Mechanistic Studies on the Rearrangement Activity of a Ring-Opening Metathesis Polymerization Catalyst: Reaction of $[Ru(H_2O)_6]^{2+}$ with Unfunctionalized Olefins

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Received January 20, 1994. Revised Manuscript Received July 6, 1994[®]

Abstract: The rearrangement of 3-phenylpropene-3,3-d_2 catalyzed by $[Ru(H_2O)_6]^{2+}$ in different solvents yields stereospecifically *trans*-phenylpropene with deuterium content on all carbons of the propyl chain. A deuterium effect of 2.3 is observed in comparison to the rearrangement of undeuterated 3-phenylpropene. Competition experiments reveal an intermolecular D transfer. The results are consistent with a stereospecific *syn* 1,2-addition− elimination of an intermediately formed metal hydride with predominant attack of the metal on position 2 of 3-phenylpropene-3,3-d_2, and also explain the selective production of *trans* products.

Introduction

Recently we reported the rearrangement of olefins in different solvents catalyzed by $[Ru(H_2O)_6]^{2+}$ (**1**) under very mild conditions.[1] Allylic ethers and alcohols are also isomerized by **1** in aqueous solution to yield enol ethers,[2] and **1** also catalyzes ring-opening metathesis polymerization (ROMP) of strained cyclic olefins.[3,4] Metathesis of acyclic olefins by **1** has been observed only in one case.[5]

A link between rearrangement activity and initiation of ROMP with **1** is still missing. Simultaneous activity for metathesis and rearrangement was observed for WCl6/EtAlCl2/EtOH where the alkylating agent contains β-hydrogen atoms.[6,7] β-Hydrogen abstraction leads to olefin generation, whereas α-hydrogen abstraction can produce a metal carbene.[8] There is strong evidence for a metal carbene to be the intermediate in Ru-catalyzed ROMP.[9-13] With ruthenium, iridium, and osmium chlorides, metal hydrides (MH) were detected during metathesis[14] and have been reported for other metals showing metathesis activity.

Rearrangements of olefins by transition metals have been extensively studied. There are two accepted mechanisms involving either intramolecular hydrogen 1,3-shift via a π-allylmetal hydride intermediate or a 1,2-addition−elimination of a metal hydride species.[8,15,16] It was only recently that the mechanism of the isomerization of functionalized olefins catalyzed by **1** in aqueous solution was reported.[17] The chelating property of functionalities such as hydroxy groups or carbonyl groups can lead to changes in the mechanism of the rearrangement and does not allow an unambiguous separation of the factors responsible for a hydrogen 1,2- or 1,3-shift. With this paper we present an extension to hydrocarbon substrates, excluding thus any possible interference of directing groups in the form of functionalities attached to the olefin.

Results and Discussion

Deuterium Distribution in Reaction Products. The distribution of deuterium in products resulting from the rearrangement of 3-phenylpropene-3,3-d_2 (**2**-d_2) with **1** was studied in order to elucidate the reaction mechanism. NMR spectra of rearranged **2**-d_2 in ethanol-d_6, acetone-d_6, THF-d_8, and diethyl ether indicate a mixture of *trans*-1-phenylpropene-1-d_1 (**3**-d_1) and *trans*-1-phenylpropene-1,3-d_2 (**3**-d_2) with partial deuteration on C_2. The ratio of **3**-d_1 to **3**-d_2 is insensitive to the solvent medium. The signals in the ^{1}H-NMR spectrum of the product mixture can be assigned as follows: 7.5−7.2 ppm (m, 5H, ar), 6.3 ppm (m, 0.9H, olefin), 1.9 ppm (m, 2.4H, methyl). The multiplet at 1.9 ppm is composed of a set of six signals typical for $RCD=CHCH_2D$ ($^3J = 6.7$ Hz, $^1J = 2.2$ Hz) and a doublet for CH_3 ($^3J = 6.8$ Hz) shifted to lower field (0.2 ppm) due to the isotope effect. The coupling constant of 6.8 Hz is the same as ^3J in undeuterated 1-phenylpropene. Residual proton resonances at 6.45 ppm are due to 2% impurities. The ^{13}C/DEPT NMR (DEPT = Distortionless Enhanced Polarization Transfer) consists of six signals in the aromatic/olefinic region, two of which are quaternary (one triplet belonging to CD). In the aliphatic region, a group of four signals is present, consisting of a triplet at 18.5 ppm (CHD2) with negative phase and a singlet at 19.0 pppm (CH3) with positive phase. No protons are

