Activation of a Cyclobutanone Carbon–Carbon Bond over an Aldehyde Carbon–Hydrogen Bond in the Rhodium-catalyzed Decarbonylation

Takanori Matsuda, Masanori Shigeno, and Masahiro Murakami*
Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Kyoto 615-8510

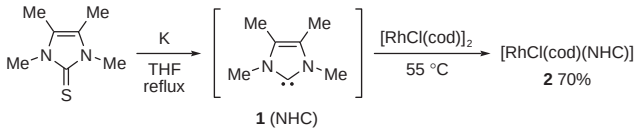
(Received December 6, 2005; CL-051505; E-mail: murakami@sbchem.kyoto-u.ac.jp)

A rhodium(I)–*N*-heterocyclic carbene complex achieved a high-yield decarbonylation reaction of cyclobutanones to selectively afford cyclopropanes. With this catalyst, a cyclobutanone having an aldehyde moiety underwent chemoselective decarbonylation of the ketonic carbonyl group with the aldehydic carbonyl group left intact.

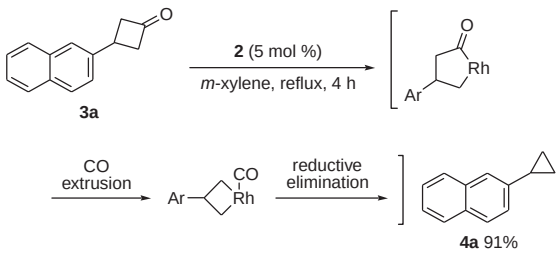
Selective activation of low polarity σ-bonds, such as carbon–hydrogen[1] and carbon–carbon bonds,[2] by transition metals presents a challenge for the development of new chemical transformations. Kinetically, a carbon–hydrogen bond generally enjoys better reactivity, and thus, adds oxidatively to a transition metal in preference to a carbon–carbon bond.[3] Decarbonylation reactions of carbonyl compounds provide a typical illustration of preferential activation of C–H bonds over C–C bonds. Whereas numerous examples with aldehydes have been reported in both stoichiometric[4] and catalytic reactions,[4a,5] decarbonylation of ketones has limited precedence.[6] Herein, we report that a neutral rhodium–*N*-heterocyclic carbene complex[7] is a peculiar decarbonylation catalyst which can specifically activate the carbon–carbon bond of a cyclobutanone in the presence of an aldehydic carbon–hydrogen bond.

Neutral monomeric complex [RhCl(cod)(NHC)][8] (**2**, NHC = 1,3,4,5-tetramethylimidazol-2-ylidene) was prepared by a procedure analogous to that for the imidazolin-2-ylidene complexes:[9] treatment of the complex $[RhCl(cod)]_2$ with 1,3,4,5-tetramethylimidazol-2-ylidene (**1**, NHC), which was generated by reductive desulfurization of the corresponding thione with potassium in THF,[10] gave **2** (Scheme 1). The complex thus produced was quite stable toward air and moisture and could be isolated by column chromatography in 70% yield.

The catalytic activity of the complex **2** for decarbonylation was examined. Both aliphatic and aromatic aldehydes were unreactive toward **2** up to 150 °C. On the contrary, cyclobutanone **3a** was decarbonylated to produce cyclopropane **4a** in 91% yield when heated at 150 °C (bath temp) in the presence of a catalytic amount of **2** (5 mol %) in *m*-xylene (Scheme 2).[11] The insertion of rhodium between the carbonyl carbon and the α-carbon was followed by carbonyl extrusion and reductive elimination. Linear ketones and ordinary less-strained cycloalkanones like 4-phenylcyclohexanone failed to undergo decarbonylation at 150 °C even with a stoichiometric amount of **2**.

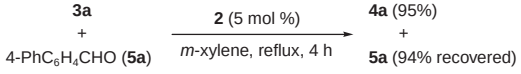


Scheme 1. Preparation of RhCl(cod)(NHC) (**2**).

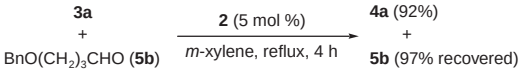


Scheme 2.

Control experiments between cyclobutanone **3a**, aromatic aldehyde **5a**, and aliphatic aldehyde **5b** were carried out to test the chemoselectivity of the decarbonylation catalyst **2** (Eqs 1 and 2). Whereas **3a** was decarbonylated by **2** to afford **4a** in high yield, both aldehydes, **5a** and **5b**, remained unchanged throughout the reaction.

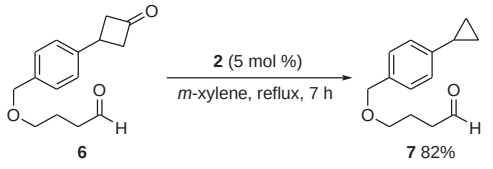


(1)



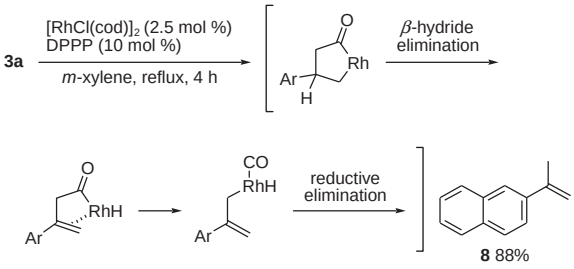
(2)

The specific reactivity of cyclobutanones toward **2** was most explicitly exemplified by the reaction of keto-aldehyde **6**. Cyclopropane **7** was exclusively formed from **6** (82% isolated yield) when **2** was used as catalyst (Eq 3). Only the ketonic carbonyl group of the cyclobutanone moiety was removed with the aldehydic carbonyl group remaining intact.



