH_3)_2$ (see Chapter 1) is observed.[70]

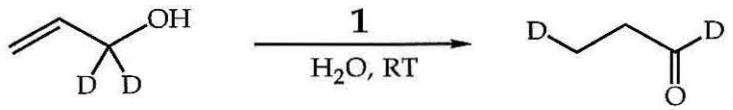
Labelling Studies. A deuterium labelling study employing allyl-*1,1-d*$_2$ alcohol **4** has been undertaken to probe the nature of the hydrogen shift during the isomerization of allylic alcohols. Compound **4** is prepared in the manner outlined by Hendrix et al.: a Diels-Alder reaction between ethyl acrylate and anthracene, followed by reduction to the alcohol with lithium aluminum deuteride, and then pyrolysis at 350-400 °C.[66] When reaction of **4** (20 eq) with **1** is carried out in D_2O at room temperature and followed by ^1H NMR spectroscopy, an equilibrium mixture of propionaldehyde-*1,2,3-d*$_3$ and the corresponding hydrate[73] is observed (eq 6a, hydrate is omitted for clarity). Integration[74] of the methyl vs. methylene peaks of the aldehyde (0.75 and 1.45 ppm, respectively) yields a ratio of 2.02 and the corresponding peaks for the hydrate (0.88 and 2.38 ppm, respectively) integrate with a ratio of 2.07.



(6a)

4

When this aqueous mixture is extracted with C_6H_6 and analyzed by ^2H NMR three peaks of equal intensity are observed at 9.3, 1.6, and 0.7 ppm. When the same reaction is carried out in H_2O and extracted with benzene the ^2H NMR spectrum contains only two resonances, of equal integration, at 9.3 and 0.7 ppm (Figure 1) indicating exclusive production of propionaldehyde-*1,3-d*$_2$ (eq 6b). The mass spectrum obtained with minimal fragmentation (GC-CIMS) is



(6b)

4

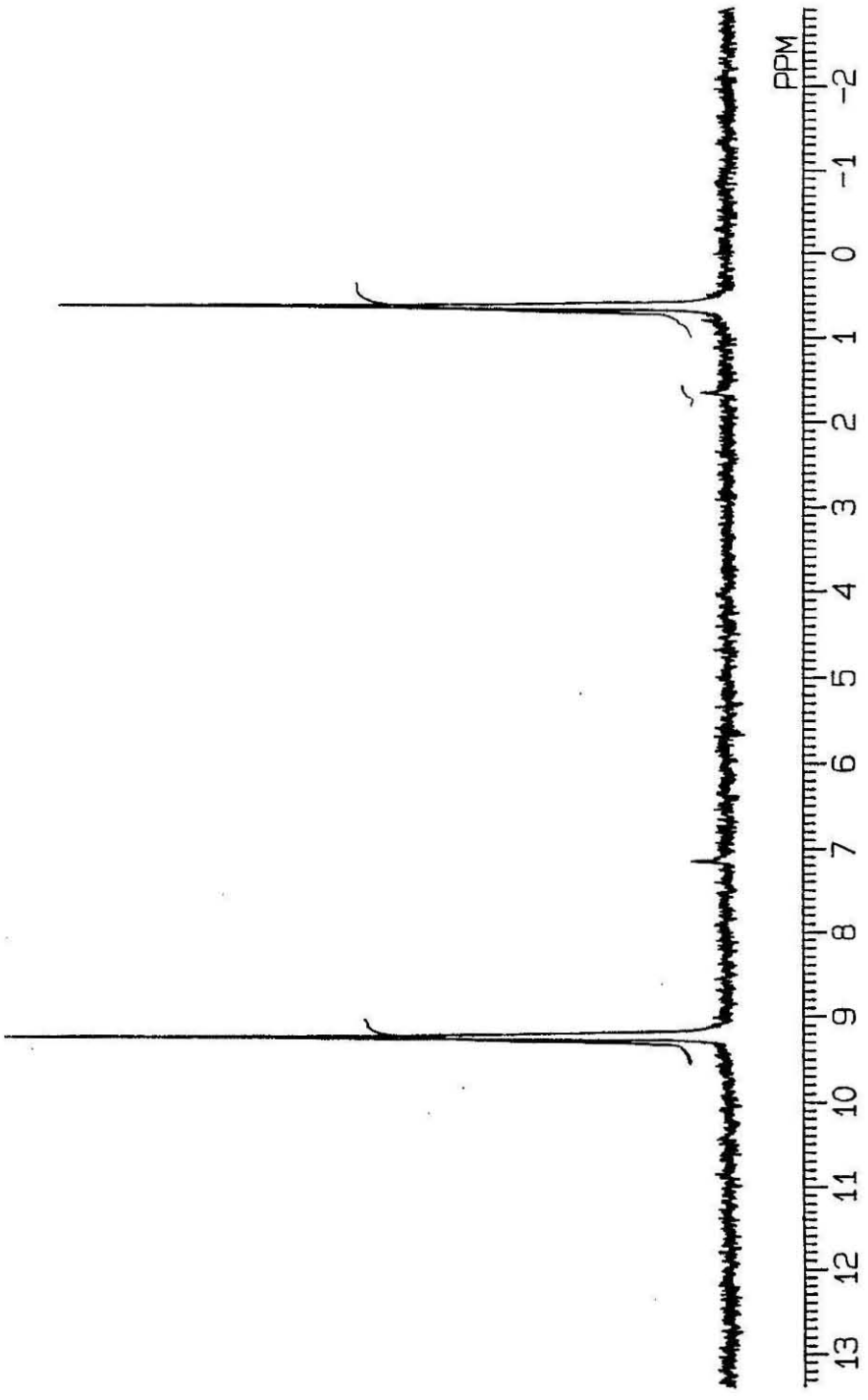
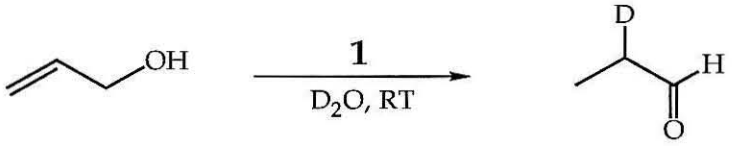


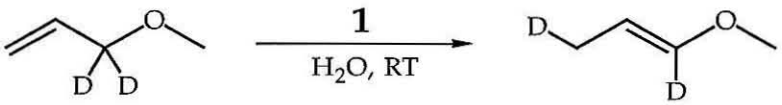
Figure 1. ^{2}H NMR (C_6D_6) spectrum of the reaction product from the aqueous (H_2O) Ru^{II}-catalyzed isomerization of allyl-*1,1-d*$_2$ alcohol.

consistent with two deuterium atoms per molecule of product. Incorporation of deuterium into the C-1 or C-3 positions of the substrate from the solvent is ruled out by the absence of deuterium in the propionaldehyde product from the isomerization of unlabelled allyl alcohol in D_2O. Analysis by ^2H NMR in C_6H_6 indicates exclusive production of propionaldehyde-2-*d* by a single resonance at 1.6 ppm, the single deuterium in the C-2 position resulting from enol tautomerization (eq 6c). The ^1H NMR confirms that there is also a single proton at this position.



(6c)

The hydrogen shift during allylic ether isomerization has been probed with the deuterium labelled substrate allyl-*1,1*-d_2 methyl ether **5**. When reaction of **5** (20 eq) with **1** in D_2O at room temperature is followed by ^1H NMR exclusive production of labelled 1-propenyl-*1,3*-d_2 methyl ether is observed(eq 7a). The

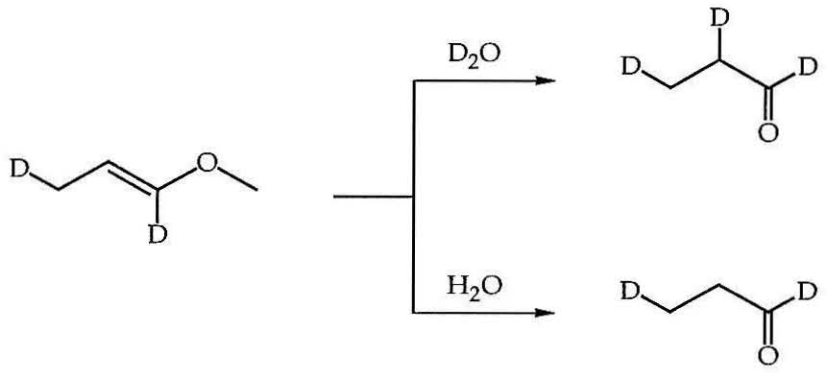


(7a)

5

resonance arising from the methyl of the propenyl moiety appears as a doublet of 1 : 1 : 1 triplets (J_{HH} = 6.6 Hz, J_{HD} = 2.2 Hz) at 1.32 ppm. Hydrolysis to propionaldehyde-*1,2,3*-d_3 and methanol subsequently occurs (eq 7b). The ^2H NMR spectrum of the C_6H_6-extracted reaction carried out in H_2O reveals the absence of deuterium on the C-2 position of propionaldehyde. Two resonances of equal integration appear at 9.3 and 0.7 ppm, indicating exclusive production of

propionaldehyde-*1,3-d*$_2$ (eq 7b), identical to the observation made with allyl-*1,1-d*$_2$ alcohol.



(7b)

The intra/intermolecularity of the allylic alcohol isomerization has been investigated through a crossover labelling study. A $^{13}C/^{2}H$ crossover, rather than a $^{1}H/^{2}H$ crossover, is designed to identify specific site-to-site crossover and allow analysis by NMR techniques, while avoiding the difficulty in observing aldehyde molecular ion peaks by mass spectrometry. Allyl-3-^{13}C alcohol **8** is

8

prepared as a solution in water (see Experimental section). After a mixture of **1**, **4**, and **8** in a 1.0 : 6.6 : 2.9 ratio is allowed to react in D_2O solution ([Ru(II)] ~ 25 mM) for 18-24 hours at room temperature, extraction of the resulting yellow solution with C_6D_6 gives a colorless solution of isotopically labelled propionaldehydes. In the ^{1}H non-decoupled ^{13}C NMR spectrum (Figure 2a) a quartet (J_{CH} = 127 Hz) at 5.79 ppm overlaps a triplet of 1 : 1 : 1 triplets (J_{CH} = 130 Hz, J_{CD} = 20 Hz) at 5.51 ppm. Based on the resonance intensities, approximately 34% of the ^{13}C label is present as $^{13}CH_2D$, the remainder being $^{13}CH_3$. No $^{13}CHD_2$ groups are observed. When the ^{13}C-labelled substrate alone is

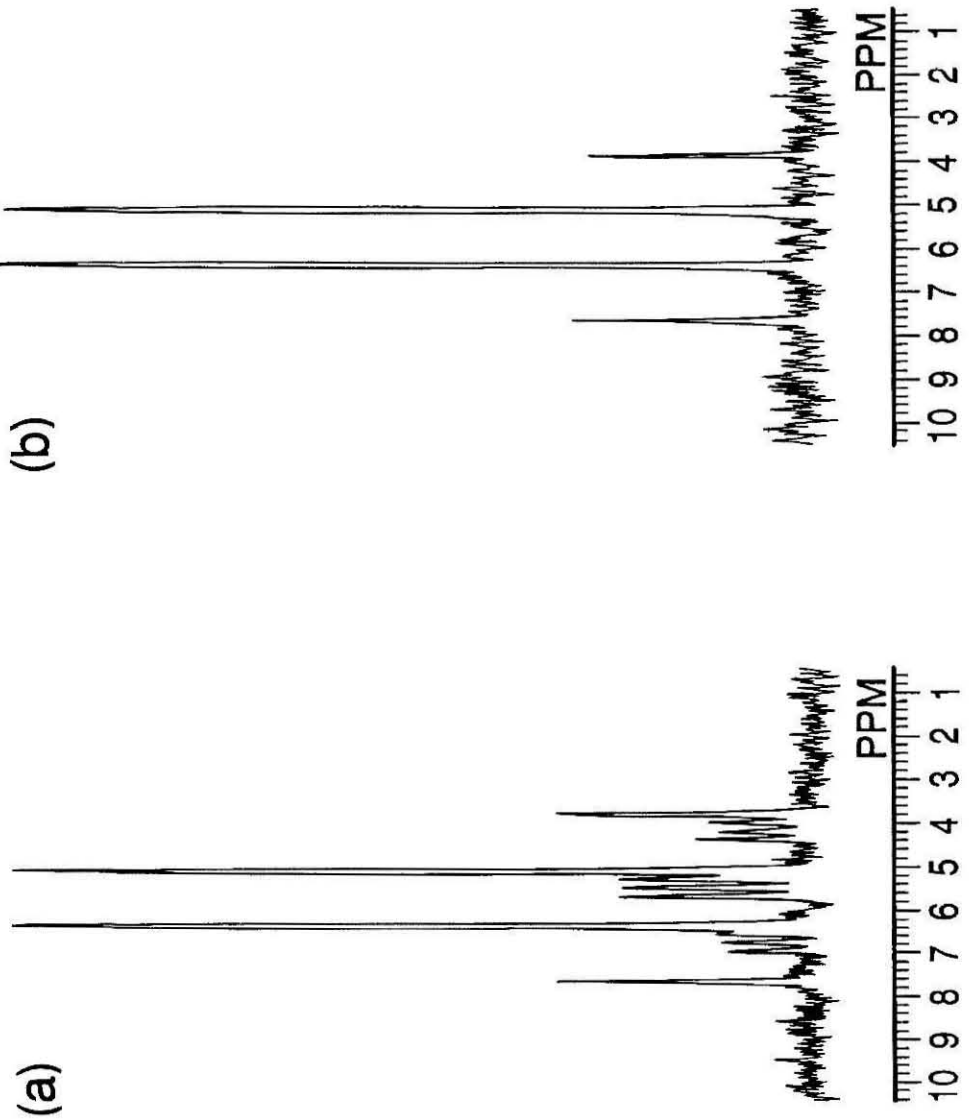


Figure 2. Methyl region of the ^{1}H-non-decoupled ^{13}C NMR (C_6D_6) of the products from the aqueous (D_2O) Ru^{II}-catalyzed isomerization of (a) allyl-*1,1-d*$_2$ alcohol and allyl-3-^{13}C alcohol and (b) allyl-3-^{13}C alcohol.

isomerized in D_2O under identical conditions the ^1H non-decoupled ^{13}C NMR spectrum (Figure 2b) contains only the quartet resonance at 5.79 ppm confirming that **4** is the source of deuterium on the methyl position of the product in the crossover experiment.

The intra/intermolecularity of the allylic ether isomerization has been investigated through a $^1H/^2H$, rather than a $^{13}C/^2H$, crossover labelling study because of synthetic difficulties. The propionaldehyde product from the isomerization of a mixture of allyl methyl ether (10 equiv.) and **5** (10 equiv.) with **1** in H_2O has been analyzed by GC-CIMS to determine the deuterium content of the labelled product. Although fragmentation by loss of the aldehyde hydrogen (or deuterium) atom precludes quantitative measurement of the relative abundancies of molecular ions for the different labelled propionaldehydes in the mass spectrum, the molecular ion pattern indicates a mixture of d_0, d_1, and d_2 propionaldehydes. A large peak at m/e 60 $(M + H)^+$ is the result of a significant amount of propionaldehyde-d_1 among the product mixture. Comparison with the mass spectra of authentic samples of propionaldehyde and propionaldehyde-*1,2*-d_2 confirms that this peak does not solely arise from fragmentation of these species.

Discussion

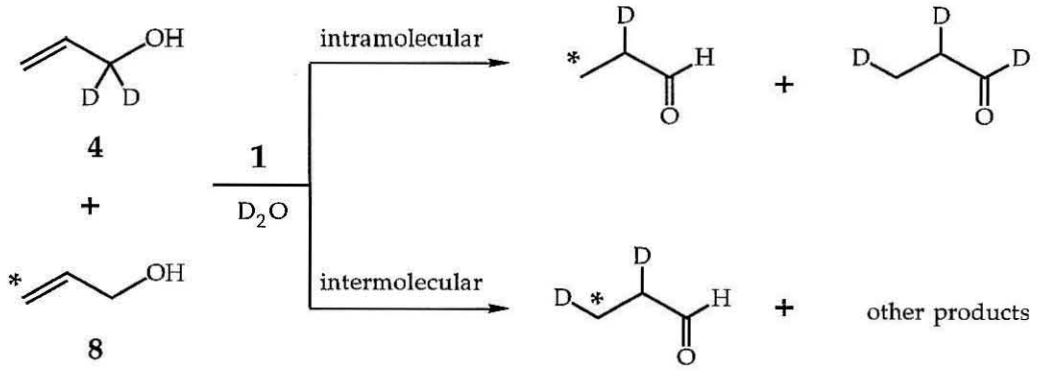
$Ru^{II}(H_2O)_6(tos)_2$ **1** is an effective catalyst for the isomerization of allylic ethers and alcohols in aqueous media. The catalyst is tolerant of substitution at all three carbons of allyl alcohol (Scheme 5). The acidity of the ruthenium(II) complex serves to hydrolyze the product enol ethers, thus making **1** a possible one-step deprotection agent for allylic ethers. The limitations of this usage are the presence of acid sensitive functional groups or basic moieties which may act as catalyst poisons, such as amines (see Chapter 1). The utility of **1** as a general isomerization catalyst for allylic substrates is undergoing further exploration.

