Dehydrogenative Formation of a (η^4-Enone)ruthenium(0) Complex as a Key Intermediate in the Catalytic Isomerization of Allylic Alcohol to Ketone

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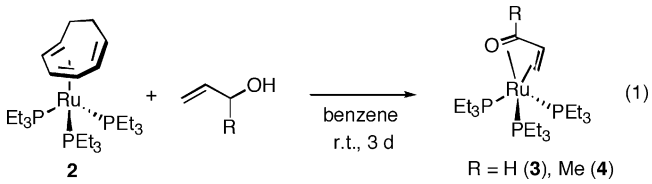
*Summary: (η^4-Enone)ruthenium(0) complexes, Ru[η^4-CH_2=CHC(R)=O](PEt_3)$_3$ (R = H (**3**), Me (**4**)), are prepared by the reactions of Ru(η^4-1,5-COD)(η^6-1,3,5-COT) (**1**)/PEt_3 and Ru(η^4-1,3,5-COT)(PEt_3)$_3$ (**2**) with allylic alcohols such as allyl alcohol and 3-buten-2-ol, respectively. Hydrogen transfer from external allyl alcohol to the coordinated η^4-3-buten-2-one ligand in **4** leads to the formation of 2-butanone and **3**, suggesting the importance of such a (η^4-enone)ruthenium complex in the ruthenium-catalyzed isomerization of allylic alcohol.*

Ruthenium-catalyzed isomerization of an allylic alcohol to a carbonyl compound is regarded as one of the most important and well-documented chemical transformations in organic synthesis.[1] Although the hydride addition−elimination process[2] and the hydrogen-abstraction process forming a η^3-allyl intermediate[3] are the most frequently encountered in the established mechanisms, an α,β-unsaturated enone-coordinated intermediate has also been proposed by Trost et al., since a small amount of enone is detected in some cases.[4] Bouwman[5] and Kirchner[6] also proposed a similar mechanism for ruthenium-catalyzed isomerization of allylic alcohol. However, the isolation or even observation of such intermediates has been lacking.

We have been studying the reactions of Ru(0) with ortho-substituted phenols and thiols, alcohols, and carboxylic acids in relation to C−H bond activation reactions promoted by a preformed ruthenium−chalcogen bond.[7] For example, reactions of Ru(η^4-1.5-COD)(η^6-1,3,5-COT) (**1**) with ortho-substituted phenols and thiols in the presence of trimethylphosphine caused dehydrogenative sp^3 C−H bond activation,[8] giving oxaruthenacycles.[7a,b] In these reactions, the unsaturated cyclic olefin ligands act as an effective hydrogen acceptor. We have now found the dehydrogenative formation of an (η^4-enone)ruthenium(0) complex as an key intermediate in the Ru-catalyzed isomerization of allyllic alcohol by the reaction of **1**/PEt_3 or Ru(η^4-1,3,5-COT)-(PEt_3)$_3$ (**2**)[9] with allylic alcohol.

Treatment of **2** with a stoichiometric amount of allyl alcohol in benzene gave (η^4-acrolein)tris(triethylphosphine)ruthenium(0) (**3**) quantitatively in 1 day at room temperature accompanied by concomitant formation of a mixture of 1,3- and 1,5-CODs (23% and 19% yields, respectively) with small amounts of cyclooctene (10%) and 1,3,5-COT (10%) (eq 1).[10] When **1** was used as the



(1)

starting complex in the presence of PEt_3 (3 equiv), the yield and formation rate significantly decreased (38% yield), probably due to the initial slow formation of **2** from **1** and concomitant side reactions. Reaction of 3-buten-2-ol also gave the analogous (η^4-3-buten-2-one)-ruthenium(0) complex **4** in 64% yield from **1**.[11] Complexes **3** and **4** were also prepared by the direct ligand exchange reaction of **2** or Ru(η^6-naphthalene)(η^4-1,5-COD) (**5**)/PEt_3 with acrolein and 3-buten-2-one, in 24% and 21% yields, respectively.

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(3) Casey, C. P.; Cyr, C. R. *J. Am. Chem. Soc.* **1973**, *95*, 2248.