® Abstract published in *Advance ACS Abstracts,* November 1, 1994.
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Table 1. Isotope Distribution in *trans*-1-Phenylpropene Resulting from Rearrangement of 2-d_2 in the Presence of **4** (Molar Ratio 2-d_2:**4** = 1:4.67)

$$PhCD_2CH=CH_2\ (2\text{-}d_2)\ +\ (OMe)_2C_6H_3CH_2CH=CH_2\ (4)$$
$$1.00 \hspace{5cm} 4.67$$

Ru(H₂O)₆²⁺

$$PhCD=CH(D)CH_3(D)$$

no. of D[a]	π-allyl	addn−elim[c]	found, %
1	1.5	80.4	79
2	98	17.6	19

no. of H[b]	π-allyl	addn−elim[c]	found
in CH₃	2.015	.2.83	2.64
in C₂	1.0	0.94	0.92
in C₁	>0	0	0

[a] Percentage of rearranged 2-d_2 containing 1 and 2 deuterium atoms. Determined by ¹H-NMR, ¹³C-NMR, and MS. [b] Integram of propyl chain resonances in ¹H NMR, approximate error ±5%. [c] Calculated with the assumption of 70% attack of the metal on position 2 of 3-phenylpropene-3,3-d_2.

observed on C_1. IR shows three signals in the region of the C−D stretching frequency (2236, 2195, 2160 cm⁻¹), consistent with deuterium contents on all three carbons of the propene chain. For an exclusive sigmatropic [1,3]-shift, no deuterium is expected on C_2, and C_1 should contain some proton since [1,3]-transfer by π-allyl intermediates is reversible in other systems.[18−20] The spectra of the reaction mixture do not change within one week at 50 °C, and reaction of 1-phenylpropene gives no 3-phenylpropene. Therefore, the rearrangement of **2** to **3** is irreversible.

Competition Experiments. In competition experiments of 2-d_2 with a nondeuterated olefin, intermolecular deuterium transfer occurs. This agrees best with a mechanism involving addition−elimination of a metal hydride (MH). In order to obtain quantitative results, an olefin with about the same rate constant for rearrangement as 2-d_2 (k_{obs} = 5.06(6) × 10⁻⁴ s⁻¹) was chosen, namely, 4-allyl-1,2-dimethoxybenzene (**4**) (k_{obs} = 4.15(6) × 10⁻⁴ s⁻¹). In analogy to the procedure described by McCormack and Orchin,[21] **4** was used in excess (2-d_2:**4** = 1:4.67) and **4** served as a source for MH and a sink for MD if each interception of MD by **4** produces 3,4-dimethoxy-1-propenylbenzene-d_1 (**5**-d_1). Table 1 shows results expected for a MH mechanism compared to experimental results. The deuterium distribution in the propene chain of rearranged 2-d_2 after the competition experiment (MH in excess) is depicted in Figure 1. In agreement with the literature,[21,22] addition of the metal on C_2 of 2-d_2 is assumed to dominate over addition on C_1 to about 70%. Since benzylic methylene hydrogens are activated, their β-elimination in the intermediate metal alkyl is kinetically favored over β-hydrogen elimination from the methyl group, leading back to the terminal olefin 2-d_2.[8] With this model, $C_6H_6CDCHCH_3$ and $C_6H_6CDCHCH_2D$ resulting from metal attack on C_2 of 2-d_2 are the two major products and $C_6H_6CDCDCH_3$ is the only important byproduct. NMR and IR measurements (three signals in the region of the C−D stretching frequency) agree with this product distribution. Again, no hydrogen incorporation on C_1 of **3** is observed.

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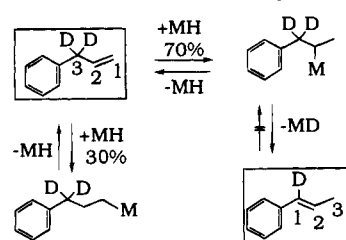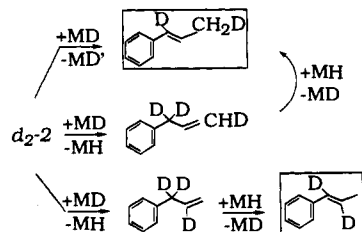
Figure 1. Product distribution in the competitive rearrangement of 2-d_2 with an excess of 4-allyl-1,2-dimethoxybenzene ([MH] ≫ [MD]).