Mechanism. The results from the ^2H and ^{13}C labelling studies place severe restrictions on a plausible isomerization mechanism but are consistent with a metal hydride isomerization mechanism involving exclusive Markovnikov addition of the metal hydride to the olefinic substrate. The isomerization of allyl-*1,1-*d_2 alcohol to exclusively propionaldehyde-*1,2,3-*d_3 in D_2O (eq 6a) and propionaldehyde-*1,3-*d_2 in H_2O (eq 6b) indicates that **1** isomerizes allyl alcohol through a selective 1,3 hydrogen shift to the intermediate enol which tautomerizes in the acidic medium.[71] The isomerization of allyl-*1,1-*d_2 methyl ether to 1-propenyl-*1,3-*d_2 methyl ether (eq 7a), and propionaldehyde-*1,3-*d_2 after hydrolysis in H_2O (eq 7b), is also indicative of a selective 1,3-hydrogen shift during allyl ether isomerization. This lack of deuterium incorporation at the C-2 position of the allyl moiety suggests that isomerization occurs through the π-allyl hydride mechanism. If the isomerization were occurring through the metal hydride addition-elimination mechanism we would expect deuterium incorporation at this site from competitive formation of a primary metal alkyl from substrate and ruthenium deuteride followed by β-hydride elimination (anti-Markovnikov addition; Scheme 2, step 2'), since formation of a primary

metal alkyl is thermodynamically favored over formation of a secondary metal alkyl. Exclusive Markovnikov addition, however, is also consistent with the lack of scrambling and exclusive formation of a 1,3 shift product.

The $^{13}C/^{2}H$ crossover experiment establishes the intermolecularity of the isomerization. An intramolecular pathway would yield only propionaldehyde-3-^{13}C and propionaldehyde-*1,3-d*$_2$, while an intermolecular pathway would statistically incorporate deuterium onto the ^{13}C-labelled site to yield propionaldehyde-3-^{13}C-3-*d* (Scheme 6) in addition to propionaldehyde-3-^{13}C.[75] The ^{1}H

Scheme 6. Inter- and Intramolecular Isomerization of **4** and **8**.



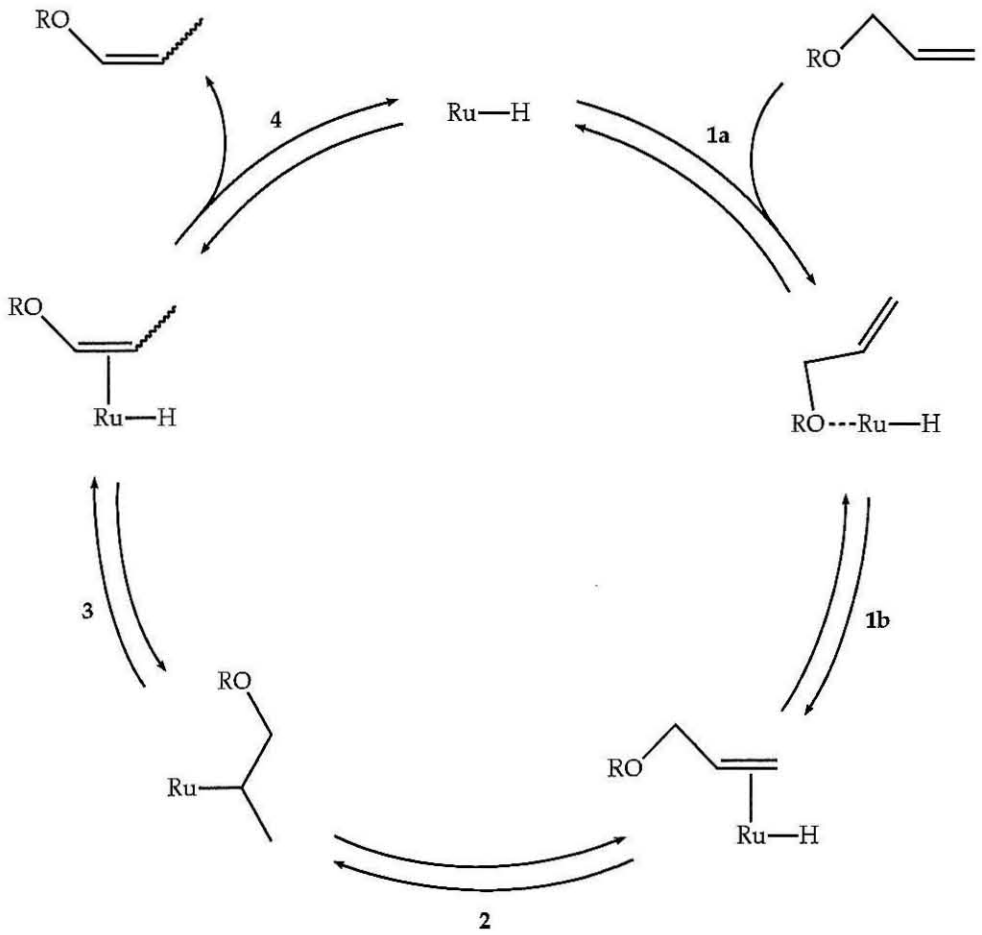
non-decoupled ^{13}C NMR spectrum of the product propionaldehydes (Figure 2a) identifies the substitution on the labelled carbon as both $^{13}CH_3$, responsible for the quartet at 5.79 ppm, and $^{13}CH_2D$, arising as the triplet of 1 : 1 : 1 triplets at 5.51 ppm. The control experiment where the isomerization of **8** is conducted in the absence of **4** (Figure 2b) definitively identifies allyl-*1,1-d*$_2$ alcohol as the source of deuterium in the crossover, ruling out incorporation of deuterium from the solvent. From the relative amounts of ^{2}H- and ^{13}C-labelled substrate, we can calculate the statistical crossover, assuming the catalyst exhibits no substrate preference, as 21%.[76] This is consistent with the observed 34% crossover, within

experimental error. The mass spectrometry results of the $^{1}H/^{2}H$ crossover between labelled and unlabelled allyl methyl ether is also indicative of intermolecularity for the isomerization of allylic ethers.

The intermolecularity of the isomerization mechanism is suggestive of the intermediacy of a metal hydride species. This, coupled with the results from the deuterium-labelling experiment, leads us to propose that addition of the metal hydride across the olefin occurs in an exclusive Markovnikov fashion to yield the secondary alkyl which subsequently undergoes β-hydride elimination to yield the enol or enol ether product. Contrary to other studies, no formation of a primary metal alkyl species occurs through anti-Markovnikov addition of the metal hydride to the olefin during the isomerization cycle as evidenced by the lack of deuterium incorporation into the C-2 position of the product aldehydes and enol ethers. We propose that the exclusive Markovnikov metal hydride addition is the result of the directing effect of the alcohol functionality.

Our modified metal hydride mechanism for the directed isomerization of allylic alcohols and ethers by aqueous ruthenium(II) is shown in Scheme 7. Pre-coordination of the substrate oxygen directs subsequent coordination of the olefin to the metal center such that insertion occurs in a Markovnikov fashion. It is possible that the trans labilizing effect of the hydride, relative to aquo, ligand favors pre-coordination of the oxygen to the trans position, thus ensuring the coordination of the olefin in a cis position with the terminal carbon proximal to the hydride. Subsequent β-hydride elimination yields the enol or enol ether which decomplexes and tautomerizes or hydrolyzes to the product aldehyde. This is the first example of a metal hydride olefin isomerization system exhibiting *exclusive* Markovnikov addition to the substrate.

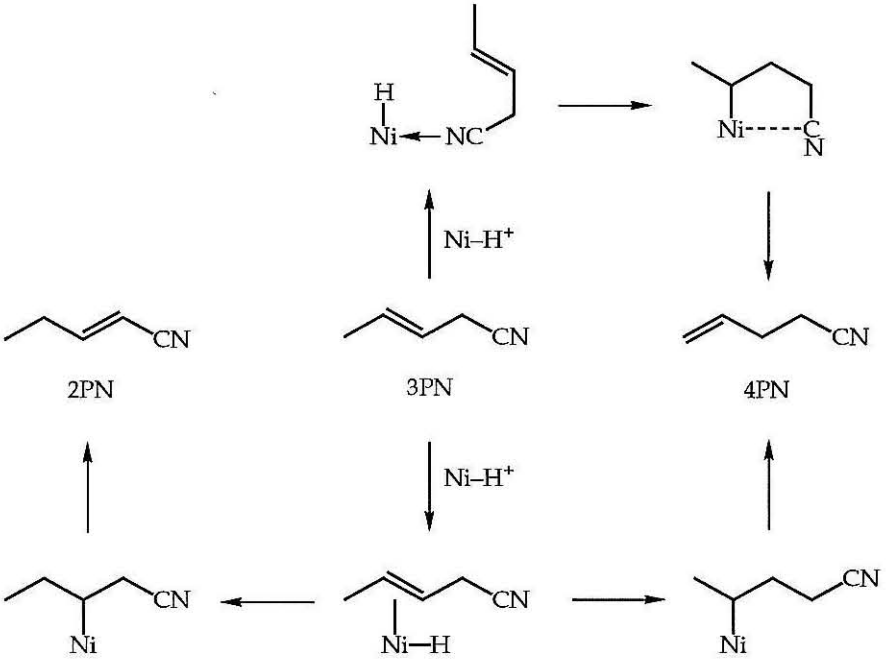
Scheme 7. Mechanism of Isomerization of Allylic Ethers and Alcohols by $Ru^{II}(H_2O)_6(tos)_2$.



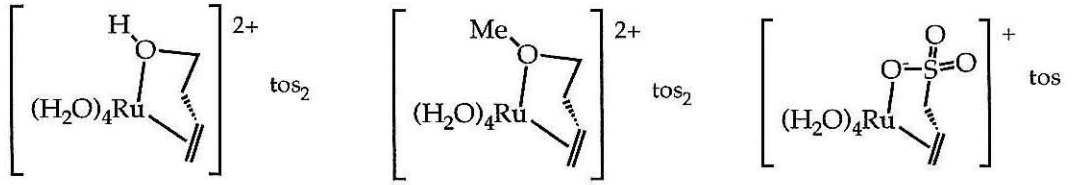
The directing effect of functional groups on the selectivity of transition metal catalysts is well precedented. Crabtree and Davis reported high stereoselectivity in the homogeneous hydrogenation of allylic and homoallylic cyclohexenols with [Ir(η^4-1,5-cyclooctadiene)(PCy_3)(C_5H_5N)]PF_6 (Cy = C_6H_{11}).[77, 78] Brown and co-workers observed moderate to high stereoselectivity in the homogeneous hydrogenation of both acyclic allylic and homoallylic alcohols[79] as well as allylic and homoallylic methylene cyclohexenols[80] with [Rh(η^4-norbornadiene)($Ph_2P(CH_2)_4PPh_2$)]BF_4. Evans and Morrissey extended this work to acyclic chiral allylic alcohols.[81, 82] Other oxygen containing functional groups such as alkoxides,[83] carboxylates,[78, 84] ethers,[78] and ketones[78] have also been shown to exhibit directing effects in transition metal-catalyzed homogeneous hydrogenation. Hydroxyls and other basic functional groups are also responsible for stereoselective transition metal-catalyzed methylenation,[85, 86] epoxidation,[87, 88] and hydroboration.[89]

Directing effects have also been observed in an olefin isomerization system. McKinney has proposed that the directing effect of a pendant cyano group is responsible for the selective isomerization of 3-pentenenitrile to 4-pentenenitrile by $HNi[P(OR)_3]_4^+$[16] High kinetic ratios of 4-pentenenitrile to 2-pentenenitrile are produced even though the thermodynamic distribution of pentenenitrile isomers is 78.3 : 20.1 : 1.6 (2PN : 3PN : 4PN). As shown in Scheme 8, the author attributes this kinetic control to nitrile-directed olefin orientation during the insertion step (upper portion of scheme). Non-directed insertion would result in a thermodynamic mixture of olefins (lower portion of scheme). In the aqueous ruthenium(II) system certain oxygen functionalities coordinate to the Ru^{II} center as demonstrated by the preparation and isolation of $Ru^{II}(H_2O)_4$-($\eta^1(O)$:η^2(C,C')-$HOCH_2CH_2CH{=}CH_2$)$(tos)_2$ **9** and the ^1H and ^{13}C NMR

Scheme 8. Kinetic Isomerization of 3-Pentenenitrile to 4-Pentenenitrile.[16]



characterization of $Ru^{II}(H_2O)_4(\eta^1(O):\eta^2(C,C')$-$CH_3OCH_2CH_2CH{=}CH_2)(tos)_2$ **10** and $Ru^{II}(H_2O)_4(\eta^1(O):\eta^2(C,C')$-$OSO_2CH_2CH{=}CH_2)(tos)$ **11** (Chapter 1).

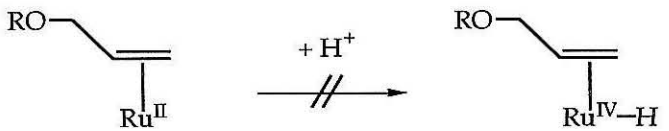


9 **10** **11**

Deuterium Incorporation. Further restrictions are placed on the mechanism in Scheme 7 by several additional observations. The total lack of deuterium incorporation into the substrate or products from D_2O, aside from the deuterium on the C-2 carbon from enol tautomerization/enol ether hydrolysis, indicates that the proposed active metal hydride does not exchange with the solvent on the timescale of the isomerizations. However, we do observe

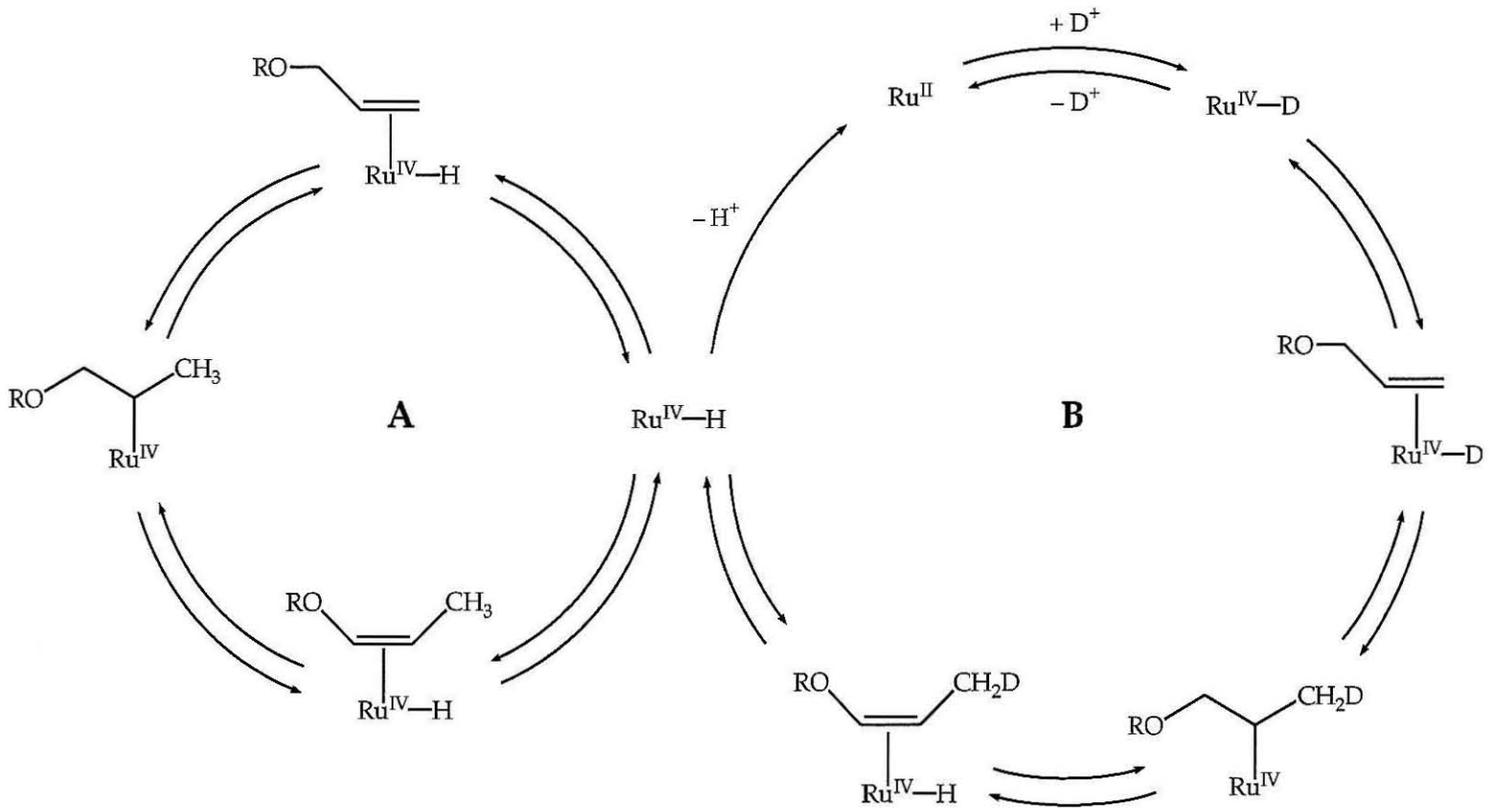
deuterium incorporation in the stoichiometric isomerization of 2-pentenoic acid to 3-pentenoic acid (vide supra) which leads us to conclude that the hydride originates from the solvent but is formed in a rate limiting step. Tolman has previously observed a similar lack of deuterium incorporation from deuterated media in a nickel hydride olefin isomerization system[51] which he attributed to a much higher rate of isomerization versus hydride exchange.

