A Novel Carbonylative Decomplexation of Alkyne-Dicobalt Hexacarbonyls: Hydrocarbamoylation of Alkynes

Takumichi Sugihara*[a], Yoshinari Okada[b], Masahiko Yamaguchi*[b], Mugio Nishizawa
[a]Faculty of Pharmaceutical Sciences, Tokushima Bunri University, Yamashiro-cho, Tokushima 770-8514, Japan
Email: taku@ph.bunri-u.ac.jp
[b]Faculty of Pharmaceutical Sciences, Tohoku University, Aobayama, Sendai 980-8578, Japan
Received 11 March 1999

Abstract: A novel carbonylative decomplexation of alkyne-dicobalt hexacarbonyls, i. e. hydrocarbamoylation of alkynes, was carried out by reaction of the complexes with 10 equiv. of primary and secondary amines.

Key words: hydrocarbamoylation, alkyne-dicobalt hexacarbonyl, carbonylation, decomplexation, amine

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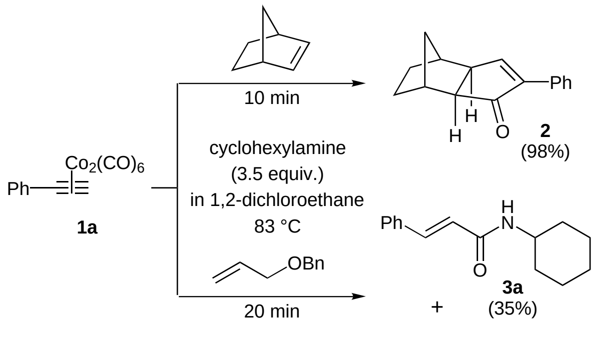
It is known that 'hard' Lewis bases, such as amines and alcohols, on low-valent organotransition metal complexes make the existing ligands labile and reactive.[1] We utilized this effect for the promotion of the Pauson-Khand reaction[2] by treatment with primary amines and ammonia.[3] The intermolecular Pauson-Khand reaction of **1a** with a reactive alkene, such as norbornene, in the presence of cyclohexylamine proceeded smoothly to give the desired cyclopentenone **2** in a good yield. In contrast, an attempted reaction of an allyl ether resulted in the recovery of the starting material. It was, however, found that **1a** was converted to an α,β-unsaturated amide **3a** in the presence of the amine (Scheme 1).



Scheme 1

This reaction corresponds to a hydrocarbamoylation of alkynes, i. e. a novel carbonylative decomplexation of alkyne-dicobalt hexacarbonyls.[4] Hydrocarbamoylation of alkynes has not been well developed and a major contribution in this area is restricted to the nickel catalyzed reaction.[5] Usually, synthesis of α,β-unsaturated amide from alkynes was carried out by hydrohalogenation followed by carbonylative amidation catalyzed by palladium complexes.[6] There is no report that cobalt carbonyl complexes mediate the hydrocarbamoylation of alkynes. Furthermore, except the Pauson-Khand reaction and the cyclotrimerization of alkynes,[7] there was no report to construct a carbon-carbon bond on the alkynes complexed with dicobalt hexacarbonyls directly. Therefore, we started to investigate this novel carbonylative decomplexation reaction. Results of the reaction of **1a** with cyclohexylamine under various conditions are summarized in Table 1.

Table 1. Reaction of **1a** with cyclohexylamine under various conditions.[a]

Entry	Cyclohexylamine (Equiv.)	Solvent	Temp. (°C)	Time (h)	Yield of **3a**[b] (%)
1	1.2	toluene	110	1	9[c]
2	3.5	toluene	110	1	52
3	3.5	toluene	110	10	54
4[d]	3.5	toluene	110	1	47
5	10	toluene	110	1	76
6	10	toluene	25	48	–[e]
7	10	benzene	80	1	64
8	10	1,2-dichloroethane	83	1	35
9	10	DME	85	1	27
10	10	chlorobenzene	110	1	80[f]

[a] All reactions were carried out in 0.2 M solution under argon atmosphere. [b] The *cis* isomer was not detected. [c] 1,2,4-triphenylbenzene was also produced in 47% yield. [d] The reaction was carried out under 1 atm of CO atmosphere. [e] **1a** was recovered in 15% yield along with phenylacetylene. [f] *N*-Cyclohexylbenzamide was also produced in 27% yield based on the molar equivalent of **1**.