With the inversed ratio (2-d_2:**4** = 10:1; MD in excess), deuterium incorporation on C_3 of rearranged **4** is dominant as indicated by ¹³C NMR. Because of the quite low signal to noise ratio, incorporation of deuterium on C_2 is not observed in ¹³C NMR. IR shows two signals in the C−D stretching frequency indicating deuterium on C_2 and C_3, but not on C_1, confirmed by ¹H NMR. The ratio of **5**-d_0 to **5**-d_1 agrees with the MH addition−elimination model.

Kinetic Measurements. The rearrangement of 2-d_2 and **2** in ethanol-d_6 shows an induction period of about 5 min (302 K) after which the decrease of reactant follows a first-order rate law for over four half-lives. The observed rate constant for the rearrangement of 2-d_2 302 K (k_{obs} = 5.06(6) × 10⁻⁴ s⁻¹) is 2.3 times smaller than the one of undeuterated **2** (k_{obs} = 1.15(3) × 10⁻³ s⁻¹). Therefore, breaking of a C−H bond is rate determining. This conclusion is supported by the observation that the rearrangement of 1-hexene to 3-hexene proceeds in a stepwise manner via 2-hexene.[1]

The possibility of the presence of a transition state with two bound reactants and transfer of H by a pseudointermolecular pathway is excluded by the first-order kinetics of the rearrangement. Intermediates of this type are probable in the dimerization process of ethylene by **1**.[23]

With these observations, there are two possible descriptions for the relative rate of the steps involved in the rearrangement process. The first involves a situation in which formation of a π-adduct between catalyst and reactant as well as dissociation of the catalyst−product adduct is fast compared to the rearrangement step. The second possibility is the formation of a ruthenium(IV) hydride species prior to substrate binding and is plausible by the product analysis of a stoichiometric rearrangement of 2-pentenoic acid.[17]

The formation of a catalytically active ruthenium(IV) hydride in a separate cycle is consistent with the observation of an induction period in the kinetic measurements of the rearrangement of 2-d_2 and **2**. The first-order kinetics indicate the presence of a steady state concentration of the active species after the induction period. Therefore, the active species must be formed in a preequilibrium which is faster than the overall reaction. The observed rate constant (k_{obs}) for the rearrangement of **2** in ethanol is linearly dependent (correlation coefficient R^2 = 0.989) on the concentration of the catalyst precursor [Ru(H₂O)₆]²⁺ in

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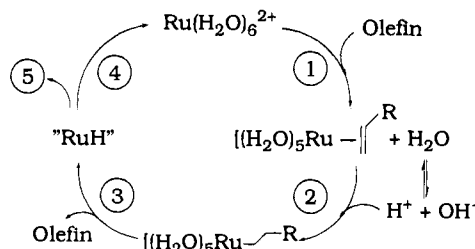*Reaction of [Ru(H₂O)₆]²⁺ with Olefins*

J. Am. Chem. Soc., Vol. 116, No. 25, 1994 11377

Figure 2. Mechanism for the initiation of the rearrangement of nonfunctionalized olefins catalyzed by $[Ru(H_2O)_6]^{2+}$: (1) formation of a ruthenium olefin complex, (2) electrophilic attack resulting in an intermediate ruthenium alkyl complex, (3) β-hydride elimination, (4) slow "reduction" to $[Ru(H_2O)_6]^{2+}$, (5) fast initiation of the catalytic cycle by addition of the ruthenium hydride to free olefin.

Figure 3. Selective formation of *trans* products: β-hydride elimination from the energetically favored conformation in the metal alkyl intermediate.

the concentration range from 1.29×10^{-3} to 1.83×10^{-2} M. This observation supports the assumption that the active species is formed in a preequilibrium.

The second-order rate constants for the formation of monoolefin complexes derived from **1** are in the range of 1.5×10^{-3} s^{-1} M^{-1} at 298 K.[24] With a large excess of substrate, the formation of the monoolefin π-complex between the substrate and **1** can be treated as a pseudo-first-order process with a rate constant of about 2.3×10^{-3} s^{-1}. The half-life for the conversion of **1** to the monoolefin complex is therefore ca. 5 min. This is 4−5 times faster than the half-life for isomerization of 2-d_2. Given an induction period of about 5 min, a monoolefin complex could be the intermediate which forms the ruthenium-(IV) hydride.