A catalytic cycle illustrating initial hydride formation from deuterated solvent is shown in Scheme 9. Free ruthenium(II) (cycle B, upper left) is oxidized to ruthenium(IV) deuteride. The substrate coordinates and undergoes a directed insertion in an exclusive Markovnikov fashion to yield a secondary metal alkyl. This metal alkyl undergoes β-hydride elimination producing the enol or enol ether product and ruthenium(IV) hydride. Cycle B, therefore, could be responsible for any observed deuterium incorporation. The ruthenium(IV) hydride can then either reduce back to ruthenium(II) or continue to isomerize substrate as shown in Cycle A, which would result isomerization without deuterium incorporation. Since we do not observe deuterium incorporation to the limits of our detection methods, Cycle A must predominate in the isomerization mechanism under the conditions studied. The rate of olefin coordination to ruthenium(IV) hydride must be much greater than reduction back to ruthenium(II). In addition, the stability of isolated ruthenium(II) allyl ethyl ether complex (see Chapter 1) suggests that deuterium cannot enter the cycle by exchange with the ruthenium(IV) hydride olefin complex (eq 8). If the reaction shown in eq 8 were occurring, the isolated ruthenium(II) allyl ethyl ether complex would decompose



(8)

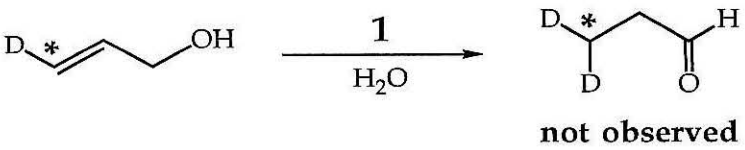
Scheme 9. Mechanism of Deuterium Incorporation during Olefin Isomerization.



to yield isomerized olefin.

The other possible origin of the initial metal hydride is the substrate itself. For instance, the olefin could coordinate to the metal center and an allylic hydrogen could be abstracted as in the first steps of the π-allyl hydride mechanism (Scheme 3). This allyl hydride could then act as the active metal hydride catalyst. However, isotopic scrambling of an olefin lacking allylic hydrogens has been observed in an independent study in this laboratory.[90] When a mixture of styrene (5 equiv.) and styrene-α,α,β-d_3 (5 equiv.) are reacted with **1** (1 equiv.) in methanol-d_4 at 55° C, incorporation of deuterium into the unlabelled styrene is observed. In the absence of labelled styrene no deuterium incorporation is observed.

The absence of di- and trideutero-^{13}C-labelled methyl groups in the alcohol crossover experiment requires the irreversibility of steps 1 and/or 2 in Scheme 7. If both substrate coordination and olefin insertion were reversible then more than one deuterium could be placed on the ^{13}C-labelled carbon through production of allyl-3-^{13}C-3-d_1 alcohol. This substrate could then be isomerized by Ru–D to yield propionaldehyde-3-^{13}C-3,3-d_2 (eq 9). The doublet of 1 : 2 : 2 : 1 quartets resonance which would arise from this $^{13}CHD_2$ group is absent from the ^{1}H non-decoupled ^{13}C NMR of the product propionaldehydes (Figure 1a).



(9)

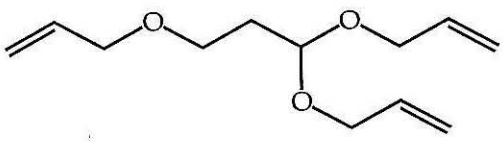
not observed

Finally, the stability of the isolated ruthenium(II) complex of allyl ethyl ether under the isomerization conditions for extended periods of time dictates

that metal hydride formation precedes olefin coordination. In other words, the substrate ruthenium(II) olefin complex is not protonated to yield an olefin hydride complex (eq 8).

Other Possible Mechanisms. The mechanism proposed above for the allylic alcohol and ether isomerizations accounts for the available data from the labelling studies as well as additional observations concerning deuterium incorporation and observed complex stabilities. The one piece of evidence not taken into account is the formation of small amounts of oxidation products during the allylic alcohol isomerizations. The central question is whether these products are formed as intermediates in the initiation, isomerization, or are the products of a parallel oxidation pathway.

An isomerization mechanism involving the intermediacy of α,β-unsaturated carbonyl species has recently been proposed by Trost and Kulawiec[25] for the selective isomerization of allylic alcohols by $(\eta^5\text{-Cp})(PPh_3)_2RuCl$. This "internal redox" mechanism (Scheme 10) involves the coordination of the allylic alcohol as a bidentate ligand. β-Hydride elimination from the coordinated alkoxide[91] leads to an enone hydride complex which rearranges to an oxaallyl species, presumably through exclusive Markovnikov addition of the metal hydride to the coordinated olefin moiety. Protonation liberates the product. This system demonstrates selectivity for allylic alcohols, leaving other alcohol and isolated olefin functionalities untouched. The authors claim that the isolation of small but detectable amounts of the acetal **12** in the presence of neat allyl alcohol is



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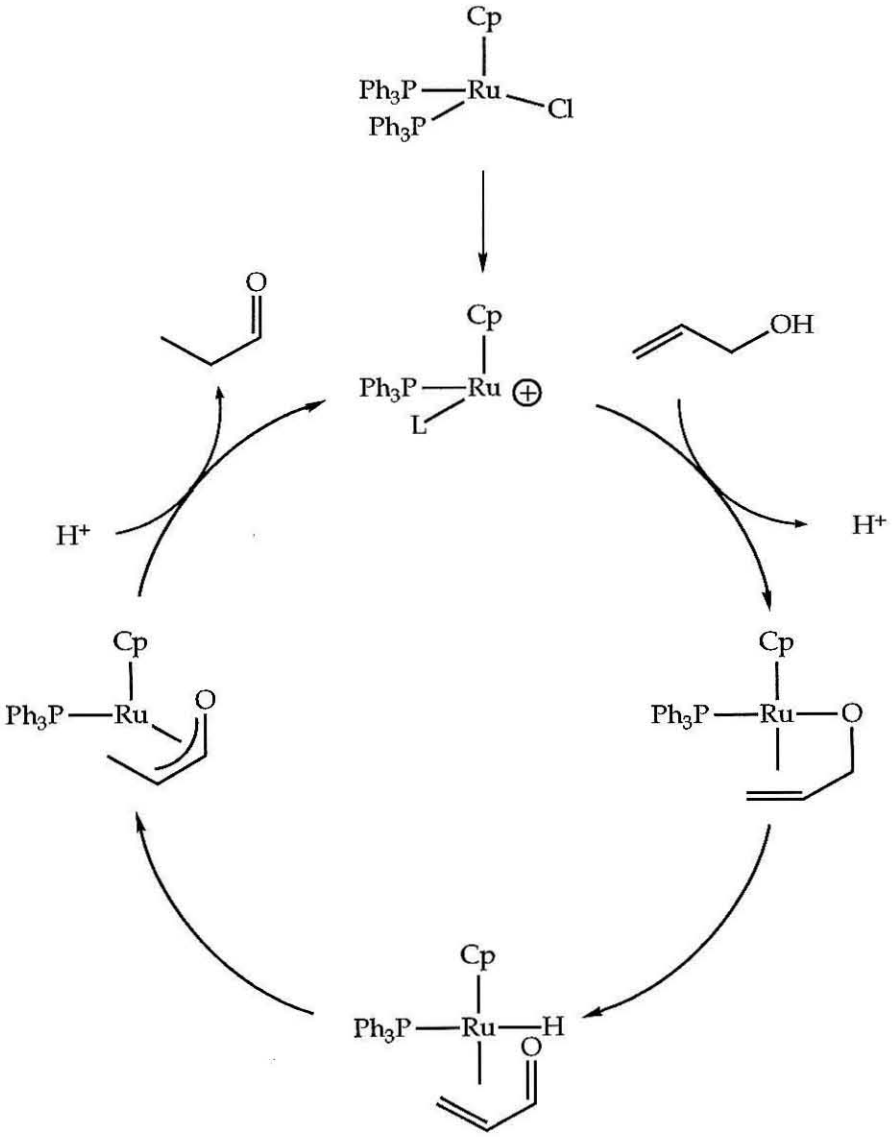
Scheme 10. Isomerization of Allylic Alcohols by η^5-Cp$(PPh_3)_2$RuCl.[25]

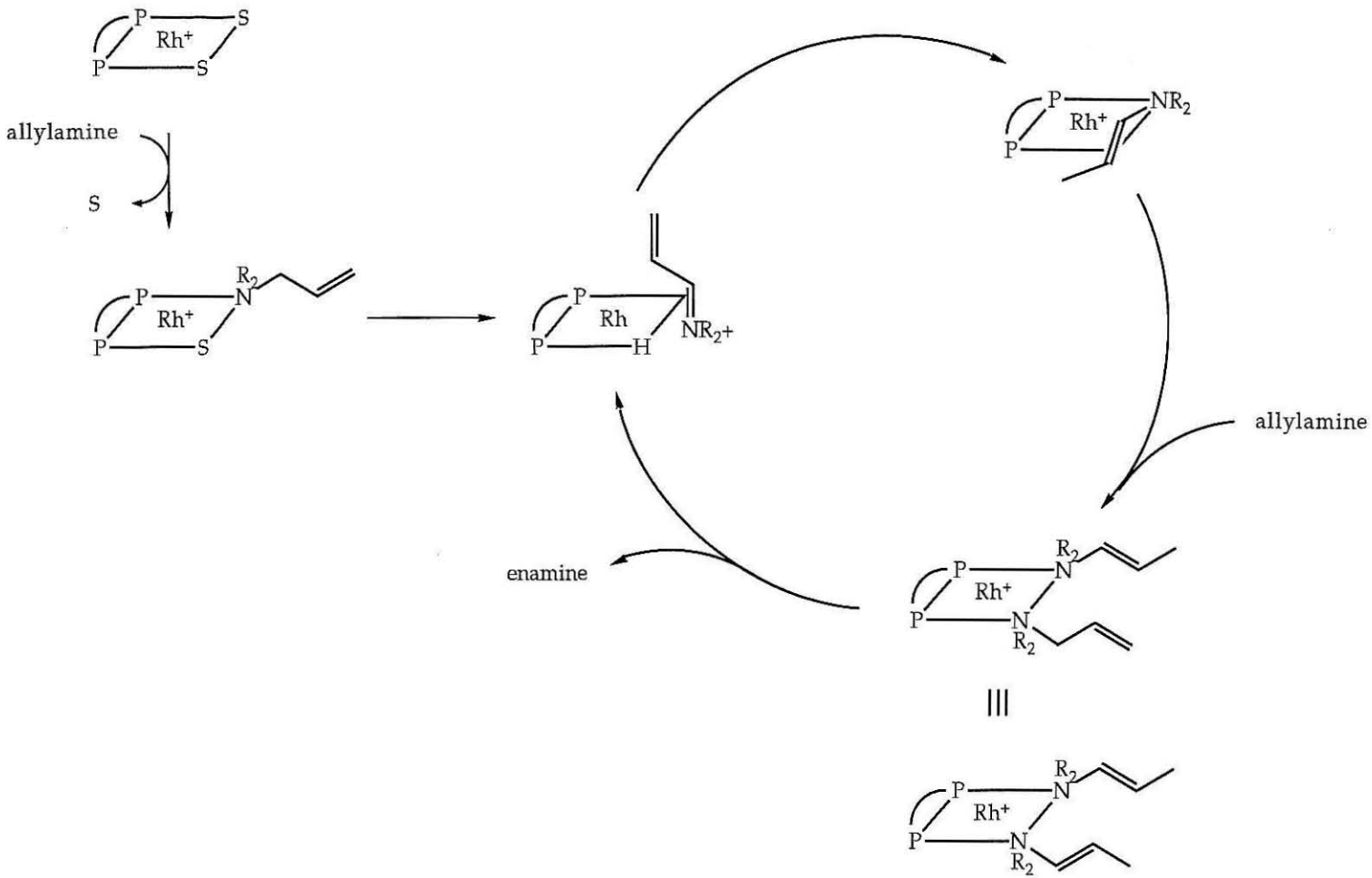


evidence for the intermediacy of the enone hydride complex. Similar selectivity is also observed in the closely related $RuCl_2(PPh_3)_3/Me_3SiOOSiMe_3$ oxidation system reported by Kanemoto et al.[92] This catalyst is also believed to oxidize the alcohol through β-hydride elimination from an alkoxide ligand.[91] No mechanistic studies were undertaken in either system.

There are differences in reactivity between our system and Trost's which shed doubt on the validity of adapting an internal redox mechanism to the aqueous ruthenium(II) system. The key difference is the inability of the organometallic system to isomerize isolated olefins, while the aqueous system can isomerize, for instance, 4-penten-1-ol to 3-penten-1-ol and 2-pentenoic acid to 3-pentenoic acid. We also observe isomerization of allyl ethers to 1-propenyl ethers, a transformation which clearly does not involve the participation of an alcohol functionality, although it may be possible that aqueous ruthenium(II) isomerizes allylic ethers and allylic alcohols by separate mechanisms. Furthermore, the intermediacy of an enone complex in the isomerization mechanism would require that free α,β-unsaturated carbonyl compound arises from decomplexation from this enone complex. We would therefore expect the amount of free α,β-unsaturated carbonyl compound produced to be dependent on the steric requirements of the enone. This does not seem to be the case, however, as crotyl alcohol yields 5-10% crotonaldehyde, but 2-methyl-2-propen-1-ol and 3-buten-2-ol yield only negligible amounts of the corresponding oxidation products while having similar or greater steric requirements than crotonaldehyde.

