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Ruthenium-Catalyzed β-Allyl Elimination Leading to Selective Cleavage of a Carbon−Carbon Bond in Homoallyl Alcohols

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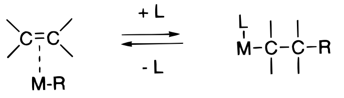
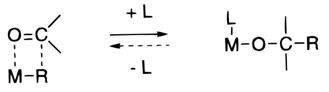
The development of efficient methods for the selective formation[1] and cleavage[2,3] of C−C bonds catalyzed by transition-metal complexes is a central and challenging subject of modern organic synthesis. Among various processes catalyzed by transition-metal complexes, alkene insertion into metal−alkyl bonds is recognized as a fundamental model reaction of alkene polymerization (eq 1 forward). The reverse reaction, i.e., C−C cleavage via β-alkyl elimination (eq 1 reverse), has recently received growing attention, especially in the field of polymer chemistry.[4] Since Watson and Roe reported the first example of β-methyl elimination in the decomposition of $(C_5Me_5)_2LuCH_2CHMe_2$,[5] several examples of reversible β-alkyl insertion-elimination at both early and late transition metal centers have been reported.[6]



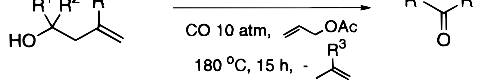
(1)



(2)

On the other hand, the addition of metal−alkyls to carbonyl compounds is another excellent method for the selective formation of C−C bonds (eq 2 forward).[7] However, since this reaction is generally irreversible, neither stoichiometric nor catalytic C−C cleavage via β-alkyl elimination from an (alkoxy)metal intermediate has yet been reported (eq 2 reverse). On the basis of our recent study of ruthenium-catalyzed C−C bond activation[3g] as well as allylruthenium chemistry,[8] we assume that successful catalytic C−C cleavage via β-alkyl elimination from an (alkoxy)-metal intermediate can be attained by using tertiary homoallyl alcohols as a substrate, since the formation of a stable allylruthenium species by β-allyl elimination should contribute significantly to the driving force of this catalytic reaction. After many trials, we finally found the first example of catalytic deallylation of tertiary homoallyl alcohols via selective cleavage of a C−C bond. We report here the development of this new catalyst system and a synthetic application of β-allyl elimination.

The treatment of tertiary homoallyl alcohol **1a** with an excess of allyl acetate in the presence of 5 mol % $RuCl_2(PPh_3)_3$ in THF under 10 atm of carbon monoxide at 180 °C for 15 h gave a deallylated product, acetophenone **2a**, in an isolated yield of 91% (eq 3). General tertiary homoallyl alcohols bearing either an aryl or alkyl substituent (**1b**−**d**) were smoothly deallylated by the present catalyst system to give the corresponding ketones (**2b**−**d**) in high isolated yields. Gas analysis showed the generation of propene (54% yield) in the reaction of **1a** and of isobutene (42% yield) in the reaction of **1d**.[9] The presence of both carbon monoxide and allyl acetate was crucial. Carbon monoxide operates as an effective π-acid.[10] While the role of allyl acetate is not yet clear, we believe that it is required for the generation and stabilization of a catalytically active ruthenium species.[11] Attempts to effect the reaction at temperatures lower than 150 °C resulted in drastically diminished yield.



(3)

1a : R^1=Ph, R^2=Me, R^3=H **2a :** 91%
1b : R^1=R^2=Ph, R^3=H **2b :** 87%
1c : R^1=R^2=Bu, R^3=H **2c :** 71%
1d : R^1=Ph, R^2=Me, R^3=Me **2d :** 85%

Several transition-metal complexes as well as ruthenium complexes were examined with regard to their ability to catalyze the deallylation of **1a** to **2a**. The results are summarized in Table 1. All of the ruthenium complexes showed catalytic activity, and among them, $RuCl_2(PPh_3)_3$ showed the highest activity. Besides ruthenium complexes, only $RhCl(PPh_3)_3$ showed a moderate catalytic activity.

