

REGIOSELECTIVE C-O BOND CLEAVAGE OF ALLYLIC PHENYL CARBONATES  
PROMOTED BY GROUP 8 TRANSITION METAL HYDRIDO COMPLEXES

Yoshinori HAYASHI, Sanshiro KOMIYA,<sup>†</sup> Takakazu YAMAMOTO,<sup>\*</sup>  
and Akio YAMAMOTO<sup>\*</sup>

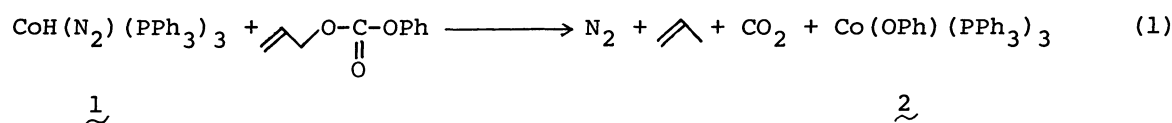
Research Laboratory of Resources Utilization, Tokyo  
Institute of Technology, 4259 Nagatsuta, Midori-ku,  
Yokohama 227

<sup>†</sup>Department of Applied Chemistry of Resources, Tokyo  
University of Agriculture and Technology, 2-24-16  
Nakamachi, Koganei, Tokyo 184

Carbon-oxygen bonds in allylic phenyl carbonates are selectively cleaved by hydrido complexes of Co, Ru and Rh to give Co(OPh)L<sub>3</sub>, RuH(OPh)L<sub>2</sub> and Rh(OPh)L<sub>3</sub> with liberation of propylene and CO<sub>2</sub>. An intermediate complex RuH(O<sub>2</sub>COEt)L<sub>3</sub> has been isolated in the reaction of RuH<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub> with allyl ethyl carbonate. Reaction mechanisms are also discussed.

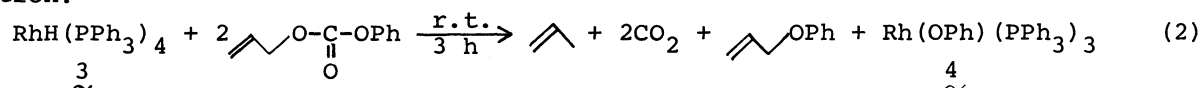
The allyl-O bond cleavage of organic substrates promoted by palladium to form π-allyl complexes and the subsequent attack of the π-allyl moiety by nucleophiles have been extensively applied to organic synthesis.<sup>1)</sup> Particularly, Pd-catalyzed C-O bond cleavage of allylic carbonates has been effectively utilized by Tsuji and others for synthesis of natural products. However, utility of transition metal complexes other than palladium to this type of reactions has been scarcely explored. Palladium(0) and nickel(0) complexes probably induce the C-O bond cleavage of allylic-O bonds by direct oxidative addition of the substrates to the metal as established in certain cases.<sup>2)</sup> On the other hand, hydrido- and alkyl-transition metal complexes may take a different course in their reactions with allylic compounds because of somewhat anionic nature of the hydrido or alkyl ligand.<sup>3)</sup> We now report the first evidence that the allylic C-O bond cleavage promoted by cobalt, rhodium and ruthenium hydrido triphenylphosphine complexes takes clearly different course from that promoted by palladium complexes.

The reaction of CoH(N<sub>2</sub>)(PPh<sub>3</sub>)<sub>3</sub>, 1, with allyl phenyl carbonate smoothly proceeds at 20 °C to give phenoxotris(triphenylphosphine)cobalt(I), 2, accompanied by evolution of equimolar amounts of dinitrogen, carbon dioxide and propylene per mol of 1.



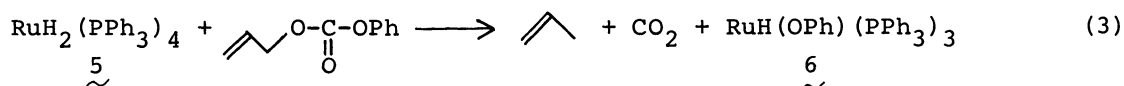
Complex 2 was fully characterized by elemental analysis, IR spectroscopy, magnetic susceptibility, X-ray structural analysis<sup>4)</sup> and chemical reactions. 2: mp (decomp); 178 °C. Found: C, 76.5; H, 5.4; Co, 6.4%. Calcd: C, 76.8; H, 5.4; Co, 6.3%. Complex 2 can be also prepared through an independent route by the reaction of 1 with phenol. Magnetic susceptibility of 2 (3.3 B.M.) suggests a high spin  $d^8$  tetrahedral structure with two unpaired electrons. IR spectrum of 2 shows a strong  $\nu(\text{C-O})$  band at  $1280\text{ cm}^{-1}$ , characteristic of transition metal phenoxide. Acidolysis of 2 with dry HCl liberates a quantitative yield of phenol per Co.

