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Direct Synthesis of Cyclopentadienones by Cobalt Carbonyl-Mediated Carbonylative Alkyne-alkyne Coupling Reaction

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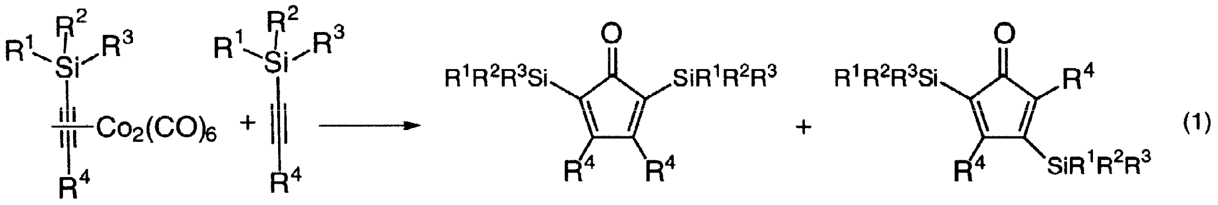
Abstract: Dicobalt carbonyl complex mediates an intermolecular carbonylative coupling reaction between alkynylsilanes. The reaction proceeds under atmospheric pressure of argon and directly provides free cyclopentadienones in high yields (up to 99%).

Keywords: Alkynes; Coupling reactions; Carbonylation; Transition metals

Cyclopentadienone is a potent compound as a synthetic intermediate. Yamazaki *et al.* reported the leading work of synthesis of cyclopentadienone by $CpCo(PPh_3)_2$-mediated alkyne-alkyne coupling, following insertion of carbon monoxide and reductive elimination of cobalt.[1] Carbonylative coupling of alkynes possessing a trimethylsilyl or aryl group mediated by $CpCo(CO)_2$[2] and $Fe(CO)_5$[3,4] has also been reported. In each reaction, however, cyclopentadienones were obtained as η^4-metal complexes. Moreover, free (uncomplexed) cyclopentadienone is generally unstable, *i.e.*, dimerization easily proceeds after oxidative treatment of the (cyclopentadienone)metal complex.

We here disclose a direct and effective synthesis of cyclopentadienones by dicobalt carbonyl complex-mediated intermolecular carbonylative alkyne-alkyne coupling reaction. This reaction could be achieved by the use of alkynylsilane, which possesses a substituent as a promoter for the coupling reaction and the other substituens as a stabilizer of the product on the silicon atom (Eq.1).



(1)

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In our initial attempt, the reaction between a dicobalt carbonyl complex of 1-(methyldiphenysilyl)-1-hexyne and the corresponding acetylene was examined in hot toluene. As a result, the dicobalt carbonyl complex was consumed at 120 °C (bath temperature) and free cyclopentadienone was obtained in moderate yield (Table 1, Entry 1). On the other hand, trimerization of alkyl- or aryl-substituted alkynes by the use of dicobalt octacarbonyl has been reported to afford substituted benzenes as a major product.[5] But in the case of the present alkynylsilane, cyclopentadienone was selectively formed. In order to improve yield, the effect of the silicon-substituent on this alkyne-alkyne coupling was investigated (Entries 2-8). The more bulky *t*-butyldiphenylsilyl group interfered with the reaction and demetallation from the alkyne complex proceeded to give free alkyne as a major product (Entry 2). The triphenyl group increased the yield (Entry 3). Moreover, introduction of an allyl group instead of a phenyl group markedly improved the reaction efficiency, and cyclopentadienone was afforded in almost quantitative yield of 99% (ratio of regioisomers A:B = 7:1) (Entry 4).[6] A less bulky group other than an allyl group on the silicon atom decreased the yield (Entries 5,6). Two allyl groups worked negatively on this reaction (Entry 7). Unlike the allyl group, a vinyl group did not operate effectively (Entry 8). These results imply that an allyldiphenylsilyl group is most appropriate for this dicobalt carbonyl complex-mediated coupling reaction. An allyl group might promote the reaction by coordination to cobalt and phenyl groups stabilize the product.

