J. Am. Chem. Soc. **1998,** *120,* 9949−9950

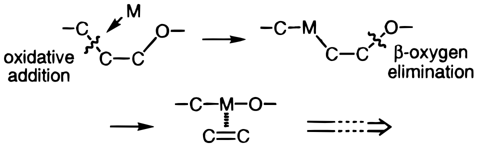
New Domino Sequences Involving Successive Cleavage of Carbon−Carbon and Carbon−Oxygen Bonds: Discrete Product Selection Dictated by Catalyst Ligands

Masahiro Murakami,* Tamon Itahashi, Hideki Amii,[†]
Kunio Takahashi, and Yoshihiko Ito*

Department of Synthetic Chemistry and Biological Chemistry
Kyoto University, Yoshida, Kyoto 606-8501, Japan

Received June 8, 1998

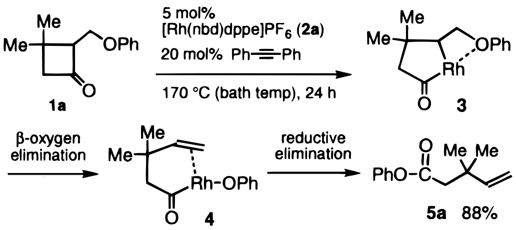
Transition metal-mediated C−C bond cleavage has received much attention in recent years.[1] Oxidative addition of a C−C bond onto a transition metal provides a direct method to break a C−C bond.[2] Catalytic reactions involving this elementary step, however, are still limited due to the inertness of C−C σ-bonds toward transition metals.[3,4] On the other hand, while common with alkali metal and alkali earth organometallics, C−O bond cleavage by β-oxygen elimination has been observed more rarely in late transition metal systems.[5,6] We recently found that the bond between the carbonyl carbon and the α-carbon of a cyclobutanone is catalytically cleaved by a rhodium(I) complex.[4] We envisaged that situating an ether linkage appropriately in the substrate would lead to development of a new domino sequence in which C−C and C−O bonds are sequentially cleaved.



(1)

We report herein successive cleavage of C−C and C−O bonds catalyzed by a cationic rhodium complex having a bidentate diphosphine ligand. Furthermore, this study provides a striking example wherein a slight modification of the tether length of an employed diphosphine ligand completely changes the reaction course.

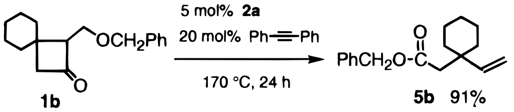
Cyclobutanone equipped with a phenoxymethyl side chain (**1a**)[7] was heated in refluxing xylene in the presence of [Rh(nbd)(dppe)]-PF_6 (**2a**, 5 mol %)[8,9] and diphenylacetylene (20 mol %). After 24 h, **1a** was consumed, and chromatographic isolation afforded olefinic ester **5a** in 88% yield.[10] The production of **5a** can be explained by assuming the pathway pictured in eq 2. Initially, rhodium(I) inserts into the bond between the carbonyl carbon and the α-carbon of **1a**.[11] The resultant five-membered cyclic acylrhodium intermediate **3** undergoes β-oxygen elimination, rather than β-hydrogen elimination[5a,6a,12] to produce acylrhodium coordinated by a C−C double bond (**4**). Subsequent reductive elimination gives rise to the olefinic ester **5a** and rhodium(I).



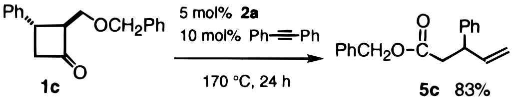
(2)

When the reaction was carried out in the absence of diphenylacetylene, the yield of **5a** decreased to 46%. It is assumed that β-oxygen elimination of **3** to form **4** is reversible and that diphenylacetylene coordinates to the rhodium of **4** to expel the olefinic moiety from the coordination sphere, thus promoting the reaction forward.

Other examples of successive cleavage of C−C and C−O bonds are shown in eqs 3 and 4. Spirocyclobutanone **1b**[7] yielded the corresponding olefinic ester **5b** in 91% yield. The reaction of cyclobutanone having a hydrogen atom at the 3-position (**1c**)[7] also resulted in the formation of olefinic ester **5c**.



(3)



(4)

A surprising ligand effect was found during the course of a detailed examination of the reaction conditions. The reaction pattern of **1a** was completely changed when the bidentate phosphine ligand dppe was replaced with dppp,[8] where the two phosphorus atoms are separated by a three-carbon tether instead of a two-carbon chain. In contrast to when the dppe was used to give the olefinic ester **5a**, the [Rh(nbd)(dppp)]PF_6-catalyzed reaction of **1a** furnished cyclopentanone **7a** in 81% isolated yield. No formation of **5a** was detected by capillary GC analysis of the

---

[†] Present address: Department of Applied Chemistry, Faculty of Engineering, Okayama University, Tsushimanaka 3-1-1, Okayama 700-0082, Japan.

