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Novel decomplexation method for alkyne–$Co_2(CO)_6$ complexes

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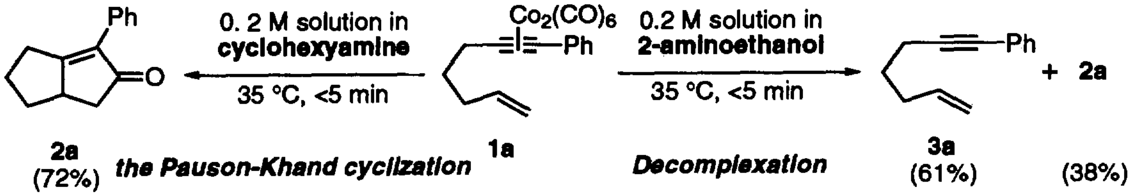
Abstract

A novel and general decomplexation method for alkyne–$Co_2(CO)_6$ complexes has been established, which treats the complexes with ethylenediamine in THF. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Decomplexation; Alkyne complexes; Carbonyl complexes; Cobalt; Ethylenediamine

Alkyne–$Co_2(CO)_6$ complexes are often used not only for protection of alkynes [1] but also as mediator for construction of new carbon–carbon bonds in the well-known Nicholas [2] and Pauson–Khand reaction [3]. In the Nicholas reaction, even if the carbon–carbon bond formation is achieved in an excellent yield, the next step, i.e. the decomplexation of alkyne–$Co_2(CO)_6$ complexes, can be cumbersome. Indeed, oxidants, such as Fe^{3+} ion [4], ceric ammonium nitrate (CAN) [5], or tertiary amine oxides [6] are usually used to carry out decomplexation, which can lead to unacceptable yields due to the propensity of the resulting alkynes to oxidation in some cases. We recently found that the Pauson–Khand reaction was carried out in cyclohexylamine at 35°C with a dramatic rate-enhancement [7]. In the course of our study on the Pauson–Khand reaction, when **1a** was treated with 2-aminoethanol, not only the Pauson–Khand reaction but also decomplexation took place to afford **3a** predominantly (Scheme 1). This result led us to investigate a novel decomplexation method for alkyne–$Co_2(CO)_6$ complexes without using oxidants [8,9].

At first, we focused on the duality of the reaction course as shown in Scheme 1 and tried to find conditions in which the decomplexation could proceed exclusively. Since we convinced that primary amines can easily react with alkyne–$Co_2(CO)_6$ complexes from our preliminary results [7], we first studied the reaction of **1a** with excess amount of chelatable diamines. The results under various conditions are summarized in Table 1 (Scheme 2).



Scheme 1.

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Table 1
The decomplexation reaction of **1a** under various conditions[a]

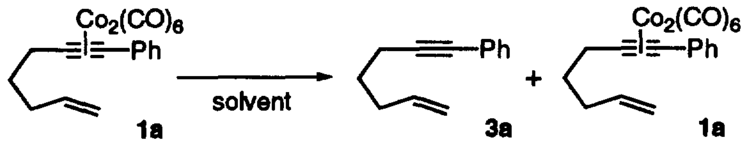
Entry	Solvent	Additive	(Eq.)	Temp (°C)	Time	Yield (%)	
						3a	**1a**
1	$H_2NCH_2CH_2NH_2$			35	5 min	97	—
2	$HN(CH_2CH_2NH_2)_2$			35	5 min	90	—
3	$(CH_2NHCH_2CH_2NH_2)_2$			35	5 min	94	—
4	THF	$H_2NCH_2CH_2NH_2$	10	25	10 h	99	—
5	THF	$H_2NCH_2CH_2NH_2$	3.5	65	5 min	94	—
6	THF	$H_2NCH_2CH_2NH_2$	2.3	65	30 min	89	—
7	THF	$H_2NCH_2CH_2NH_2$	1.2	65	2 h	75[b]	5
8	EtOH	$Fe(NO_3)_3 \cdot 9H_2O$	4.5	25	4 h	77[b]	—
9	CH_2Cl_2	NMO[c]	1.5	25	10 h	—[d]	—

[a] All reactions were carried out in 0.2 M solution. [b] The undetermined polar byproducts were also produced. [c] NMO, *N*-methylmorpholine *N*-oxide. [d] **2a** was produced in 97% yield instead of **3a**.