An internal redox mechanism similar to Trost's has been proposed by Inoue et al.[93] for the asymmetric isomerization of allyl amines by $[Rh(binap)S_2]^+$ (binap = 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl; S = solvent or other coordinative molecule).[52-54] This "nitrogen triggered" mechanism (Scheme 11) is

Scheme 11. Isomerization of Allylamines by Rhodium Biphosphines Complexes.[93]

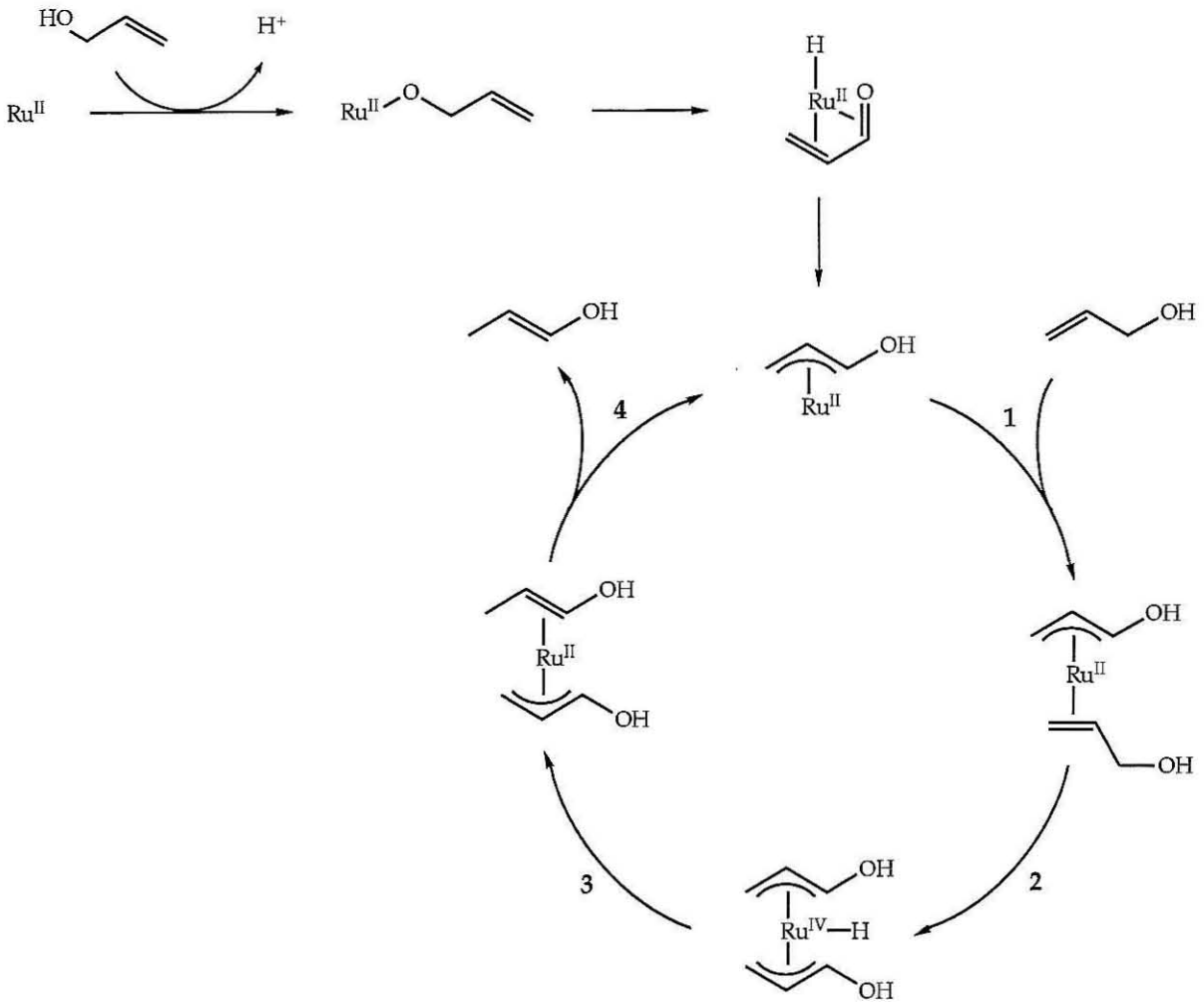


based on ^{1}H and ^{31}P NMR studies, kinetic measurements, and deuterium labelling experiments, and is very similar to the mechanism proposed by Trost. Convincing evidence for the necessity of the amine functionality for isomerization activity is the displacement of solvent from $[Rh(binap)S_2]^+$ by triethylamine to form [Rh(binap)(S)(triethylamine)]$^+$ but not by 2-methyl-2-butene. More importantly, the rate of isomerization of diethylgeranylamine is inhibited by addition of triethylamine but not affected by the presence of a large excess of 2-methyl-2-butene.

As stated before, the alcohol functionality is not necessary for the isomerization of double bonds in the aqueous ruthenium(II) system, nor is the reaction inhibited by excess alcohol. Isomerization of allyl alcohol can be carried out in neat methanol and occurs at approximately the same rate as in water. However, excess olefin inhibits the isomerization reaction.[94] We are also able to prepare olefin complexes in methanol solution and isolated olefin complexes of aqueous ruthenium(II) do not decompose through loss of olefin when dissolved in methanol (see Chapter 1). In addition, the rhodium system is intramolecular as shown by the absence of mono-deuterated enamine by GC-MS in the products of the isomerization of a mixture of non-labelled and *dideutero* allyl amines (eq 3).[29] The aqueous ruthenium(II) system, however, is intermolecular (vide supra).

A possible mechanistic pathway involving oxidation intermediates and intermolecular reactivity is shown in Scheme 12. This mechanism still does not account for the isomerization of non-activated olefins or allyl ethers, but could still be a parallel mechanism for the isomerization of allylic alcohols. Selective 1,3-hydrogen shift is guaranteed by the intermediacy of π-allyl species and cross-over between substrates occurs in steps 2-3. As drawn, the symmetry of the bis(π-allyl) intermediate requires step 2 to be reversible. If this is the case,

Scheme 12. Alternate Mechanism of Isomerization of Allylic Alcohols by $Ru^{II}(H_2O)_6(tos)_2$.



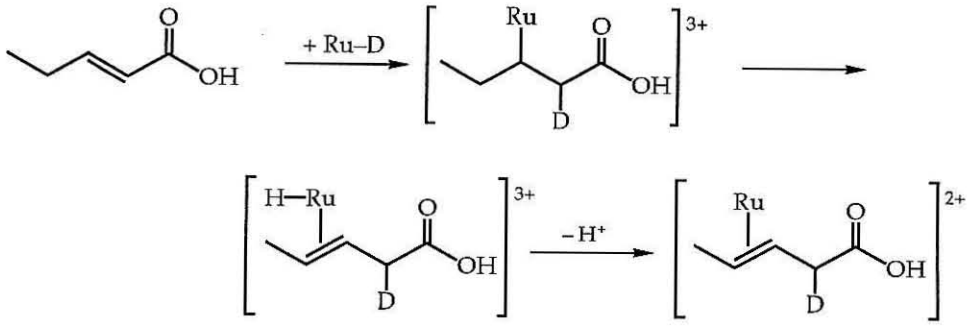
multiple crossovers may take place between substrates, producing, for instance, propionaldehyde-3-^{13}C-1,3-d_2 and unlabelled propionaldehyde. These products, which would not be produced from the mechanism in Scheme 7, could be detected by mass spectrometry. Unfortunately, extensive ion fragmentation precludes analysis of the product mixture of the experiment shown in Scheme 6 by mass spectrometry. We, therefore, have been unable to rule out the mechanism in Scheme 12.

Oxidation of allylic alcohols may indeed be a pathway independent of olefin isomerization. However, non-activated alcohols such as methanol, ethanol, and various other primary aliphatic alcohols are not oxidized by aqueous ruthenium(II). When benzyl alcohol is reacted with **1** (10 : 1) in water no benzaldehyde is formed within 24 h at room temperature or for extended time at 65 °C.

Non-Allylic Substrates. The selective deuteration of only one of the C-2 hydrogens during the formation of **7** from **1** and free 2-pentenoic acid in D_2O is also indicative of specific addition of metal-hydride across an olefin bond. In this case it is directed by the carboxylic acid functionality. The irreversibility of the formation of this complex is evidenced by (a) the lack of exchange between these two diastereotopic positions on the NMR time scale—the olefin complex is inert and olefin is not exchanging between metal sites—and (b) the presence of exactly one deuterium at the C-2 position—reversibility would result in a greater enrichment of deuterium at this position. We are therefore observing the original metal-deuteride formed from Ru^{II} and D^+ in the form of the deuterium at C-2. Since the addition/isomerization/complex formation sequence is irreversible, metal hydride is not liberated and we see essentially 100% deuterium incorporation. This is in contrast to allyl alcohol isomerization and all other isomerizations

where metal hydride is liberated (i.e., the reaction is catalytic). A reaction sequence is shown in Scheme 13.

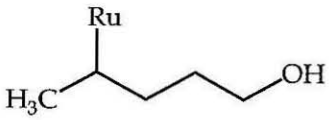
Scheme 13. Isomerization of 2-Pentenoic Acid in D_2O by $Ru^{II}(H_2O)_6(tos)_2$.



The stability of homoallylic substrates such as 3-buten-1-ol and 3-penten-1-ol with regard to isomerization has been observed previously in a system which is claimed to isomerize olefins through a π-allyl hydride mechanism.[30] This stability was attributed to the formation of a stable chelate structure which prevented allylic hydrogen abstraction by the metal. We have prepared such a chelate complex of aqueous ruthenium(II) with 3-buten-1-ol.[70] However, in the aqueous ruthenium(II) system, metal hydride formation precedes olefin coordination and insertion. The stability of the olefin complex, therefore, should not be responsible for the olefin's stability towards isomerization. An alternate explanation is that the 3-buten-1-ol quickly binds to all metal sites and prohibits the formation of metal hydride. However, 3-penten-1-ol does not isomerize although, as an internal olefin, it is a relatively weak complexing agent.

We note, however, that the ratio of *cis/trans* 3-penten-1-ol during the isomerization of 4-penten-1-ol is 40 : 60 as observed by ^1H NMR, while after all 4-penten-1-ol is consumed the ratio changes to 27 : 73, indicating that 3-penten-1-ol is still reacting with ruthenium hydride but in such a way as to only isomerize

the double bond geometry. There are two possible explanations for this. Either (a) the alcohol oxygen is directing the addition of the olefin to the ruthenium hydride to yield a ruthenium alkyl species such as **13** which can only β-eliminate



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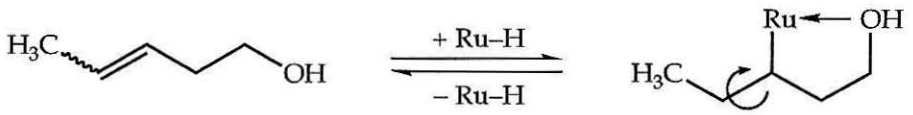
to give 4-penten-1-ol or 3-penten-1-ol or (b) coordination of the alcohol oxygen to the metal center in the ruthenium alkyl species shown in eq 10 prevents β-



(10)

elimination to yield 2-penten-1-ol. Both possibilities allow *cis/trans* isomerization of the double bond. The interaction of the terminal olefin 3-buten-1-ol with the catalyst in this fashion would have to be probed through labelling studies. We do acknowledge, however, the additional possibility that 3-buten-1-ol does bind the metal well enough to prevent hydride formation from unbound ruthenium(II) while 3-penten-1-ol does not. Ruthenium hydride can form and *cis/trans* isomerize this olefin. Complete binding of the catalyst is surely the reason why diallyl ether does not undergo isomerization in the presence of **1**.

Summary

Olefin isomerization of allylic ethers and alcohols of various substitution patterns is catalyzed by aqueous ruthenium(II) under mild conditions. Non-allylic olefins are also isomerized, although homoallylic alcohols exhibit stability towards isomerization. Labelling studies indicate that isomerization occurs by a modified metal hydride addition-elimination mechanism involving exclusive Markovnikov addition to the double bond directed by the oxygen functionality of the substrate. The mechanistic experiments detailed here illustrate that although a 1,3-hydrogen shift strongly implies a π-allyl hydride mechanism for transition-metal-catalyzed olefin isomerization, ruling out the metal hydride addition-elimination mechanism by establishing the intramolecularity of the process is of increased importance with functionalized substrates because of the directing power of functional groups in transition-metal catalysis. An observed 1,3-hydrogen shift might be the result of directed olefin insertion and is not in itself evidence for the π-allyl metal hydride mechanism. The applicability of these mechanistic results towards a metathesis initiation mechanism is discussed in Chapter 3.

Experimental

General Procedures. All manipulations involving air- and/or moisture-sensitive compounds were carried out using standard high vacuum or Schlenk techniques. Argon was purified by passage through columns of BASF RS-11 (Chemalog) and Linde 4Å molecular sieves. Solids were transferred and stored in a N_2-filled Vacuum Atmospheres glove box equipped with a MO-40-1 purification train, a DK-3E Dri-Kool conditioner, and a Dri-Cold Freezer.

Instrumentation. NMR spectra were recorded on a JEOL FX-90Q (89.6 MHz ^1H, 22.5 MHz ^{13}C), a JEOL GX-400 (399.65 MHz ^1H, 61.25 MHz ^2H, 100.40 MHz ^{13}C), a Varian XL-200 (200 MHz ^1H), Varian EM-390 (90 MHz ^1H) and a Bruker AM-500 (500.14 MHz ^1H, 76.78 MHz ^2H). Proton chemical shifts are referenced to internal residual solvent protons. Carbon chemical shifts are referenced to the carbon signal of the deuterated solvents. Deuterium chemical shifts are referenced to natural abundance deuterium in the solvent. Gas chromatography analyses were performed on a Shimadzu GC-Mini-2 flame-ionization instrument equipped with a 50 m capillary column and a Hewlett-Packard model 3390A integrator. Low-resolution mass spectrometry analyses were performed on a Hewlett-Packard model 5970 mass selective detector in conjunction with a Series 5890 GC equipped with a 15 m SE-30 capillary column or at the Southern California Mass Spectrometry Facility at the University of California, Riverside. Elemental analysis was performed at the analytical facilities of the California Institute of Technology.

Materials. Benzene, diethyl ether, and tetrahydrofuran were distilled from sodium-benzophenone ketyl. Methylene chloride was distilled from calcium hydride. Dried, degassed solvents were stored under argon in dry glass

vessels equipped with Teflon valve closures. Water was either house deionized or purchased from Aldrich (HPLC grade) and degassed prior to use. Chloroform-*d* and benzene-d_6 were purchased from Cambridge Isotope Laboratories and used as received. Deuterium oxide was purchased from Aldrich or Cambridge Isotope Laboratories and degassed prior to use. Allyl alcohol, 3-buten-1-ol, and 4-penten-1-ol were purchased from Aldrich and purified by distillation. Anthracene, ethyl acrylate, sodium hydride, iodomethane, 4-(dimethylamino)-pyridine, solketal (2,2-dimethyl-1,3-dioxolane-4-methanol), trimethylacetyl chloride, and (±)-3-cyclohexenyl-1-methanol were purchased from Aldrich and used as received. Lithium aluminum deuteride was purchased from Aldrich and purified by soxhlet extraction into anhydrous diethyl ether and stored as a solid in the dark before use. Sodium periodate was purchased from EM Science and used as received. Bromobenzene was purchased from Aldrich and distilled under argon before use. Thin-layer chromatography (TLC) was performed on precoated TLC plates (silica gel 60 F-254, EM Reagents). Flash chromatography was performed by the method of Still et al.[95] using silica gel 60 (230-400 mesh ATM, EM Reagents). Reagent grade petroleum ether (35-60 °C), pentane, and ethyl acetate were used without further purification. Paul Bernhard is gratefully acknowledged for initial samples of $Ru^{II}(H_2O)_6(tos)_2$ [2] and for a modified procedure for its preparation prior to publication.[1] All samples of $Ru^{II}(H_2O)_6(tos)_2$ prepared in this laboratory were according to the literature procedure.[1] The preparation of Allyl-*1,1*-d_2 alcohol was outlined by Hendrix et al.[66] and is reported in full below.

General Isomerization Procedure. Olefin (0.1-0.2 mmol) is added to a solution of $Ru^{II}(H_2O)_6(tos)_2$ (5.5 mg, 0.01 mmol) in degassed water (0.5 mL). The solution is stirred at room temperature or 45 °C for a period of 12-48 hours

during which time it turns from pale pink to yellow. The reaction is monitored by ^{1}H NMR or TLC. After completion, the product aldehyde is isolated by ether extraction (3 x 100 μL) and distilled.

9,10-Dihydro-9,10-ethano-11-carboethoxyanthracene. Anthracene (15.3 g, 86 mmol) was dissolved in ethyl acrylate (200 mL) and the solution was heated to reflux for 48 h. The solution was cooled to room temperature, excess ethyl acrylate was removed in vacuo, and the residue was washed with pentane and dried at reduced pressure to yield 21.7 g (78 mmol, 91%) of the product as a white solid. ^{1}H NMR ($CDCl_3$): δ7.25 (m, 4H), 7.07 (m, 4H), 4.65 (d, 1H), 4.31 (t, 1H), 4.03 (m, 2H), 2.84 (m, 1H), 2.17 (m, 1H), 1.96 (m, 1H), 1.18 (t, 3H).

9,10-Dihydro-9,10-ethano-11-(methanol-d_2)-anthracene. 9,10-Dihydro-9,10-ethano-11-carboethoxyanthracene (21.7 g, 78 mmol) was added slowly to a slurry of lithium aluminum deuteride (LAD) (2.7 g, 64 mmol) in THF (400 mL) at room temperature. The slurry was heated to reflux for 24 h during which time all solids dissolved. The reaction was then cooled to room temperature and then worked up by the standard procedure[96] followed by a pentane wash to yield 16.2 g (68 mmol, 87% yield) of the product as a white solid. Residual proton content at the methanol carbon was less than 2% as measured by ^{1}H NMR. ^{1}H NMR ($CDCl_3$): δ7.26 (m, 4H), 7.10 (m, 4H), 4.40 (d, 1H, J = 2.2), 4.25 (t, 1H, J = 2.7), 2.14 (br, 1H), 1.92 (ddd, 1H, J = 2.9, 10.3, 12.2), 1.33 (br s, 1H), 1.06 (ddd, 1H, J = 2.7, 4.9, 12.2).

Allyl-*1,1-d*$_2$ Alcohol. 9,10-Dihydro-9,10-ethano-11-(methanol-d_2)-anthracene was heated to 350-400 °C under argon with the use of a sand bath. After 30 min a slight vacuum was applied and the product was collected in a receiver flask cooled to 77 °K. Residual proton content at C-1 was less than 2% as

measured by ^{1}H NMR. The product was freeze-pump-thaw degassed at 77 °K and stored at room temperature in a glass vessel equipped with a Teflon valve closure. ^{1}H NMR ($CDCl_3$): δ 5.96 (dd, 1H, J = 10.3, 16.6), 5.26 (d, 1H, J = 16.6), 5.13 (d, 1H, J = 10.3). ^{2}H NMR ($CHCl_3$): δ 4.33 (s).