A synthetic application of the present reaction is demonstrated in the following ring-opening reaction of cyclic homoallyl alcohols (eq 4). The treatment of **1e** under the present reaction conditions gave the ring-opening product, unsaturated ketone **3**, as a mixture of olefinic isomers (8-en:7-en = 26:74, total 76% yield).

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[2] For reviews, see: (a) Bishop, K. C. *Chem. Rev.* **1976**, *76*, 461. (b) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245. (c) Jennings, P. W.; Johnson, L. L. *Chem. Rev.* **1994**, *94*, 2241.

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[4] (a) Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* **1985**, *18*, 51. (b) Resconi, L.; Piemontesi, F.; Franciscono, G.; Abis, L.; Fiorani, T. *J. Am. Chem. Soc.* **1992**, *114*, 1025. (c) Kesti, M. R.; Waymouth, R. M. *J. Am. Chem. Soc.* **1992**, *114*, 3565. (d) Yang, X.; Jia, L.; Marks, T. J. *J. Am. Chem. Soc.* **1993**, *115*, 3392. (e) Hajela, S.; Bercaw, J. E. *Organometallics* **1994**, *13*, 1147 and references therein.

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[7] Addition of allylorganometallics to carbonyl compounds, see: Roush, W. R. In *Comprehensive Organic Synthesis*: Trost, B. M.; Fleming, I., Eds.; Pergamon: Oxford, U.K., 1991; Vol. 2, pp 1−53.

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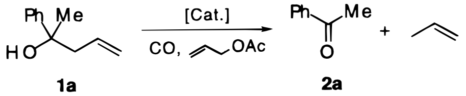
[9] In the reaction of **1d**, a small amount (0.36 mmol) of propene was generated from allyl acetate (30 mmol) together with isobutene (1.68 mmol, 42%) from **1d**.

[10] After the reaction, $RuCl_2(PPh_3)_3$ was quantitatively converted into *cis*-$RuCl_2(CO)_2(PPh_3)_2$ (Stephenson, T. A.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1966**, *28*, 945). In addition, carbon monoxide can be replaced by maleic anhydride (yield of **1a**, 65%; see the Supporting Information). These results indicate that carbon monoxide and maleic anhydride may coordinate to an active ruthenium center and promote the reductive elimination of propene from a (hydrido)(allyl)ruthenium intermediate, as well as control the electronic condition of an active ruthenium center.

[11] Oxidative addition of allyl trifluoroacetate to Ru(0) has already been reported, see: Komiya, S.; Kabasawa, T.; Yamashita, K.; Hirano, M.; Fukuoka, A. *J. Organomet. Chem.* **1994**, *471*, C6.

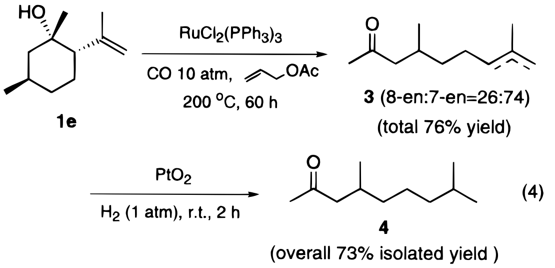
S0002-7863(98)00714-8 CCC: \$15.00

Table 1. Catalytic Activity of Several Transition-Metal Complexes in Deallylation of **1a** to **2a**[a]



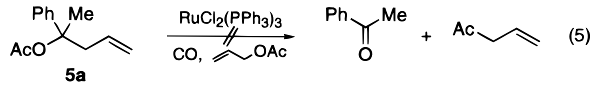
catalyst	yield of **2a** (%)[b]
RuCl$_2$(PPh$_3$)$_3$	(91)
cis-RuCl$_2$(CO)$_2$(PPh$_3$)$_2$	65
Cp*RuCl(cod)	64
Ru$_3$(CO)$_{12}$[c]	45
RhCl(PPh$_3$)$_3$	53
NiBr$_2$(PPh$_3$)$_2$	0
PdCl$_2$(PPh$_3$)$_2$	0
cis-PtCl$_2$(PPh$_3$)$_2$	0

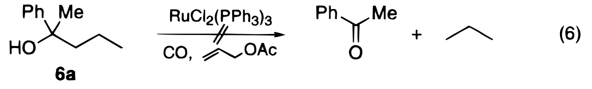
[a] Compound **1a** (4.0 mmol), catalyst (0.20 mmol), allyl acetate (30 mmol), THF (8.0 mL), CO (10 atm), 180 °C, 15 h. [b] GLC yield (isolated yield). [c] Ru$_3$(CO)$_{12}$ (0.067 mmol).

