

# Novel Functional Group Transformation from Acetylene Cobalt Complex to Ketone via Ligand Exchange

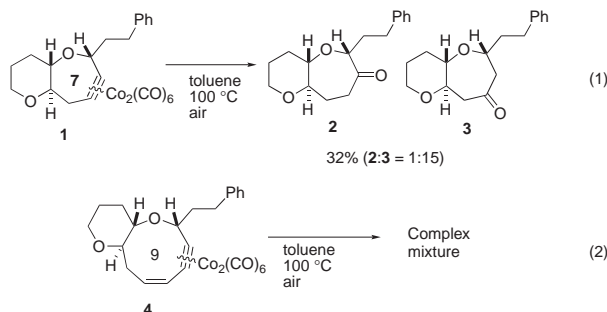
Akinari Hamajima, Hiroyuki Nakata, Masako Goto, and Minoru Isobe\*  
 Laboratory of Organic Chemistry, School of Bioagricultural Sciences, Nagoya University,  
 Chikusa-ku, Nagoya 464-8601

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A new transformation of acetylene dicobalt tetracarbonyl dppm complexes was found to convert to ketones with high regioselectivity under ligand exchange condition.

Acetylene dicobalt hexacarbonyl complexes are used in the organic synthesis of natural products<sup>1</sup> largely as a protecting group,<sup>2</sup> substitution reaction at its adjacent position (Nicholas reaction)<sup>3</sup> and the Pauson–Khand reaction.<sup>4</sup> As for the complexes situated at the acyclic positions, there exist various regeneration methods back into acetylenes with some oxidants.<sup>2,5,6</sup> As for the cyclic complexes, however, only little has been known for the conversion into the corresponding acetylenes<sup>7</sup> or olefins<sup>8</sup> due to the strain of the acetylene moiety. During the course of synthetic studies toward ciguatera known as a marine neurotoxin causing ciguatera poisoning, we reported the reductive decomplexation of dicobalt hexacarbonyl acetylenes into *cis*-olefins or vinylsilanes.<sup>9</sup> In the synthetic studies on the central part of ciguatera, high-pressure hydrogenation of the cobalt complex gave the desired ketone as a major product.<sup>10</sup> At that time, high-pressure hydrogenation was the only method for conversion of acetylene cobalt complex to ketone in a single step. Since this reaction mechanism was unclear, it was difficult to improve for a practically useful method.

A 7-membered ring cobalt complex **1** was exposed to air under heating condition to give two ketones of regioisomer (Eq 1). But application of this condition to 9-membered ring cobalt complex **4** resulted in affording a complex mixture (Eq 2). It implied that a carbonyl ligand of acetylene cobalt complex was removed by heating to result in a formation of coordinatively unsaturated complex and then coordinating with molecular oxygen to give the ketone. No 7-membered ring acetylene can exist because of the ring strain, therefore, the coordinatively unsaturated complex shows longer-life. On the other hand, 9-membered acetylene can exist, so the coordinatively unsaturated complex decomposed easily.



If a coordinatively unsaturated complex could somehow be stabilized, ketone formation would apply for 9-membered ring.

We expected that some ligand-exchange complexes<sup>11</sup> might satisfy these requirements directed to the ketone synthesis.

Table 1 summarizes the effects of some ligands. We clearly observed the ligand-exchange compound on the TLC, when 9-membered ring acetylene cobalt complex **4** was treated with triphenylphosphine. After 1 or 2 h, the ligand exchange cobalt complex was converted to the corresponding acetylene **5** (Entry 1). In this case, no 9-membered ring-ketone **6** was obtained, but the result suggested the potentiality to stabilize coordinatively unsaturated complex via ligand exchange by a phosphine group. Then, we attempted to employ a bidentate ligand. Treatment of the acetylene cobalt complex with dppm at 60 °C gave acetylene dppm dicobalt tetracarbonyl complex. After stirring for 1 or 2 days at the same temperature, dppm complex was converted to the desired ketone **6** in moderate yield (Entry 2). Treatment with two-methylene diphosphine ligand, dppe or bis(diphenylphosphino)benzene, gave a mixture of ligand exchanged complex and simply decomplexed acetylene **5**. After stirring for several hours, both of the desired ketone **6** and the acetylene **5** were isolated (Entries 3 and 4). Treatment with three or four-methylene diphosphine ligand gave only decomplexed acetylene **5** (Entries 5 and 6). These results imply that bidentate ligands longer than dppe similarly behave like triphenylphosphine. Thus, ligand-exchange with dppm gave the best result among others as shown in Table 1.

Table 2 summarizes the result of ketone-formation with dppm under various ways of oxygen introduction. In Entry 1, treatment of the cobalt complex **4** with 1.5 equiv. of dppm under open air gave **6** in lower yield. In Entry 2, treatment of **4** under controlled air condition gave **6** in moderate yield, but not reproducible. Entries 1 and 2 show that it is difficult to obtain ketone in a steady yield only by a controlled amount of air. In Entry 3, addition of excess dppm gave the ketone **6** reproducibly in moderate yield. In Entry 4, using of excess dppm under pure

Table 1.

Entry	Ligand	Time/h	Yield/%	<b>5</b>	<b>6</b>
1	PPh <sub>3</sub>	4	80	0	
2	dppm	22	trace	46	
3	dppe	15	18	28	
4	dppBz	15	45	28	
5	dppp	14	80	0	
6	dppb	14	80	0	

Table 2.

Entry	dpmm (equiv.)	Conditions	Time	Yield
1	1.5	open air	5 h	21%
2	1.5	air injected by syringe	15 h	47%
3	15	open air	8 h	55%
4	15	O <sub>2</sub>	3 h	45%
5	15	sealed (non oxygen condition)	24 h	0% <sup>a</sup>

<sup>a</sup>dpmm complex 7 was recovered in quantitative yield.

Table 3.

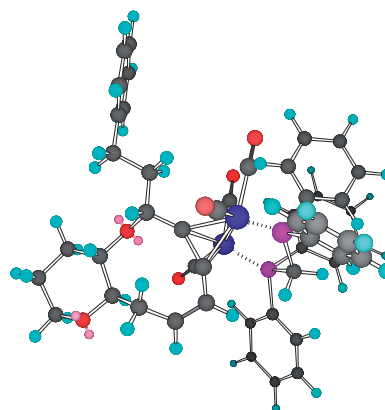
Entry	Substrates	dpmm	Products
100 °C, air			
1			
2			
3			
4			

oxygen condition gave the ketone **6** rapidly in almost the same yield. Under non-oxygen condition (Entry 5), on the other hand, no ketone was obtained, instead dpmm complex **7** was recovered in quantitative yield.

In the Table 3 are depicted some examples of the conversion of cyclic or acyclic cobalt complex into the corresponding ketones under optimized condition. Contrary to the result of Eq 1, treatment of **1** with dpmm gave the regioisomer **2** as the major product (Entry 2).

A hypothetical mechanism of this selectivity with cyclic cobalt complex may be as follows: Opposite side of alkyl side chain is less hindered, so that dpmm was exchanged for two carbon monoxide in the less hindered side as shown in Figure 1. Finally, molecular oxygen attack cobalt atom from less hindered side opposite to dpmm, and consequently, the oxygen atom is shifted toward this carbon to give the ketone.

Thus, we found some ligand-exchanged cobalt complexes exposed to air under heating to give the corresponding ketone

Figure 1. Possible 3D structure of **7**.

in moderate yields, which would widely provide a new method for organic synthesis.

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