

Silicon-Tethered Cyclocarbonylation of Alkynes

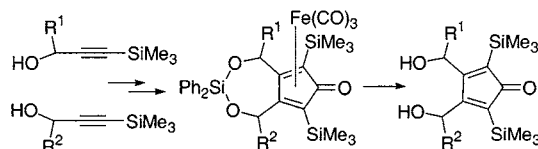
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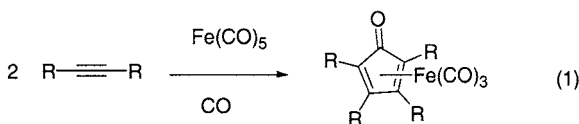
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ABSTRACT



Temporary union of alkynes in the $\text{Fe}(\text{CO})_5$ -promoted cyclocarbonylation provides a method for carbonylative cross-coupling of alkynes to construct unsymmetrically substituted cyclopentadienones.

It is known that $\text{Fe}(\text{CO})_5$ -promoted cyclocarbonylation¹ can provide a method for the construction of five-membered carbocyclic ring systems, which is potentially useful owing to the occurrence of such rings in a diverse range of natural product molecules.² Although there are a number of examples of homocoupling via this reaction where two alkynes react with $\text{Fe}(\text{CO})_5$ in CO atmosphere to give the symmetrically substituted cyclopentadienone- $\text{Fe}(\text{CO})_3$ complexes (eq 1),³ no example of cross-coupling of two alkynes has been reported to the best of our knowledge.



We report here a method for cross-coupling of alkynes via “silicon tethered”⁴ $\text{Fe}(\text{CO})_5$ -promoted cyclocarbonylation, which consists of linking two alkynes into a silyl acetal, subjecting the resulting diyne to cyclocarbonylation, and disengaging the metal and the tether moiety. Tethering the two alkyne reaction partners of $\text{Fe}(\text{CO})_5$ -promoted cyclo-

carbonylation makes this reaction intramolecular, thereby leading to better yield and regioselectivity than are generally associated with intermolecular reactions. Shibata et al. have reported a related silicon-tethered diyne homocoupling promoted by octacarbonyldicobalt.⁵ Our strategy was first tested with a simple substrate **1**, which was obtained by the reaction of trimethylsilylpropynol⁶ with dichlorodiphenylsi-

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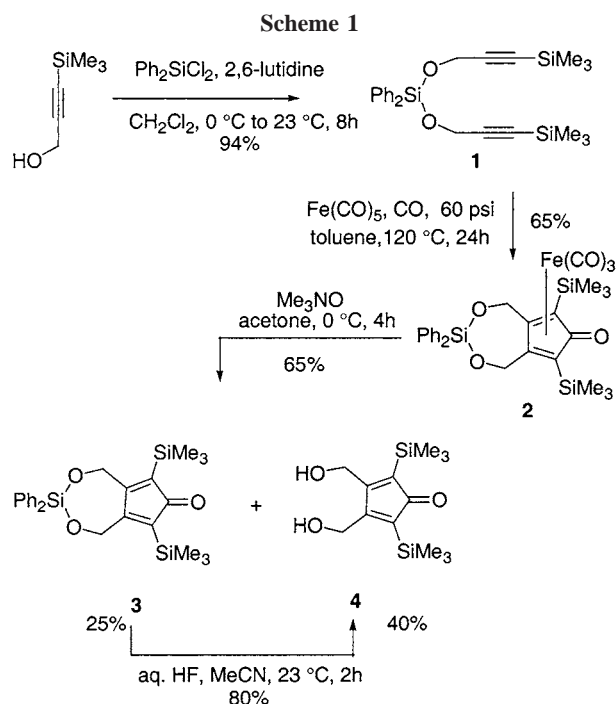
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lane in the presence of base. The substrate **1**, which has two alkyne reaction units connected by a silyl acetal moiety, underwent cyclocarbonylation in good yield considering that the reaction involves seven-membered ring formation.⁷

Treatment of the resulting cyclopentadienone–Fe(CO)₃ complex **2** with Me₃NO⁸ afforded two products, **3** and **4**,⁹ without the known possible problems³ such as dimerization of cyclopentadienone or migration of one double bond and accompanying desilylation. Removal of the tether moiety in **3** was completed by treatment with HF (Scheme 1).¹⁰ Also,