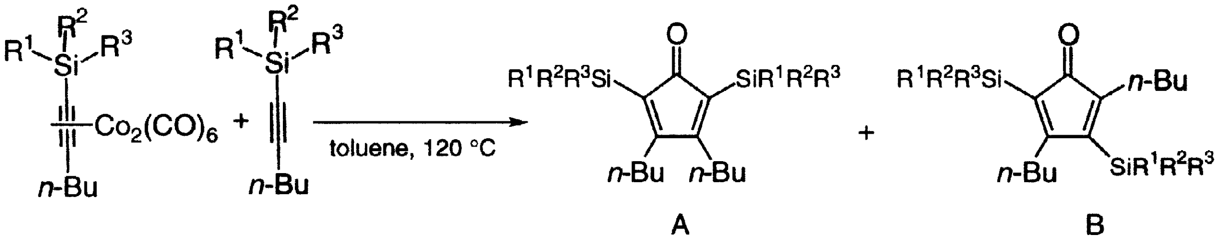

Table 1. Effect of silyl group on alkyne-alkyne coupling reaction.

Entry	R^1	R^2	R^3	Yield / % (A:B)[a]
1	Me	Ph	Ph	67 (2:1)
2	*t*-Bu	Ph	Ph	6 (>100:1)[b]
3	Ph	Ph	Ph	77 (3.5:1)
4	**allyl**	**Ph**	**Ph**	**99 (7:1)**
5	allyl	Ph	Me	48[c]
6	allyl	Me	Me	trace
7	allyl	allyl	Ph	13 (10:1)
8	vinyl	Ph	Ph	40 (2:1)

[a] Molar ratio. Dicobalt carbonyl complex:alkyne = 1:3. Yield is based on dicobalt carbonyl complex. [b] Regio isomer B could not be detected. [c] Regioisomer A and B (28%, 8:1) and isomerized products which possess methylphenyl(1-propenyl)silyl group (ca. 20%).

This coupling reaction was examined under several reaction conditions (Table 2). Under atmospheric pressure of carbon monoxide, the reaction proceeded slowly to afford the cycloproduct in lower yield (Entry 2). Dimethoxyethane (DME) could be also utilized as a solvent and cyclopentadienone was provided in high yield of 85% (Entry 3). At lower reaction temperature prolonged reaction time is necessary (Entry 4).

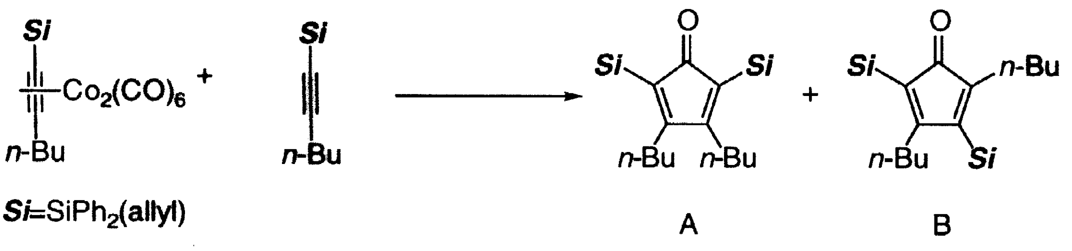

Table 2. The carbonylative alkyne-alkyne coupling under several reaction conditions.

Entry	Bath temp. /℃	Solvent	Time / h	Yield / % (A:B)[a]
1	120	toluene	2	99 (7 : 1)
2[b]	120	toluene	12	36 (10 : 1)
3	120	DME	3	85 (3 : 1)
4	90	DME	20	45 (9 : 1)

[a] Molar ratio. Dicobalt carbonyl complex:alkyne = 1:3. Yield is based on dicobalt carbonyl complex.
[b] The reaction was performed under atmospheric pressure of carbon monoxide.

Various alkynes possessing an allyldiphenylsilyl group on its terminal position were submitted to the dicobalt carbonyl complex-mediated coupling reaction in toluene (Table 3). The corresponding cyclopentadienones were obtained in high yields of 85-99% (Entries 1-3). The regioselectivity increased by the introduction of a less bulky substituent on the terminal position (Entries 3,4).[7] In the coupling of silyl acetylene which has no substituent on its terminal position, only symmetrical cyclopentadienone was selectively formed in 70% (A:B = >100:1) (Entry 4).

