

Bis(allyl)–Ruthenium(IV) Complexes as Highly Efficient Catalysts for the Redox Isomerization of Allylic Alcohols into Carbonyl Compounds in Organic and Aqueous Media: Scope, Limitations, and Theoretical Analysis of the Mechanism

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Abstract: The catalytic activity of the bis(allyl)–ruthenium(IV) dimer [$\{\text{Ru}(\eta^3\text{-}\eta^3\text{-C}_{10}\text{H}_{16})(\mu\text{-Cl})\text{Cl}\}_2$] ($\text{C}_{10}\text{H}_{16}$ = 2,7-dimethylocta-2,6-diene-1,8-diy)l (**1**), and that of its mononuclear derivatives [$\text{Ru}(\eta^3\text{-}\eta^3\text{-C}_{10}\text{H}_{16})\text{Cl}_2(\text{L})$] ($\text{L} = \text{CO}, \text{PR}_3, \text{CNR}, \text{NCR}$) (**2**) and [$\text{Ru}(\eta^3\text{-}\eta^3\text{-C}_{10}\text{H}_{16})\text{Cl}(\text{NCMe})_2[\text{SbF}_6]$] (**3**), in the redox isomerization of allylic alcohols into carbonyl compounds, both in tetrahydrofuran and in water, is reported. In particular, a variety of allylic alcohols have been quantitatively isomerized using [$\{\text{Ru}(\eta^3\text{-}\eta^3\text{-C}_{10}\text{H}_{16})(\mu\text{-Cl})\text{Cl}\}_2$] (**1**) as catalyst, the reactions proceeding in all cases faster in water. Remarkably, complex **1** has been found to be the most efficient catalyst reported to date for this particular transformation, leading to TOF and TON values up to 62 500 h⁻¹ and 1 500 000, respectively. Moreover, catalyst **1** can be recycled and is capable of performing allylic alcohol isomerizations even in the presence of conjugated dienes, which are known to be strong poisons in isomerization catalysis. On the basis of both experimental data and theoretical calculations (DFT), a complete catalytic cycle for the isomerization of 2-propen-1-ol into propenal is described. The potential energy surfaces of the cycle have been explored at the B3LYP/6-311+G(d,p)//B3LYP/6-31G(d,p) + LAN2DZ level. The proposed mechanism involves the coordination of the oxygen atom of the allylic alcohol to the metal. The DFT energy profile is consistent with the experimental observation that the reaction only proceeds under heating. Calculations predict the catalytic cycle to be strongly exergonic, in full agreement with the high yields experimentally observed.

Introduction

New achievements in organic synthesis have appeared very rapidly as part of the increasing academic and industrial interest in fulfilling the fundamental principles of “Green Chemistry”.¹ Among the most important challenges of modern chemistry, organic reactions in water are of primary interest especially when they are performed under catalytic conditions.² As a matter of fact, the development of metal-mediated catalytic transformations in aqueous media represents one of the cornerstones of modern organometallic chemistry.^{3,4} Although the hydrophobic character of most organic compounds may be a drawback, the

recovery of the organic products from an aqueous medium can be easily achieved by phase separation. Simultaneously, the concept of atom economy, that is, all atoms of the reactant end up in the final product, has emerged as a desirable goal in chemical reactions.⁵

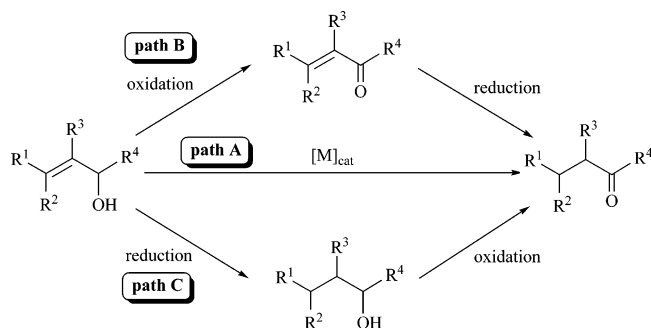
To address both issues, that is, atom economical organic catalytic reactions in water, much effort has been done during the past few years.^{3,4} Isomerization reactions are typical examples of atom economical reactions because no byproducts are generated. Among them, the isomerization of allylic alcohols into the corresponding carbonyl compounds is an economically

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- See, for example: (a) Li, C. J. *Chem. Rev.* **1993**, *93*, 2023–2035. (b) Lubineau, A.; Auge, J.; Queneau, Y. *Synthesis* **1994**, 741–760. (c) Li, C. J.; Chan, T. H. *Organic Reactions in Aqueous Media*; John Wiley & Sons: New York, 1997. (d) Lindström, U. M. *Chem. Rev.* **2002**, *102*, 2751–2772. (e) Li, C. J. *Chem. Rev.* **2005**, *105*, 3095–3165.

- See, for example: (a) Kalck, P.; Monteil, F. *Adv. Organomet. Chem.* **1992**, *34*, 219–284. (b) Herrmann, W. A.; Kohlpaintner, C. W. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1524–1544. (c) *Aqueous Organometallic Chemistry and Catalysis*; Horváth, I. T., Joó, F., Eds.; Kluwer: Dordrecht, 1995. (d) *Aqueous-Phase Organometallic Catalysis: Concepts and Applications*; Cornils, B., Herrmann, W. A., Eds.; Wiley-VCH: Weinheim, 1998. (e) Hanson, B. E. *Coord. Chem. Rev.* **1999**, *185–186*, 795–807. (f) Joó, F. *Aqueous Organometallic Catalysis*; Kluwer: Dordrecht, 2001. (g) Pinault, N.; Bruce, D. W. *Coord. Chem. Rev.* **2003**, *241*, 1–25.
- Thematic issues of journals have been devoted to the catalytic applications of water-soluble organometallic compounds. See, for example: (a) *J. Mol. Catal. A: Chem.* **1997**, *116*, 1–316. (b) *Catal. Today* **1998**, *42*, 371–478. (c) *Adv. Synth. Catal.* **2002**, *344*, 219–451.
- See, for example: (a) Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 259–281 and references therein. (b) Trost, B. M. *Acc. Chem. Res.* **2002**, *35*, 695–705 and references therein.

Scheme 1. Transformation of Allylic Alcohols into Saturated Carbonyl Compounds

important process because it provides a simple synthetic route to very valuable raw materials in organic synthesis. Although pioneering transformations were performed thermally by the treatment with acids, bases, or by using heterogeneous catalysts, new synthetic approaches based in homogeneous catalysis (see path A in Scheme 1) are preferred because they generally proceed with much more efficiency, improving also the selectivities.⁶ This one-pot internal redox process represents a useful and elegant shortcut to carbonyl compounds, which otherwise would require a two-step sequence of oxidation and reduction reactions (paths B or C in Scheme 1).⁶ Several group 6, 8, 9, and 10 metal complexes have been found to be active catalysts for this transformation.⁶ In particular, the best performances in terms of both selectivity, turnover frequencies (TOF), and turnover numbers (TON) have been reported using iron, ruthenium, and rhodium compounds.⁶

Surprisingly, the catalytic isomerization of allylic alcohols into carbonyl compounds in aqueous media has been scarcely studied.⁶ The reactions are usually performed under biphasic (water/organic solvent) conditions using as catalysts transition-metal complexes containing water-soluble ligands (either isolated or generated in situ), which allows the catalyst recycling by phase separation. These include: [Ni(COD)₂]/DPPBTS (COD = 1,5-cyclooctadiene; DPPBTS = tetrasulfonated 1,4-bis(diphenylphosphino)butane),^{7a} [RhCl(COD)(PAr₃)] (PAr₃ = carboxylated triarylphosphines),^{7b} RhCl₃/TPPTS or Rh₂(SO₄)₃/TPPTS (TPPTS = P(*m*-C₆H₄SO₃Na)₃),^{7c} [Rh(COD)(SULPHOS)] (SULPHOS = ⁻O₃S-C₆H₄-CH₂C(CH₂PPh₂)₃),^{7d} [Rh(COD)(TPMP)₂][BF₄] (TPMP = Ph₂P(*p*-C₆H₄PO₃Na)₂),^{7e} and [RuCl₂(η⁶-arene){P(CH₂OH)₃}] (arene = C₆H₆, C₆Me₆, *p*-cymene).^{7f,8} The hexa-aquoruthenium(II) complex [Ru(H₂O)₆][Tos]₂ (Tos = *p*-toluenesulfonate) has also proven to be an active

catalyst for the isomerization of allylic alcohols and ethers in pure aqueous solution.⁹ In addition, the catalytic systems [Rh(CO)₂(μ-Cl)₂],¹⁰ *mer*-[RuCl₃(DMSO)(phen)] (DMSO = dimethyl sulfoxide; phen = 1,10-phenanthroline),¹¹ *cis,cis*-[RuCl₂(DMSO)₂(phen)],¹¹ and [Ru(acac)₃]/phen/TsOH (acac = acetylacetonate; TsOH = *p*-toluenesulfonic acid)¹² have been used for allylic alcohols isomerization in monophasic water/organic solvent mixtures.