The induction periods in the rearrangement of **2** catalyzed by $[Ru(H_2O)_6](trif)_2$ are only moderately sensitive to the choice of solvent. Addition of trifluoromethanesulfonic acid (10 equiv relative to the catalyst) to diethyl ether prior to addition of **2** results in an increase of k_{obs} by a factor of approximately 20. In the acidified diethyl ether, the rearrangement starts immediately without an induction period. These observations are best explained by assuming protonation of a catalyst precursor of the type $[(H_2O)_5Ru(\eta^2\text{-olefin})]^{2+}$ to yield a ruthenium alkyl complex. This species will then react by β-elimination to a ruthenium hydride complex which will start the catalytic cycle. In nonacidified, aprotic media, the free water molecule which results from the ligand substitution by the olefin can act as the proton source. This proposed mechanism for the initiation is depicted in Figure 2.

Hydrogen Exchange with Solvent. Monitoring the magnitude of the M + 1 peak by GC−MS in the rearrangement of 1-octene allows the determination of the deuterium exchange with solvent. Change of ethanol to ethanol-d_6 does not affect the magnitude of the M + 1 peak of the products. Neither does the addition of H_2O or of D_2O in ethanol-d_6. After the rearrangement of nondeuterated **2** in deuterated solvents, no D is observed in NMR or IR. Therefore, no deuterium exchange with solvent is observed, indicating that deuterium exchange between metal hydride and solvent is slow compared to rearrangement. Once a metal hydride has started a cycle, the hydrogens are transferred between the substrate molecules without interference from the solvent.

If the attack of a preformed ruthenium(IV) hydride to olefin is the first step in the catalytic cycle, deuterium incorporation into rearrangement products should be observed in deuterated solvents. This was shown to be the case in the stoichiometric reaction of **1** with 2-pentenoic acid.[17] Even if metal hydride formation would be slow compared to the steps involved in the
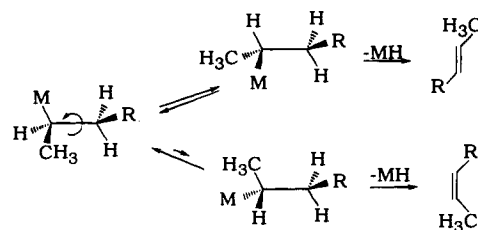
rearrangement cycle, increasing the catalyst concentration should result in an enhanced D incorporation by increasing the concentration of the active species. With a catalyst amount of up to 20 mol %, no D incorporation is observed. We suggest that the substrate shows a marked preference for coordinated metal hydride. Such behavior has also been described in the rearrangement of allylic benzene with $HCo(CO)_4$.[21]

Selectivity. The rearrangement of unfunctionalized olefins catalyzed by the precursor **1** selectively produces the *trans* isomers, tested by ^1H NMR ($^3J_{olefin}$ = 16−18 Hz and small NOE effect) and by comparison of GC retention times with commercial standards. This result furthermore supports a MH addition−elimination mechanism (see Figure 3). The intermediate metal alkyl formed by *syn* addition of MH on the olefin rotates readily around the C−C bond. This rotation is fast compared to β-elimination. A *syn* β-elimination from the energetically favored conformation produces the *trans* product. Our model for the rationalization of the selective formation of *trans* products only holds for a transition state in which the conformational modes are not restricted by chelating effects resulting from pendent functional groups. Therefore, the observed formation of *trans*- and *cis*-3-penten-1-ol (27:73) from the rearrangement of 4-penten-1-ol is due to the directing power of the hydroxy group and shows that functionalities can influence the mechanism of the rearrangement to a considerable extent.[17]

Additional experiments support this hypothesis. Thus, 3-methylbutene rearranges very slowly due to the methyl substituent which introduces a substantial rotational barrier in the metal alkyl intermediate. Therefore, β-hydrogen elimination occurs on the methyl group, which results in the formation of the reactant. With 2-allyl-1-methoxybenzene, only the *trans* product is formed. With 2-allylphenol, 30% *cis* isomer is produced probably due to stabilization of a cisoid transition state by chelating of the OH group with the catalyst. Rearrangement of internal *cis*-olefin (e.g., *cis*-2-hexene) also results in *trans* products. Such a behavior is excluded if a π-allyl mechanism predominates.[25]

Catalyst Recovery. In rearrangement experiments with catalyst contents up to 20 mol %, ^1H-NMR resonances typical for $[(H_2O)_5Ru(\eta^2\text{-olefin})]^{2+}$ are observed. For the rearrangement of functionalized olefins, such species have been isolated.[17] Upon addition of new substrate, the rearrangement starts again with an increased initiation period. This shows that the catalyst precursor is not deactivated by formation of an olefin complex, consistent with a quite small formation constant K_1 = 112 (25 °C) for the model compound $[(H_2O)_5Ru(\eta^2\text{-2,5-dihydrofuran})]^{2+}$.[26]

The situation seems to be analogous to the "catalyst" recovery in the ring-opening metathesis polymerization of 7-oxanorbornenes catalyzed by **1**.[3] In ROMP with **1**, it was shown that

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the formation of the active carbene species is very slow compared to propagation.[26] Therefore, only a small part of the catalyst precursor is transformed to the active species. The major part is bound as an olefin complex, which can be recovered.