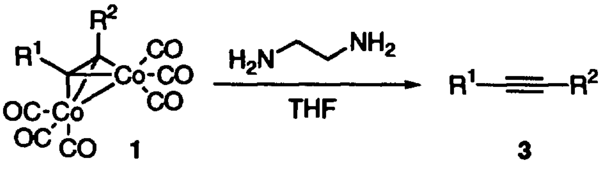
When ethylenediamine was used as a solvent, the desired decomplexation exclusively proceeded in a short reaction time to give **3a** in an excellent yield (entry 1). Although the use of diethylenetriamine and triethylenetetramine as solvents also promoted decomplexation (entry 2 and 3), the simplest one, i.e. ethylenediamine, gave the cleanest results. Reducing the amount of ethylenediamine to ten equivalents still allowed to carry out the reaction in a reasonable time (10 h) at 25°C (entry 4). At more elevated temperature, the amount of ethylenediamine could be reduced down to 3.5 equivalents with respect to the complex, and the reaction was completed in a short time (entry 5). Entries 6 and 7 showed that the use of smaller amount of the diamine slowed down the reaction and decreased the yield of **3a**. Among various solvents such as toluene, 1,4-dioxane, 1,2-dichloroethane, and 1,2-dimethoxyethane, tetrahydrofuran (THF) has proven to be the best for both conditions, i.e. with 3.5 equivalents of the amine at 65°C (Conditions A) and with ten equivalents of ethylenediamine at 25°C (Conditions B) [10]. Under previously published conditions [4], polar byproducts were also formed (entry 8). When **1a** was treated with *N*-methylmorpholine *N*-oxide (NMO) in dichloromethane, the bicyclic enone **2a** was produced in an excellent yield (entry 9) [11]. The present method should become an important alternative procedure for the decomplexation of alkyne–$Co_2(CO)_6$ complexes without using oxidants.

With these suitable conditions for decomplexation in our hand, we investigated its scope (Scheme 3; Table 2). In most of the cases shown in Table 2 (except entry 12), the desired decomplexation was finished within 30 min at 65°C and within 1 day at 25°C to afford the original alkynes **3** in excellent yields. Protection of alcohol moieties of the side chain was not necessary for decomplexation (entries 3, 5 and 13). Terminal alkynes could also undergo this reaction (entry 7). It is also worth pointing out that amides and sulfides did not affect the reaction course to give the original alkynes in good yields (entries 8–10). The trimethylsilyl group on the alkynyl carbon, which is sometimes used as a protective groups for terminal alkynes, mostly survived under conditions A, while nearly half of it was cleaved during decomplexation under conditions B presumably due to the longer reaction time (entry 11). In contrast, when 1-benzyloxy-5-trimethysilyl-4-pentyne (**3l**) was treated under both conditions A and B, **3l** was recovered in quantitative yield. The cobalt in the reaction mixture might be responsible for the cleavage of the trimethylsilyl group in the present case (entry 11). On the other hand, the triethylsilyl group survived under both conditions despite a longer reaction time (entry 12). It should be mentioned that decomplexation of simple propargyl ether–$Co_2(CO)_6$ complexes such as 1-benzyloxy-2-propyne did not work under both conditions.

Considering the mechanisms, sterically less hindered amines such as primary ones might come close to the



Scheme 2.



Scheme 3.

Co atom of alkyne–$Co_2(CO)_6$ complexes and displace one of the CO to give **4** (Scheme 4). The driving force for the substitution reaction is thought to be strong affinity between cobalt and nitrogen. It is known that 'hard' ligands, which contain a N or O atom, on metal–carbonyl complexes make the existing CO ligands labile and therefore facilitate the ligand substitution reaction [12]. The amine on the complex might trigger to open up a vacant coordination site due to its labilizing effect to form complexes such as **5**. When an existing olefin is accessible to this site, the Pauson–Khand reaction could proceed as we reported previously (i.e. **5**→**6**→**7**) [7]. In contrast, when chelatable diamines are used instead of monoamines, the vacant coordination site could be filled by the other amino group to form a chelate complex such as **8**. The resulting complex becomes more electron-rich and might start to release the alkyne **3**. The mechanisms of reactions of alkyne–$Co_2(CO)_6$ complexes with amines, which presented in the above hypothesis, are currently under further investigation.

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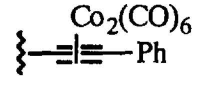
Table 2
The decomplexation reaction of alkyne–$Co_2(CO)_6$ complexes **1**[a]

Entry	**1**	R_1	R_2	Conditions A[b]		Conditions B[c]	
				Time (min)	Yield of **3** (%)	Time (h)	Yield of **3** (%)
1	**b**	Ph	Ph	10	94	10	98
2	**c**	Ph	CH_2OBn	30	98	5	97
3	**d**	Ph	CH_2OH	10	90	24	92
4	**e**	*n*-Bu	CH_2OBn	20	92	20	96
5	**f**	Ph	$C(CH_3)_2OH$	15	97	24	100
6	**g**	Ph	$(CH_2)_2OBn$	10	98	10	99
7	**h**	H	$(CH_2)_2OBn$	10	92	10	98
8	**i**	Ph	$(CH_2)_2NHBz$	15	93	8	90
9	**j**	Ph	$(CH_2)_2NHTs$	15	88	10	84
10	**k**	Ph	$(CH_2)_2SPh$	15	94	8	92
11	**l**	Me_3Si	$(CH_2)_3OBn$	15	85[d]	20	47[e]
12	**m**	Et_3Si	$(CH_2)_3OBn$	60	93	60	94
13	**n**	Ph	$(CH_2)_3OH$	20	90	20	80
14	**o**	Ph	$(CH_2)_3OTBDPS$	20	94	20	95
15	**p**	Ph		10[f]	99[g]	7[h]	98[g]