Remarkably, we have recently reported that the mononuclear bis(allyl)-ruthenium(IV) complex [Ru(η³:η²:η³-C₁₂H₁₈)Cl₂] (C₁₂H₁₈ = dodeca-2,6,10-triene-1,12-diyl) is an active catalyst for this particular transformation, showing an extremely high performance (TOF values up to 55 000 h⁻¹; TON values up to 10⁶).¹³ As far as we know, this complex represents the first example of a Ru(IV) catalyst for this isomerization reaction.⁶ With these precedents in mind, and continuing with our studies aimed at discovering new catalytic systems, in this paper we report that the dinuclear bis(allyl)-ruthenium(IV) complex {[Ru(η³:η³-C₁₀H₁₆)(μ-Cl)Cl₂] (C₁₀H₁₆ = 2,7-dimethylocta-2,6-diene-1,8-diyl) (**1**), as well as its mononuclear derivatives [Ru(η³:η³-C₁₀H₁₆)Cl₂(L)] (L = CO, PR₃, CNR, NCR) (**2**) and [Ru(η³:η³-C₁₀H₁₆)Cl(NCMe)₂][SbF₆] (**3**) (see Figure 1), are also highly efficient catalysts for the isomerization of allylic alcohols into carbonyl compounds in both organic and aqueous media. In particular, the parent complex **1** provides the following remarkable features: (i) it is the most efficient catalyst described to date,⁶ (ii) its catalytic activity is maintained at very low catalyst loadings and can be recycled with only partial deactivation after three or four runs, (iii) it is a readily available air-stable solid,¹⁴ and (iv) it remains active in the presence of isoprene in contrast to the loss of activity observed for almost all of the known catalysts.¹⁵

Moreover, on the basis of both experimental data and theoretical calculations, a complete catalytic cycle is described. The most relevant feature of the mechanism is that it involves the formation of a π-oxoallyl intermediate, in contrast to the classical alkyl and π-allyl intermediates commonly proposed for this isomerization reaction.⁶ Although the involvement of a π-oxoallyl intermediate has been previously postulated by B. M. Trost and co-workers starting from half-sandwich ruthenium(II) catalysts,¹⁶ no theoretical confirmation was provided. Herein, we report for the first time a theoretical study showing the key role of the oxygen atom of the allylic alcohols, which enables

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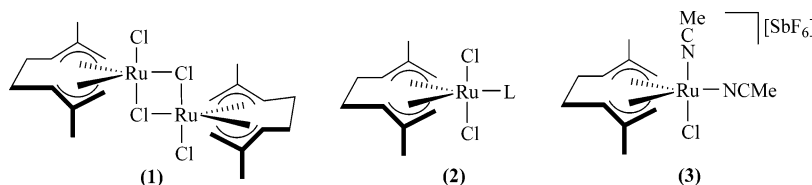


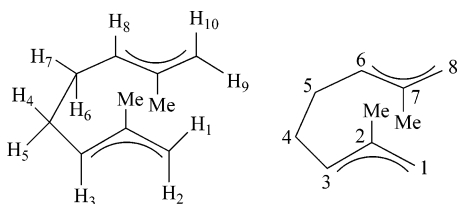
Figure 1. Bis(allyl)–ruthenium(IV) catalysts used in this work.

the chelate coordination of the substrate to the metal favoring the catalytic activity.

Experimental Section

The manipulations were performed under an atmosphere of dry nitrogen using vacuum-line and standard Schlenk techniques. Solvents were dried by standard methods and distilled under nitrogen before use. All reagents were obtained from commercial suppliers and used without further purification with the exception of compounds [$\text{Ru}(\eta^3\text{-C}_{10}\text{H}_{16})(\mu\text{-Cl})\text{Cl}]_2$ (**1**),¹⁴ [$\{\text{Ru}(\eta^6\text{-arene})(\mu\text{-Cl})\text{Cl}\}_2$] (arene = C_6H_6 , *p*-cymene, C_6Me_6),¹⁷ [$\text{RuCl}_2(\text{PPh}_3)_3$],¹⁸ [$\text{Ru}(\eta^5\text{-C}_9\text{H}_7)\text{Cl}(\text{PPh}_3)_2$],¹⁹ [$\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{PPh}_3)_2$],²⁰ [$\text{Ru}(\eta^3\text{-C}_{10}\text{H}_{16})\text{Cl}_2(\text{L})$] (L = CO (**2a**),^{21a} PPh_3 (**2e**),^{21a} PPr_3 (**2g**),^{21c} $\text{P}(\text{OMe})_3$ (**2h**),^{21c} CN^tBu (**2i**),^{21c} NH_2Ph (**2j**),^{21d} NCMe (**2k**)^{21b}), and [$\text{Ru}(\eta^3\text{-C}_{10}\text{H}_{16})\text{Cl}(\text{NCMe})_2$][SbF_6] (**3**),^{21f,g} which were prepared by following the methods reported in the literature. Infrared spectra were recorded on a Perkin-Elmer 1720-XFT spectrometer. The C and H analyses were carried out with a Perkin-Elmer 2400 microanalyzer. GC measurements were made on Hewlett-Packard HP6890 equipment using a HP-INNOWAX cross-linked poly(ethylene glycol) (30 m, 250 μm) or a Supelco Beta-Dex 120 (30 m, 250 μm) column. GC/MS measurements were performed on Agilent 6890N equipment coupled to a 5973 mass detector (70-eV electron impact ionization) using a HP-IMS column. NMR spectra were recorded on a Bruker DPX-300 instrument at 300 MHz (^1H), 121.5 MHz (^{31}P), or 75.4 MHz (^{13}C) using SiMe_4 or 85% H_3PO_4 as standards. DEPT experiments have been carried out for all of the compounds reported.

The numbering for protons and carbons of the 2,7-dimethylocta-2,6-diene-1,8-diyl skeleton is as follows:



Synthesis of Complexes [$\text{Ru}(\eta^3\text{-C}_{10}\text{H}_{16})\text{Cl}_2(\text{PR}_3)$] ($\text{PR}_3 = \text{PMe}_3$ (2b**), PMe_2Ph (**2c**), PMePh_2 (**2d**), $\text{P}(p\text{-C}_6\text{H}_4\text{OMe})_3$ (**2f**)).** The corresponding phosphine ligand (2 mmol) was added, at room temperature,

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to a solution of complex [$\{\text{Ru}(\eta^3\text{-C}_{10}\text{H}_{16})(\mu\text{-Cl})\text{Cl}\}_2$] (**1**) (0.616 g; 1 mmol) in 20 mL of dichloromethane. After the mixture was stirred for 10 min, the solvent was removed under vacuum and the resulting yellow solid residue was washed with hexanes (3 \times 10 mL) and dried in vacuo. **2b**: Yield 91% (0.699 g). Anal. Calcd for $\text{RuC}_{13}\text{H}_{25}\text{Cl}_2\text{P}$: C, 40.63; H, 6.56. Found: C, 40.57; H, 6.54. IR (KBr, cm^{-1}): ν 501 (w), 573 (w), 678 (w), 736 (w), 783 (w), 801 (w), 821 (w), 850 (m), 948 (vs), 1025 (w), 1095 (w), 1261 (w), 1285 (m), 1304 (w), 1315 (w), 1344 (w), 1384 (m), 1418 (m), 1456 (w), 1495 (w), 2853 (m), 2908 (m), 2977 (m). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ -4.78 (s) ppm. ^1H NMR (CD_2Cl_2): δ 1.58 (d, 9H, $^3J_{\text{HP}} = 10.3$ Hz, PCH_3), 2.15 (s, 6H, CH_3), 2.69 (m, 2H, H_4 and H_6), 2.97 (d, 2H, $^3J_{\text{HP}} = 4.8$ Hz, H_2 and H_{10}), 3.39 (m, 2H, H_5 and H_7), 4.09 (d, 2H, $^3J_{\text{HP}} = 9.1$ Hz, H_1 and H_9), 4.93 (m, 2H, H_3 and H_8) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 16.90 (d, $^1J_{\text{CP}} = 33.9$ Hz, PCH_3), 20.97 (s, CH_3), 36.99 (s, C_4 and C_5), 63.70 (d, $^2J_{\text{CP}} = 5.7$ Hz, C_1 and C_8), 108.07 (d, $^2J_{\text{CP}} = 10.2$ Hz, C_3 and C_6), 122.08 (d, $^2J_{\text{CP}} = 1.2$ Hz, C_2 and C_7) ppm. **2c**: Yield 89% (0.794 g). Anal. Calcd for $\text{RuC}_{18}\text{H}_{27}\text{Cl}_2\text{P}$: C, 48.44; H, 6.10. Found: C, 48.39; H, 6.25. IR (KBr, cm^{-1}): ν 493 (s), 573 (w), 679 (s), 694 (s), 712 (s), 750 (s), 787 (m), 846 (m), 914 (vs), 941 (vs), 964 (w), 1002 (w), 1029 (m), 1109 (m), 1183 (w), 1199 (w), 1279 (m), 1294 (m), 1312 (m), 1325 (w), 1343 (w), 1383 (s), 1436 (s), 1453 (m), 1496 (w), 2855 (m), 2908 (m), 3001 (m), 3073 (m). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 1.27 (s) ppm. ^1H NMR (CD_2Cl_2): δ 1.91 and 2.00 (d, 3H each, $^2J_{\text{HP}} = 10.0$ Hz, PCH_3), 2.14 (s, 6H, CH_3), 2.70 (m, 2H, H_4 and H_6), 2.99 (d, 2H, $^3J_{\text{HP}} = 4.2$ Hz, H_2 and H_{10}), 3.43 (m, 2H, H_5 and H_7), 3.70 (d, 2H, $^3J_{\text{HP}} = 9.7$ Hz, H_1 and H_9), 5.02 (m, 2H, H_3 and H_8), 7.45–7.65 (m, 5H, Ph) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 14.42 and 15.30 (d, $^1J_{\text{CP}} = 35.5$ Hz, PCH_3), 21.29 (s, CH_3), 37.30 (s, C_4 and C_5), 66.88 (d, $^2J_{\text{CP}} = 5.3$ Hz, C_1 and C_8), 107.80 (d, $^2J_{\text{CP}} = 9.5$ Hz, C_3 and C_6), 123.52 (s, C_2 and C_7), 128.65–140.41 (m, Ph) ppm. **2d**: Yield 93% (0.946 g). Anal. Calcd for $\text{RuC}_{23}\text{H}_{29}\text{Cl}_2\text{P}$: C, 54.33; H, 5.75. Found: C, 54.36; H, 5.54. IR (KBr, cm^{-1}): ν 477 (m), 514 (s), 524 (m), 700 (s), 736 (s), 743 (s), 756 (s), 787 (w), 801 (w), 821 (w), 857 (w), 890 (vs), 969 (w), 1000 (w), 1023 (m), 1096 (w), 1167 (w), 1198 (w), 1286 (m), 1313 (w), 1343 (m), 1381 (m), 1417 (m), 1438 (s), 1486 (w), 2860 (m), 2921 (m), 2989 (m), 3003 (m), 3056 (m). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 4.42 (s) ppm. ^1H NMR (CD_2Cl_2): δ 2.14 (s, 6H, CH_3), 2.18 (s, 3H, PCH_3), 2.63 (m, 2H, H_4 and H_6), 3.08 (d, 2H, $^3J_{\text{HP}} = 2.9$ Hz, H_2 and H_{10}), 3.43 (m, 2H, H_5 and H_7), 3.96 (d, 2H, $^3J_{\text{HP}} = 10.0$ Hz, H_1 and H_9), 5.14 (m, 2H, H_3 and H_8), 7.35–7.96 (m, 10H, Ph) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 14.11 (d, $^1J_{\text{CP}} = 32.0$ Hz, PCH_3), 21.03 (s, CH_3), 37.24 (s, C_4 and C_5), 67.42 (s, C_1 and C_8), 108.22 (d, $^2J_{\text{CP}} = 8.2$ Hz, C_3 and C_6), 123.42 (s, C_2 and C_7), 128.10–138.00 (m, Ph) ppm. **2f**: Yield 92% (1.215 g). Anal. Calcd for $\text{RuC}_{31}\text{H}_{37}\text{O}_3\text{Cl}_2\text{P}$: C, 56.37; H, 5.65. Found: C, 56.64; H, 5.86. IR (KBr, cm^{-1}): ν 501 (w), 541 (s), 613 (w), 622 (w), 642 (w), 718 (w), 798 (s), 826 (m), 862 (w), 960 (w), 1028 (m), 1088 (m), 1112 (w), 1182 (s), 1252 (vs), 1286 (s), 1382 (w), 1409 (w), 1441 (m), 1458 (m), 1500 (s), 2835 (m), 2853 (m), 2910 (m), 2957 (m), 2999 (m), 3066 (m). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 22.39 (s) ppm. ^1H NMR (CD_2Cl_2): δ 2.24 (s, 6H, CH_3), 2.63 (m, 2H, H_4 and H_6), 3.02 (s, 2H, H_2 and H_{10}), 3.43 (m, 2H, H_5 and H_7), 3.79 (s, 9H, OCH_3), 4.41 (d, 2H, $^3J_{\text{HP}} = 9.4$ Hz, H_1 and H_9), 5.20 (m, 2H, H_3 and H_8), 6.85–7.65 (m, 12H, Ph) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 20.80 (s, CH_3), 37.20 (s, C_4 and C_5), 55.61 (s, OCH_3), 67.42 (d, $^2J_{\text{CP}} = 4.7$ Hz, C_1 and C_8), 108.59 (d, $^2J_{\text{CP}} = 10.4$ Hz, C_3 and C_6), 113.10–160.82 (m, C_6H_4 , C_2 and C_7) ppm.