(3)

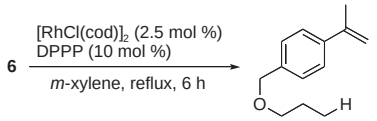
The anomalous behavior of [RhCl(cod)(NHC)] (**2**) as the decarbonylation catalyst led us to compare **2** with other rhodium complexes. A neutral rhodium(I)–phosphine complex formed in



Scheme 3.

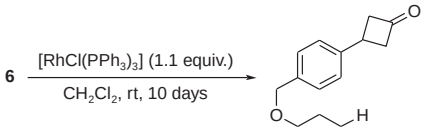
situ from $[RhCl(cod)]_2$ and DPPP[8] furnished not **4a** but olefin **8** from **3a** through a decarbonylation process involving β-hydride elimination (Scheme 3).[6d,12]

Furthermore, no chemoselectivity was observed in the decarbonylation reaction of **6** in the presence of the Rh(I)–DPPP complex; both the aldehydic and ketonic carbonyl groups were decarbonylated to afford 1-isopropenyl-4-propoxymethylbenzene (**9**) in 84% yield (Eq 4).



9 84% (4)

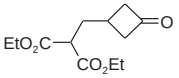
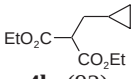
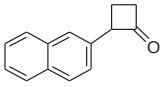
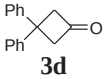
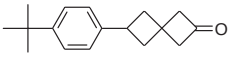
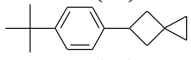
A chemoselectivity opposite to that provided by **2** was observed when **6** was treated with a stoichiometric amount of the Wilkinson's complex at room temperature. Only the aldehydic carbonyl group was decarbonylated with the cyclobutanone carbonyl remaining intact in the product **10** (Eq 5).[13] Thus, it proved that aldehydes and cyclobutanones possess similar reactivities toward rhodium-mediated decarbonylation and that an appropriate choice of the ligand system can result in opposite chemoselectivity.



10 83% (5)

Other examples of the decarbonylation of cyclobutanones using the Rh–NHC complex **2** are listed in Table 1. An active hydrogen of **3b** remained intact during decarbonylation (Entry 1). In the case of 2-(2-naphthyl)cyclobutanone (**3c**), 9% of (*E*)-1-(2-naphthyl)propene (**11**), formed through β-hydride elimination, was obtained as another decarbonylation product together with the major product, cyclopropane **4a** (83%) (Entry 2). 3,3-Disubstituted cyclobutanone **3d** requires a longer reaction time to reach full conversion, probably due to steric reasons (Entry 3). On the other hand, spiro[3.3]heptan-2-one **3e**, with constrained geminal disubstituents at the 3-position, was decarbonylated much more rapidly than **3d** (Entry 4). During decarbonylation of **3e** with **2**, β-carbon elimination did not follow the insertion step of rhodium, unlike the case of a ring-expansion reaction of an analogous spiro compound catalyzed by $[Rh(dppp)_2]Cl$.[14]

Table 1. Decarbonylation of cyclobutanones **3b–3e** using **2**[a]

Enrty	3	Time/h	4 (%yield[b])
1	 **3b**	6	 **4b** (92)
2	 **3c**	8	**4a**[c] (83)
3	 **3d**	84	 **4d** (90)
4	 **3e**	2	 **4e** (86)

[a]Cyclobutanone **3** (0.60 mmol) and Rh–NHC complex **2** (0.03 mmol, 5 mol %) were heated in refluxing *m*-xylene (3.0 mL). [b]Isolated yield. [c]Obtained as a mixture with (*E*)-1-(2-naphthyl)-propene (**11**) (9%).

In summary, the present study provides an intriguing example of preferential activation of a C–C bond over a C–H bond. The unique potential of NHC complexes for synthetic purposes is inferred from the contrasting chemoselectivies observed in decarbonylation. Mechanistic explanation of the marked contrast and application to other catalytic process are the subjects of further studies in our laboratory.

References and Notes

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8 Abbreviations: cod = cycloocta-1,5-diene, DPPP = 1,3-bis(diphenylphosphino)propane.

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11 Decarbonylation of **3a** with [RhCl(cod)(1,3-dimethylimidazol-2-ylidene)] under otherwise identical conditions gave **4a** in 82% yield.

12 Catalyst with 1/2 ratio of Rh/DPPP exhibited a higher activity than that with 1/1 ratio.

13 Decarbonylation of **3a** in the presence of 1.1 equiv. of $[RhCl(PPh_3)_3]$, which failed to occur at rt, proceeded in refluxing *m*-xylene (4 days) to afford a mixture of **4a** (7%), **8** (25%), and **11** (23%, $E/Z = 90/10$).

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Published on the web (Advance View) February 11, 2006; DOI 10.1246/cl.2006.288