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Preliminary Communication

A convenient synthesis of hexacarbonyldicobalt complexes of chiral (non-racemic) terminal alkoxyacetylenes

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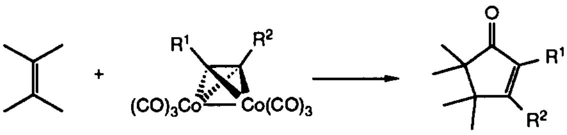
Abstract

The hexacarbonyldicobalt complexes of chiral (non-racemic) unsubstituted terminal alkoxyacetylenes have been synthesized for the first time by a novel procedure that involves one-pot transformation of a chiral alcohol to the corresponding trimethylsilylated alkoxy acetylene, followed by complexation and protodesilylation (also one-pot). The synthesis is efficient and amenable to the preparation of multigram quantities.

Key words: Cobalt; Carbonyl; Alkoxyacetylene; Asymmetric synthesis; Pauson–Khand reaction

1. Introduction

Complexation of a carbon–carbon triple bond to the hexacarbonyldicobalt grouping is very useful in organic synthesis. For example, the hexacarbonyldicobalt moiety can protect a carbon–carbon triple bond in the presence of a variety of reagents [1], promote carbocation formation [2], facilitate the separation of diastereomers [3], stabilize a thermally labile alkyne [4], and, perhaps most interestingly, mediate the reaction of an alkyne with an alkene and carbon monoxide to form a cyclopentenone in the Pauson–Khand reaction [5] (Scheme 1).



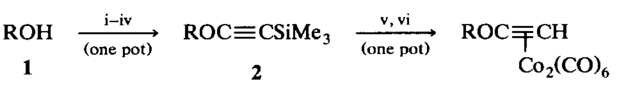
Scheme 1.

We have recently described an effective enantioselective version of the intramolecular Pauson–Khand reaction [6] based on chiral (non-racemic) alkoxyenynes [7]. A related research programme devoted to the development of an enantioselective version of the intermolecular reaction using terminal alkoxyacetylenes has until now been unsuccessful due to the extremely low yields (≤ 10%) encountered in the complexation of the chiral unsubstituted alkoxyacetylenes. In this communication we report a novel procedure for the efficient synthesis of these hexacarbonyl-μ-(η-alkoxyethyne)dicobalt(*Co–Co*) complexes.

2. Results and discussion

Octacarbonyldicobalt tends to induce the polymerization of unsubstituted terminal alkoxyacetylenes, which results in low yields of the corresponding complexes. This problem, however, can be largely circumvented through substitution on the other acetylenic carbon. Thus, the yield of the complexation of tert-butoxytrimethylsilylacetylene is *ca.* 4-fold greater than in the case of the non-silylated compound and that of *trans*-2-phenylcyclohexyloxypropyne is *ca.* 8 times higher than with the non-methylated derivative [6b].

In an effort to improve the efficiency of the preparation of the hexacarbonyldicobalt complexes of unsubstituted terminal alkoxyacetylenes, we examined various terminal substituents that could, in theory, be removed after complexation. While attempts to complex bromo- and iodo-alkoxyacetylenes [7b] were not promising, it was discovered that the trimethylsilylated derivatives **2**, prepared typically in one pot [7a] from the corresponding alcohols **1**, could be efficiently transformed to their hexacarbonyldicobalt complexes (Scheme 2). Furthermore, it was found that these derivatives, without isolation, underwent an unprecedented, remarkably facile desilylation on treatment with methanol-potassium carbonate to give the desired dicobalt complexes of the terminal alkoxyacetylenes **3**



$$\underset{\mathbf{1}}{\text{ROH}} \xrightarrow[\text{(one pot)}]{\text{i–iv}} \underset{\mathbf{2}}{\text{ROC}{\equiv}\text{CSiMe}_3} \xrightarrow[\text{(one pot)}]{\text{v, vi}} \underset{\mathbf{3}}{\underset{\text{Co}_2(\text{CO})_6}{\text{ROC}{\equiv}\text{CH}}}$$

Scheme 2. Reagents and conditions: i, KH, THF, 20°C; ii, Cl_2CCHCl, THF, −50 to 20°C; iii, LiBu, −70 to −40°C; iv, Me_3SiCl, THF, −78°C; v, $[Co_2(CO)_8]$, pentane, 20°C; vi, K_2CO_3–MeOH, 20°C.