General Procedure for the Catalytic Isomerization of Allylic Alcohols into Carbonyl Compounds. In a Schlenk tube fitted with a condenser, the corresponding allylic alcohol, ruthenium catalyst precursor, and cocatalyst (if required) were dissolved in THF or water (20 mL), and the reaction mixture was stirred at 75 °C for the indicated time. The course of the reaction was monitored by regular sampling and analysis by gas chromatography. The identity of the resulting saturated carbonyl compounds was assessed by comparison with commercially available pure samples (Aldrich Chemical Co. or Acros Organics) and by their fragmentation in GC/MS.

Isomerization of 1-Octen-3-ol into Octan-3-one under Preparative Conditions. Under nitrogen atmosphere, 1-octen-3-ol (6.3 mL, 40 mmol), dimer **1** (0.025 g, 0.04 mmol), Cs₂CO₃ (0.053 g, 0.163 mmol), and water (200 mL) were introduced in a Schlenk flask, and the reaction mixture was stirred at 75 °C for 20 min (quantitative conversion by GC). The resulting aqueous solution was then saturated with NaCl and extracted with dichloromethane (2 × 50 mL). The combined organic extracts were dried over MgSO₄, concentrated, and purified by column chromatography over silica gel, using diethyl ether as eluent, to give 4.82 g (37.6 mmol) of analytically pure octan-3-one (94% yield).

Theoretical Methods. The potential energy surfaces (PESs) corresponding to the processes involved in the redox isomerization of allylic alcohols into carbonyl compounds catalyzed by the Ru(IV) complexes have been explored using density functional theory (DFT)²² with the Becke 3-parameter Lee–Yang–Parr^{23,24} (B3LYP) hybrid functional.

We have carried out all of the geometry optimizations using Pople's 6-31G(d,p) basis sets for H, C, O, Cl atoms²⁵ and the LANL2DZ effective core potential²⁶ for ruthenium. All of the geometrical parameters were fully optimized, and all of the structures located on the PESs were characterized as minima or transition structures by computing the corresponding Hessian matrices, examining the number of imaginary frequencies from them. The energy predictions were improved by carrying out single-point calculations with Pople's valence triple-zeta 6-311+G(d,p) basis set.²⁷

Solvation effects (water and tetrahydrofuran) have been estimated by using a continuum solvent description: the so-called polarized continuum model (PCM).²⁸

The Gaussian98 and Gaussian03 packages of programs²⁹ were used to carry out the calculations.

Results and Discussion

Catalytic Isomerization of Allylic Alcohols into Carbonyl Compounds in THF. First, we checked the catalytic activity of dimer **1** [$\{\text{Ru}(\eta^3\text{-}\eta^3\text{-C}_{10}\text{H}_{16})(\mu\text{-Cl})\text{Cl}\}_2$] (**1**) in the isomerization of a simple model, 1-octen-3-ol (see Table 1). Thus, when a 0.2 M THF solution of 1-octen-3-ol was refluxed for 24 h with a catalytic amount of **1** (0.2 mol % in Ru), octan-3-one was formed in 96% yield (see entry 1 in Table 1). The rate of this isomerization process can be enhanced upon addition of a

Table 1. Isomerization of 1-Octen-3-ol into Octan-3-one Catalyzed by the Dinuclear Bis(allyl)-Ruthenium(IV) Complex **1**^a

entry	cocatalyst	yield (%) ^b	time	TOF (h ⁻¹) ^c
1	none	96	24 h	20
2	Li ₂ CO ₃ (0.2 mol %)	100	3 h	167
3	Na ₂ CO ₃ (0.2 mol %)	100	55 min	545
4	K ₂ CO ₃ (0.2 mol %)	100	90 min	333
5	Cs ₂ CO ₃ (0.2 mol %)	100	35 min	857
6	Cs ₂ CO ₃ (0.4 mol %)	100	10 min	3000
7	Cs ₂ CO ₃ (2 mol %)	100	10 min	3000
8	AgSbF ₆ (0.2 mol %)	62	18 h	17

^a All of the reactions were performed under N₂ atmosphere at 75 °C using 4 mmol of 1-octen-3-ol (0.2 M in THF). Substrate/Ru ratio: 500:1.

^b Yield of octan-3-one determined by GC. ^c Turnover frequencies ((mol product/mol Ru)/time) were calculated at the time indicated in each case.

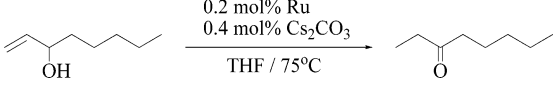
catalytic amount of base as cocatalyst.³⁰ Among all alkaline carbonates M₂CO₃ (M = Li, Na, K, and Cs) tested, the best results were obtained with Cs₂CO₃ (entry 5 vs entries 2–4; in all cases, a 1:1 Ru/base ratio was used), which leads to the quantitative transformation of the unsaturated alcohol into the saturated ketone in only 35 min (TOF = 857 h⁻¹). We have also screened the optimal Ru/Cs₂CO₃ ratio performing experiments with 1:1 to 1:10 molar ratios, and we have observed that a notable improvement occurs by increasing the Cs₂CO₃/Ru mol ratio up to 2 (entry 6 (TOF = 3000 h⁻¹) vs 5 (TOF = 857 h⁻¹)). The addition of an excess of base has no influence on the reaction rate (entry 7 vs 6). To check whether Cs₂CO₃ acts as base or chloride abstractor, the isomerization of 1-octen-3-ol by complex **1** was studied using AgSbF₆ as cocatalyst under the same reaction conditions (substrate/Ru/AgSbF₆ ratio: 500:1:1). In this case, only 62% of conversion was attained after 18 h of reflux (entry 8; to be compared to entry 5), indicating clearly that Cs₂CO₃ acts mainly as a base.

In accord with these results, a substrate/Ru/Cs₂CO₃ ratio of 500:1:2 was considered as the optimal reaction conditions for the rest of our catalytic studies. Remarkably, under these reaction conditions, the dimeric complex [$\{\text{Ru}(\eta^3\text{-}\eta^3\text{-C}_{10}\text{H}_{16})(\mu\text{-Cl})\text{Cl}\}_2$] (**1**) is by far much more active (TOF = 3000 h⁻¹) than the classical ruthenium(II) catalysts [$\{\text{Ru}(\eta^6\text{-arene})(\mu\text{-Cl})\text{Cl}\}_2$] (arene = C₆H₆,^{7f} *p*-cymene,^{30a} C₆Me₆^{7f}), [RuCl₂(PPh₃)₃],³⁰ [Ru(η⁵-C₉H₇)Cl(PPh₃)₂],^{16b} and [Ru(η⁵-C₅H₅)Cl(PPh₃)₂]¹⁶ (TOF = 1–500 h⁻¹; entries 2–7 vs entry 1 in Table 2),³¹ its efficiency being even higher than that shown by the mononuclear ruthenium(IV) complex [Ru(η³:η²:η³-C₁₂H₁₈)Cl₂] recently reported by us (TOF = 3000 vs 429 h⁻¹; entry 1 vs entry 8).¹³

It is also worth mentioning that the exceptional high activity of complex **1** is retained at lower catalyst loadings. For example, using 10⁻⁴ or 6.67 × 10⁻⁵ mol % of Ru, 1-octen-3-ol (0.2 M in THF; substrate/Ru/Cs₂CO₃ ratio: 1 000 000:1:2 or 1 500 000:1:2) can be quantitatively transformed into octan-3-one within 16 (TOF = 62 500 h⁻¹; entry 9 in Table 2) or 36 h (TOF = 41 666 h⁻¹; entry 10 in Table 2), leading to the highest turnover