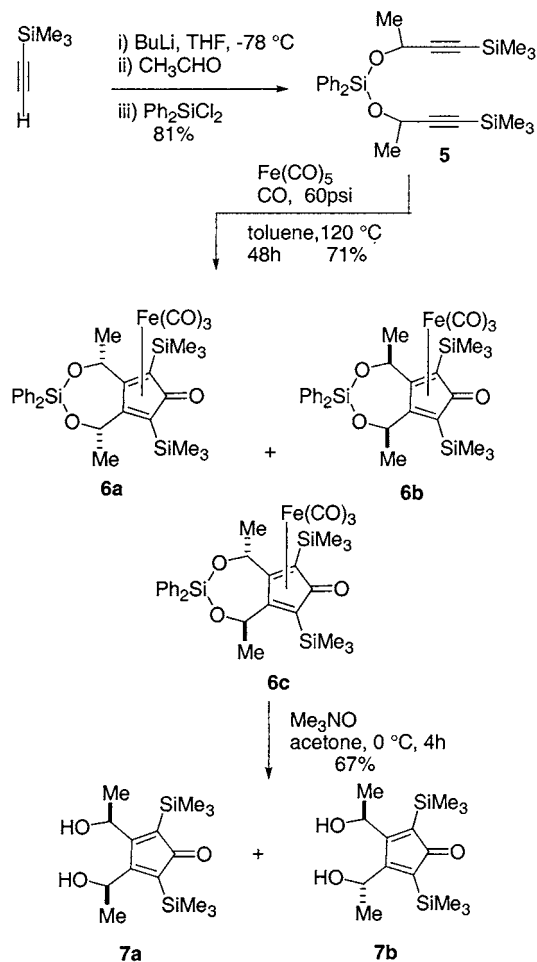
a sterically more demanding substrate **5** was prepared from trimethylsilylacetylene by a one-pot process involving sequential treatment with *n*-BuLi,¹¹ acetaldehyde, and dichlorodiphenylsilane. The cyclocarbonylation of diyne **5** over 48 h gave all the possible diastereomers **6a**, **6b**, and **6c** in a ratio of ca. 1:1:1.2, which gave two diastereomers **7a** and *rac*-**7b** after demetalation and concomitant desilylation by Me₃NO treatment (Scheme 2). However, the same reaction for 24 h gave a 1:1 mixture of **6a** and **6b** in 44% yield, with only a trace amount of **6c**. Me₃NO treatment of this mixture gave only **7a** in 42% yield.

The inseparable mixture of Fe(CO)₃ complexes **6a**, **6b**, and **6c** was analyzed by comparison of the ¹H NMR spectrum of the mixture with that of (*S,S*)-**6c**, which was synthesized from commercially available (*S*)-3-butynol (Scheme 3).

These results indicate that the *meso* diastereomer of **5** reacts faster than the (*S,S*)- or (*R,R*)-diastereomer. The

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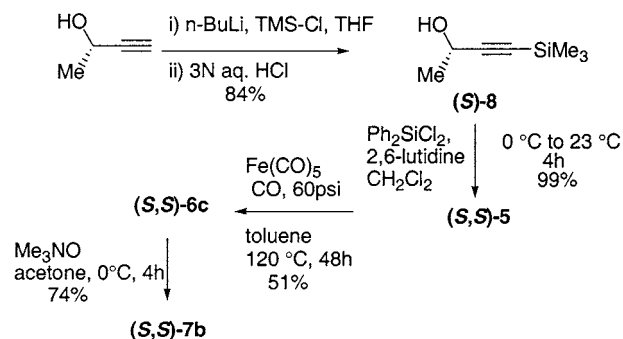
Scheme 2



putative intermediate, the tricarbonyl[bis-(η^2 -alkyne)]iron complex, may be considered to account for the reactivity difference between two diastereomers. The tricarbonyl[bis-(η^2 -alkyne)]iron complexes,¹² which would be formed by the sequential replacement of two CO ligands by two alkyne units of the diyne **5**, are depicted by **RS-9** and **SS-9** (Figure 1).