Summary and Conclusions

The mechanism of the rearrangement of acyclic olefins catalyzed by **1** is best described by a 1,2-addition−elimination of a metal hydride which is formed in a preequilibrium. This metal hydride attacks the olefinic substrate to form a metal alkyl intermediate. β-Hydride elimination of the energetically most stable rotamer is the rate-determining step in the rearrangement cycle, leading to a metal hydride−product complex. This "activated" metal hydride starts a new cycle considerably faster than uncoordinated metal hydride. This model agrees with the mechanism proposed for the rearrangement of functionalized olefins in aqueous solution.[17] The observed predominant hydrogen 1,3-shift in the work of these authors can be interpreted either as an effect of the directing influence of functional groups attached to the olefin or as evidence for an interfering π-allyl hydride mechanism. Our results indicate clearly that also, with nonfunctionalized substrate, the mechanism follows a 1,2-addition−elimination sequence. In addition to intermolecular hydrogen transfer, the distribution of deuterium in products of rearranged **2-d_2** combined with a selective attack of the intermediate metal hydride species on C_2 is fully consistent with this mechanism. Moreover, the selective formation of *trans* products is fully compatible with this model.

The mechanism is supported by the characteristics of the ROMP activity of **1**. In that system, predominating β-hydride abstraction in a ruthenium alkyl intermediate explains the slow initiation and low concentration of the active carbene species resulting from the unfavorable α-hydride abstraction.[26]

Experimental Section

Reagents. Deuterated solvents were used as received. Olefins were distilled prior to use. **2-d_2** was synthesized in 98% purity. The impurities consisted of 1.5% undeuterated propenylbenzene and 0.5% undeuterated allylbenzene (GC). [Ru(H$_2$O)$_6$](tos)$_2$ and [RuH$_2$O)$_6$](trif)$_2$ were prepared according to the literature.[27]

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Instrumentation. All NMR measurements were done on either a Bruker AC-300 or a Bruker AC-400. For IR measurements, a Perkin-Elmer FTIR 1720 x with a selected resolution of 2 cm^{-1} was used. GC analyses were obtained on a HP-5890 with a HP Ultra 2 column (column length 10 m; diameter 0.2 mm; stationary phase 5% diphenylpolysiloxane; layer thickness 0.11 μm; carrier gas He; temperature program 40−220 °C with 3 °C/min). For GC−MS characterizations a FISONS VG AutoSpec Q with a 16 m HP Ultra 2 column was used throughout.

Catalytic Rearrangements. For a typical rearrangement experiment, 3.0 mg of **1** was dissolved in 0.5 mL of argon-saturated solvent and 100 μL of the olefin was added by the septum technique. The mixture was then allowed to stand in a thermostated bath (typically 40 °C).

Sample Treatment for IR and GC−MS Measurements. For analysis the products were separated from the catalyst by dilution with water and extraction with ether. A passage through a neutral silica gel column and elution with hexane/ether followed.

Kinetic Studies. Kinetic measurements were performed on a Bruker AC-400. The first-order rate constants for the rearrangement of deuterated and undeuterated allylbenzene were determined by following the increase of product signals and the decrease of reactant signals with time at 302 K in the ^{1}H-NMR spectra. For each value of k, three independent measurements were done. The reaction mixture was composed of 5.2 mg of **1**, 100 μL of **2-d_2**, and 0.4 mL of ethanol-d_6.

The dependence of k_{obs} on the catalyst concentration in the rearrangement of **2** was determined by following the reaction kinetics by GC. The catalyst concentration was varied from 1.29×10^{-3} to 1.83×10^{-2} M in four steps. In order to exclude effects resulting from changes in the ionic strength, these measurements were carried out in a 0.5 M ethanolic solution of lithium trifluoromethanesulfonate. The induction periods in ethanol and diethyl ether were determined in the same manner.

Supplementary Material Available: ^{1}H-NMR spectrum of a competition experiment, ^{1}H- and ^{13}C-NMR and DEPT spectra of the rearrangement of **2-d_2**, and IR spectra of isolated products in the C−D stretching region (5 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.