Reaction of Allyl-*1,1-d*$_2$ Alcohol with $Ru^{II}(H_2O)_6(tos)_2$. To a clean dry NMR tube equipped with a Teflon valve closure was added allyl-*1,1-d*$_2$ alcohol (12 mg, 0.20 mmol) and water (H_2O or D_2O) (400 μL) and the sample was degassed by three freeze-pump-thaw cycles at 77 °K. $Ru^{II}(H_2O)_6(tos)_2$ (5.5 mg, 0.010 mmol) was added under a flow of argon and the reaction was monitored by ^{1}H NMR in the case of D_2O samples. Integration of the ^{1}H NMR (D_2O) was measured under conditions of low pulse angle of (≤ 15°) and long pulse delay (≥ 10 s) to insure relaxation of all spins between accumulations. After the reaction was complete the solution was extracted with C_6H_6 (3 x 200 μL) The resulting C_6H_6 solution was vacuum transferred at 77 °K to a clean dry NMR tube and sealed under dynamic vacuum with a torch. The ^{2}H NMR spectrum was recorded at room temperature.

9,10-Dihydro-9,10-ethano-11-(methoxymethyl-*d*$_2$)-anthracene. 9,10-Dihydro-9,10-ethano-11-(methanol-d_2)-anthracene (10.0 g, 42 mmol) was added slowly to a slurry of sodium hydride (2.0 g, 83 mmol) and iodomethane (11.9 g, 84 mmol) in THF (200 mL) at 0 °C. The mixture was stirred overnight and allowed to warm to room temperature. Standard aqueous workup yielded 7.2 g (29 mmol, 68%) of product as a white solid. ^{1}H NMR ($CDCl_3$): δ 7.25 (m, 4H), 7.08 (m, 4H), 4.36 (d, 1H, J = 2.4), 4.23 (t, 1H, J = 2.7), 3.27 (s, 3H), 2.20 (br, 1H), 1.91 (ddd, 1H, J = 2.9, 10.0, 12.2), 1.00 (ddd, 1H, J = 2.7, 4.9, 12.2).

Allyl-*1,1-d*$_2$ Methyl Ether. 9,10-Dihydro-9,10-ethano-11-(methoxymethyl-d_2)-anthracene was heated to 350-400 °C under argon with the use of a sand bath. After 30 min a slight vacuum was applied and the product was collected in a receiver flask cooled to 77 °K. Residual proton content at C-1 was less than 2% as measured by ^{1}H NMR. The product was freeze-pump-thaw degassed at 77 °K and stored at room temperature in a glass vessel equipped with a Teflon valve closure. ^{1}H NMR ($CDCl_3$): δ 5.88 (dd, 1H, J = 10.5, 17.3), 5.25 (d, 1H, J = 17.3), 5.17 (d, 1H, 10.5), 3.32 (s, 3H).

Reaction of Allyl-*1,1-d*$_2$ Methyl Ether with $Ru^{II}(H_2O)_6(tos)_2$. To a clean dry NMR tube was added allyl-*1,1-d*$_2$ methyl ether (17 mg, 0.24 mmol), water (H_2O or D_2O) (400 μL), and $Ru^{II}(H_2O)_6(tos)_2$ (6.7 mg, 0.012 mmol). The sample was degassed by three freeze-pump-thaw cycles at 77 °K and sealed under dynamic vacuum with a torch. The reaction was monitored by ^{1}H NMR in the case of D_2O samples. After the reaction was complete the solution was extracted with C_6H_6 (3 x 200 μL) The resulting C_6H_6 solution was vacuum transferred at 77 °K to a clean dry NMR tube and sealed under dynamic vacuum with a torch. The ^{2}H NMR spectrum was recorded at room temperature.

1-Trimethylacetyloxy-2,3-acetonidoglycerine. 4-(Dimethylamino)-pyridine (DMAP) (0.1 g) was dissolved in pyridine (30 mL) in a clean, dry flask. Solketal (2,2-dimethyl-1,3-dioxolane-4-methanol) (13.2 g, 0.10 mol) was added and the solution was cooled to 0 °C with an ice bath. Pivaloyl chloride (trimethylacetyl chloride) (18.1 g, 0.15 mol) was added by syringe. After the addition, during which white solids began to precipitate, the mixture was stirred at 0 °C and allowed to warm to room temperature over 12 h. After this time the white slurry was poured into ice water (50 mL) and the organic layer separated. The aqueous layer was extracted with methylene chloride (3 x 20 mL) and the

organic solutions were combined and dried over $NaSO_4$. Residual solvent and side products (pivalic acid) were distilled away at 3-4 torr. Further distillation at 50 microns yielded 16.2 g (75 mmol, 75%, b.p. 65-70 °C) of product as a colorless liquid. ^1H NMR ($CDCl_3$): δ 4.28 (m, 1H), 4.10 (m, 2H), 4.04 (dd, 1H), 3.75 (dd, 1H), 1.42 (s, 3H), 1.34 (s, 3H), 1.19 (s, 9H).

2,3-Dihydroxypropyl Pivalate. 1-Trimethylacetyloxy-2,3-acetonido-glycerine (16 g, 74 mmol) was dissolved in THF (600 mL). To this solution was added hydrochloric acid (370 mL, 1 N) and the mixture was stirred at room temperature. The reaction was followed by ^1H NMR. After completion (ca. 2.5 h) the mixture was poured into methylene chloride (500 mL) and sodium bicarbonate (37 g) was added carefully to neutralize the aqueous layer. The organic layer was separated and the remaining aqueous layer was extracted with methylene chloride (3 x 100 ml). The organic solutions were combined, dried over $MgSO_4$, and rotovapped to yield 12.1 g (69 mmol, 93%) product as a white solid which can be recrystallized from methylene chloride/pentane. ^1H NMR ($CDCl_3$): δ 4.16 (m, 2H), 3.19 (m, 1H), 3.67 (m, 1H), 3.57 (m, 1H), 2.50 (d, 1H, J = 5.4), 2.11 (dd, 1H, J = 5.9, 6.6), 1.20 (s, 9H). Anal. Calcd for $C_8H_{16}O_4$: C, 54.53; H, 9.15. Found: C, 54.40; H, 8.82.

2-Trimethylacetyloxyacetaldehyde. This procedure was adapted from Shiao et al.[97] 2,3-Dihydroxypropyl pivalate (1.76 g, 10 mmol) was dissolved in methylene chloride (100 mL). To this solution was added a solution of sodium periodate ($NaIO_4$) (22.5 g, 105 mmol) in water (200 mL) and the emulsion was stirred at room temperature. The reaction was followed by TLC. After completion the organic layer was separated and washed with water (50 mL). Removal of solvent in vacuo afforded 1.44 g (10 mmol, 100%) of the product as a colorless

liquid which was stored at -50 °C to prevent decomposition. ^{1}H NMR ($CDCl_3$): δ 9.53 (s, 1H), 4.60 (s, 2H), 1.22 (s, 9H).

Phenyl Lithium. A solution of butyllithium in hexanes (140 mL, 2.5 M, 0.35 mol) was added dropwise over 75 min to a solution of bromobenzene (55.0 g, 0.35 mol) in hexane (400 mL) at –20 °C. After stirring for an additional hour at –20 °C the solution was cooled to –50 °C and stored overnight. The solution was then warmed to room temperature. The solvent was removed in vacuo to leave a white solid which was washed with hexane (3 x 50 mL) and dried in vacuo to yield the product as a fluffy white solid (27.6 g, 94%). A titration assay (*s*-butanol, 1,10-phenanthroline indicator) indicated the solid to be 100% lithium reagent.

Allyl-3-*^{13}C* Alcohol. 2-Trimethylacetyloxyacetaldehyde (560 mg, 3.9 mmol) was added slowly to a stirred solution of methylene-^{13}C-triphenyl-phosphorane (1.43 g, 5.2 mmol) in C_6H_6 (80 mL) at 5 °C and then the solution was warmed to room temperature. All the volatile components of this reaction were then vacuum transferred at 77 °K to a clean flask and the solvent was distilled through a 21-cm Vigreaux column. The crude allyl-3-^{13}C pivalate was added by syringe to a diethyl ether (15 mL) solution of phenyl lithium (0.82 g, 9.8 mmol) and the reaction was allowed to stir at room temperature for 8 h. Extraction of the reaction mixture with water (3 x 1 mL) yields an aqueous solution of **3** which is vacuum transferred at 77 °K to remove the lithium salts and stored degassed in a glass vessel equipped with a Teflon valve closure. Traces of ether can be removed by pentane extraction followed by removal of residual pentane by solvent evaporation in vacuo at 0 °C. Yield based on 2-trimethylacetyloxy-acetaldehyde was approximately 10% based on ^{1}H NMR integration versus an

internal standard. ^{1}H NMR (D_2O): δ 5.82 (m, 1H), 5.09 (dd, 1H, J_{HH} = 17.5, J_{CH} = 55.4), 5.00 (dd, 1H, J_{HH} = 10.5, J_{CH} = 59.2), 3.92 (t, 1H, J = 5.1).

Reaction of Allyl-3-^{13}C Alcohol and Allyl-1,1-d_2 Alcohol with $Ru^{II}(H_2O)_6(tos)_2$. To a clean dry NMR tube equipped with a Teflon valve closure was added 400 µL of a solution of allyl-3-^{13}C alcohol in water (H_2O or D_2O). Allyl-1,1-d_2 alcohol was added by syringe and the sample was degassed by three freeze-pump-thaw cycles at 77 °K. $Ru^{II}(H_2O)_6(tos)_2$ was added under a flow of argon and the reaction was monitored by ^{1}H NMR in the case of D_2O samples. After the reaction was complete the solution was extracted with C_6D_6 (3 x 200 µL). The resulting C_6D_6 solution was vacuum transferred at 77 °K to a clean dry NMR tube and sealed under dynamic vacuum with a torch. The ^{13}C NMR spectrum was recorded at room temperature.

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(75) The total list of possible products for this crossover experiment includes the previously mentioned propionaldehyde-*3*-^{13}C and propionaldehyde-*1,3*-d_2 as well as propionaldehyde-*1*-*d*. More products are possible if steps1 and/or 2 in Scheme 7 are reversible.

(76) With a 6.6 : 2.9 ratio of **4** to **8**, Ru–X (X = H or D) reacts with **4** and **8** in a 69 : 31 ratio, assuming no substrate preference. When Ru–X reacts with **4**, Ru–D is produced and when Ru–X reacts with **8**, Ru–H is produced. Therefore, Ru–D is the active catalyst 69% of the time. Since Ru–D will then react with **8** 31% of the time, we should see 0.31 x 0.69 = 21% crossover.

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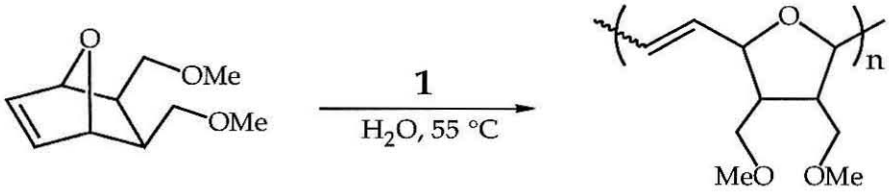
CHAPTER 3

Aqueous Ruthenium(II)-Catalyzed Ring-Opening Metathesis Polymerization of 7-Oxanorbornene Derivatives: Acyclic Olefin Chain Transfer

Introduction

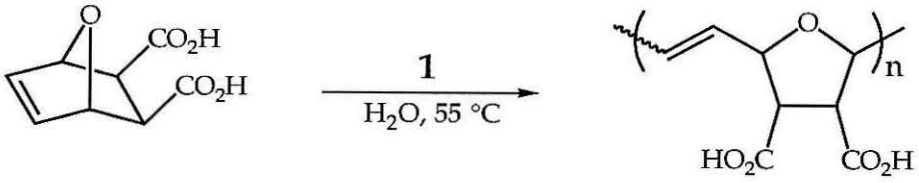
Our interest in the coordination complex $Ru^{II}(H_2O)_6(tos)_2$ **1**[1, 2] stems from its activity as a catalyst for the ring-opening metathesis polymerization (ROMP)[3-6] of strained cyclic olefins. A large variety of norbornene and 7-oxanorbornene derivatives can be polymerized to high molecular weight polymer in water or aqueous ethanol at temperatures in excess of 55 °C in the presence of **1**.[7-11] It is presumed that the active ROMP catalyst is actually a ruthenium alkylidene species, although the initiation mechanism involving transformation from the catalyst precursor **1** and the strained cyclic monomer to a ruthenium alkylidene or metallacycle is presently unknown. Studies aimed at understanding this initiation mechanism have focused on the monomer 5,6-*exo*-bis(methoxymethyl)-7-oxabicyclo[2.2.1]hept-2-ene **2** due to its low initiation times, high conversion to polymer, and the formation of a ruthenium(II) monoolefin complex of **2** during the course of the polymerization.[10]



2 **poly(2)**

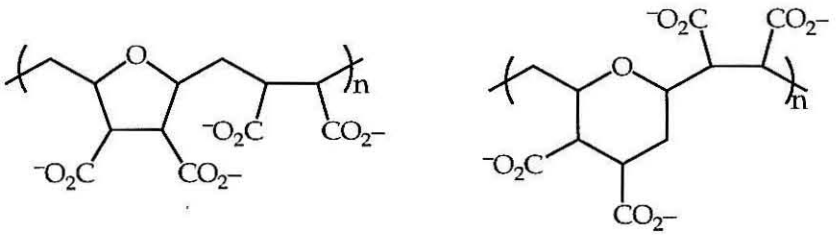
The molecular weight of poly(**2**) produced in this system is rather high, approximately 300-1,300K.[9, 10] The properties of a polymeric material are highly dependent upon its molecular weight, as well as its polydispersity and microstructure[12] and for some applications high MW polymer is undesirable. It may be of use, therefore, to be able to control the molecular weight of the polymeric materials produced in this system to address a wider variety of applications. For instance, when hydrogenated, the metathesis polymer[13] of 5,6-

exo-dicarboxylate-7-oxabicyclo[2.2.1]hept-2-ene **3** is similar in structure to the clinically useful polyanionic material DIVEMA, a copolymer of maleic anhydride and divinyl ether.[14-17] DIVEMA is prepared through radical polymerization methods and contains high-molecular weight fractions which are toxic. The molecular weight is not easily altered. The molecular weight of metathesis



3 **poly(3)**

polymers may be regulated through chain-transfer techniques.[5] Successful implementation of these techniques to the aqueous ruthenium(II) system could yield samples of poly(**3**) of relatively low molecular weight. The clinical utility of such polyanionic polymers would be enhanced by their lower toxicity.



DIVEMA

Previous studies from these laboratories have demonstrated that $Ru^{II}(H_2O)_6(tos)_2$ itself, and, more importantly, the ROMP catalyst derived from it, are tolerant of a wide range of organic functionality.[8-11, 18] This functionality includes alcohols, ketones, and esters which severly disable metathesis catalysts based on the early transition metals. This tolerance for functional groups has allowed us to manufacture polymers with various functionality along the

polymer chain, thus imparting various mechanical and chemical properties to these polymers.[8, 9] Chain transfer reactions effected with acyclic olefins containing functional groups would result in telechelic polymers with specific functionalized end groups.[19-23] Such species are useful for the production of larger polymeric materials and block copolymers,[21, 22, 24] and cross metathesis of functionalized, terminal olefins would be an important synthetic route to α,γ-disubstituted olefins.[25-27] Successful chain transfer with acyclic olefins in this system would also have mechanistic implications, providing evidence that the active catalyst is, in fact, a ruthenium alkylidene which undergoes metathesis with acyclic olefins. The relative reactivity of chain transfer agents in this system can be compared with those in classical metathesis systems.

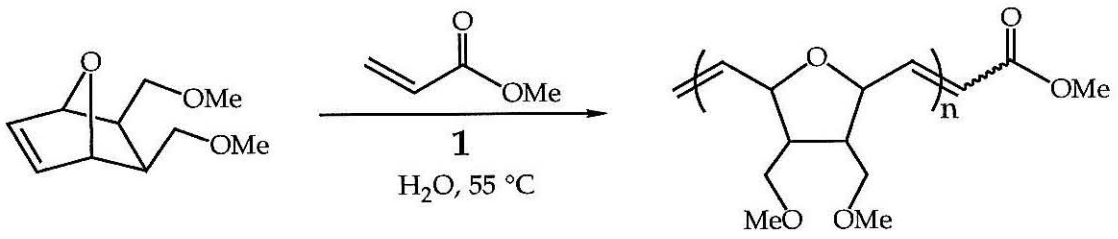
In this chapter we explore the reactivity of acyclic olefins within the ROMP system based on **1** in an attempt to control the molecular weight of polymeric materials produced in this system and to gather evidence on the intermediacy of a ruthenium alkylidene active catalytic species. The studies detailed in chapters 1 and 2 revealed olefins which do not undergo isomerization and are, therefore, suited to this study.