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(5) ven der Drift, R. V.; Bouwman, E.; Drent, E. *J. Organomet. Chem.* **2002**, *650*, 1.

(6) Slugovc, C.; Rüba, E.; Schmid, R.; Kirchner, K. *Organometallics* **1999**, *18*, 4230.

(7) (a) Hirano, M.; Kurata, N.; Marumo, T.; Komiya, S. *Organometallics* **1998**, *17*, 501. (b) Hirano, M.; Kurata, N.; Komiya, S. *J. Organomet. Chem.* **2000**, *607*, 18. (c) Kanaya, S.; Komine, N.; Hirano, M.; Komiya, S. *Chem. Lett.* **2001**, 1284. (d) Komiya, S.; Hirano, M. *Dalton* **2003**, 1439.

(8) Abbreviations used in this text: COD = cyclooctadiene, C_8H_{12}; COT = cyclooctatriene, C_8H_{10}.

(9) Komiya, S.; Planas, J. G.; Onuki, K.; Lu, Z.; Hirano, M. *Organometallics* **2000**, *19*, 4051.

(10) **3**: ^{1}H NMR (300.4 Hz, C_6D_6) δ 0.77 (dt, J_{H-P} = 13.1 Hz, J_{H-H} = 7.6 Hz, 9H, PCH_2CH_3), 0.9 (m, CH_2=CH, obscured by signals due to PEt_3), 1.02 (dt, J_{H-P} = 12.5 Hz, J_{H-H} = 7.7 Hz, 9H, PCH_2CH_3), 1.17 (dt, J_{H-P} = 12.9 Hz, J_{H-H} = 7.6 Hz, 9H, PCH_2CH_3), 1.29 (m, 6H, PCH_2CH_3), 1.5 (m, CH_2=CH, obscured by signals due to PEt_3), 1.60 (m, 6H, PCH_2CH_3), 1.94 (m, 6H, PCH_2CH_3), 4.81 (brs, =CHCHO), 7.26 (brs, CHO); ^{13}C{^{1}H} NMR (75.5 Hz, C_6D_6) δ 9.1 (s, PCH_2CH_3), 9.2 (d, J_{C-P} = 3 Hz, PCH_2CH_3), 22.2 (dd, J_{C-P} = 16, 3 Hz, PCH_2CH_3), 24.1 (d, J_{C-P} = 16 Hz, PCH_2CH_3), 24.4 (dt, J_{C-P} = 22, 3 Hz, PCH_2CH_3), 26.2 (dt, J_{C-P} = 31, 4 Hz, CH_2=CH), 75.6 (s, =CHCHO), 115.0 (s, CO); ^{13}C NMR (75.5 Hz, C_6D_6) δ 9.1 (m, PCH_2CH_3), 9.2 (m, PCH_2CH_3), 22.2 (m, PCH_2CH_3), 24.1 (m, PCH_2CH_3), 24.4 (m, PCH_2CH_3), 26.2 (ddt, J_{C-H} = 145 Hz, J_{C-P} = 31, 4 Hz, CH_2=CH), 75.6 (dd, J_{C-H} = 161, 18 Hz, =CHCHO), 115.0 (d, J_{C-H} = 177 Hz, CHO). ^{31}P{^{1}H} NMR (121.6 Hz, C_6D_6): δ 19.5 (d, J = 33 Hz, 1P), 25.5 (d, J = 16 Hz, 1P), 44.0 (dd, J = 33, 16 Hz, 1P); HRMS (FAB; *m/z*) found 512.2007, calcd for $C_{21}H_{49}OP_3Ru$ 512.2040. Anal. Calcd for $C_{21}H_{49}OP_3Ru$: C, 49.30; H, 9.65. Found: C, 49.97; H, 10.24.