Similar C-O bond cleavage reaction takes place in the reaction of  $\text{RhH}(\text{PPh}_3)_4$ , 3, with allyl phenyl carbonate at room temperature. In this case, a decarboxylation reaction of allyl phenyl carbonate catalyzed by 3 partly takes place in the same reaction system to give allyl phenyl ether (ca. 1 mol/3), carbon dioxide (ca. 2 mol/3), propylene and  $\text{Rh}(\text{OPh})(\text{PPh}_3)_3$ , 4, according to the following equation.

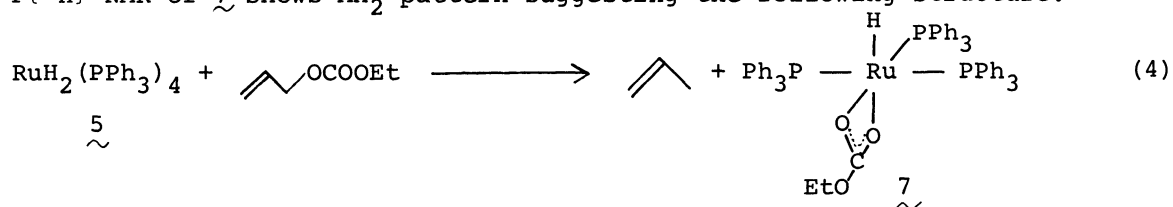


Prolonged reaction time increases the yield of  $\text{CO}_2$  and allyl phenyl ether. The isolated complex, 4, is characterized by elemental analysis as well as by comparing its IR data with those reported in the literature.<sup>5)</sup>

Reaction of  $\text{RuH}_2(\text{PPh}_3)_4$ , 5, with allyl phenyl carbonate also proceeded to afford  $\text{RuH}(\text{OPh})(\text{PPh}_3)_3$ , 6,<sup>6)</sup> with liberation of quantitative amounts of  $\text{C}_3\text{H}_6$  and carbon dioxide.

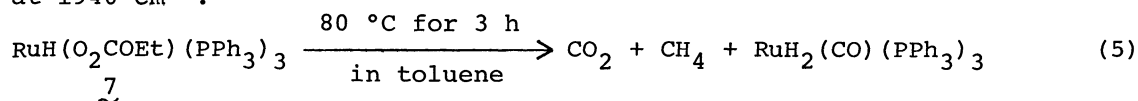


Generation of the phenoxide complexes on interaction of these hydrido complexes with allyl phenyl carbonate suggests the intermediate formation of phenylcarbonato complexes. Although the phenylcarbonato complex was not isolated in these reactions, probably owing to the rapid decarboxylation, an analogue of the supposed intermediate,  $\text{RuH}(\text{O}_2\text{COEt})(\text{PPh}_3)_3$  (7), was isolated in the reaction of  $\text{RuH}_2(\text{PPh}_3)_4$  with allyl ethyl carbonate with concomitant evolution of one equivalent of propylene. Complex 7 was characterized by IR and NMR spectroscopy and elemental analysis. 7: Found: C, 69.9; H, 5.2%. Calcd: C, 70.0; H, 5.3%.  $^1\text{H-NMR}$  (in  $\text{CD}_2\text{Cl}_2$  at room temperature):  $\delta$ : -18.66 (1H, q,  $J=28.3$  Hz) for  $\text{Ru-H}$ ; 0.86 (3H, t,  $J=6.8$  Hz) for  $\text{OCH}_2\text{CH}_3$ ; 3.55 (2H, q,  $J=6.8$  Hz) for  $\text{OCH}_2\text{CH}_3$ .  $^{31}\text{P}\{^1\text{H}\}\text{-NMR}$  of 7 shows  $\text{AX}_2$  pattern suggesting the following structure.<sup>7)</sup>



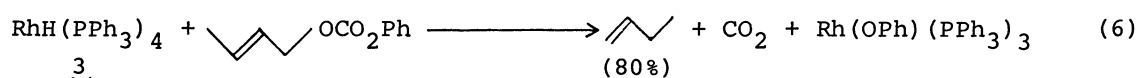
In fact, thermolysis of ethylcarbonato complex 7 at 80 °C in toluene caused decarboxylation liberating  $\text{CO}_2$  (100%) and  $\text{CH}_4$  (82%). The resulting complex was

characterized as  $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$  (75%) based on IR spectrum showing the  $\nu(\text{C}=\text{O})$  band at  $1940 \text{ cm}^{-1}$ .<sup>8)</sup>