Results and Discussion

Acyclic terminal olefins act as effective molecular weight regulators in the aqueous ruthenium(II) metathesis system. When monomer **2** is added to a solution of **1** and regulator in water at 55-65 °C, polymerization proceeds with very little change in initiation time but the polymer produced is of intermediate molecular weight (M_n = 10-15 K). If the precatalyst is incubated with the regulator for 15 min at 55-65 °C before addition of monomer, oligomeric polymer samples are produced. End groups corresponding to the regulator can be identified by NMR and IR spectroscopy in both the oligomeric and intermediate MW samples. Methyl acrylate and 3-buten-1-ol were used as regulators in this study. Acyclic olefins which were found to isomerize in the presence of **1** (see Chapter 2) were avoided. Previous use of olefins isomerized by **1** as successful molecular weight regulators has been reported for other ruthenium ROMP systems.[28, 29] However, the catalyst systems studied are not active olefin isomerization catalysts and do not isomerize the regulating olefin before chain transfer takes place.

When *exo*-5,6-bis(methoxymethyl)-7-oxabicyclo[2.2.1]hept-2-ene **2** is added to a solution of methyl acrylate and $Ru^{II}(H_2O)_6(tos)_2$ in water a 55 °C ($[Ru^{II}]$ = 0.01 M; monomer : regulator : Ru :: 57 : 10 : 1) polymerization commences within 1 min as evidenced by an increase in the turbidity of the mixture. After 1 h at 55 °C the mixture is cooled and dissolved in ethanol. Addition of water results in a white precipitate which is isolated by centrifugation. The isolated polymer, after drying at reduced pressure, is a clear viscous oil in contrast to the opaque, rubbery material obtained in the absence of regulator. Yields of polymer ranged from 60-87%. Analysis of the sample by gel permeation chromatography (GPC) reveals a bimodal molecular weight

distribution evidenced by a shoulder towards lower molecular weight. Both the molecular weight and polydispersity index (PDI) of the regulated polymer are different from poly(**2**) produced in the absence of regulator. The M_n of this sample (11.5K) demonstrates the large attenuation effected by the regulator on the molecular weight of poly(**2**), a sample of which has an M_n of 293K when prepared under identical conditions without regulator. The PDI of regulated polymer ranges from 2.7-3.0, greater than that of unregulated polymer (2.05). Samples of poly(**2**) prepared in aqueous ethanol have polydispersities as low as 1.2.[30] Increasing the amount of regulator to 75 eq/Ru has a neglible effect on the M_n and PDI relative to the samples produced with only 10 eq/Ru. Acrylate endgroups can be detected in these low molecular weight polymer samples by both ^{1}H NMR (singlet resonances at 3.6-3.7 ppm) and IR (weak intensity resonance at 1718 cm^{-1}) spectroscopy.

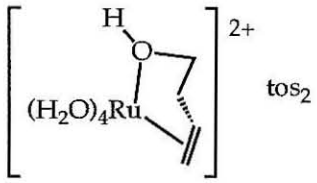


2

Oligomeric products can be produced under slightly different conditions. When the regulator (methyl acrylate) and ruthenium(II) catalyst are heated in water solution at 55 °C for 15 min the solution turns from pale red to yellow indicating the formation of the ruthenium(II)-regulator olefin complex. Addition of monomer at this stage results in a slightly cloudy reaction mixture after 1-2 min. After 1 h at 55 °C the mixture is extracted with diethyl ether and the ether solution is evaporated to dryness. The clear viscous oil is obtained in variable

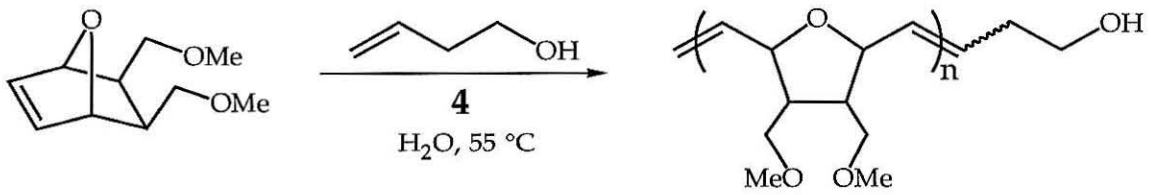
yields, depending on polymerization time. Analysis of the sample by GPC indicates a mixture of oligomeric species as evidenced by the multimodal low molecular weight distribution (Figure 1).

A similar mixture of oligomers can be produced using 3-buten-1-ol as the regulator through either the incubation method, as described above, or by using isolated $Ru^{II}(H_2O)_4(\eta^1(O):\eta^2(C,C')\text{-}HOCH_2CH_2CH{=}CH_2)(tos)_2$ **4** as the catalyst.



4

Polymerization of **2** by **4** in the presence of free 3-buten-1-ol at 55 °C in water yields a similar oligomeric mixture as evidenced by the GPC (Figure 1).[31] This regulator is more effective than methyl acrylate: as shown in Figure 1, a [3-buten-1-ol]/[**2**] ratio of 0.18 produces an oligomer mixture of similar molecular weight and dispersity as a [methyl acrylate]/[**2**] ratio of 1.33. The M_n of oligomer samples produced with a [3-buten-1-ol]/[**2**] ratio of 0.89 is extremely low (1.6K)



2

and the PDI is 1.5. Distinct peaks can be seen in the GPC trace but the relatively low resolution precludes assignment of actual structures from the apparent molecular weights of individual peaks. By scaling the apparent weights of the

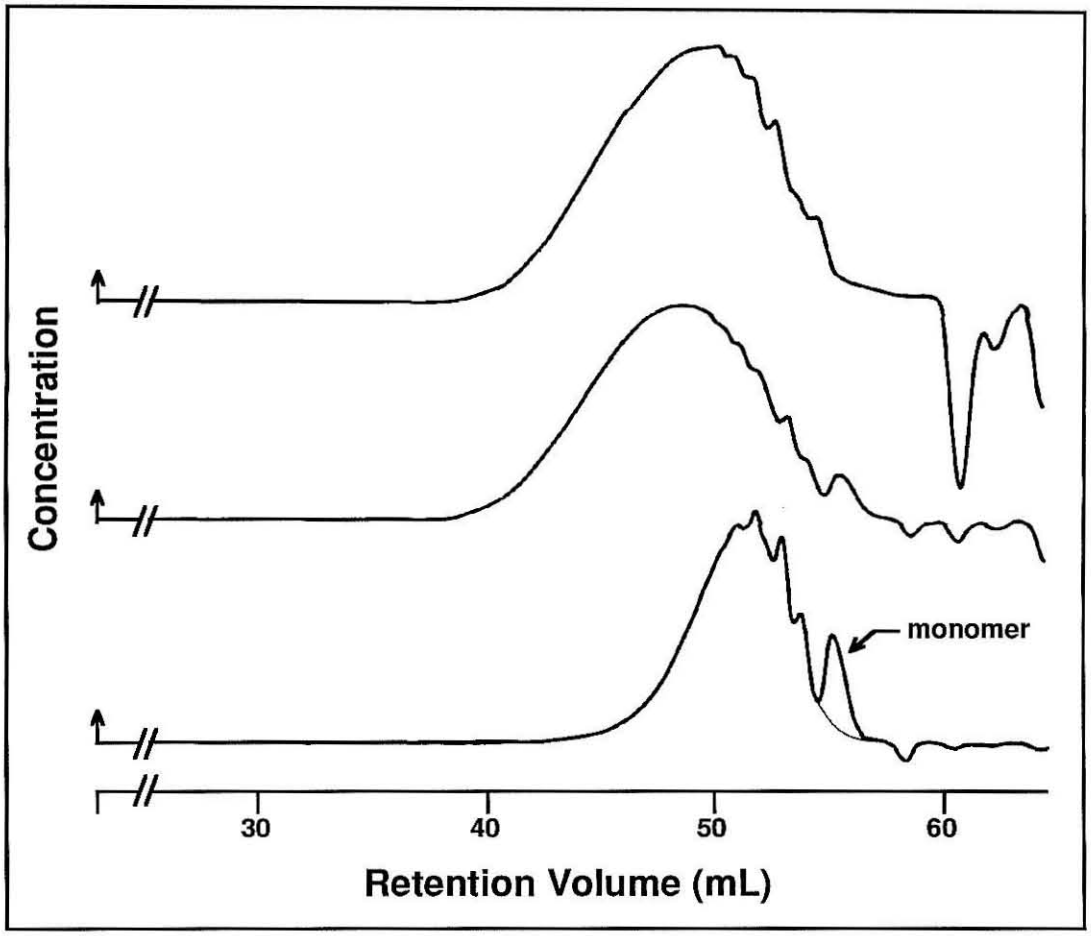
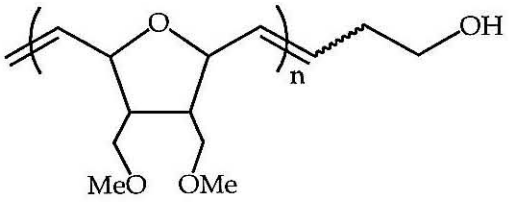


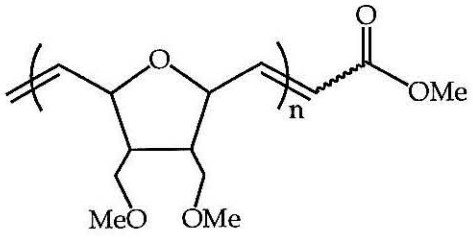
Figure 1. GPC traces of samples of poly(**2**) produced by **1**-catalyzed ROMP in the presence of acyclic olefins. Top: [methyl acrylate]/[**2**] = 1.33. Middle: [3-buten-1-ol]/[**2**] = 0.18. Bottom: [3-buten-1-ol]/[**2**] = 0.89.

oligomer peaks to the apparent weight of the residual monomer peak, however, we can obtain corrected weights of 272, 347, 489, and 609. While we cannot satisfactorily assign these peaks to the calculated weights of the expected telomers (Figure 2), it is clear from these data that we have produced a sample dominated by very low molecular weight oligomers. High resolution GPC analysis confirms this conclusion (Figure 3).

Preliminary investigations into the structure of the oligomers were made by NMR. We have identified both alkylidene moities from the 3-buten-1-ol regulator in the ^1H NMR spectrum of the oligomer sample utilizing both one- and two-dimensional NMR techniques. A fully assigned two-dimensional ^1H-^1H shift correlation (COSY) NMR spectrum of an oligomer mixture produced from a



n	C	MW
1	14	256
2	24	440
3	34	624
4	44	808
5	54	992



n	C	MW
1	14	270
2	24	454
3	34	638
4	44	822
5	54	1004

Figure 2. Structures and molecular weights for the first five members of the unsymmetrical telomer series from the 3-buten-1-ol and methyl acrylate regulated polymerizations of *exo*-5,6-bis(methoxymethyl)-7-oxabicyclo[2.2.1]norbornene **2**.

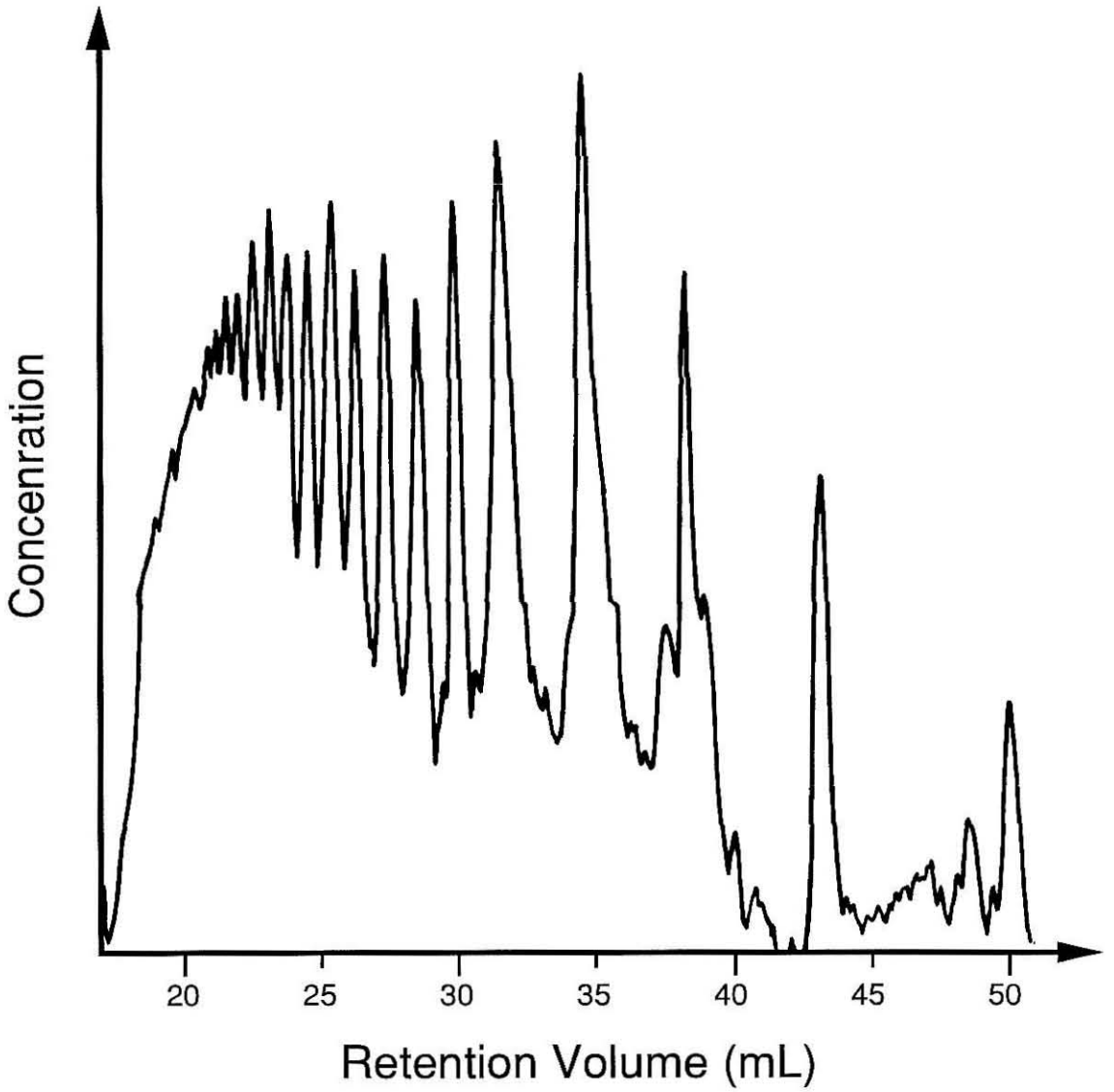


Figure 3. High resolution GPC trace of poly(**2**) regulated with 3-buten-1-ol ([3-buten-1-ol]/[**2**] = 0.89).