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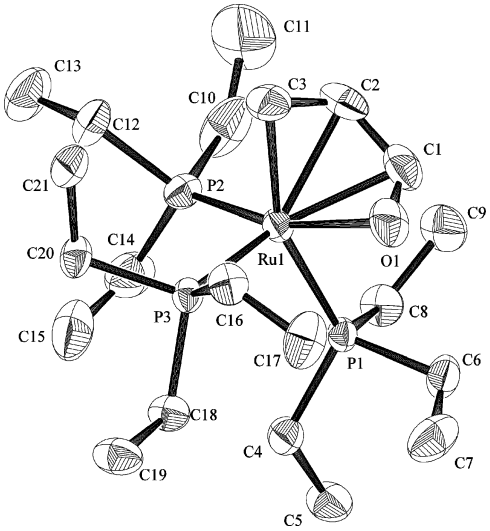
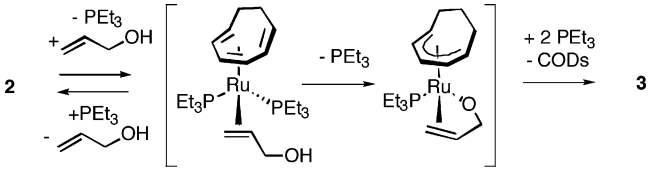


Figure 1. Molecular structure of **3**. All hydrogen atoms are omitted for clarity. Ellipsoids represent 50% probability.

Complex **3** was sufficiently soluble in pentane, and single crystals of **3** were grown from a cold pentane solution. An X-ray structure analysis of **3** unequivocally revealed the η^4 coordination of the acrolein molecule to ruthenium, as shown in Figure 1.[12] Long C(2)═C(3) (1.443(7) Å) and C(1)═O(1) (1.313(6) Å) bonds as well as a short C(1)−C(2) bond (1.389(7) Å) of the acrolein ligand suggest significant contribution of an oxaruthenacyclopentene structure in **3**, though all four atoms are located in the bonding distances to ruthenium (Figure 1). However, **3** is essentially considered as a five-coordinated complex of a highly distorted trigonal bipyramid consisting of two phosphorus and C═C double bonds in the equatorial plane and the other phosphorus and carbonyl ligands in apical positions, because C(3) is regarded as an sp^2-hybridized carbon from its J(C−H) value of 146 Hz. Thus, complex **3** is basically regarded as an enone-coordinated ruthenium(0) complex.[13] In the ^{1}H NMR of **3**, the formyl proton is found at δ 7.26 (br) and three vinylic protons at δ 4.81 (br), 1.6, and 0.9, where the last two signals are confirmed only by H−H COSY and C−H shift correlation spectra. All three triethylphosphine ligands are magnetically inequivalent, giving an AMX pattern in the ^{31}P{^{1}H} NMR spectrum, showing its rigid structure in solution. Although such stereochemical rigidity of the five-coordinate complex **3** is relatively rare, it can be understood by some contribution of an oxaruthenacyclopentene structure as discussed above.

The reaction is considered to start by an initial protonation of the COT ligand, giving an (allyloxo)(η^5-cyclooctadienyl)ruthenium(II) intermediate (Scheme 1).

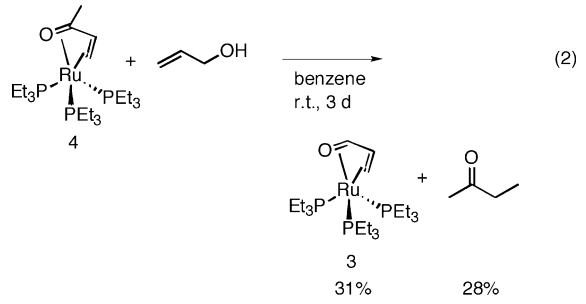
Scheme 1



This process seems to require the prerequisite coordination of allyl alcohol, since 1-propanol having pK_a values analogous to that of allyl alcohol showed no reactivity toward **2** at 70 °C at all (pK_a: allyl alcohol, 15.5; 1-propanol, 16.1). Then, the OH proton is trapped by the COT ligand to form an (allyloxo)(η^5-cyclooctadienyl)ruthenium(II) intermediate,[14] from which β-hydrogen elimination of the allyloxo ligand takes place followed by eventual liberation of 1,3- and 1,5-CODs, giving **3** or **4**. Although the present reaction mechanism essentially resembles the sp^3 C−H bond activation of 2,6-xylenol by **1** in the presence of a tertiary phosphine ligand to give an oxaruthenacycle,[7] the result suggests that prior coordination of an olefinic C═C double bond to Ru is indispensable for the reactions of less acidic aliphatic alcohols.