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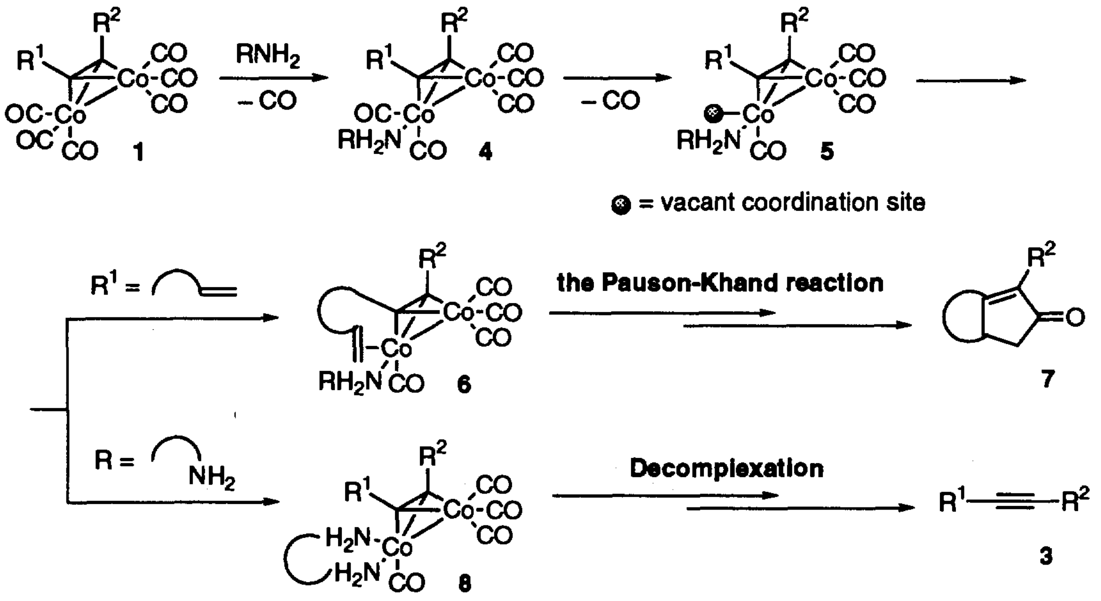
[a] All reactions were carried out in 0.2 M solution. [b] Conditions A: A mixture of the complex and 3.5 molecular equivalents of ethylenediamine in THF was stirred at 65°C. [c] Conditions B: A mixture of the complex and ten molecular equivalents of ethylenediamine in THF was stirred at room temperature. [d] The desilylated acetylene, 1-benzyloxy-4-pentyne, was also produced in 8% yield. [e] The desilylated acetylene, 1-benzyloxy-4-pentyne, was also produced in 38% yield. [f] Seven molecular equivalents of ethylenediamine were used. [g] **3p** is 1,4-diphenyl-1,3-butadiyne. [h] Twenty molecular equivalents of ethylenediamine were used.



Scheme 4.

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[10] The typical experimental procedures for conditions A: Under an argon atmosphere, a mixture of **1a** (543 mg, 1.19 mmol) and ethylenediamine (0.28 ml, 4.19 mmol) in THF (5.6 ml) was stirred at 65°C for 5 min. After cooling, Et_2O and water were added to the reaction mixture. The organic layer was separated, washed with 3% HCl aq. and sat. $NaHCO_3$ aq. successively, dried over $MgSO_4$, and concentrated. The resulting residue was passed through silica gel pad (*n*-hexane) to give **3a** (190 mg, 94%) as a colorless oil. For conditions B: Under an argon atmosphere, ethylenediamine (0.82 ml, 12.3 mmol) was added to a solution of **1a** (562 mg, 1.23 mmol) in THF (6.2 ml) at 25°C. After 10 h, Et_2O and water were added to the reaction mixture. The organic layer was separated, washed with 3% HCl aq. and sat. $NaHCO_3$ aq. successively, dried over $MgSO_4$, and concentrated. The resulting residue was passed through silica gel pad (*n*-hexane) to give **3a** (207 mg, 99%) as a colorless oil.

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