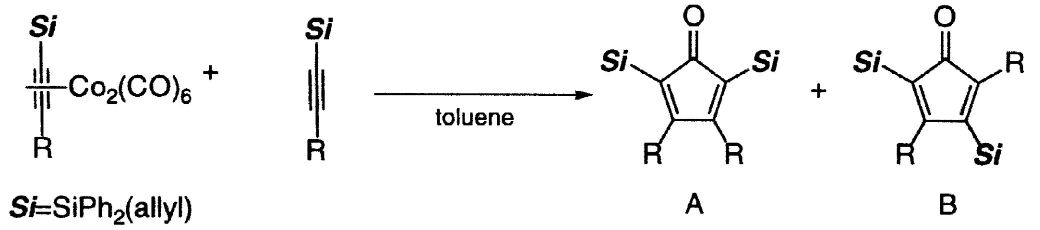

Table 3. The carbonylative coupling of various alkynes.

Entry	R	Bath temp. / ℃	Yield / %	Ratio (A:B)[a]
1	*n*-Bu	120	99	7 : 1
2	Ph	120	85	4 : 1
3	Me	100	91	10 :1
4	H	100	70	>100 :1[b]

[a] Molar ratio. Dicobalt carbonyl complex:alkyne = 1:3. Yield is based on dicobalt carbonyl complex. [b] Regio isomer B could not be detected.

Carbonylative coupling is a powerful method for the construction of a five-membered ring system. But synthetic utilization of a carbonylative alkyne-*alkyne* coupling reaction has remained relatively unexplored compared with carbonylative alkyne-*alkene* coupling (Pauson-Khand reaction).[8] Dicobalt carbonyl-mediated intermolecular carbonylative alkyne-*alkyne* coupling reaction effectively proceeds by the introduction of an allyldiphenysilyl group on alkyne. This reaction directly provides synthetically useful uncomplexed cyclopentadienones in high yields. The present results indicate further utility of the carbonylative alkyne-*alkyne* coupling reaction.

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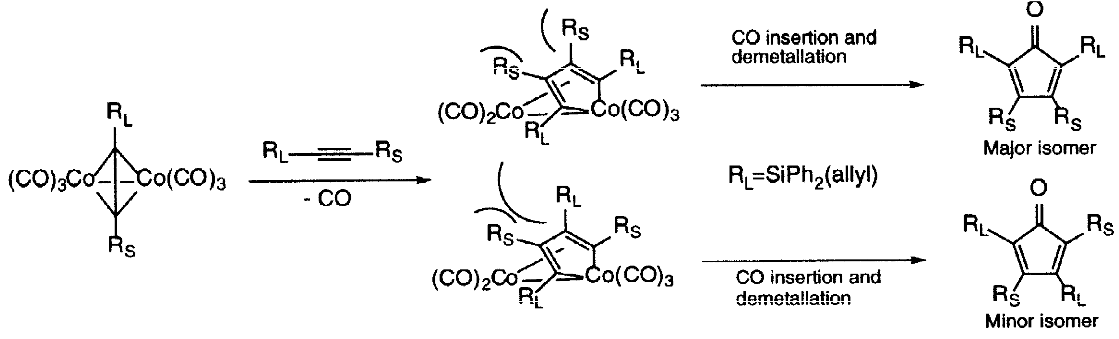
6. Typical experimental procedure (Table 1, Entry 4) is as follows: A toluene solution (2 ml) of 1-(allyldiphenysilyl)-1-hexyne-dicobalt hexacarbonyl complex (68.2 mg, 0.12 mmol) and 1-(allyldiphenylsilyl)-1-hexyne (107.0 mg, 0.35 mmol) in a 30-ml round-bottomed flask with reflux condenser was immersed in a hot oil bath (120 ℃). The reaction mixture was stirred for 2 h, then the resulting precipitates were removed by filtration through a small pad of silica gel using a mixed eluent of hexane and ethyl acetate (5/1,*v/v*). Purification of the crude products by thin-layer chromatography afforded pure cyclopentadienone in 99% yield (regioisomer A: 63.4 mg, 0.10 mmol, 86%, regioisomer B: 9.4 mg, 0.015 mmol, 13%).
7. Proposed mechanism: An allyldiphenylsilyl group on alkyne probably operates as a large substituent (R$_L$), which might control regioselectivity .



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