Catalytic isomerization of a secondary allylic alcohol to ketone proceeded smoothly in the presence of 5 mol % of **2** in benzene at 70 °C. For example, 3-buten-2-ol, 1-phenylallyl alcohol, and cyclohexenyl alcohol were isomerized to 2-butaone (59%), propionylbenzene (64%), and cyclohexanone (86%) in benzene in 2 h at 70 °C.

To further verify the isomerization mechanism via an (η^4-enone)ruthenium intermediate, the cross-reaction of the (η^4-3-buten-2-one)ruthenium(0) complex **4** with allyl alcohol was carried out in C_6D_6 at room temperature (eq 2). The coordinated 3-buten-2-one was in fact



hydrogenated to 2-butanone, giving the (η^4-acrolein)ruthenium complex **3**.[15] The result indicates that the coordinated η^4-enone is hydrogenated by the external allyl alcohol to give a saturated ketone with concomitant formation of the (η^4-acrolein)ruthenium(0) complex **3**. Therefore, the (η^4-enone)ruthenium complex is considered to be one of the important key intermediates in the ruthenium-catalyzed isomerization of allylic alcohol to ketone. However, no apparent reverse reaction of **3** with 3-buten-2-ol took place, probably due to higher thermodynamic stability of **3** as compared to that of **4**.

(11) **4**: this complex was characterized spectroscopically; ^{1}H NMR (300.4 Hz, C_6D_6) δ 0.59 (br q, CH_2═CH), 0.78−1.26 (m, PCH$_2$CH_3), 1.32 (m, PCH_2CH$_3$), 1.6 (m, CH_2═CH, obscured by signals due to PEt$_3$), 1.71 (m, PCH_2CH$_3$), 1.95 (qui, J = 7.1 Hz, PCH_2CH$_3$), 2.39 (d, J = 3.6 Hz, ═CHC(CH_3)O), 4.64 (brs, ═CHC(CH$_3$)O); ^{31}P{^{1}H} NMR (121.6 Hz, C_6D_6) δ 13.9 (dd, J = 32, 5 Hz, 1P), 25.3 (dd, J = 15, 4 Hz, 1P), 45.2 (dd, J = 32, 15 Hz, 1P).

(12) Crystal data for **3**: $C_{21}H_{49}OP_3Ru$, FW = 511.61, monoclinic, $P2_1/n$ (No. 14), a = 8.866(4) Å, b = 18.635(4) Å, c = 16.021(5) Å, β = 100.57(3)°, V = 2601(1) Å^3, Z = 4, D_{calcd} = 1.306 g/cm^3, R = 0.038, R_w = 0.052, 4094 unique reflections with $I > 3\sigma(I)$.

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(14) Analogous protonations to the η^6-cyclooctatriene ligand in **2** or **1** by phenol or 3-butenoic acid are known to give (η^5-cyclooctadienyl)ruthenium(II) complexes:[7] Osakada, K.; Grohmann, A.; Yamamoto, A. *Organometallics* **1990**, *9*, 2092.

(15) Reaction of **4** with allyl alcohol at room temperature for 3 days in C_6D_6 (%/**4**): **3** (31%), 2-butenone (28%).

Unfortunately, catalytic isomerization of primary allyl alcohols such as allyl alcohol, crotyl alcohol, prenyl alcohol, and 3-phenylallyl alcohol by **2** failed. In these reactions, facile decarbonylation of allylic alcohols by **2** took place to kill the catalytic activity. In fact, the IR spectrum of the recovered complex from the reaction of **2** with allyl alcohols shows strong ν(CO) bands at 1900 (vs), 1928 (sh), 1973 (s), and 2036 (s) cm^{-1} due to uncharacterized carbonyl complexes, and corresponding alkenes and alkanes were also detected in the gas phase.[16] Such decarbonylation reactions of saturated aldehydes are well-known processes in the Ru-catalyzed Tishchenko-type dimerization of saturated aldehydes.[17] The success of the catalytic isomerization of allylic alcohol to ketone but not to aldehyde may be due to the absence of a facile decarbonylation process of the product ketone. It is noted that inefficient but catalytic disproportionation to saturated alcohol and α,β-unsaturated aldehyde also occurred in these reactions, though the mechanism of this self-transfer hydrogenation process is not clear at present.