(1) For a review, see: Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245.

(2) (a) Suggs, J. W.; Jun, C.-H. *J. Am. Chem. Soc.* **1984**, *106*, 3054. (b) Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 7346. (c) Hughes, R. P.; King, M. E.; Robinson, D. J.; Spotts, J. M. *J. Am. Chem. Soc.* **1989**, *111*, 8919. (d) Bennett, M. A.; Nicholls, J. C.; Rahman, A. K. F.; Redhouse, A. D.; Spencer, J. L.; Willis, A. C. *J. Chem. Soc., Chem. Commun.* **1989**, 1328. (e) Suzuki, H.; Takaya, Y.; Takemori, T. *J. Am. Chem. Soc.* **1994**, *116*, 10779. (f) Rybtchinski, B.; Vigalok, A.; Ben-David, Y.; Milstein, D. *J. Am. Chem. Soc.* **1996**, *118*, 12406. (g) Jun, C.-H. *Organometallics* **1996**, *15*, 895 and references therein.

(3) (a) Noyori, R.; Odagi, T.; Takaya, H. *J. Am. Chem. Soc.* **1970**, *92*, 5780. (b) Kaneda, K.; Azuma, H.; Wayaku, M.; Teranishi, S. *Chem. Lett.* **1974**, 215. (c) Suggs, J. W.; Jun, C.-H. *J. Chem. Soc., Chem. Commun.* **1985**, 92. (d) Huffman, M. A.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1993**, *115*, 4895. (e) Edelbach, E. L.; Lachicotte, R. J.; Jones, W. D. *J. Am. Chem. Soc.* **1998**, *120*, 2843. (f) Liou, S.-Y.; van der Boom, M. E.; Milstein, D. *Chem. Commun.* **1998**, 687 and references therein.

(4) (a) Murakami, M.; Amii, H.; Ito, Y. *Nature* **1994**, *370*, 540. (b) Murakami, M.; Amii, H.; Shigeto, K.; Ito, Y. *J. Am. Chem. Soc.* **1996**, *118*, 8285. (c) Murakami, M.; Takahashi, K.; Amii, H.; Ito, Y. *J. Am. Chem. Soc.* **1997**, *119*, 9307.

(5) (a) Komiya, S.; Shindo, T. *J. Chem. Soc., Chem. Commun.* **1984**, 1672. (b) Komiya, S.; Srivastava, R. S.; Yamamoto, A.; Yamamoto, T. *Organometallics* **1985**, *4*, 1504. (c) Oishi, S.; Kihara, N.; Hosaka, A. *Chem. Lett.* **1985**, 621. (d) Steinborn, D *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 401 and references therein.

(6) For isolation of stable (β-oxyalkyl)metal complexes, see: (a) Majima, T.; Kurosawa, H. *Chem. Soc., Chem. Commun.* **1977**, 610. (b) Zlota, A. A.; Frolow, F.; Milstein, D. *J. Am. Chem. Soc.* **1990**, *112*, 6411. (c) Chatt, J.; Vallarino, L. M.; Venanzi, L. M. *J. Chem. Soc.* **1957**, 2496. (d) Ref 5a.

(7) Cyclobutanones **1a**−**d** were readily prepared by [2 + 2] cycloaddition of the corresponding allylic ethers with dichloroketene and the subsequent dechlorination with zinc.

(8) nbd = 2,5-norbornadiene, dppe = $Ph_2PCH_2CH_2PPh_2$, dppp = $Ph_2P(CH_2)_3$-PPh_2, and dppb = $Ph_2P(CH_2)_4PPh_2$.

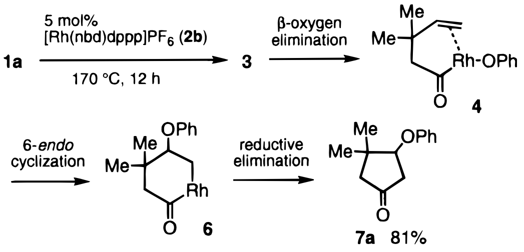
(9) The hexafluorophosphate complexes **2a**−**c** were prepared according to a literature procedure for preparation of analogous tetrafluoroborate complexes: Green, A.; Kuc, T. A.; Taylor, S. H. *J. Chem. Soc. A* **1971**, 2334. The details of the syntheses and crystal structures will be reported separately.

(10) Monitoring the reaction by capillary GC revealed that decarbonylated cyclopropane **8a** was formed as a sole side product (∼4.5%), and formation of cyclopentanone **7a** was not observed.

(11) Whereas a less substituted α-bond is cleaved in the hydrogenolysis of an ordinary cyclobutanone,[4b] the more substituted α-bond is cleaved in the present case. It is likely that coordination of the ether linkage to rhodium facilitates insertion into the more substituted but proximate α-bond.

(12) Milstein, D.; Calabrese, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 3773.