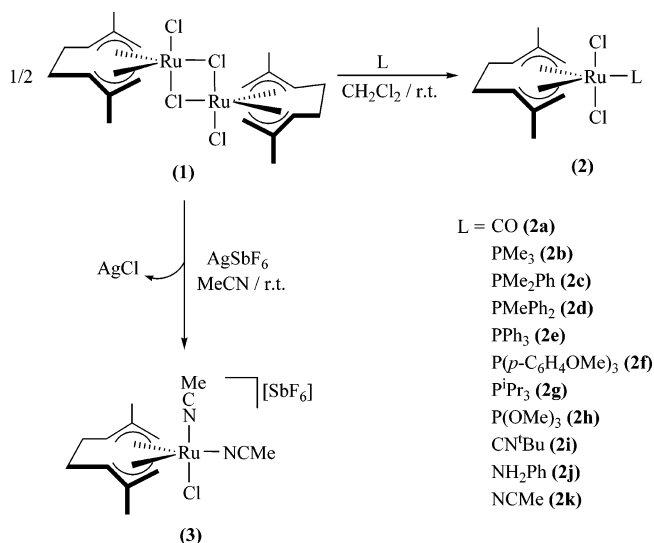
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- (31) TOF values of 285, 33, and 8 h⁻¹ have been previously reported for the isomerization of 1-octen-3-ol by using [RuCl₂(PPh₃)₃], [$\{\text{Ru}(\eta^6\text{-}p\text{-cymene})(\mu\text{-Cl})\text{Cl}\}_2$], and [Ru(η⁵-C₅H₅)Cl(PPh₃)₂], respectively, as catalysts and 3 equiv of K₂CO₃ as cocatalyst. See ref 30a.

Table 2. Ruthenium-Catalyzed Isomerization of 1-Octen-3-ol into Octan-3-one^a


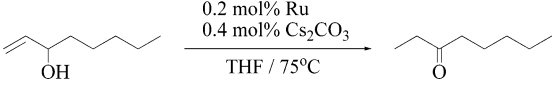
entry	catalyst	yield (%) ^b	time	TOF (h ⁻¹) ^c
1	[{Ru(η^3 : η^3 -C ₁₀ H ₁₆)(μ -Cl)Cl} ₂] (1)	100	10 min	3000
2	[{Ru(η^6 -C ₆ H ₆)(μ -Cl)Cl} ₂]	100	60 min	500
3	[{Ru(η^6 - <i>p</i> -cymene)(μ -Cl)Cl} ₂]	100	90 min	333
4	[{Ru(η^6 -C ₆ Me ₆)(μ -Cl)Cl} ₂]	100	4 h	125
5	[RuCl ₂ (PPh ₃) ₃]	92	22 h	21
6	[Ru(η^5 -C ₉ H ₇)Cl(PPh ₃) ₂]	38	22 h	9
7	[Ru(η^5 -C ₅ H ₅)Cl(PPh ₃) ₂]	1	22 h	<1
8	[Ru(η^3 : η^2 : η^3 -C ₁₂ H ₁₈)Cl ₂]	100	70 min	429
9 ^d	[{Ru(η^3 : η^3 -C ₁₀ H ₁₆)(μ -Cl)Cl} ₂] (1)	100	16 h	62 500
10 ^e	[{Ru(η^3 : η^3 -C ₁₀ H ₁₆)(μ -Cl)Cl} ₂] (1)	100	36 h	41 666

^a All of the reactions were performed under N₂ atmosphere at 75 °C using 4 mmol of 1-octen-3-ol (0.2 M in THF). Substrate/Ru/Cs₂CO₃ ratio: 500:1:2. ^b Yield of octan-3-one determined by GC. ^c Turnover frequencies ((mol product/mol Ru)/time) were calculated at the time indicated in each case. ^d Reaction performed with a substrate/Ru/Cs₂CO₃ ratio of 1 000 000:1:2. ^e Reaction performed with a substrate/Ru/Cs₂CO₃ ratio of 1 500 000:1:2.

Scheme 2. Synthesis of the Mononuclear Bis(allyl)-Ruthenium(IV) Complexes **2** and **3**

number values (TON = 10⁶ and 1.5 × 10⁶, respectively) reported to date for this catalytic transformation.^{6,32}

The catalytic activity of the dimeric complex **1** raised the question whether the active catalyst is a dinuclear or mononuclear species. In this respect, the catalytic activity of a series of mononuclear derivatives [Ru(η^3 : η^3 -C₁₀H₁₆)Cl₂(L)] (**2a–k**) and [Ru(η^3 : η^3 -C₁₀H₁₆)Cl(NCMe)₂][SbF₆] (**3**) (see Scheme 2), in the isomerization of 1-octen-3-ol into octan-3-one, was studied (results are summarized in Table 3).^{21,33} Although all of the complexes tested have been found to be active catalysts, longer reaction times are in general required to obtain the

Table 3. Isomerization of 1-Octen-3-ol into Octan-3-one Catalyzed by Mononuclear (2,7-Dimethylocta-2,6-diene-1,8-diyl)-Ruthenium(IV) Complexes^a


entry	catalyst	yield (%) ^b	time	TOF (h ⁻¹) ^c
1	[Ru(η^3 : η^3 -C ₁₀ H ₁₆)Cl ₂ (CO)] (2a)	100	85 min	353
2	[Ru(η^3 : η^3 -C ₁₀ H ₁₆)Cl ₂ (PMe ₃)] (2b)	100	29 h	17
3	[Ru(η^3 : η^3 -C ₁₀ H ₁₆)Cl ₂ (PMe ₂ Ph)] (2c)	100	29 h	17
4	[Ru(η^3 : η^3 -C ₁₀ H ₁₆)Cl ₂ (PMePh ₂)] (2d)	100	8.5 h	59
5	[Ru(η^3 : η^3 -C ₁₀ H ₁₆)Cl ₂ (PPh ₃)] (2e)	100	7.5 h	67
6	[Ru(η^3 : η^3 -C ₁₀ H ₁₆)Cl ₂ {P(<i>p</i> -C ₆ H ₄ OMe) ₃ }] (2f)	100	6.5 h	77
7	[Ru(η^3 : η^3 -C ₁₀ H ₁₆)Cl ₂ (P ^{<i>i</i>} Pr ₃)] (2g)	100	40 min	750
8	[Ru(η^3 : η^3 -C ₁₀ H ₁₆)Cl ₂ {P(OMe) ₃ }] (2h)	100	90 min	333
9	[Ru(η^3 : η^3 -C ₁₀ H ₁₆)Cl ₂ (CN ^{<i>t</i>} Bu)] (2i)	100	4 h	125
10	[Ru(η^3 : η^3 -C ₁₀ H ₁₆)Cl ₂ (NH ₂ Ph)] (2j)	100	60 min	500
11	[Ru(η^3 : η^3 -C ₁₀ H ₁₆)Cl ₂ (NCMe)] (2k)	100	12 min	2500
12	[Ru(η^3 : η^3 -C ₁₀ H ₁₆)Cl(NCMe) ₂][SbF ₆] (3)	100	12 min	2500

^a All of the reactions were performed under N₂ atmosphere at 75 °C using 4 mmol of 1-octen-3-ol (0.2 M in THF). Substrate/Ru/Cs₂CO₃ ratio: 500:1:2. ^b Yield of octan-3-one determined by GC. ^c Turnover frequencies ((mol product/mol Ru)/time) were calculated at the time indicated in each case.

saturated ketone in quantitative yield when compared to dimer **1** (see entries 1–10; TOF = 17–750 h⁻¹ to be compared to 3000 h⁻¹ using **1**). Only complexes [Ru(η^3 : η^3 -C₁₀H₁₆)Cl₂(NCMe)] (**2k**) and [Ru(η^3 : η^3 -C₁₀H₁₆)Cl(NCMe)₂][SbF₆] (**3**), containing labile acetonitrile ligands, have shown a catalytic performance comparable to that of **1** (entries 11 and 12; TOF = 2500 h⁻¹). This seems to indicate that dimer **1** acts as a catalyst precursor of an active mononuclear species “[Ru(η^3 : η^3 -C₁₀H₁₆)Cl]”.

Catalytic Isomerization of Allylic Alcohols into Carbonyl Compounds in Water. Several bis(allyl)-ruthenium(IV) complexes derived from **1** are prone to coordinate water, and some of them show a significant solubility in aqueous media (e.g., [Ru(η^3 : η^3 -C₁₀H₁₆)(H₂O)(κ^2 -*O*,*O*-CH₃CO₂)] [BF₄], [Ru(η^3 : η^3 -C₁₀H₁₆)(H₂O)(κ^1 -*O*-CF₃SO₃)₂] [BF₄], or [Ru(η^3 : η^3 -C₁₀H₁₆)(κ^3 -*N,N,N*-terpy)] [BF₄]₂ (terpy = 2,2':6',2''-terpyridine) among others).³⁴ Although the hydrolytic sensitivity of metal–carbon bonds has been a major drawback of organometallic chemistry, the remarkable stability of these species toward water is explained on the basis of the high electronegativity of ruthenium in the +4 oxidation state. This fact confers a greater covalency to the resulting metal–carbon bonds, which consequently become quite resistant to hydrolytic conditions.³⁵

(32) (a) TON values up to 3000 (TOF up to 36 000 h⁻¹) have been reported for the isomerization of 2-propen-1-ol into propionaldehyde using complexes [Ru(η^5 -C₅H₅)(PR₃)(NCMe)₂][PF₆] (PR₃ = PPh₃, PCy₃) as catalysts: Slugovc, C.; Růba, E.; Schmid, R.; Kirchner, K. *Organometallics* **1999**, *18*, 4230–4233. (b) TON values up to 6000 have also been reported for the isomerization of 3-buten-2-ol into butan-2-one using complex [Ru(η^5 -C₅H₅)Cl(PPh₃)₂] as catalyst and AgOTf (silver *p*-toluenesulfonate) as cocatalyst (a TOF value > 200 000 h⁻¹ has been claimed): see ref 16c. (c) We have reported TON values up to 10⁶ (TOF up to 55 000 h⁻¹) for the isomerization of 1-octen-3-ol into octan-3-one using complex [Ru(η^3 : η^2 : η^3 -C₁₂H₁₈)Cl₂] as catalyst and Cs₂CO₃ as cocatalyst: see ref 13.

