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LETTERS

Reductive Decomplexation of Biscobalthexacarbonyl Acetylenes into Olefins

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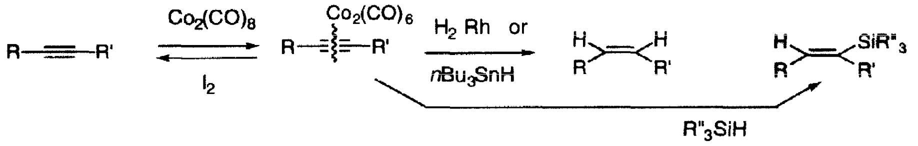
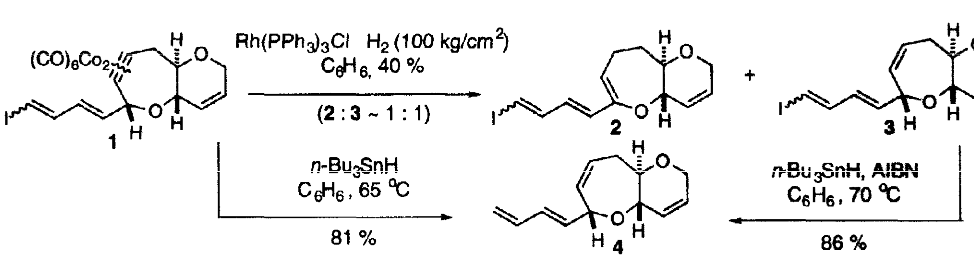
Abstract : *The decomplexation of acetylene biscobalthexacarbonyl complexes can usually be achieved under oxidative condition. We had found other reductive conditions with endo-cyclic complexes, and recently other reductive conditions with both endo- and exo-cyclic complexes using either tributyltin hydride or triethylsilane. The original acetylene derivatives were transformed selectively either into the corresponding cis olefins or cis-vinylsilanes.* © 1998 Elsevier Science Ltd. All rights reserved.

Acetylene biscobalthexacarbonyl complexes[1] are widely used as protection of triple bonds[2] as well as *C*-*C*-bond and *C*-*O*-bond formation reactions,[3,4] and thus they have been applied to natural product syntheses.[5] The most common decomplexation is oxidative procedure leading to the original triple bond, but this condition is limited to the *exo*-cyclic cases. In *endo*-cyclic complexes, on the other hand, only the method for decomplexation was high pressure hydrogenation using Rh-catalyst to provide olefinic cyclic ethers.[6, 7] Recently Kuwajima reported Birch reduction for such decomplexation.[8] In the present paper we describe two additional decomplexation protocols applicable to either *exo*- or *endo*-cyclic acetylene Co-complexes as shown in eq. 1.



eq. 1

During the course of our synthetic studies toward a part of marine natural product, gambiertoxin 4B,[9] we employed the biscobalthexacarbonyl complex strategy and examined above high pressure decomplexation with **1** in the presence of Wilkinson catalyst to obtain the vinyl iodides **2** or **3**, and the latter was treated with tributyltin hydride in the presence of AIBN to provide the de-iodinated olefin **4**. During the initial hydrogenation of **1**, however, double bond-transposition occurred partially to obtain the vinyl ether **2**. We then found that treatment of **1** with tributyltin hydride even without AIBN directly afforded **4** as a single product without double bond migration in 81% yield (Scheme 1).

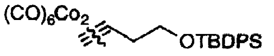
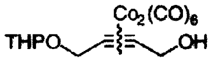
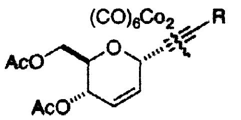
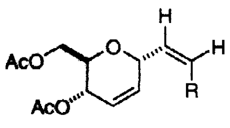
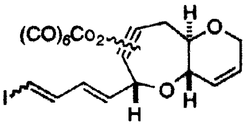
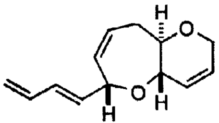
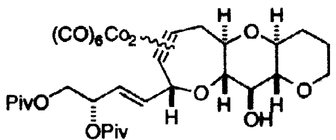
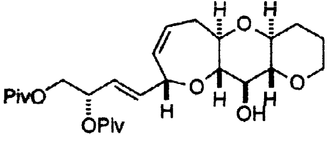
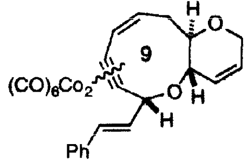
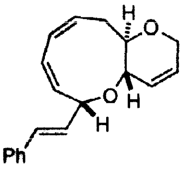
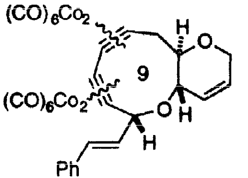
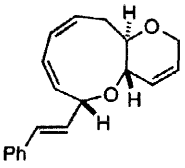


Scheme 1

PII: S0040-4039(98)00281-0

Reductive decomplexation of biscobalthexacarbonyl complexwith tinhydride. Various examples showing general applicability of this new decomplexation with tin hydride are summarized in Table 1, that includes both *endo*- and *exo*-cyclic acetylene-biscobalthexacarbonyl complexes. Common reaction conditions were heating of a 0.01-0.035M solution in benzene solvent at 65 °C with 10-12 equiv. *n*-Bu_3SnH for 2 h.