When 1.2 equiv. of the amine were used, the desired **3** was produced in a low yield along with 1,2,4-triphenylbenzene (Entry 1). Increase in the amount of the amine improved the yield (Entries 1, 2, and 5), and use of more than 10 equiv. of the amine under argon atmosphere gave the satisfactory result (Entry 5). Comparison of Entries 2-4 revealed that the employment of prolonged reaction time and a carbon monoxide atmosphere did not have an influence on the reaction. While the decomplexation proceeded at lower temperatures (Entry 6), the desired hydrocarbamoylation took place at higher temperatures (Entry 5). Solvents had an influence on the efficiency of the reaction. Although the use of 1,2-dichloroethane, which is the best solvent in the primary amine-promoted Pauson-Khand reaction,[3] and 1,2-dimethoxyethane (DME) did not provide satisfactory results (Entries 8 and 9), the reaction underwent efficiently in aromatic solvents such as toluene, benzene, and chlorobenzene (Entries 5, 7, and 10). Since N-cyclohexylbenzamide was produced in the reaction in chlorobenzene (Entry 10), the activated cobalt complexes formed from **1a** and the amine oxidatively added to the carbon-chlorine bond of the chlorobenzene. The best conditions for the hydrocarbamoylation are as the follow: 10 equiv. of amines in toluene at 110 °C. Since formation of alkyne-dicobalt hexacarbonyls usually undergoes in quantitative yields, the present reaction demonstrates that alkynes can be converted into trans α,β-unsaturated amides in good yields via two steps conversions. We then continued investigation of the scope of the reaction and the results are summarized in Table 2.

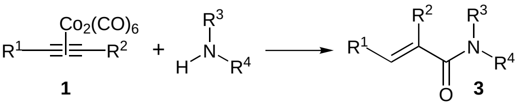
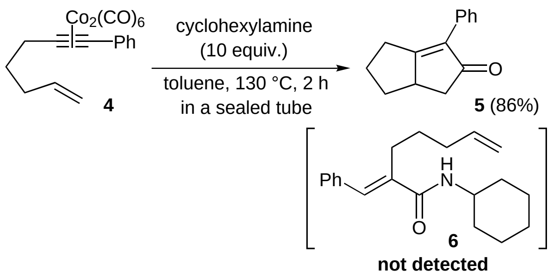


Table 2. Reaction of alkyne-dicobalt hexacarbonyls **1** with various amines.[a]

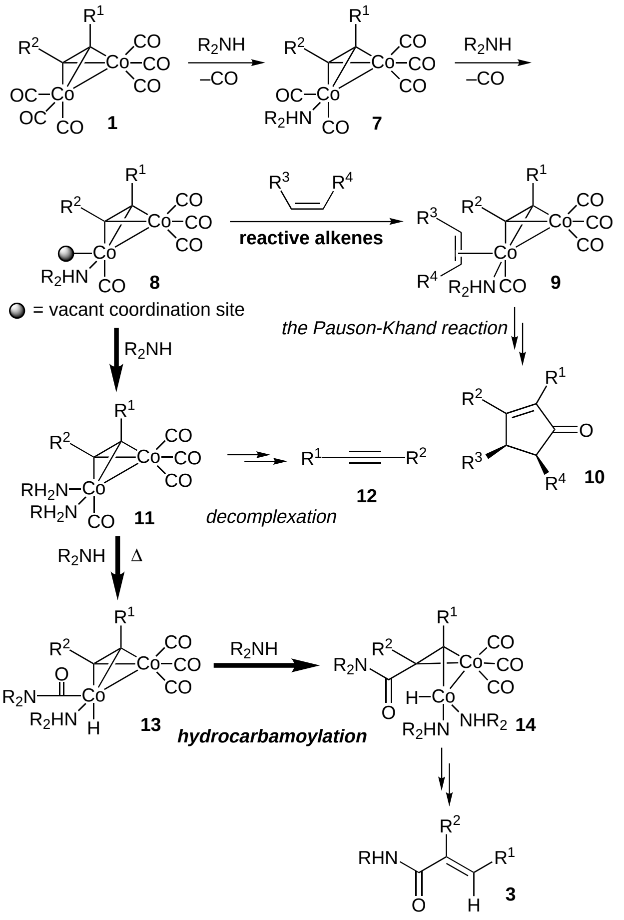
Entry	Complex			Amine		Solvent	Temp.	Time	Yield of **3**[b]	
	1	R^1	R^2	R^3	R^4		(°C)	(h)	**3**	(%)
1	**a**	Ph	H	H	Bn	toluene	110	2	**e**	82
2	**a**	Ph	H	H	PhC(Me)H[c]	toluene	110	1	**f**	74
3	**a**	Ph	H	H	*c*-Oct[d]	toluene	110	2	**g**	65
4	**a**	Ph	H	H	*t*-Bu	toluene	130[e]	10	**h**	31
5	**a**	Ph	H	H	Ph	xylene	140	10	**i**	–[f]
6	**a**	Ph	H	Et	Et	toluene	130[e]	4	**j**	47
7	**b**	*n*-Bu	H	H	Cy[g]	xylene	140	2	**k**	63
8	**b**	*n*-Bu	H	H	Bn	toluene	110	2	**l**	68
9	**b**	*n*-Bu	H	H	PhC(Me)H[c]	toluene	110	2	**m**	68
10	**b**	*n*-Bu	H	H	*c*-Oct[d]	toluene	130[e]	2	**n**	60
11	**c**	*n*-Pr	*n*-Pr	H	Cy[g]	xylene	140	2	**o**	64
12	**c**	*n*-Pr	*n*-Pr	H	Bn	toluene	110	1	**p**	72
13	**c**	*n*-Pr	*n*-Pr	H	PhC(Me)H[c]	toluene	110	1	**q**	62
14	**d**	Ph	Ph	H	Cy[g]	toluene	110	2	**r**	10[h]