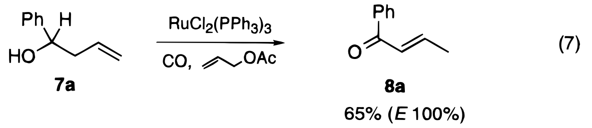


Hydrogenation of **3** by PtO$_2$ catalyst gave the saturated ketone **4** in an overall isolated yield of 73%. Thus, the present reaction may offer a novel method for the catalytic ring-opening reaction of general 2-vinylcycloalkanols.[12]

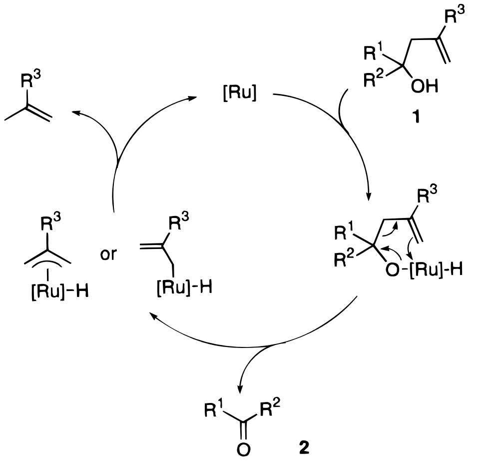
The following reactions using **5a**, **6a**, and **7a**, illustrated in eqs 5−7, provided insight into the mechanism. First, treatment of **5a** did not give **2a** at all, which indicates that the first step of the reaction is oxidative addition of a hydroxy group of **1a** to ruthenium. Second, the failure of the depropylation of **6a** to **2a** suggests that the driving force of this reaction is the formation of an allylruthenium species. Furthermore, substrate **7a**, which has both a β-hydrogen and a β-allyl group, gave the α,β-unsaturated ketone **8a** exclusively via β-hydrogen elimination.







Scheme 1



Considering all of our findings, the most plausible mechanism is illustrated in Scheme 1. The initial step might consist of oxidative addition of the hydroxy group in **1** to an active ruthenium center. Subsequent β-allyl elimination from an (alkoxy)ruthenium intermediate gives ketone **2** together with a (hydrido)(allyl)ruthenium intermediate, which undergoes reductive elimination to give propene. Carbon monoxide may promote the final reductive elimination of propene as an effective π-acid (vide supra).

In summary, we have developed the first and practical ruthenium-catalyzed deallylation of tertiary homoallyl alcohols via selective cleavage of a C−C bond. The mechanistic aspects and scope of the transfer−allylation reaction[13] are currently under investigation, but we believe that this C−C bond cleavage involves the first β-alkyl (β-allyl) elimination from an (alkoxy)ruthenium intermediate in its catalytic cycle.

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Supporting Information Available: Experimental details and characterization of compounds **1e** and **4** (4 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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[12] The thermal ring-opening reaction (retro-ene reaction) of 2-vinylcyclohexanols is generally carried out in the vapor phase at ca. 500 °C. Marvell, E. N.; Rusay, R. *J. Org. Chem.* **1977**, *42*, 3336.

[13] The following novel ruthenium-catalyzed transfer−allylation of aldehydes with **1a** or **1d** also supports the formation of an allylruthenium intermediate. For example, the treatment of benzaldehyde with an equimolar amount of **1a** or **1d** in the presence of RuCl$_2$(PPh$_3$)$_3$ catalyst and an excess amount of allyl acetate in THF gave the transfer-allylated product, (*E*)-1-phenyl-2-buten-1-one (**8a**) and 3-methyl-1-phenylbut-2-en-1-one (**9a**) in yields of 68 and 35%, respectively (eq 8). Of course, no reaction occurred in the absence of **1a** or **1d**, even in the presence of allyl acetate.