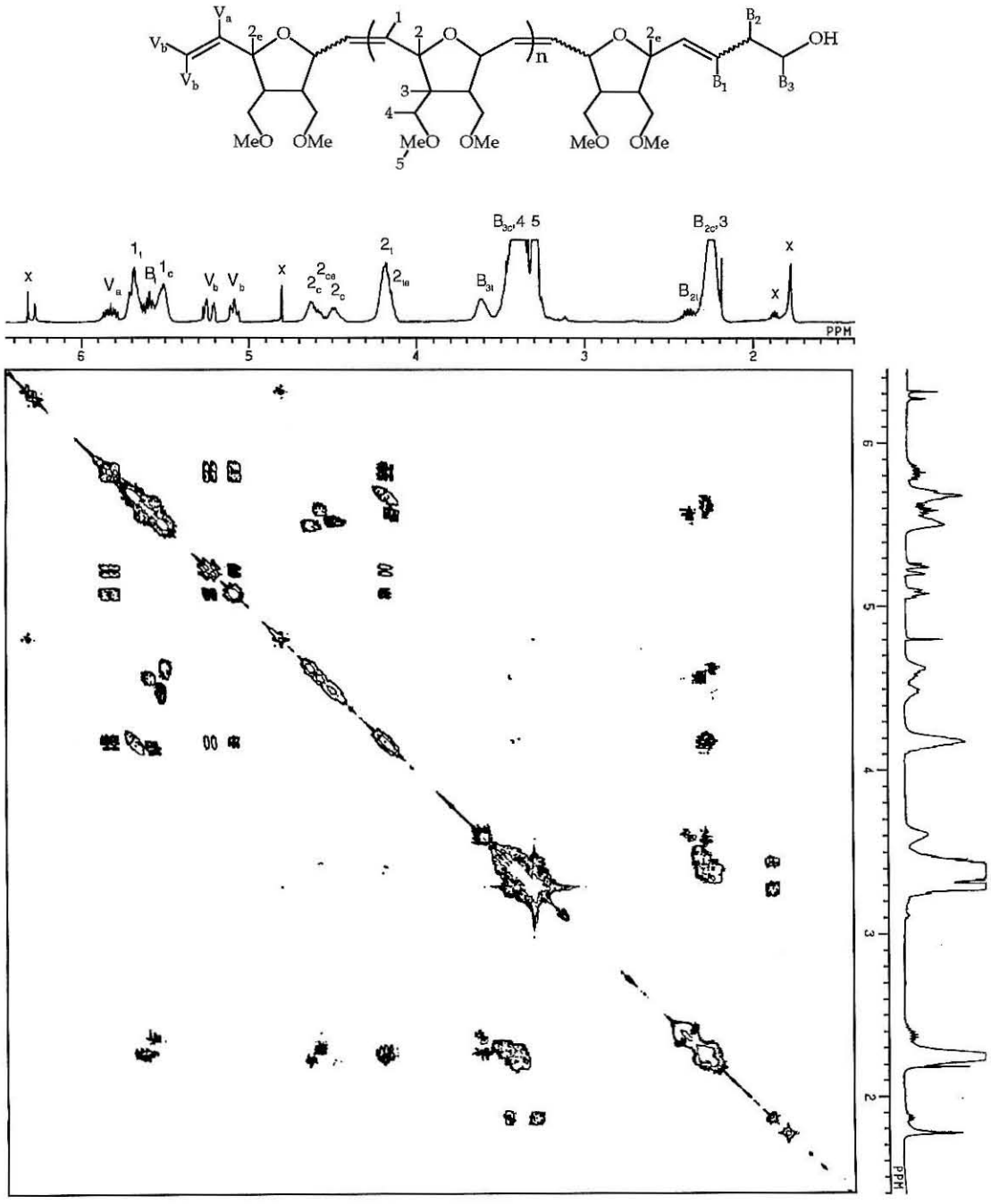


Figure 4. Two-dimensional ^{1}H-^{1}H shift correlation (COSY) NMR spectrum of poly(**2**) regulated with 3-buten-1-ol ([3-buten-1-ol]/[**2**] = 0.89). (Symmetrized matrix).

3-buten-1-ol-regulated (50 eq/Ru) polymerization is shown in Figure 4. The resonances for the bulk polymer are assigned in direct comparison with a spectrum of high molecular weight poly(**2**). Note that the olefin protons, as well as the allylic protons, of the polymer backbone are split in terms of the *cis* or *trans* configuration of the double bond to which they are attached or adjacent to. In addition, the *cis* allylic proton gives rise to two resonances at 4.5 and 4.6 ppm. This inequivalence may be the result of polymer tacticity (meso and racemic dyads).[32] In fact, close examination of the cross peaks of a two-dimensional ^{1}H-^{1}H shift correlation (COSY) NMR spectrum of high molecular weight poly(**2**)[32] reveals that both olefin resonances, as well as the *trans* allylic resonance, are also composed of two peaks, but the shift inequivalence is practically undetectable in the 1D spectrum.

The peaks for the alkylidene moieties are essentially the remaining peaks in the spectrum. The vinyl end group is at 6.84 (=CH–), 5.33 and 5.10 (CH_2=) ppm, typical for a terminal olefin ^{1}H NMR spectrum. It is unclear why the upfield terminal vinyl proton resonance at 5.10 ppm appears as a triplet while the resonance at 5.33 is a doublet, but we note that selective decoupling of the olefin resonance at 6.84 ppm collapses both terminal vinyl resonances to broad singlets. In addition, both resonances appear as doublets in CD_2Cl_2 solvent. All three vinyl protons are coupled to the *trans* allylic proton at 4.2 ppm, but not to the *cis* allylic proton. The small allylic coupling between the terminal vinyl protons and the allylic proton is readily detectable in the COSY spectrum. The butenol end group is at 5.6 (–CH=), 3.6 (–CH_2O–), and 2.4 (=CHCH_2–) ppm. The olefin resonance is coupled to both the *trans* allylic proton at 4.2 ppm , as well as the *cis* allylic proton at 4.5-4.6 ppm. This allylic proton which is coupled to the butenol end group actually resonates at a different chemical shift between the

bulk polymer *cis* allylic protons at 4.5 and 4.6 ppm. This is clearly seen upon inspection of the cross peaks in the ^{1}H-^{1}H COSY spectrum (Figure 4). In addition, the cross peak for the butenol end group olefin/*trans* allylic proton interaction is slightly upfield of the polymer olefin/*trans* allylic proton interaction. We therefore are able to identify the spectral location of polymer protons which are directly adjacent to the regulator end-groups. The resonances at 3.6 ($-CH_2O-$) and 2.4 ($=CHCH_2-$) ppm may arise from only those protons adjacent to *trans* double bonds, with the *cis*-adjacent resonances overlapping with the bulk polymer peaks at 3.4 and 2.3 ppm. This conclusion is drawn from the presence of two cross peaks arising from coupling between the *cis* and *trans* olefin protons of the end group, as identified by their coupling to the *cis* and *trans* allylic protons of the polymer, and the allylic protons of the end group ($=CHCH_2-$) in the region 2.3-2.4 ppm. These resonances, in turn, couple with two separate peaks in the region 3.4-3.7 ppm, separate from bulk polymer crosspeaks, allowing us to identify *cis*- and *trans*-adjacent $-CH_2O-$ end group resonances. A similar analysis can be performed on an oligomer sample prepared using methyl acrylate as the regulator.[33]

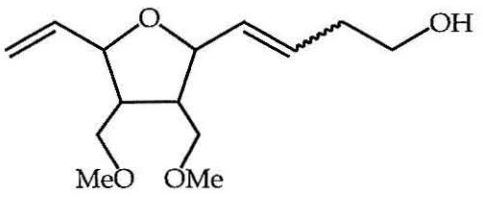
End group resonances for this sample are also observed in the ^{13}C NMR. The terminal vinyl carbons resonate at 140.0 (=CH–) and 115.5 ($CH_2=$) ppm. The butenol carbons resonate at 134.5 (–CH=), 129.5 (=CH–), and 62.0 ($-CH_2O-$) ppm. The resonances for the two different end groups are approximately equal in intensity. The ^{13}C NMR resonances arising from C-3 of poly(**2**) at 47-49 ppm are indicative of the *cis*/*trans* configuration of the double bonds of the polymer backbone. The peaks at 48.8, 47.9, 47.5, and 47.2 ppm arise from carbons in *cis-cis*, *cis-trans*, *trans-cis*, and *trans-trans* dyads, respectively. The complications arising from the end group on these resonances, however, precludes the

determination of the *cis/trans* ratio of this sample. The appearance of the C-2 resonances at 77 and 82 ppm, however, indicate that the microstructure of this low molecular weight sample is similar to poly(**2**) produced in the absence of regulator. In general, acyclic olefin molecular weight regulators have little effect on the *cis* content of the bulk polymer.[5]

While the ^{1}H and ^{13}C NMR data indicates that there are approximately equal amounts of the two alkylidene end groups in the sample, it does not yield information regarding the end groups of individual telomers. If the regulating olefin is represented as Q_1Q_2, where Q_1 and Q_2 are the alkylidene moieties of the unsymmetrical regulating olefin, then three telomer series can be produced: $Q_1(M)_nQ_1$, $Q_1(M)_nQ_2$, and $Q_2(M)_nQ_2$, where M is the ring-opened monomer unit. The unsymmetrical series for both 3-buten-1-ol and methyl acrylate regulated polymerization of **2** are shown in Figure 2. While we have been implying the existence of only this series, we can see in the high resolution GPC trace that all three series are present by inspection of the n = 1 peak. Two small shoulders, one at higher and the other at lower retention time, flank this peak and most likely correspond to the symmetrical series of telomers. The high relative yield of the unsymetrical series is characteristic for polymerization in the presence of terminal acyclic olefins.[34, 35, 36, 37] Regulation with an internal olefin, however, usually produces a ratio of the telomer series closer to the statistical 1 : 2 : 1. Unfortunately, molecular weight regulation with the internal olefin *cis*-3-penten-1-ol resulted in only small amounts of oligomeric products which could not be analyzed by high resolution GPC.

The alcohol functionality on the butenol end group imparts sufficient non-volatility to the telomers to preclude extensive characterization of the 3-buten-1-ol regulated polymer sample by gas chromatography (GC). Only two peaks of

similar retention times are observed when the telomer sample is run through a capillary GC column (SE-30) at 250 °C. GC-Mass Spectrometry (GC-MS) analysis by electron ionization (EI) failed to reveal parent ion peaks. Fragmentation upon ionization resulted in high-mass peaks for both GC peaks of only 211 e/m. Chemical ionization (CI) techniques, however, allowed observation of parent ion peak by HRMS at m/e 257.1753 (MH^+).[38] We therefore assign these peaks to the two isomers (*cis* and *trans*) of structure **5** (cf. Figure 2, n = 1). The MS peak at 211 e/m presumably arises from loss of a $-CH_2CH_2OH$ fragment yielding a stable allyl radical, or a methoxymethyl group. The corresponding asymmetrical telomer (structure **6**, cf. Figure 2, n = 1) from the methyl acrylate regulated polymerization of **2** was also identified by GC-HRMS (CI) (m/e = 271.1545 (MH^+)).[38]



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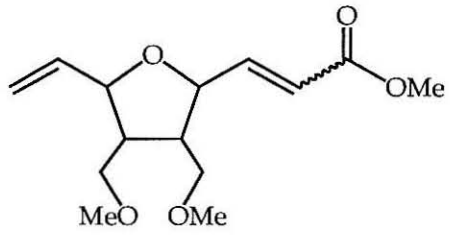


6

As mentioned earlier, our initial observations indicated that 3-buten-1-ol is a more effective molecular weight regulator than methyl acrylate in this aqueous ruthenium(II) metathesis system. More detailed studies were carried out on the effects of acyclic olefin concentration on polymer molecular weight.[38] The slopes of plots of $1/N_n$ versus $[Q_1Q_2]/[\text{Monomer}]$ are the chain transfer constants, the ratio of the chain transfer rate constant to the propagation rate constant, for a given acyclic olefin. Although the absolute values of chain transfer constants are unreliable, comparison of relative values is possible provided that polymerizations are run under similar conditions.[5] Constants of 0.21 and 0.04 for

3-buten-1-ol and methyl acrylate, respectively, confirm our initial observations regarding the relative regulating effects of these two olefins. Chain transfer reactivity increases with increasing distance between the olefin and ester functionalities in both classical systems[23, 39] and ours.[38] In addition, internal olefins such as methyl 2-pentenoate are even poorer chain transfer agents than methyl acrylate.[38] These observations regarding the effectiveness of various chain transfer agents are consistent with the expected reactivity of well-characterized homogeneous alkylidene complexes. The debilitating effect of an electron withdrawing group on the ability of an olefin to undergo metathetical cleavage has been observed before in both chain transfer reactions[23, 40] and acyclic self- and cross-metathesis.[39] The greater steric requirements of internal versus terminal olefins impede their reactivity with well-characterized transition-metal alkylidene complexes such as W(CH-*t*-Bu)(NAr)$(OR)_2$.[41]

Metathesis Initiation Mechanism. Still under scrutiny is the mechanism of initiation of this metathesis catalyst system. The perplexing question, and one that addresses the major difference between this system and the majority of classical catalyst systems of the early transition metals, is the path by which the metal is initially alkylated. The majority of homogeneous metathesis and ROMP catalyst systems based on the early transition metals are either binary or ternary mixtures composed of a transition metal complex and an alkylating agent based on aluminum, tin, magnesium, lead, bismuth, or zinc.[4] In these systems transmetallation of the alkyl fragments occurs and subsequent rearrangement on the transition metal center affords the metathesis active alkylidene complex. However, in the aqueous ruthenium(II) system, and in other metathesis systems which contain neither transition metal carbon bonds nor alkylating agent cocatalysts, formation of a metal carbon bond must occur through reaction of the

metal center with the olefinic substrate as these are the only reactants.

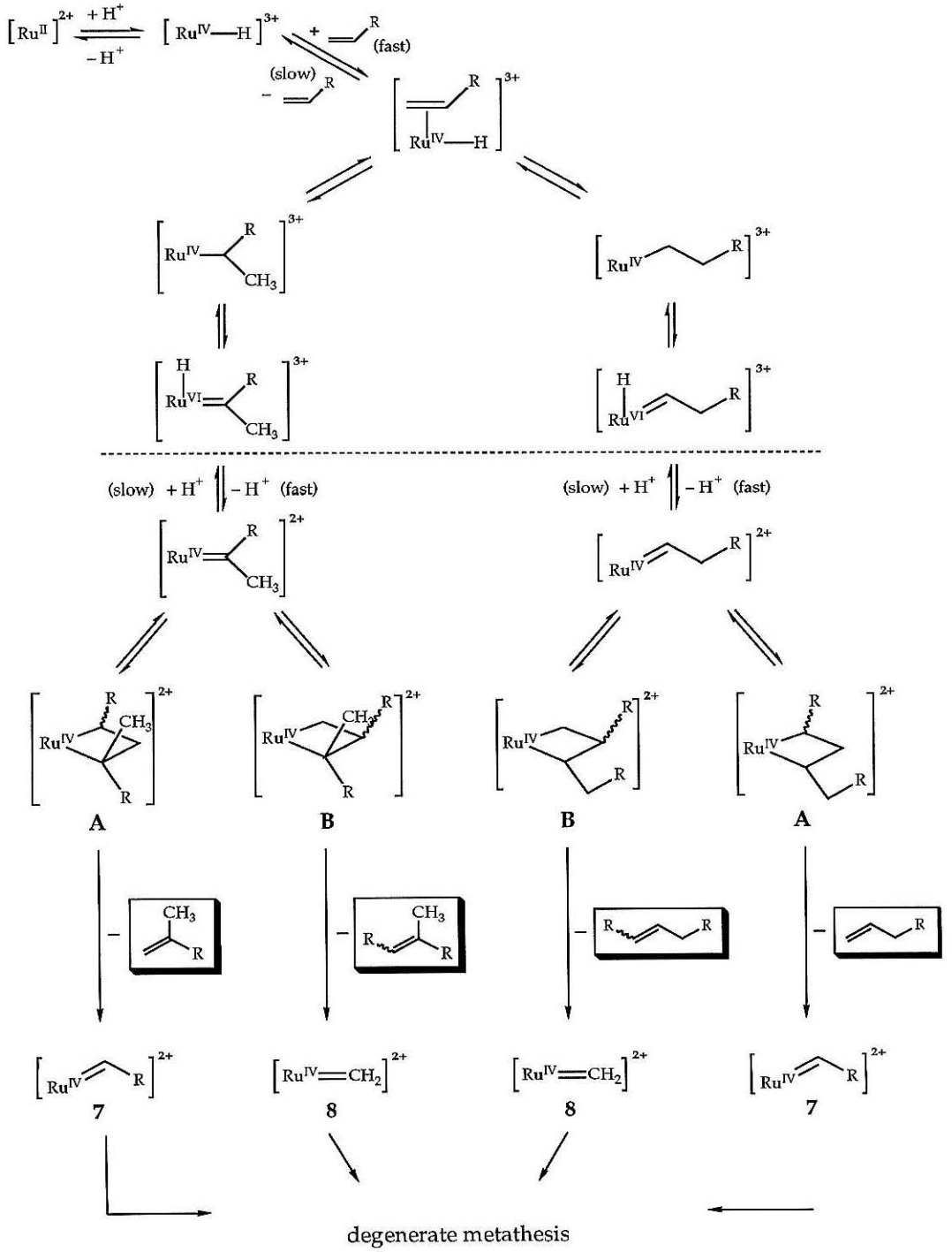
The activity of the catalyst precursor **1** as an olefin isomerization catalyst and evidence implicating the intermediacy of a metal hydride species in these isomerizations (see Chapter 2) leads us to propose the metathesis initiation mechanism in Scheme 1. This scheme essentially links the olefin isomerization mechanism with a metathesis initiation mechanism. The initiating species for both reactions is the proposed ruthenium(IV) hydride[42] formed through protonation of ruthenium(II). The reactions above the dotted line are the initiation and propagation steps of isomerization, as proposed in Chapter 2, including metal protonation, olefin coordination, and olefin insertion (Markovnikov on the left, anti-Markovnikov on the right). Subsequent α-elimination generates the alkylidene hydride species shown. This step is included in the isomerization mechanism based on preliminary results regarding the isotopic crossover between styrene and styrene-α,α,β-d_3 in methanol in the presence of **1**.[38] Deprotonation of the alkylidene hydride yields a ruthenium(IV) alkylidene complex which we believe to be the active catalyst. Shown in the scheme are the four possible metallacycles resulting from [2 + 2] addition of the olefin to the two different alkylidene species. Productive retro [2 + 2] cleavage of metallacycles of type **A** yields two different olefins (highlighted) with (n + 1) carbons, where n is the number of carbons in the substrate olefin, and a substituted alkylidene **7**. Productive retro [2 + 2] cleavage of metallacycles of type **B** yields two different olefins (highlighted) with [n + (n – 1)] carbons and ruthenium methylidene **8**. The propagating alkylidenes **7** and **8** continue to catalyze metathesis, although predominantly degenerate, producing substrate olefin.

