

Journal of Organometallic Chemistry 554 (1998) 163-166

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

Takumichi Sugihara *, Hitoshi Ban, Masahiko Yamaguchi

Faculty of Pharmaceutical Sciences, Tohoku University, Aobayama, Sendai 980-8578, Japan

Received 1 September 1997; received in revised form 13 October 1997

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 wellknown 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 Fe³⁺ 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).





* Corresponding author. Tel.: + 81 22 2176814; fax: + 81 22 2176811; e-mail: taku@mail.pharm.tohoku.ac.jp

⁰⁰²²⁻³²⁸X/98/\$19.00 © 1998 Elsevier Science S.A. All rights reserved. *PII* S0022-328X(97)00679-7

Table 1					
The decomplexation	on reaction	of 1a	under	various	conditions ^a

Entry	Solvent	Additive	(Eq.)	Temp (°C)	Time	Yield (%)	
						3 a	1a
1	H2NCH2CH2NH2			35	5 min	97	_
2	HN(CH ₂ CH ₂ NH ₂) ₂			35	5 min	90	
3	(CH ₂ NHCH ₂ CH ₂ NH ₂) ₂			35	5 min	94	
4	THF	H2NCH2CH2NH2	10	25	10 h	99	
5	THF	H ₂ NCH ₂ CH ₂ NH ₂	3.5	65	5 min	94	
6	THF	H ₂ NCH ₂ CH ₂ NH ₂	2.3	65	30 min	89	
7	THF	H ₂ NCH ₂ CH ₂ NH ₂	1.2	65	2 h	75 ^b	5
8	EtOH	$Fe(NO_3)_3 \cdot 9H_2O$	4.5	25	4 h	77 ^ь	
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 1,2dimethoxyethane, 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-Co₂(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 (31) was treated under both conditions A and B, 31 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-Co₂(CO)₆ complexes such as 1-benzyloxy-2propyne did not work under both conditions.

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





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

Table 2 The decomplexation reaction of alkyne $-Co_2(CO)_6$ complexes 1^a

 \mathbf{R}_2

Entry

1

 R_1

1	ь.	DI-	D1-	10	04	10	00	
1	D	Pn	Ph CH OD	10	94	10	98	
2	c	Ph	CH ₂ OBn	30	98	5	97	
3	d	Ph	CH ₂ OH	10	90	24	92	
4	e	<i>n</i> -Bu	CH ₂ OBn	20	92	20	96	
5	f	Ph	C(CH ₃) ₂ OH	15	97	24	100	
6	g	Ph	(CH ₂) ₂ OBn	10	98	10	99	
7	h	Η	(CH ₂) ₂ OBn	10	92	10	98	
8	i	Ph	$(CH_2)_2 NHBz$	15	93	8	90	
9	j	Ph	(CH ₂) ₂ NHTs	15	88	10	84	
10	k	Ph	$(CH_2)_2$ SPh	15	94	8	92	
11	1	Me ₃ Si	(CH ₂) ₃ OBn	15	85 ^d	20	47°	
12	m	Et ₃ Si	(CH ₂) ₃ OBn	60	93	60	94	
13	n	Ph	$(CH_2)_3OH$	20	90	20	80	
14	0	Ph	(CH ₂) ₃ OTBDPS	20	94	20	95	
15	р	Ph		10 ^f	99 ^g	7 ^h	98 ^g	
			$\begin{array}{c} \operatorname{Co}_2(\operatorname{CO})_6\\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ $					

Conditions A^b

Time (min)

reported previously (i.e. $5 \rightarrow 6 \rightarrow 7$) [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.

Acknowledgements

Yield of 3 (%)

The authors kindly thank Mamiko Yamada for her valuable technical assistance. This work was supported in part by grants from the Japan Society of Promotion of Science (Research for the Future Program) and the Ministry of Education, Science, Sports, and Culture, Japan (no. 08404050 & 09771890). The authors would also like to thank Dr Christophe Coperét at the Scripps Research Institute for his kind advice during the preparation of this manuscript.

Conditions B^c

Yield of 3 (%)

Time (h)

^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-4pentyne, 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.