Table 1 Decomplexation of acetylene biscobalthexacarbonyl with *n*-Bu_3SnH.

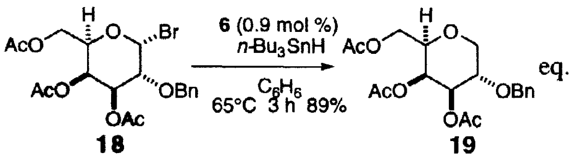
entry	substrate		product		yield (%)
1		**5**		**12**	60
2		**6**		**13**	64
3		**7**: R = H		**14**	55
4		**8**: R = TMS		**15**	64
5		**1**		**4**	81
6		**9**		**16**	82
7		**10**		**17**	61
8		**11**		**17**	35

Typical experimental details follow with the complex **1** into **4** for example. A mixture of cobalt complex **1** (76.5 mg, 126 μmol) and tributyltin hydride (400 μl, 1.51 mmol) in benzene (3.5 ml) was degassed and then heated to 65 °C with stirring. After 1 h the reaction mixture was cooled to rt and concentrated *in vacuo*. The residue was purified by silica gel column chromatography to afford product **4** (20.5 mg, 10.0 μmol, 81%)[10] as a colorless and analytically pure oil.

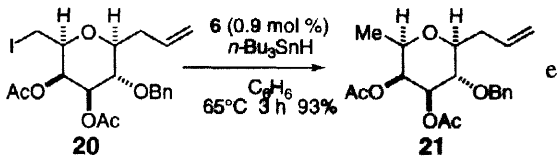
Among above examples in Table 1, we found that (i) the free hydroxyl group does not interfere the decomplexation, (ii) both terminal and di-substituted acetylene complexes work well, (iii) di-substituted acetylenes go to *cis*-olefins, (iv) *endo*-cyclic complexes give the corresponding *cis*-olefins without double bond-migration at 65 °C. Higher reaction temperatures exceeding 70 °C, however, afforded a mixture with double bond-migration products. Even the bis-(biscobalt)-complex **11** was converted to the conjugated diene **17** with *n*-Bu_3SnH.

In all examples in Table 1, no radical starter such as AIBN was used to result in the successful decomplexation. This fact suggests that the Co-complex itself may act as an initiator for radical reactions. To prove this suggestion, two independent reactions of dehalogenation such as eq. 2 and 3 were examined with a

Co-complex in the presence or absence of radical quencher. Thus, a benzene solution of the substrates **18** and **20** was heated at 65 °C for 3 h with a catalytic amount of Co-complex **6** (0.9 mol %) and excess amount of *n*-Bu$_3$SnH (3 equiv.). The bromine or iodine atoms was removed to yield the products **19** and **21**, respectively. On the other hand, no reaction happened in the presence of a radical inhibitor, galvinoxyl. These experiments led us to conclude that Co-complex can initiate radical reaction by itself.



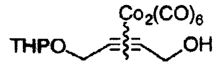
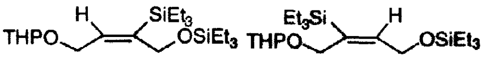
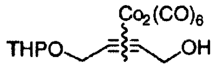
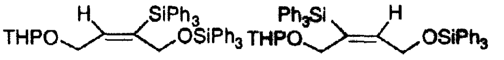
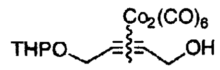
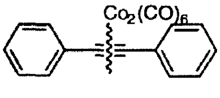
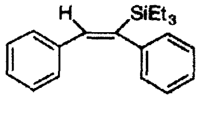
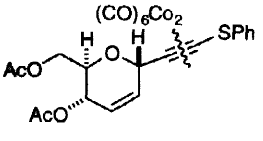
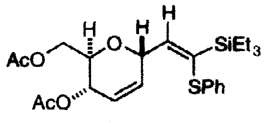
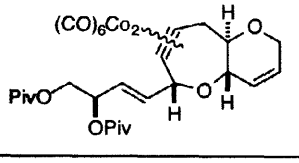
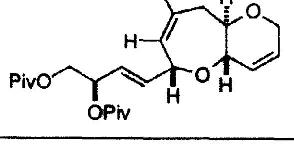
18 **19** eq. 2