Future Studies. Evidence for such a mechanism would include

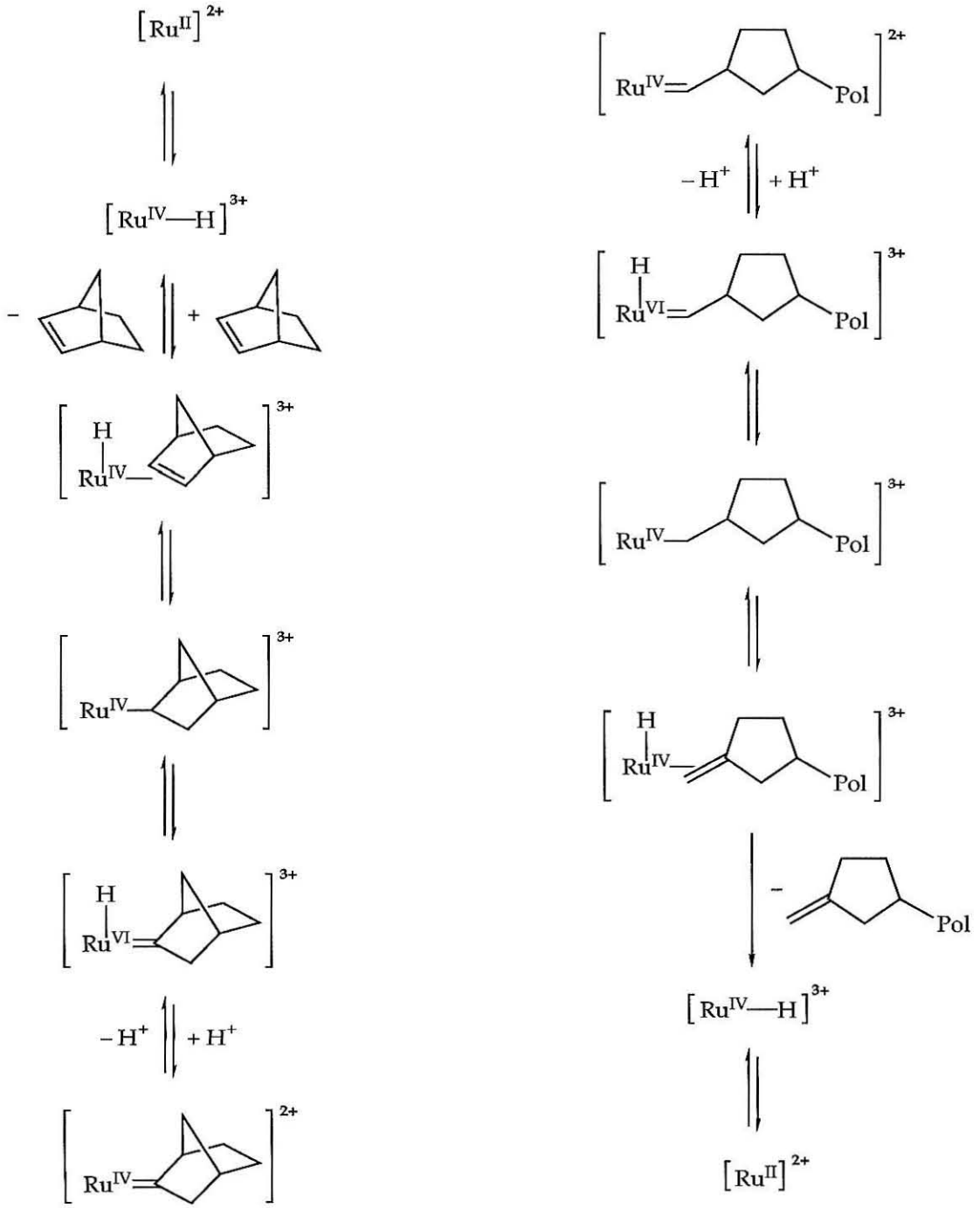
observation of the four highlighted olefins which all contain n + 1 or n + (n – 1) carbons. These four new olefins have not been observed when **1** is reacted with terminal olefins such as styrene and methyl acrylate. In fact, cross-metathesis of acyclic olefins catalyzed by **1** has never been observed. Attempts to observe degenerate metathesis of acyclic olefins through isotopic labelling studies have been complicated by crossover due to olefin isomerization. Self- and cross-metathesis of acyclic olefins by a ruthenium catalyst has been observed in only one system. Marciniec and co-workers have reported that the self-metathesis of tris(alkoxy)vinylsilanes and their cross metathesis with various terminal and internal olefins is catalyzed by $RuCl_3 \cdot nH_2O$ and $RuCl_2(PPh_3)_3$.[43-47]

The initiation mechanism, when applied to a norbornene structure, would result in an alkylidene, and hence an initiation polymeric end group, as shown in Scheme 2. Prior to the chain transfer studies detailed above, observation of polymer end groups in this system has been hampered by the high molecular weight of the polymers formed. However, the end groups observed and identified in the oligomer samples are derived from only the added acyclic olefin chain transfer agent. This indicates that the ruthenium alkylidene formed during the chain transfer process is kinetically stable and initiates a new polymer chain (see Scheme 3). If the new ruthenium alkylidene, presumably the unsubstituted methylene complex due to the preferred formation of β-substituted metallacycles,[48, 49] were not stable and decomposed before initiating another polymer chain, the isolated oligomers would all contain an initiating end group. Further studies in this area will entail utilizing acyclic olefins for chain transfer reactions which are substituted in such a way as to render the ruthenium alkyidene resulting from chain transfer to be unstable or inactive (degradative chain transfer). Possibilities include triflate and halogen substituted olefins.

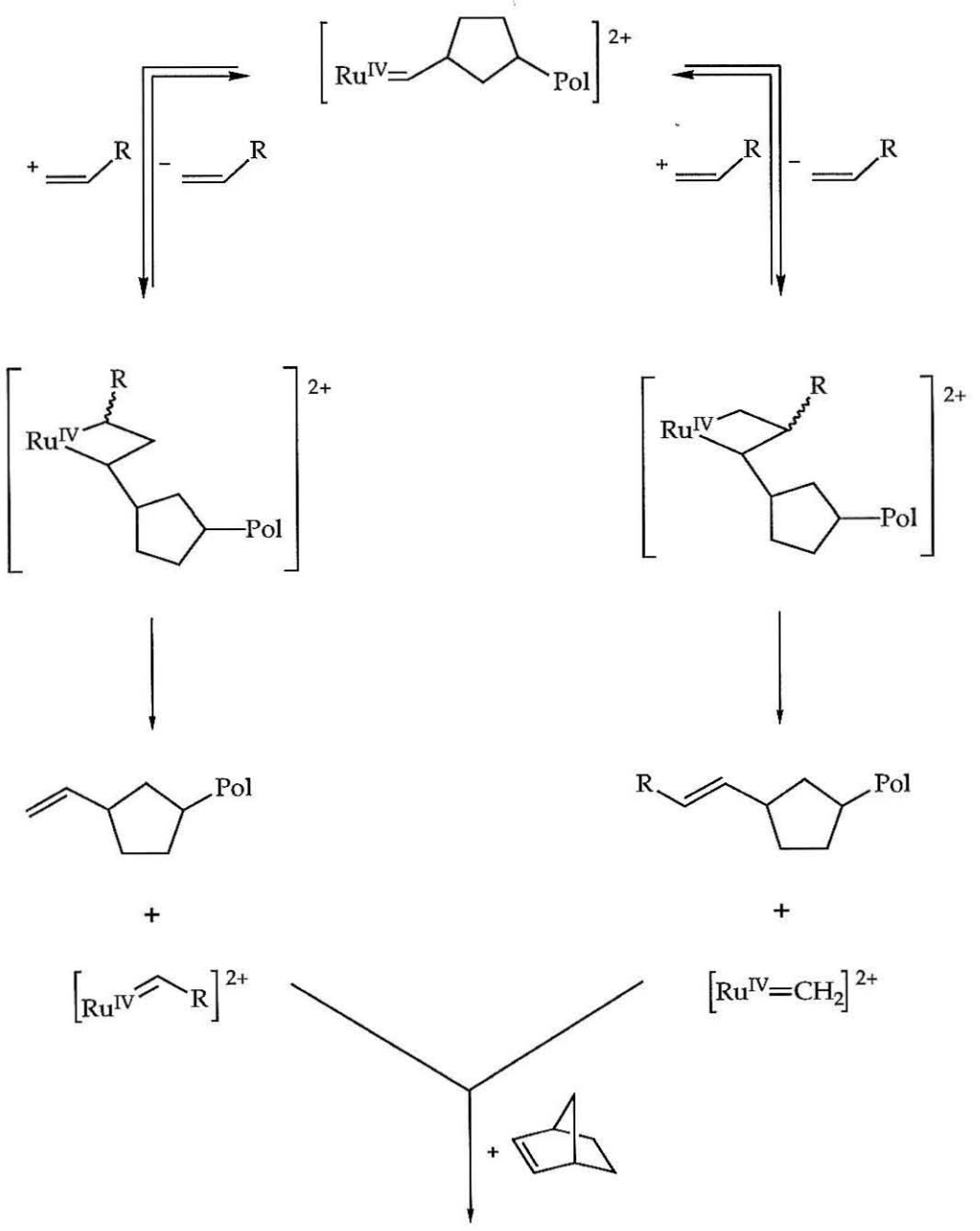
Scheme 1. Proposed Metathesis Initiation Mechanism.



Scheme 2. Initiation and Termination Sequences for Polymerization.



Scheme 3. Acyclic Olefin Chain Transfer with a Ruthenium Alkylidene.



Summary

Acyclic terminal olefins are effective chain transfer agents in the ROMP of 7-oxanorbornene derivatives by $Ru^{II}(H_2O)_6(tos)_2$, providing the first example of acyclic olefin metathesis in this system. The molecular weight of polymer samples produced varied from 11.5K to less than 2K depending on the acyclic olefin : monomer ratio and whether the precatalyst was $Ru^{II}(H_2O)_6(tos)_2$ or the ruthenium(II) complex of the acyclic olefin. End groups corresponding to the alkyidene moieties of the acyclic olefin in oligomeric samples of poly(5,6-*exo*-bis(methoxymethyl)-7-oxabicyclo[2.2.1]hept-2-ene) were identified by ^1H and ^{13}C NMR analysis. The unsymmetrical monomeric units **5** and **6** from regulation with methyl acrylate and 3-buten-1-ol, respectively, were identified by a combination of GC-MS and EI-HRMS. The relative effectiveness of various acyclic olefins as chain transfer agents corresponds to the expected and observed reactivity of a homogeneous alkylidene complex. A metathesis initiation mechanism for this system has been proposed involving a kinetically stable ruthenium(IV) hydride formed by protonation of ruthenium(II).

Experimental

General Procedures. All manipulations involving air- and/or moisture-sensitive compounds were carried out using standard high vacuum or Schlenk techniques. Argon was purified by passage through columns of BASF RS-11 (Chemalog) and Linde 4Å molecular sieves. Solids were transferred and stored in a N_2-filled Vacuum Atmospheres glove box equipped with a MO-40-1 purification train, a DK-3E Dri-Kool conditioner, and a Dri-Cold Freezer.

Instrumentation. NMR spectra were recorded on a JEOL FX-90Q (89.6 MHz ^1H, 22.5 MHz ^{13}C), a JEOL GX-400 (399.65 MHz ^1H, 61.25 MHz ^2H, 100.40 MHz ^{13}C), a Varian XL-200 (200 MHz ^1H), Varian EM-390 (90 MHz ^1H) and a Bruker AM-500 (500.14 MHz ^1H, 76.78 MHz ^2H). Proton chemical shifts are referenced to internal residual solvent protons. Carbon chemical shifts are referenced to the carbon signal of the deuterated solvents. Deuterium chemical shifts are referenced to natural abundance deuterium in the solvent. Gas chromatography analyses (GC) were performed on a Shimadzu GC-Mini-2 flame-ionization instrument equipped with a 50 m capillary column and a Hewlett-Packard model 3390A integrator. Low-resolution mass spectrometry analyses were performed on a Hewlett-Packard model 5970 mass selective detector in conjunction with a Series 5890 GC equipped with a 15 m SE-30 capillary column or at the Southern California Mass Spectrometry Facility at the University of California, Riverside. High resolution mass spectrometry was performed by the analytical services department at the E. I. Du Pont de Nemours Co. Infrared spectra of polymer solutions (CH_2Cl_2) were recorded in NaCl solution cells on a Perkin-Elmer 1600 Series FT-IR. Elemental analysis was performed at the analytical facilities of the California Institute of Technology. Gel permeation chromatography (GPC) was performed on a homemade HPLC

intrument employing an Altex model 110A pump, a Rheodyne model 7125 injector with a 100μL injection loop, three Shodex Styragel size exclusion columns (KF 803, KF 804, and KF 805), and a Knauer differential refractometer. Methylene chloride was used as the eluent at 1.0 mL/min. Molecular weights are reported relative to narrow molecular weight polystyrene standards. GPC samples (0.5 wt%) were filtered through a 0.5 μm filter prior to injection. High resolution GPC was graciously performed by Prof. Wilhelm Risse of the Phillips Universitat, Marburg, West Germany.

Two-Dimensional ^{1}H-^{1}H Correlated NMR Spectra. The data were acquiredusing a JEOL GX-400 NMR spectrometer operating at 399.65 MHz proton frequency. The pulse sequence was 90°–t_1–90°–ACQTM–PD and the phases of the pulses and receiver were cycled to provide quadrature detection in f_1 and selection of "P-type" peaks. The ^{1}H 90° pulse width was measured on each individual sample by searching for the 180° null and was typically 8.0 μs on the 5mm ^{1}H probe. The f_2 spectral width was chosen at a minimum to accomodate all peaks in the one-dimensional spectrum and the pulse delay (PD) was minimally 2.0 s. One dummy scan was taken before each slice to eliminate non-equilibrium magnetization. A minimum of 8 transients of 2 K data points were collected for 512 increments of t_1. The data were apodized with a sine-bell window function and Fourier transformed in both dimensions. The absolute value spectrum was calculated and then symmetrized if necessary.

Materials. Benzene, diethyl ether, and tetrahydrofuran were distilled from sodium-benzophenone ketyl and methylene chloride was distilled from calcium hydride. Dried degassed solvents were stored under argon in dry glass vessels equipped with Teflon valve closures. Water was either house deionized or purchased from Aldrich (HPLC grade) and degassed prior to use. Chloro-

form-*d* and benzene-d_6 were purchased from Cambridge Isotope Laboratories and used as received. Deuterium oxide was purchased from Aldrich or Cambridge Isotope Laboratories and degassed prior to use. 3-Buten-1-ol was purchased from Aldrich and purified by passage through reagent grade alumina before use. Methyl acrylate was purchased from Aldrich and stored degassed in a dry glass vessel equipped with a Teflon valve closure after being vacuum tranferred from calcium hydride. Thin-layer chromatography (TLC) was performed on precoated TLC plates (silica gel 60 F-254, EM Reagents). Flash chromatography was performed by the method of Still et al.,[50] using silica gel 60 (230-400 mesh ATM, EM Reagents). Reagent grade petroleum ether (35-60 °C) and ethyl acetate were used without futher purification. 5,6-*exo*-Bis(methoxymethyl)-7-oxabicyclo[2.2.1]hept-2-ene,[9] was published by literature procedures. Paul Bernhard is gratefully acknowledged for initial samples of $Ru^{II}(H_2O)_6(tos)_2$[2] and for a modified procedure for its preparation prior to publication.[1] All samples of $Ru^{II}(H_2O)_6(tos)_2$ prepared in these laboratories were according to the literature procedure.[1]

General Polymerization Procedure. The following procedure produces oligomeric polymer samples as described in the text: To a solution of $Ru^{II}(H_2O)_6(tos)_2$ (6 mg, 0.011 mmol) in degassed water (1 mL) under argon is added the molecular weight regulator by syringe. The solution is heated at 55 °C for 15 min during which time the color changes from pale red to deep yellow. 5,6-*exo*-Bis(methoxymethyl)-7-oxabicyclo[2.2.1]norbornene (100 μL, 0.62 mmol) is added and the mixture is left at 55 °C for 1-2 hours. The cloudy yellow mixture was allowed to cool to room temperature, extracted with diethyl ether (3 x 1 mL), dried over $MgSO_4$, and evaporated to a clear residue. Yields are dependent on reaction time for a given concentration of acyclic olefin and varied from 50-95%.

Intermediate molecular weight (11.5K) polymer samples can be prepared using a modified procedure in which the monomer is added to the catalyst/acyclic olefin solution less than 4 min after addition of the acyclic olefin.

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