(33) The coordination chemistry of the dimeric Ru(IV) complex [{Ru(η^3 : η^3 -C₁₀H₁₆)(μ -Cl)Cl}₂] (**1**), although much less developed, is clearly related to that of the classical arene–Ru(II) dimers [{Ru(η^6 -arene)(μ -Cl)Cl}₂], allowing the preparation of mononuclear adducts via chloride bridges cleavage and abstraction. For a review on the chemistry of **1**, see: (a) Cadierno, V.; Crochet, P.; García-Garrido, S. E.; Gimeno, J. *Curr. Org. Chem.* **2006**, *10*, 165–183. For reviews on the chemistry of [{Ru(η^6 -arene)(μ -Cl)Cl}₂] dimers, see: (b) Le Bozec, H.; Touchard, D.; Dixneuf, P. H. *Adv. Organomet. Chem.* **1989**, *29*, 163–247. (c) Bennett, M. A. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, 1995; Vol. 7, pp 549–602. (d) Bennett, M. A. *Coord. Chem. Rev.* **1997**, *166*, 225–254. (e) Pigge, F. C.; Coniglio, J. J. *Curr. Org. Chem.* **2001**, *5*, 757–784.

(34) See, for example: (a) Sommerer, S. O.; Palenik, G. J. *Organometallics* **1991**, *10*, 1223–1224. (b) Steed, J. W.; Tocher, D. A. *Polyhedron* **1992**, *11*, 2729–2737. (c) Kavanagh, B.; Steed, J. W.; Tocher, D. A. *J. Chem. Soc., Dalton Trans.* **1993**, 327–335. (d) Belchem, G.; Schreiber, D. H. A.; Steed, J. W.; Tocher, D. A. *Inorg. Chim. Acta* **1994**, *218*, 81–87. (e) Wache, S. J. *Organomet. Chem.* **1995**, *494*, 235–240.

(35) The application of high oxidation state organometallic derivatives in aqueous catalysis has been recently highlighted: Poli, R. *Chem.-Eur. J.* **2004**, *10*, 332–341 and references therein.

Table 4. Isomerization of Various Allylic Alcohols Catalyzed by the Bis(allyl)–Ruthenium(IV) Complex **1** in THF and Water^a

Entry	Substrate	Product	Catalyst concentration	THF Yield ^b /time/TOF ^c	THF/Cs ₂ CO ₃ Yield ^b /time/TOF ^c	H ₂ O Yield ^b /time/TOF ^c	H ₂ O/Cs ₂ CO ₃ Yield ^b /time/TOF ^c
1			0.2 mol% Ru	96/24 h/20	100/10 min/3000	100/40 min/750	100/15 min/2000
2			0.2 mol% Ru	97/24 h/20	100/15 min/2000	100/15 min/2000	100/15 min/2000
3			0.2 mol% Ru	82/24 h/17	100/20 min/1500	100/10 min/3000	100/15 min/2000
4			0.2 mol% Ru	73/24 h/15	100/50 min/600	100/15 min/2000	100/15 min/2000
5			0.2 mol% Ru	100/14 h/36	100/84 min/357	100/20 min/1500	100/20 min/1500
6			1 mol% Ru	69/24 h/3	100/60 min/100	100/20 min/300	100/20 min/300
7			5 mol% Ru	76/24 h/<1	100/2 h/10	100/60 min/20	100/15 min/80
8			5 mol% Ru	7/24 h/<1	100/6 h/3	92/24 h/<1	100/3 h/7
9			5 mol% Ru	47/24 h/<1	100/4.5 h/4	100/60 min/20	100/60 min/20
10			10 mol% Ru	44/24 h/<1	100/5 h/2	100/2.5 h/4	100/90 min/7
11			10 mol% Ru	23/24 h/<1	100/3.5 h/3	100/3 h/3	100/2.5 h/4
12			10 mol% Ru	8/40 h/<1	47/40 h/<1	57/40 h/<1	71/40 h/<1 ^d
13			10 mol% Ru	1/40 h/<1	7/40 h/<1	18/40 h/<1	32/40 h/<1 ^e

^a All of the reactions were performed under N₂ atmosphere at 75 °C using 4 mmol of the corresponding allylic alcohol (0.2 M in THF or H₂O). When Cs₂CO₃ was used as cocatalyst, it was added in a 2:1 molar ratio with respect to Ru. ^b Yield of the corresponding aldehyde or ketone determined by GC. ^c Turnover frequencies ((mol product/mol Ru)/time) were calculated at the time indicated in each case. ^d 91% yield after 31 h if the reaction is performed at 90 °C. ^e 89% yield after 40 h if the reaction is performed at 90 °C.

Taking advantage of this property, we decided to study the isomerization of 1-octen-3-ol catalyzed by complex **1** in aqueous medium. Remarkably, the reaction proceeds at higher rates than those observed in THF either in the presence or in the absence of Cs₂CO₃. For instance, in the absence of Cs₂CO₃, octan-3-one was quantitatively obtained in only 40 min versus 96% yield after 24 h in THF (see entry 1 in Table 4). These observations seem to suggest that the higher polarity of water versus THF favors the dissociation of the chloride ligands in complex **1** as well as the deprotonation of the alcohol to form the corresponding oxo-allyl anion (see the theoretical analysis section). Noteworthy, the reaction profile of this isomerization process is characterized by an induction period of several minutes (see Figure 2), indicating the slow formation of the real active species in the catalytic cycle.³⁶ Moreover, deactivation of the active species does not occur after total consumption of the allylic alcohol. Thus, after a regular catalytic test, no induction period was observed upon addition of a second charge of substrate (Figure 2).

Catalyst **1** is also very efficient in the isomerization of a variety of allylic alcohols, proving the wide scope of this catalytic transformation (results are summarized in Table 4). As a general trend, the isomerization process was found to take place faster in water than in THF (see columns 7 and 8 vs 5 and 6, respectively), and, for most of the substrates tested, a quantitative formation of the saturated carbonyl compound is achieved without Cs₂CO₃ (see column 7 in Table 4). As far as

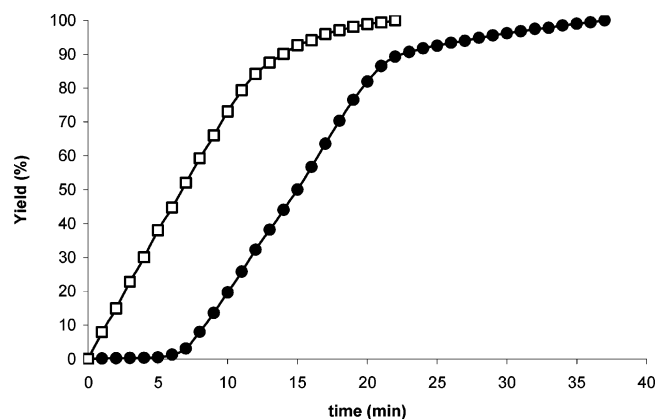


Figure 2. Isomerization of 1-octen-3-ol into octan-3-one catalyzed by complex **1** in water and in the absence of Cs₂CO₃ (reaction performed under N₂ atmosphere at 75 °C using 4 mmol of 1-octen-3-ol (0.2 M in H₂O)). Yield of octan-3-one as a function of time (●, first charge; □, second charge).

the allylic alcohols are concerned, there is a strong dependence upon the substitution of the carbon–carbon double bond as previously observed with other catalytic systems.³⁷ Thus, the monosubstituted alcohols 1-octen-3-ol, 1-hepten-3-ol, 1-hexen-3-ol, 1-penten-3-ol, and 3-buten-2-ol (see entries 1–5) are readily isomerized in aqueous medium using a ruthenium charge of 0.2 mol %, leading to TOF values of 750–3000 h^{−1} without Cs₂CO₃ or 1500–2000 h^{−1} with Cs₂CO₃. Efficient transforma-

(36) Induction periods have been systematically observed in all catalytic reactions regardless of the solvent (THF or water) or the presence of cocatalysts.

(37) It is well known that the isomerization of allylic alcohols becomes more difficult as the number of substituents increases on the C=C double bond. See ref 6.

tion of allyl alcohol into propanal has also been observed using 1 mol % of Ru (entry 6; TOF = 300 h⁻¹ in water).³⁸ The high catalytic activity of complex **1** at a lower loading (10⁻⁴ mol % of Ru) has also been confirmed for the isomerization of 3-buten-2-ol into butan-2-one in water and in the absence of Cs₂CO₃ (100% yield in 24 h, TON = 10⁶, TOF = 41 667 h⁻¹). In contrast, when 1,1- and 1,2-disubstituted allylic alcohols are used, longer reaction times and higher Ru loadings (5–10 mol %) are required to achieve total conversions (entries 8–12; TOF = 1–20 h⁻¹ in water). In the case of trisubstituted allylic alcohols such as 3-methyl-2-buten-1-ol (entry 13), complex **1** was found to be almost inactive at 75 °C. Thus, after 40 h, only 32% yield of 3-methyl-butylaldehyde could be obtained using **1** (10 mol % of Ru) in water and in the presence of Cs₂CO₃. Nevertheless, with the reactions performed at a higher temperature (90 °C), 3-methyl-butylaldehyde could be obtained in 89% yield after 40 h.³⁹

In contrast to almost all known catalysts for allylic alcohols isomerization, which fail in the presence of conjugated dienes,¹⁵ catalyst **1** remains active in the presence of isoprene. As an example, in the presence of 15 mmol of isoprene, 4 mmol of 1-octen-3-ol (0.2 M in water) can be quantitatively isomerized into octan-3-one within 170 min using 0.1 mol % of **1** (0.2 mol % of Ru; without Cs₂CO₃; TOF = 176 h⁻¹ to be compared to entry 1 in Table 4).⁴⁰ Nevertheless, it should be noted that the isoprene poisoning observed for dimer **1** is much more severe than that previously observed by us for the mononuclear bis-(allyl)-ruthenium(IV) complex [Ru(η³:η²:η³-C₁₂H₁₈)Cl₂] (C₁₂H₁₈ = dodeca-2,6,10-triene-1,12-diyl).¹³ Two major deactivation routes have been proposed: (i) the preferential coordination of the diene versus the substrate, and (ii) the formation of stable π-allyl complexes after reaction of the diene with metal-hydride intermediates.^{11,15} Apparently, coordination of isoprene to the Ru(IV) unit [Ru(η³:η³-C₁₀H₁₆)Cl₂], via chloride bridges cleavage in dimer **1**, seems to be favored versus isoprene coordination to [Ru(η³:η³-C₁₂H₁₈)Cl₂], via displacement of the olefinic C=C bond of the dodeca-2,6,10-triene-1,12-diyl chain in the mononuclear complex [Ru(η³:η²:η³-C₁₂H₁₈)Cl₂].