20 **21** eq. 3

Hydrosilative decomplexation of biscobalthexacarbonyl complex with silicon hydride We found that an alternative decomplexation of the acetylene biscobalthexacarbonyl complex occurred by heating in benzene solution at 65 °C with triethyl- or triphenyl-silane to afford the corresponding vinylsilanes. Various examples are summarized in Table 2. The reaction proceeded all in *cis*-mode with little effect of the free hydroxyl group to geometric isomerism. Silylation of the OH-group (entry 1, 2) in the butyndiol derivative **6** was avoided by addition of ethanol as co-solvent (entry 3). In entry 4, a relatively stronger condition was necessary [high temperature (80 °C) and for long reaction period (15 h)] to complete the hydrosilative decomplexation. In cases of non-symmetric acetylene biscobalthexacarbonyl complexes (entry 5 and 6), exclusively high regio- and stereo-selectivity was found in the product vinyl silanes. These cases suggest that the bulky silyl group remained away from the more sterically crowded substituent.[11]

Table 2 **Decomplexation of acetylene biscobalthexacarbonyl with R$_3$SiH.**

entry	substrate	silane/solvent	product (yield %/ ratio)
1	 **6**	Et$_3$SiH C$_6$H$_6$	 **25a** **25b** (65 % / ~1:1)
2	 **6**	Ph$_3$SiH C$_6$H$_6$	 **26a** **26b** (49 % / ~1:1)
3	 **6**	Ph$_3$SiH C$_6$H$_6$-EtOH	 **27a** **27b** (64 % / ~6:4)
4	 **22**	Et$_3$SiH C$_6$H$_6$	 **28** (78 %)
5	 **23**	Et$_3$SiH C$_6$H$_6$	 **29** (87 %)
6	 **24**	Et$_3$SiH C$_6$H$_6$	 **30** (74 %)

A typical hydrosilation of a solution of phenylthioacetylene cobalt complex **23** (65.3 mg, 103 mmol) in triethylsilane (2.0 ml) was heated to 65 °C for 2h. After cooling to rt the reaction mixture was concentrated in vacuo and purified by silica gel column chromatography to afford **29** (41.7 mg, 90.3 μmol, 87%) as a colorless oil.

As a summary we report two new reductive decomplexation of acetylene biscobalthexacarbonyl complexes with tin hydride or silicon hydride. In the cases where *n*-Bu_3SnH was used for decomplexation, the original triple bond was transformed into a *cis* double bond. Decomplexation by R_3SiH (R= Et, Ph) afforded *cis*-vinylsilanes which may still be useful for further transformation in the synthetic scheme. All products formed in these reactions were exclusively from the *cis*-addition.

Acknowledgement This research was financially supported by a Grant-In-Aids for Scientific Research from the Ministry of Education, Science, Sports and Culture and by JSPS-RFTF. S. H. is grateful to JSPS for a Research Fellowships for Young Scientists. Special thanks are due to Mr. S. Kitamura in Nagoya University for the measurement of elemental analysis and high resolution mass spectra.

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9. Murata, M.; Legrand, A. M.; Ishibashi, Y.; Fukui, M.; Yasumoto, T. *J. Am. Chem. Soc.* **1990**, *112*, 4380-4386.
10. Compound 4: $[\alpha]_D^{29}$ -9.2° (*c* = 0.45, $CHCl_3$); ^1H-NMR (400 MHz, $CDCl_3$), δ = 2.38 (1H, ddq, *J* = 16.0, 10.5, 3.0 Hz, H-8a), 2.61 (1H, ddd, *J* = 16.0, 8.0, 3.5 Hz, H-8b), 3.27 (1H, ddd, *J* = 10.5, 8.0, 3.5 Hz, H-9), 4.00 (1H, dt, *J* = 8.0, 3.0 Hz, H-10), 4.08-4.25 (2H, m, H-13), 4,63 (1H, m, H-5), 5.10-5.15 (1H, m, H-1a), 5.19-5.26 (1H, m, H-1b), 5.65-5.90 (5H, m, H-4*, H-6, H-7, H-11, H-12), 6.28-6.40 (2H, m, H-2, H-3*); ^{13}C-NMR (75.4 MHz, $CDCl_3$) δ = 34.5, 65.5, 74.8, 78.2, 79.1, 117.8, 127.3, 127.7, 127.9, 131.5, 133.9, 134.5, 136.5; IR (KBr): ν = 2931, 2858, 1733, 1288, 1139, 1108, 1072, 1020, 902, 676 cm^{-1}; Anal. calcd. for $C_{13}H_{16}O_2$ C: 76.44, H: 7.89, found C: 76.56, H: 7.62.
11. To our best knowledge, this type of hydrosilation reaction has never been reported. We appreciate the referee's kind suggestion to cite here that the hydrosilation of olefins in the presence of $Co_2(CO)_8$ was reported in: Magomedov, G. K. I.; Andrianov, K. A.; Shkolnik, O. V.; Izmailov, B. A.; Kalinin, V. N. *J. Organomet. Chem.* **1978**, *149*, 29-36.