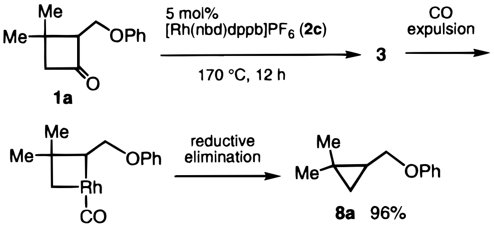
reaction mixture.[13] It is likely that, as is the case with dppe, the olefin-coordinated acylrhodium intermediate **4** is initially formed through successive cleavage of C−C and C−O bonds. Then, instead of undergoing direct reductive elimination, **4** recyclizes to a six-membered acylrhodium **6**[14] by addition of the Rh−O linkage across the C−C double bond[15] in a 6-*endo* mode.[16] Finally, reductive elimination forming a C−C bond affords **7a**.



(5)

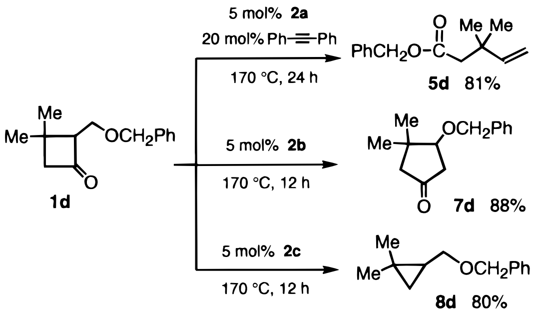
When an analogous reaction of **1a** catalyzed by [Rh(nbd)(dppp)]PF_6 (**2b**) was carried out in the presence of diphenylacetylene (20 mol %), the olefinic ester (**5a**) was produced (76%) in preference to **7a** (9%). This result can be explained by assuming that diphenylacetylene drives out the internal coordination of the olefinic moiety of **4** to disfavor recyclization.

A third distinct and exclusive reaction pathway of **1a** was identified when the bidentate diphosphine ligand dppp was replaced with dppb.[8] As reported previously,[4b] **1a** having an ether side chain underwent simple decarbonylation when catalyzed by [Rh(nbd)(dppb)]PF_6 (**2c**).[9] Decarbonylated cyclopropane **8a**, keeping the ether side chain intact, was exclusively formed (96%).[17] The wider P−Rh−P angle with dppb may cause larger steric repulsions to favor a four-membered rhodacycle rather than a five-membered one, thus promoting expulsion of the carbonyl group from the five-membered cyclic skeleton.



(6)

Similar discrete product selection dictated by the diphosphine ligand was observed with the benzyl ether analogue **1d**[7] of the cyclobutanone **1a** as shown in eq 7.



(7)

Among the three pathways, however, the reaction that forms cyclopentanone lacks generality. For example, olefinic ester **5b** was obtained in 86% yield from cyclobutanone **1b** even when **2b** was used as the catalyst.[18]

In summary, new rhodium-catalyzed domino sequences were identified in which C−C and C−O bonds were successively cleaved. A highlight is that the reaction patterns of the cyclobutanones **1a** and **1d** are affected enormously by the employed bidentate diphosphine ligand. As the length of the carbon tether between two phosphorus atoms was extended from ethylene to trimethylene to tetramethylene, different compounds, ring-opened olefinic ester, recyclized cyclopentanone, or decarbonylated cyclopropane, were obtained respectively from the same reactant. The mechanistic explanation for this unprecedented dramatic divergence deserves careful study but could be very difficult to work out. While the observed divergence presently requires certain substitutions in the substrate, it clearly demonstrates the possibility of controlling the reaction course itself by slight modifications of the ligand of a transition metal catalyst.

Acknowledgment. Support from Monbusho (Grant-in-Aid for Scientific Research on Priority Areas, No. 283: Innovative Synthetic Reactions) is gratefully acknowledged.

Supporting Information Available: Experimental details and characterization for **5**, **7**, and **8** (2 pages, print/PDF). See any current masthead page for ordering and Web access instructions.

JA981993S

---

[13] Decarbonylated cyclopropane **8a** was observed by GC as the only side product (∼12%).

[14] Campbell, R. E., Jr.; Lochow, C. F.; Vora, K. P.; Miller, R. G. *J. Am. Chem. Soc.* **1980**, *102*, 5824.

[15] For addition of a Rh−O linkage across a C−C double bond, see: Evans, J. A.; Russell, D. R.; Bright, A.; Shaw, B. L. *Chem. Commun.* **1971**, 841.

[16] Alternatively, recyclization of **4** by addition of the Rh−C linkage across the C−C double bond in a *5-endo* mode followed by reductive elimination forming a C−O bond is also conceivable for the production of **7a**.

[17] Neither **5a** nor **7a** was detected by GC.

[18] The reaction of **1b** catalyzed by the dppb complex **2c** afforded the corresponding decarbonylated cyclopropane **8b** in 93% yield, being in accordance with other examples.