We also note that catalyst **1** can be recycled at least three or four times after the isomerization of 3-buten-2-ol, 1-penten-3-ol, and 1-hexen-3-ol (0.2 M in water; 0.2 mol % of Ru and 0.4 mol % of Cs₂CO₃) into the corresponding ketones, which can be easily separated from the aqueous solution by fractional distillation (see Table 5). This feature, along with the activity observed in the presence of isoprene, is an additional proof of the utility of these catalysts, which show an unprecedented performance for the catalytic isomerization of allylic alcohols in water. Moreover, because all of these isomerization reactions

Table 5. Isomerization of Allylic Alcohols Catalyzed by Complex **1**: Catalyst Recycling^a

entry	substrate	cycle	yield (%) ^b	time	TOF (h ⁻¹) ^c	TON ^d	
1	<i>n</i> = 0	1	100	20 min	1500	500	
		2	100	20 min	1500	1000	
		3	100	35 min	857	1500	
		4	18	24 h	4	1590	
2	<i>n</i> = 1	1	100	15 min	2000	500	
		2	100	25 min	1200	1000	
		3	100	2.5 h	200	1500	
		4	15	24 h	3	1575	
3	<i>n</i> = 2	1	100	15 min	2000	500	
		2	100	20 min	1500	1000	
		3	100	25 min	1200	1500	
		4	100	50 min	600	2000	
		5	7	24 h	1	2035	

^a All of the reactions were performed under N₂ atmosphere at 75 °C using 4 mmol of the corresponding allylic alcohol (0.2 M in water). Substrate/Ru/Cs₂CO₃ ratio: 500:1:2. ^b Yield of the corresponding ketone determined by GC. ^c Turnover frequencies ((mol product/mol Ru)/time) were calculated at the time indicated in each case. ^d Cumulative TON values.

can be performed in a preparative scale (a representative example is shown in the Experimental Section), the basic research presented here is believed to be of interest to synthetic chemists and to find wide applications in different synthetic programs soon.

Mechanistic Aspects. From a mechanistic point of view, the catalytic isomerization of allylic alcohols is based on the well-known ability of transition-metal complexes to migrate carbon-carbon double bonds.⁴¹ Thus, in the case of allylic alcohols, such a migration generates an enol intermediate, which readily tautomerizes into the thermodynamically more stable carbonyl compound. Over the years, two different mechanisms have been proposed for this isomerization reaction (**A** and **B** in Scheme 3).⁶

(i) The Alkyl Mechanism. In this case, the catalyst is a metal-hydride complex that can be either isolated or generated in situ. The first step in the catalytic cycle involves the π-coordination of the allylic alcohol to the metal through the C=C bond. Subsequent insertion of the alkene moiety into the M-H bond generates metal-alkyl species, which evolve, via β-hydrogen elimination, into the corresponding η²-enol complex. In the final step, the decomplexation of the enol regenerates the starting metal-hydride catalyst. Significantly, in this mechanism, an intermolecular hydrogen transfer takes place. R. H. Grubbs and co-workers have demonstrated, using labeled compounds, that this mechanism is operative when [Ru(H₂O)₆]-[Tos]₂ is used as precatalyst.^{9c}

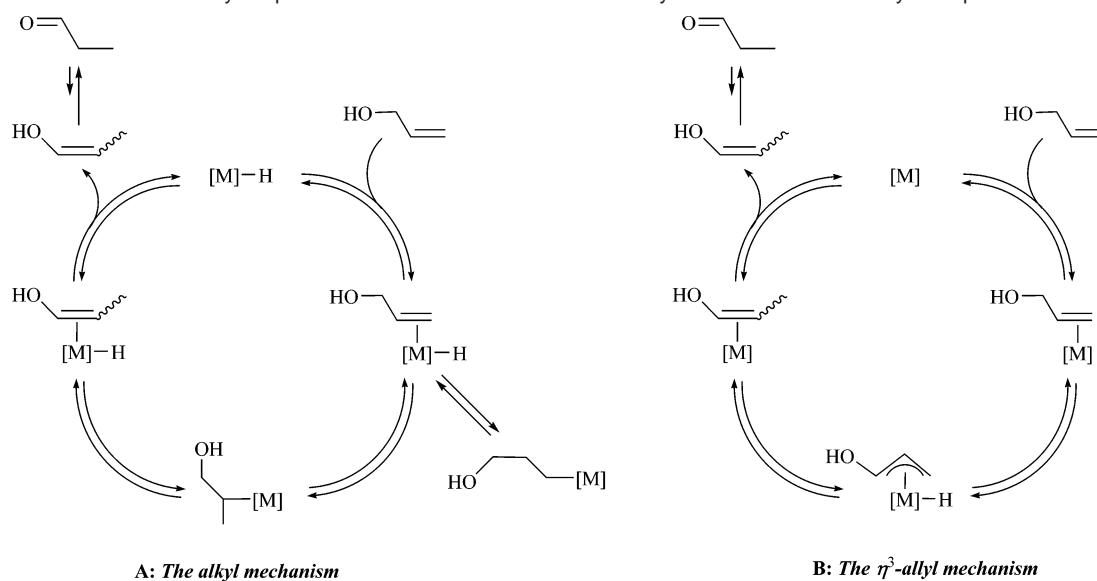
(ii) The η³-Allyl Mechanism. The catalytic cycle starts again with the π-coordination of the alkene moiety to an unsaturated metal fragment that does not contain a M-H bond. Formal oxidative addition of one of the C-H single bonds of the alkene generates a π-allyl metal-hydride intermediate, which evolves, by reductive elimination, into the corresponding η²-enol complex. As in the previous mechanism, decoordination regenerates

(38) In contrast, due probably to steric reasons, the isomerization of 1-phenyl-2-propen-1-ol requires at least 5 mol % of Ru to achieve 100% conversion in reasonable reaction times (TOF values up to 80 h⁻¹; see entry 7 in Table 4).

(39) A systematic study on the influence of the temperature (from 40 to 100 °C) on the catalytic activity of complex **1** has been carried out using the isomerization of 1-octen-3-ol into octan-3-one as model reaction (0.2 M in water; 0.2 mol % of Ru; without Cs₂CO₃). Selected results are as follows: *T* = 60 °C, 88% yield after 24 h (TOF = 18 h⁻¹); *T* = 70 °C, 100% yield after 1.5 h (TOF = 333 h⁻¹); *T* = 80 °C, 100% yield after 20 min (TOF = 1500 h⁻¹); *T* = 90 °C, 100% yield after 10 min (TOF = 3000 h⁻¹); *T* = 100 °C, 100% yield after 7 min (TOF = 4286 h⁻¹). Very low conversions (<27%) were observed after 24 h when *T* < 60 °C.

(40) Isoprene resistance was also observed in THF solution. Thus, in the presence of 15 mmol of isoprene, 4 mmol of 1-octen-3-ol (0.2 M in THF) can be quantitatively isomerized into octan-3-one within 50 min using 0.1 mol % of **1** and 0.4 mol % of Cs₂CO₃ (TOF = 600 h⁻¹ to be compared to entry 1 in Table 4).

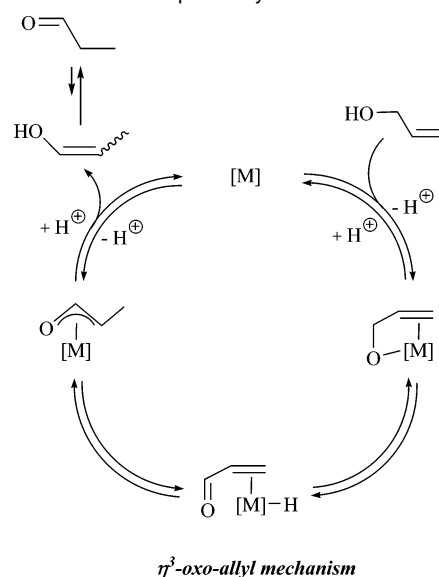
(41) (a) Masters, C. *Homogeneous Transition-Metal Catalysis*; Chapman and Hall: London, 1981; pp 70–89. (b) Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis*; John Wiley & Sons: New York, 1992; pp 9–24. (c) Herrmann, W. A. In *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornils, B., Herrmann, W. A., Eds.; VCH: Weinheim, 1996; Vol. 2, pp 980–991.