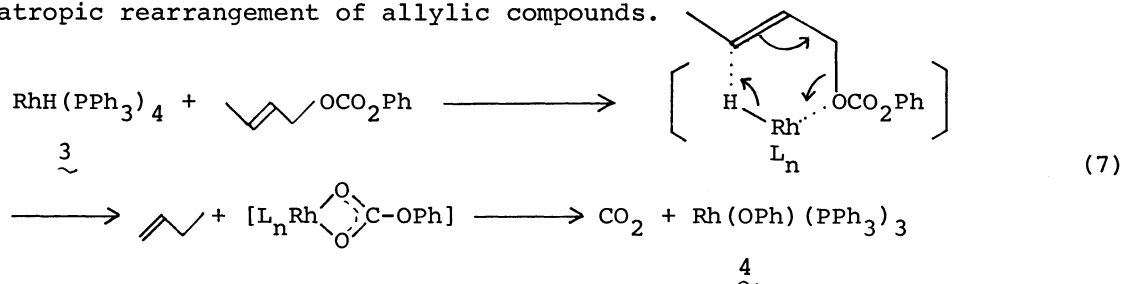


The carbonyl complex  $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$  and methane have been probably formed by further thermolysis of an ethoxo complex formed by decarboxylation of **7**.

In order to obtain further insight into mechanism of the C-O bond cleavage of allyl phenyl carbonate, reaction of substituted allyl phenyl carbonates were examined. The reaction of **3** with an excess amount of 2-butenyl phenyl carbonate liberated  $\text{CO}_2$  and only 1-butene.



The high regioselectivity in the product olefin in the C-O bond cleavage demonstrated in the present study strongly suggests involvement of the following  $\text{S}_{\text{N}}2'$  type reaction mechanism accompanying the double bond shift, similar to the sigmatropic rearrangement of allylic compounds.

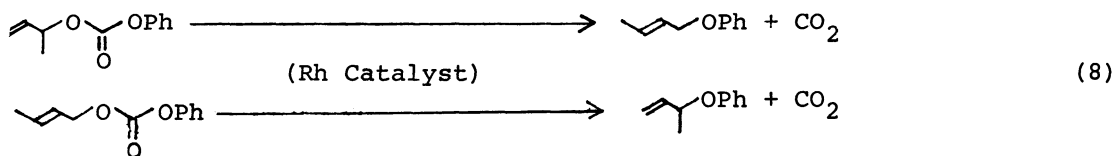


The actual reaction of **3** with the allylic phenyl carbonate may proceed through insertion of the allylic double bond into Rh-H bond followed by  $\beta$ -elimination of the phenylcarbonato entity by rhodium. Formation of 1-butene as the sole reaction product in the reaction of **3** with the allylic phenyl carbonate are not compatible with the direct oxidative addition of allylic phenyl carbonate to Rh(I) followed by reductive elimination of the hydrido-allylic ligands. The process would yield 2-butene from 2-butenyl phenyl carbonate in disagreement with the present result. The reaction of **3** with 1-methyl-2-propenyl phenyl carbonate liberated  $\text{CO}_2$  and a mixture of 1-butene and 2-butene, the ratio between 1-butene and 2-butene depending on reaction conditions. The formation of 2-butene in this reaction is elucidated by a similar  $\text{S}_{\text{N}}2'$  mechanism to that depicted above, whereas 1-butene seems to originate from the reaction of **3** with 2-butenyl phenyl ether which was formed by a  $\text{Rh}(\text{OPh})(\text{PPh}_3)_3$ -catalyzed decarboxylation of 1-methyl-2-propenyl phenyl carbonate (*vide infra*, Eq. 8 and Mechanism). Actually, evolution of  $\text{CO}_2$  prior to that of butenes was observed in the reaction of **3** with 1-methyl-2-propenyl phenyl carbonate, and a reaction of **3** with 2-butenyl phenyl ether gave 1-butene.

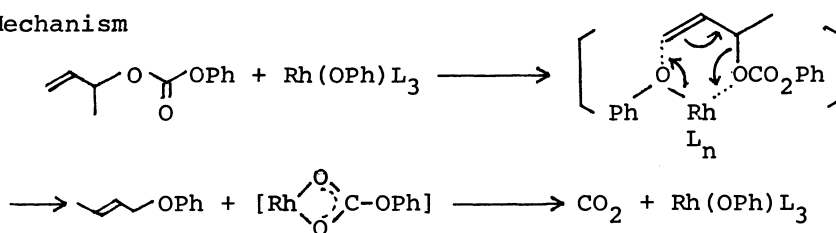
Similar reaction of **1** and **5** with the allylic phenyl carbonates with the  $\text{CH}_3$ -substituent have been less clear-cut than those of Eq. 6, and mixtures of 1-butene and 2-butene have been produced. The butenes may have been formed by isomerization of 2-butene and 1-butene, originally produced as in Eq. 6, catalyzed by the hydrido complexes **1** and **5** which are known to catalyze the double

bond migration.<sup>9)</sup>

The regioselectivity in the allyl-O bond cleavage promoted by the cobalt, rhodium, and ruthenium complexes different from that promoted by palladium complexes provides an opportunity for synthetic applications. One example is the decarboxylative allylic ether formation from allylic carbonate catalyzed by rhodium complexes.



Mechanism



The details of these catalytic reactions will be reported separately.<sup>10)</sup>

#### References

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