Heating of **3** in toluene at 80 °C caused liberation of ethylene in 67% yield over 7 h.[18] In this reaction, initial oxidative addition of the formyl C−H bond of acrolein to Ru may take place, giving an acryloyl(hydrido)-ruthenium(II) intermediate from which decarbonylation takes place to give a hydrido(carbonyl)(vinyl)ruthenium-(II) intermediate followed by reductive elimination of ethylene. Addition of 10 equiv of triethylphosphine/equiv of **3** showed no apparent retardation or acceleration effect on this reaction, suggesting no involvement of prior dissociation or association of phosphine ligand in this reaction. When hydrogen gas (0.1 MPa) was introduced into the benzene solution of **3** at room temperature, a mixture of *trans*- and *cis,mer*-dihydrido(carbonyl)-tris(triethylphosphine)ruthenium(II) complexes were quantitatively formed with liberation of ethane.[19] Since **3** itself is stable under these conditions, hydrogen is considered to enhance the decarbonylation process. The result is understood by considering the initial hydrogenation of the C=C double bond of the coordinated acrolein to give propanal, which smoothly and oxidatively adds to Ru to give an acyl(hydrido)ruthenium(II) species followed by decarbonylation and reductive elimination to give ethane. As a whole, dihydrogen is considered to induce the formal oxidative addition of aldehyde.

In summary, the present results display the importance of an (η^4-enone)ruthenium intermediate in ruthenium-catalyzed isomerization of allylic alcohol, which is formed by dehydrogenation of allylic alcohol. In these reactions, the η^5-cyclooctadienyl ligand in **2** or allylic alcohol is considered to act as a hydrogen acceptor.

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Supporting Information Available: Physical and crystallographic data for **3**; crystallographic data are also available as a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) Reactions of **2** with excess allylic alcohols at 70 °C for 2 h in C_6D_6 (%/**2**): for allyl alcohol, propanol (240%), C_2H_4 (45%), C_2H_6 (19%), C_3H_6 (22%); for prenyl alcohol, 3-methylbutan-1-ol (840%), 3-methyl-2-buten-1-one (320%), isobutane (14%), isobutene (26%); for cinnamyl alcohol, 3-phenylpropanol (700%), cinnamaldehyde (280%), styrene (189%), ethylbenzene (nd).

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(18) IR analysis of the resultant complex suggests the formation of an uncharacterized monocarbonyl complex. IR (KBr, cm^{-1}): 2925 (vs), 1922 (vs), 1457 (s), 1376 (m), 1035 (m), 764 (m).

(19) *cis,mer*-$RuH_2(CO)(PEt_3)_3$ was quantitatively obtained by the treatment of **3** with H_2 (0.1 MPa) at 50 °C with evolution of ethane (95%) and characterized spectroscopically. ^{1}H NMR (300.4 MHz, C_6D_6): δ −9.79 (dtd, J_{H-P} = 75, 29 Hz, J_{H-H} = 6 Hz, 1H, Ru−*H* trans to PEt_3), −8.38 (qd, J_{H-P} = 25 Hz, J_{H-H} = 6 Hz, 1H, trans to CO), 1.03 (m, 9H, PCH_2CH_3), 1.12 (m, 18H, PCH_2CH_3), 1.42 (m, 6H, PCH_2CH_3), 1.55 (m, 12H, PCH_2CH_3). ^{31}P{^{1}H} NMR (121.6 MHz, C_6D_6): δ 28.2 (t, J_{P-P} = 21 Hz, 1P, *P*Et_3), 39.7 (d, J_{P-P} = 21 Hz, 2P, *P*Et_3). IR (KBr, cm^{-1}): 2980−2880 (m), 1919 (vs), 1458 (m), 1420 (m), 1375 (m), 1253 (w), 1030 (s), 764 (s), 709 (m), 620 (m).