Scheme 3. Mechanisms Commonly Proposed for the Redox Isomerization of Allylic Alcohols into Carbonyl Compounds

the catalyst and gives the free enol, which tautomerizes into the corresponding carbonyl. In this case, an intramolecular hydrogen transfer is involved. Because the oxidation state of the metal has to be raised by two, this mechanism has been usually proposed for low-valent transition-metal catalysts.⁶ In particular, Branchadell and Grée have recently demonstrated by means of DFT calculations that such a mechanism is operative in the conversion of allylic alcohols to carbonyl compounds catalyzed by the $\text{Fe}(\text{CO})_3$ unit.⁴²

The two pathways described above, which have been well established for the metal-catalyzed isomerization of unfunctionalized olefins, do not assign a specific role to the oxygen atom of the allylic alcohols during the catalytic cycle. Moreover, they cannot explain why some catalysts isomerize allylic alcohols faster than unfunctionalized alkenes,¹⁶ or even exclusively.^{11,12} To account for these facts, a third mechanism, invoking coordination of the oxygen atom to the metal,⁴³ has been recently proposed by Trost and Kulawiec for the isomerization of allylic alcohols catalyzed by $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{PPh}_3)_2]$ (the η^3 -oxo-allyl mechanism; see Scheme 4).^{16b}

The first step in the catalytic cycle involves deprotonation of the allylic alcohol and chelate coordination of the resulting α,β -unsaturated alkoxide to the metal. Subsequent β -hydrogen elimination yields an enone–metal–hydride species, which, after re-addition of the hydride ligand to the substrate, generates a π -oxo-allyl complex. Final protonation releases the enol and regenerates the starting complex. The initial formation of the α,β -unsaturated alkoxide is in agreement with the improvement of the catalytic activity usually observed in the presence of bases.³⁰ Experimental evidence, using deuterium-labeled substrates, suggests that several half-sandwich ruthenium(II) cata-

Scheme 4. Mechanism Proposed by B. M. Trost

lysts operate through this mechanism.^{15,16,32a,44} In our case, the rate enhancement observed in the catalytic activity of complex **1** upon addition of Cs_2CO_3 as cocatalyst, along with the fact that this complex is inactive in the isomerization of simple olefins such as 1-hexene or 1-dodecene, seems to suggest that a π -oxo-allyl type mechanism (Scheme 4) operates. In the next section, we will present a theoretical analysis on such a mechanism.

Theoretical Analysis of the Isomerization of 2-Propen-1-ol into Propenal. In the following theoretical analysis, we will focus on the mononuclear alkoxo- π -olefin complex **4** (Figure 3), analogous to the Ru(II) species proposed in Trost's mechanism (Scheme 4), that according to our experimental results can be proposed as the catalytic active species. We have introduced minimal modelization substituting the methyl groups of the 2,7-dimethylocta-2,6-diene-1,8-diyl ligand in **4** by hydrogens.

(42) Branchadell, V.; Crévisy, C.; Grée, R. *Chem.-Eur. J.* **2003**, *9*, 2062–2067.

(43) In this context, Noyori and co-workers have demonstrated that isomerization of allylic amines catalyzed by complexes $[\text{Rh}(\text{BINAP})\text{L}_2][\text{ClO}_4]$ (BINAP = 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl; L = acetone, methanol, amines, etc.) involves the initial coordination of nitrogen to Rh. This was confirmed by trapping intermediates, variable-temperature NMR experiments, and ab initio calculations. (a) Tani, K. *Pure Appl. Chem.* **1985**, *57*, 1845–1854. (b) Inoue, S.; Takaya, H.; Tani, K.; Otsuka, S.; Sato, T.; Noyori, R. *J. Am. Chem. Soc.* **1990**, *112*, 4897–4905. (c) Yamakawa, M.; Noyori, R. *Organometallics* **1992**, *11*, 3167–3169. (d) For a review on catalytic isomerization of allylamines, see: Otsuka, S. *Acta Chem. Scand.* **1996**, *50*, 353–360.

(44) (a) van der Drift, R. C.; Bouwman, E.; Drent, E.; Kooijman, H.; Spek, A. L.; van Oort, A. B.; Mul, W. P. *Organometallics* **2002**, *21*, 3401–3407. (b) Standfest-Hauser, C. M.; Lummerstorfer, T.; Schmid, R.; Kirchner, K.; Hoffmann, H.; Puchberger, M. *Monatsh. Chem.* **2003**, *134*, 1167–1175.

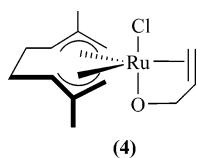
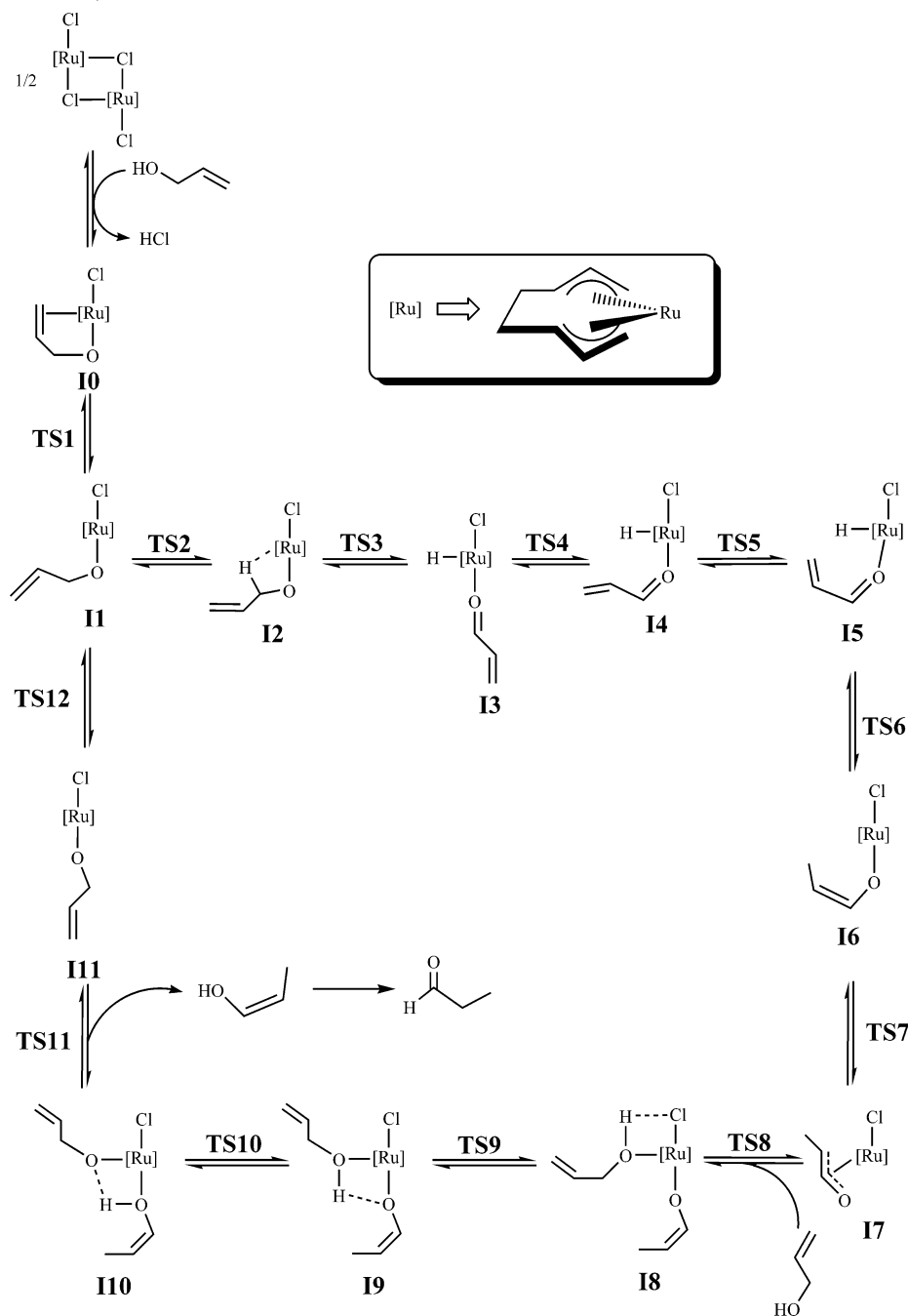


Figure 3. The proposed active species in the isomerization of 2-propen-1-ol into propanal catalyzed by complex **1**.

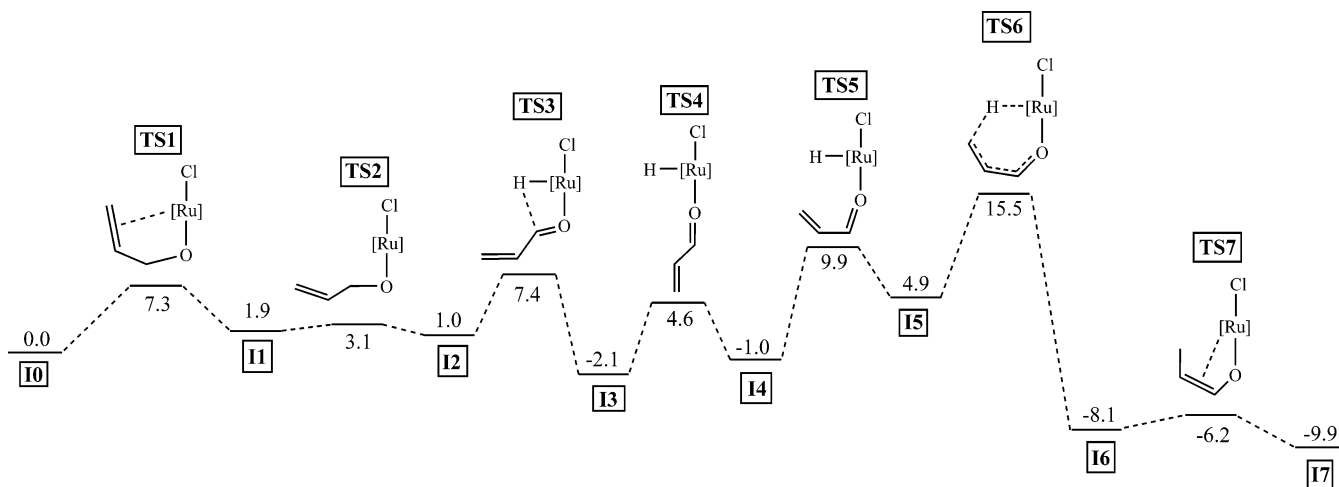
To keep the computational cost of the present work within reasonable limits, we have not considered mechanisms involving protonations, and, therefore, the results of our theoretical analysis should apply to the experimental observations in basic media. On the other hand, we focused on a general mechanism valid for the two solvents experimentally employed (water and THF) without explicit participation of individual solvent molecules