References

- For recent reviews, see, (a) S.G. Davis, in: Organotransition Metal Chemistry: Applications to Organic Synthesis, Pergamon, Oxford, 1986, pp. 86–90. (b) H. Kunz, H. Waldmann, in: E.W. Abel, F.G. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, vol. 6, Elsevier, New York, 1995, pp. 692–693.
- [2] For recent reviews, see, (a) K.M. Nicholas, Acc. Chem. Res. 20 (1987) 207. (b) A.J.M. Caffyn, K.M. Nicholas, in: E.W. Abel, F.G. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, vol. 12, Elsevier, New York, 1995, pp. 685–702.
- [3] For recent reviews, see, (a) P.L. Pauson, in: A. de Meijere, H. tom Dieck (Eds.), Organometallics in Organic Synthesis, Springer-Verlag, Berlin, 1987, pp. 233–246. (b) N.E. Shore, Chem. Rev. 88 (1988) 1081. (c) N.E. Shore, in: L.A. Paquette (Ed.), Organic Reactions, vol. 40, Wiley, New York, 1991, pp. 1–90. (d) N.E. Shore, in: B.M. Trost, I. Fleming (Eds.), Comprehensive Organic Synthesis, vol. 5, Pergamon, Oxford, 1991, pp. 1037–1064. (e) N.E. Shore, in: E.W. Abel, F.G. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, vol. 12, Elsevier, New York, 1995, pp. 703–739.
- [4] K.M. Nicholas, R. Pettit, Tetrahedron Lett. 12 (1971) 3475.
- [5] (a) D. Seyferth, M.O. Nestle, A.T. Wehman, J. Am. Chem. Soc. 97 (1975) 7417. (b) C. Descoins, D. Samain, Tetrahedron Lett. 17 (1976) 745. (c) J.E. O'Boyle, K.M. Nicholas, Tetrahedron Lett. 21 (1980) 1595. (d) K.M. Nicholas, M. Mulvaney, M. Bayer, J. Am. Chem. Soc. 102 (1980) 2508.
- [6] For Me₃NO, see, S.L. Schreiber, T. Sammakia, W.E. Crowe, J. Am. Chem. Soc. 108 (1986) 3128.
- [7] T. Sugihara, M. Yamada, H. Ban, M. Yamaguchi, C. Kaneko, Angew. Chem. Int. Ed. Engl. 36 (1997) 2801.
- [8] Reductive decomplexation methods have been reported but all of them provide the corresponding alkenes instead of the original

alkynes. See, (a) M. Isobe, C. Yenjai, S. Tanaka, Synlett (1994) 916. (b) S. Hosokawa, M. Isobe, Synlett (1995) 1179. (c) T. Nakamura, T. Matsui, K. Tanino, I. Kuwajima, J. Org. Chem. 62 (1997) 3032. (d) S. Hosokawa, M. Isobe, in: Abstract of 72nd Annual Meeting of the Chemical Society of Japan, Tokyo, March 1997, p. 816.

- [9] There is a report that the $Co_2(CO)_6$ complex of 1-trimethylsilyl-1alkyne derivatives can be decomplexated with concomitant desilylation by the treatment with *n*-Bu₄NF. The applicability of this method, however, is unknown. See ref. [6].
- [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, Et₂O and water were added to the reaction mixture. The organic layer was separated, washed with 3% HCl aq. and sat. NaHCO3 aq. successively, dried over MgSO₄, 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, Et₂O and water were added to the reaction mixture. The organic layer was separated, washed with 3% HCl aq. and sat. NaHCO3 aq. successively, dried over MgSO4, and concentrated. The resulting residue was passed through silica gel pad (n-hexane) to give 3a (207 mg, 99%) as a colorless oil.
- [11] For the tertiary amine oxide-promoted Pauson-Khand reaction, see, (a) S. Shambayati, W.E. Crowe, S.L. Schreiber, Tetrahedron Lett. 31 (1990) 5289. (b) N. Jeong, Y.K. Chung, B.Y. Lee, S.H. Lee, S.-E. Yoo, Synlett (1991) 204.
- [12] For instance, see, C.M. Lukehart, in: Fundamental Transition Metal Organometallic Chemistry, Brooks/Cole, Monterey, 1985, pp. 63–67.