[a] All reactions were carried out in the presence of 10 equiv. of the amine in 0.2 M solution under argon atmosphere. [b] The *cis* isomer was not detected. [c] (*R*)-1-phenylethylamine was used. [d] *c*-Oct-NH_2 is cyclooctylamine. [e] The reaction was carried out in a sealed tube. [f] The corresponding α,β-unsaturated amide was not detected. [g] Cy-NH_2 is cyclohexylamine. [h] Decomplexation reaction also proceeded to give diphenylacetylene in 75% yield.

The reaction with primary amines having primary or secondary alkyl groups, such as benzylamine, (R)-1-phenylethylamine, and cyclooctylamine, proceeded smoothly to give the corresponding amides in good yields (Entries 1-3). In contrast, when tert-butylamine and diethylamine were used, the products were obtained in moderate yields (Entries 4 and 6). The steric bulkiness around the nitrogen atom has an influence on the hydrocarbamoylation. Since the reaction with aniline did not proceed (Entry 5), the electron density on the nitrogen atom also played an important role. Complexes derived from alkyl substituted alkynes could be converted into the corresponding amides in good yields by treatment with primary amines (Entries 7-13). The reaction of the complex derived from diphenylacetylene was cumbersome and decomplexation proceeded predominantly (Entry 14). When **4** was treated with cyclohexylamine under the same conditions, **5** was produced as a sole product with no sign of the formation of **6** (Scheme 2). In the presence of alkenes at the suitable position, the Pauson-Khand reaction is faster than the hydrocarbamoylation.



Scheme 2



Scheme 3

The proposed mechanisms are shown in Scheme 3. The first step of the reaction is considered as the ligand substitution reaction of one of the CO in **1** with the amines followed by liberation of the CO to produce the coordinatively unsaturated complex **8**. As shown in Scheme 1 and 2, alkenes, if present and sufficiently reactive, then occupy the vacant coordination site to produce **9**, which undergoes the Pauson-Khand reaction. When reactive alkenes are absent, a second amine coordinates to the cobalt to produce **11**. Since **11** is unstable due to the electronic effects of the coordinated amines, the alkyne ligand is liberated at the ambient temperature and finally the decomplexation occurs as shown in Entry 6 in Table 1. At higher temperatures, insertion of CO to the cobalt-amine bond undergoes smoothly to yield **13**, and then the reaction ended up with the formation of the α,β-unsaturated amide **3**.

It is clear that the reaction underwent in regioselective manner. In carbometallation and acylmetallation reactions, it is known that metals usually prefer to be located at the α-position of the phenyl group due to the metal-directing effect of the phenyl susbtituent.[8] Thus, the carbamoyl group might be transferred first from the cobalt to the terminal alkyne carbon to produce **14**, in which one of the cobalt is located on the internal carbon. Subsequent protonation and decomplexation gives the trans α,β-unsaturated amide **3**. The mechanisms of reactions of alkyne-dicobalt hexacarbonyls with amines are currently under investigation.

Acknowledgement

This work is supported in part by grants from the Japan Society of Promotion of Science (No. RFTF 97P00302) and the Ministry of Education, Science, Sports, and Culture, Japan (No. 09771890).

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Article Identifier:
1437-2096,E;1999,0,06,0768,0770,ftx,en;Y06399ST.pdf