Scheme 5. The Complete Catalytic Cycle for the Isomerization of 2-Propen-1-ol into Propanal (For a Detailed Drawing of All Structures, See the Supporting Information)

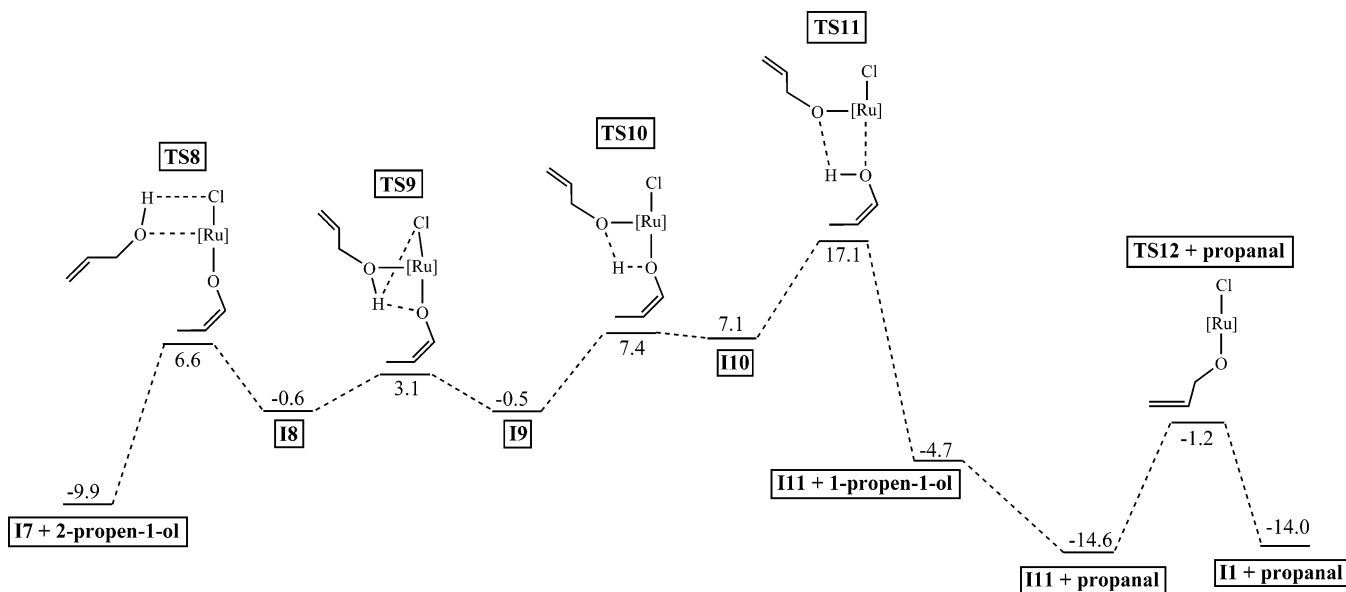


on the reaction coordinate. A schematic and complete catalytic cycle is shown in Scheme 5. The energy profile is collected in Schemes 6 and 7, and the geometrical parameters for all of the structures are provided as Supporting Information (Figure S1; information about the relative Gibbs free energies for all of the structures on the PESs is collected in Table S5).

Scheme 6 shows that the alkoxo- π -olefin complex **10** evolves into the 16-electron alkoxo intermediate **11** through the transition structure **TS1** involving a moderate energy barrier. An alternative route proposed by Trost and Kulawiec^{16b} for Ru(II) complexes (see Scheme 4) in which the oxygen atom of the hydroxyl group decoordinates from ruthenium at the same time that the allylic hydrogen migrates to form the ruthenium hydride bond was less favorable energetically.⁴⁵ Apparently, the oxygen

Scheme 6. Energy Profile for the First Part of the Catalytic Cycle (For a Detailed Drawing of All Structures, See the Supporting Information)^a

^a ΔG values (kcal/mol) including solvation (H_2O) effects are given. A temperature of 348.15 K and a pressure of 1 atm were assumed.

Scheme 7. Energy Profile for the Second Part of the Catalytic Cycle (For a Detailed Drawing of All Structures, See the Supporting Information)^a

^a ΔG values (kcal/mol) including solvation (H_2O) effects are given. A temperature of 348.15 K and a pressure of 1 atm were assumed.

atom is more strongly coordinated to the electrophilic Ru(IV) center than in the case of Trost–Kulawiec’s Ru(II) complexes, the Ru–O bond cleavage requiring therefore more energy.

After a β -elimination process, involving the intermediate **I2** and transition structures **TS2** and **TS3**, the enal-hydride **I3** is formed. Suitable rotations (**I3** \rightarrow **I5**) of the *O*-coordinated enal ligand, to allow the insertion of the olefinic moiety into the Ru–H bond, generate the enolate intermediate **I6**. Finally, transition structure **TS7** leads to the $\eta^3(O,C,C)$ -oxo-allyl intermediate **I7**. All of these transformations involve rather small energy barriers (see Scheme 6). The experimental observation that the catalyst is inactive in the isomerization of single olefins strongly supports the formation of this η^3 -oxo-allyl complex, in agreement with the mechanism proposed by Trost and Kulawiec (Scheme 4).^{16b}

Direct addition of 2-propen-1-ol to **I7**, leading to the intermediate **I8**, takes place through a transition structure **TS8** with a moderate energy barrier of 16.5 kcal/mol (see Scheme 7). The following steps in the cycle, involving intermediates **I8**–**I11**, which are formed through relatively moderate energy barriers (**TS9**, **TS10**, and **TS11**), account for the formal exchange of the coordinated enolate ligand in **I8** by the incoming 2-propen-1-ol (Scheme 7). Dissociation of the enol ligand in **I10**, through the transition structure **TS11**, leads to the 16-electron alkoxo complex **I11**. A suitable rotation involving **TS12** gives rise to the intermediate **I1**, closing the catalytic cycle (see Scheme 5). The formed enol spontaneously tautomerizes into the more stable propanal, which is the desired final product of the studied process.

Our experimental results show that the formation of carbonyl compounds from allylic alcohols, catalyzed by the bis(allyl)–ruthenium(IV) complexes, takes place only by increasing the

(45) An anonymous referee contributed in a decisive manner to elucidate this important point.

temperature ($T > 60^\circ$) as mentioned above.³⁹ The DFT calculations suggest that the **I7** \rightarrow **III** transformation in Scheme 7, involving a global energy barrier of 27 kcal/mol, is responsible for the required activation.⁴⁶ The ΔG free energy of the whole cycle is -15.9 kcal/mol. Therefore, it is clearly an exergonic cycle, in full agreement with the high yields experimentally observed for the isomerization reaction of allyl alcohols into carbonyl compounds catalyzed by the bis(allyl)-ruthenium(IV) complex [$\{\text{Ru}(\eta^3\text{-}\eta^3\text{-C}_{10}\text{H}_{16})(\mu\text{-Cl})\text{Cl}_2\}$] (**1**) (see Table 4).

Conclusions

In this work, we have shown that the air-stable bis(allyl) ruthenium(IV) dimer [$\{\text{Ru}(\eta^3\text{-}\eta^3\text{-C}_{10}\text{H}_{16})(\mu\text{-Cl})\text{Cl}_2\}$] (**1**) as well as its mononuclear derivatives [$\text{Ru}(\eta^3\text{-}\eta^3\text{-C}_{10}\text{H}_{16})\text{Cl}_2(\text{L})$] ($\text{L} = \text{CO}, \text{PR}_3, \text{CNR}, \text{NCR}$) (**2**) and [$\text{Ru}(\eta^3\text{-}\eta^3\text{-C}_{10}\text{H}_{16})\text{Cl}(\text{NCMe})_2$]-[SbF_6] (**3**) are highly efficient catalysts for the redox isomerization of allylic alcohols into carbonyl compounds. In particular, complex **1** has been found to be the most efficient catalyst reported to date for this isomerization reaction (TOF and TON values up to $62\,500\text{ h}^{-1}$ and $1\,500\,000$, respectively). Moreover, the transformation can be performed in water, and the catalyst can be recycled up to four times with only partial deactivation.

The potential energy surfaces corresponding to the catalytic cycle were explored. Our calculations support a variant of the mechanism proposed by Trost and Kulawiec for the catalytic isomerization of allylic alcohols into carbonyl compounds, based on alkoxo- π -olefin ruthenium complexes as the active species, in which the cleavage of the Ru(IV)-olefin versus Ru(IV)-O bond is preferred. According to the DFT calculations, the reaction steps involving the addition of a 2-propen-1-ol molecule

to the intermediate η^3 -oxo-allyl complex, and the subsequent dissociation of the formed enol ligand, lead to a global energy barrier (27 kcal/mol), which is consistent with the experimentally observed activation required for the studied reactions to proceed. Calculations also predict the whole catalytic cycle to be strongly exergonic (-15.9 kcal/mol), in full agreement with the high yields experimentally observed.

All of these theoretical and experimental facts together with the catalytic activity shown by the ruthenium(IV) catalyst in the presence of isoprene (in contrast to the loss of activity found with other catalysts) disclose a powerful tool for the synthesis of carbonyl compounds in an environment friendly manner. Because the synthesis of aldehydes and ketones using readily available dienes as raw materials, via a hydration/isomerization sequence, is nowadays an important goal,⁴⁷ the use of this catalytic process provides a valuable synthetic approach, which in addition can be performed in water.

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Supporting Information Available: Full ref 29 and Cartesian coordinates, energetic data (relative and absolute energies), and some representative geometrical parameters for all of the structures located at the PESs. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(46) A rough estimate of the half-life time based on the computed barrier height (using 1 M standard state) leads to a value close to 5 min, which extrapolates rather well to the experimental total reaction times reported in entry 6 in Table 4 (20–60 min). Cramer, C. J. *Essentials of Computational Chemistry. Theory and Models*; Wiley: New York, 2002.

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