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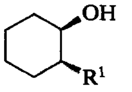
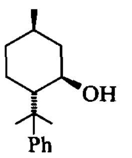
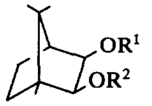
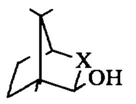
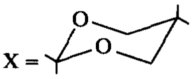
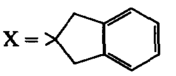
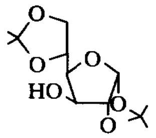
TABLE 1. Preparation of silylated alkoxyacetylenes **2** and hexacarbonyldicobalt complexes **3**

ROH (1)		Yield of **2** (%)	Yield of **3** (%)
	**a**, R^1 = phenyl	67	90
	b, R^1 = 2,4,6-trimethylphenyl	48	88
	c, R^1 = 9-phenanthryl	37	78
	**d**	67	74
	**e** R^1 = H, R^2 = -$CH_2{}^tBu$	81 [a]	82 [b]
	f R^1 = -$CH_2{}^tBu$, R^2 = H	76 [a]	45 [b]
	**g** X = 	80 [a]	82 [b]
	h X = 	94	74
	**i**	57 [c]	50

[a] Yield of non-silylated alkoxyacetylene.

[b] Overall yield from non-silylated alkoxyacetylene.

[c] Intermediate alkoxy dichloro olefin purified by SiO_2 chromatography, then treated in diethyl ether with n-butyllithium followed by chlorotrimethylsilane.

in excellent yield [8]. Several examples of this conversion are provided in Table 1.

In contrast to the reported instability and poor Pauson–Khand reactivity of the complex of ethoxyacetylene [5b], these higher-molecular-weight chiral complexes can be handled and stored for long periods without appreciable decomposition, and we found to our considerable satisfaction, that they react smoothly and selectively with representative olefins in the intermolecular Pauson–Khand reaction. These and related results will be published in the near future [9].

3. Typical experimental procedures

3.1. *Silylated alkoxyacetylene* **2a**

To 2.51 g (62.6 mmol) of oil-free potassium hydride suspended in 20 ml of tetrahydrofuran at 20°C under argon was added dropwise with stirring 5.50 g (31.2 mmol) of (1*R*,2*S*)-(−)-2-phenylcyclohexanol in 50 ml of tetrahydrofuran. After evolution of dihydrogen was complete, the mixture was cooled to −50°C, treated with 4.11 g (31.3 mmol) of trichloroethylene in 30 ml of tetrahydrofuran, and then allowed to warm to 20°C. After being stirred for 1.5 h, the brown reaction mixture was treated dropwise at −78°C with 31.3 ml (78.2 mmol) of a 2.5 M solution of n-butyllithium in hexane. After 0.5 h at −78 to −50°C, the mixture was recooled to −78°C and 12.0 ml (10.3 g, 94.6 mmol) of freshly distilled chlorotrimethylsilane in 20 ml of tetrahydrofuran was added dropwise. After being stirred at −78°C for 10 min, the mixture was poured into aqueous sodium bicarbonate and the crude product was isolated with pentane in the usual manner and purified by dry-column chromatography (silica gel pretreated with 3% v/v of triethylamine) with hexane to afford 5.70 g (67%) of **2a** as a white, crystalline solid: mp 69–70°C (pentane); $[\alpha]_D^{25}$ −59° (*c* 1.2, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.22 (m, 5H); 4.11 (m, 1H), 2.71 (m, 1H), 1.97–1.28 (m, 8H), 0.06 (s, 9H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 142.3 (C), 128.4 (CH), 127.6 (CH), 126.7 (CH), 107.8 (C), 89.9 (CH), 49.1 (CH), 38.4 (C), 33.8 (CH_2), 30.9 (CH_2), 25.5 (CH_2), 24.7 (CH_2), 0.72 (CH_3); IR (KBr) 3070, 3050, 3010, 2950, 2850, 2180, 1600, 1240, 840, 750, 700 cm^{-1}; mass spectrum (EI), *m/z* 272 (M^+), 91 (100%); Anal. Calcd for $C_{17}H_{24}OSi$: C, 74.94; H, 8.88. Found: C, 74.82; H, 8.86%.

3.2. Hexacarbonyldicobalt complex 3a

To a solution of 2.00 g (7.35 mmol) of the above silylated alkoxyacetylene **2a** in 120 ml of pentane at 20°C was added 2.68 g (7.83 mmol) of octacarbonyldicobalt and the resulting mixture was stirred for 1.5 h, whereupon the pentane was evaporated. The residue was dissolved in 120 ml of methanol and 1.00 g of solid potassium carbonate was then added. After being stirred for 2 h at 20°C, the mixture was extracted with pentane, which was then filtered through a short column of alumina and the solvent was evaporated to give 3.20 g (90%) of **3a** as a viscous, dark-red oil: ^{1}H NMR (80 MHz, $CDCl_3$) δ 7.44–7.13 (m, 5H); 5.41 (s, 1H), 3.81 (m, 1H), 2.72 (m, 1H), 2.40–0.80 (m, 8H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 142.9 (C), 134.6 (C), 128.4 (CH), 127.8 (CH), 126.7 (CH), 88.8 (CH), 53.2 (CH), 50.3 (CH), 33.8 (CH_2), 31.1 (CH_2), 25.6 (CH_2), 24.5 (CH_2); IR (film) 3060, 3040, 3010, 2900, 2850, 2085, 2045, 2010, 1510, 1040, 750, 700 cm^{-1}.

Acknowledgments

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