Due to the *pseudo* 1,3-diaxial interaction between phenyl and methyl that is unavoidable in **SS-9**, the formation of **SS-9**

Scheme 3



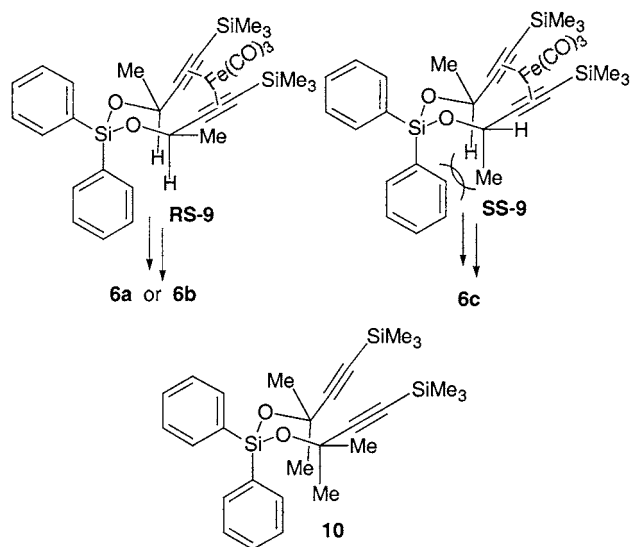
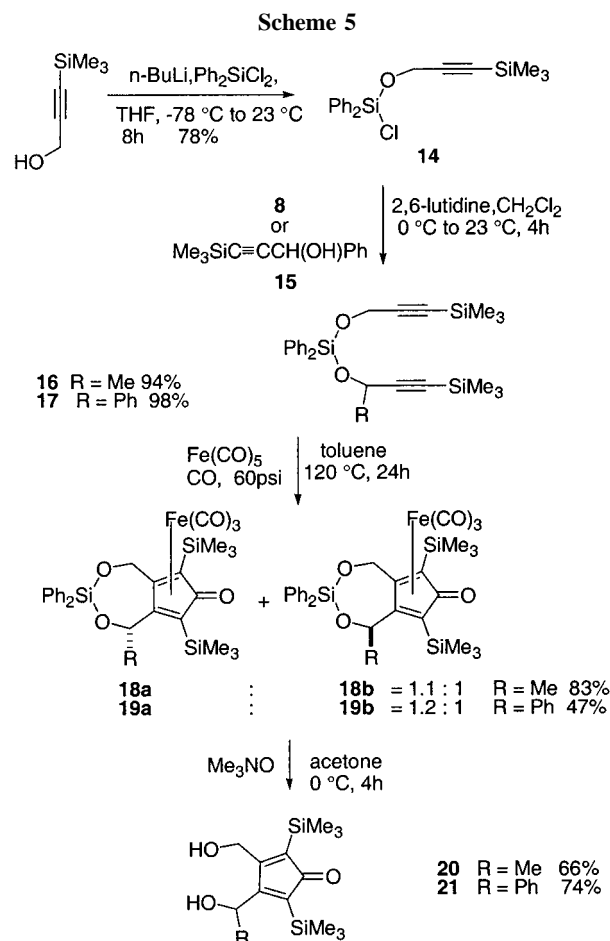
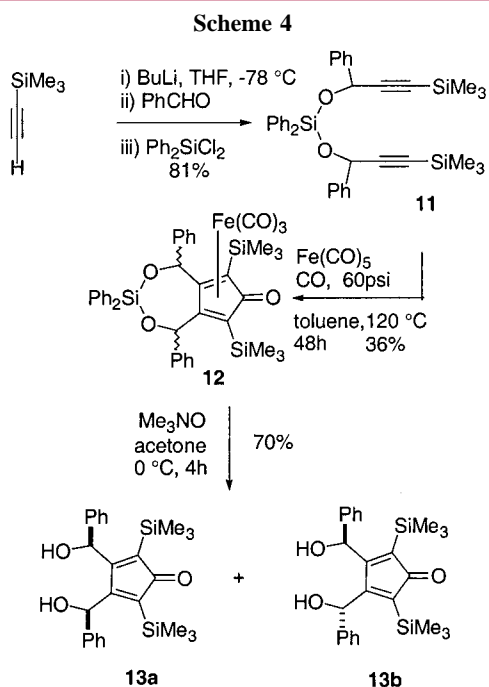


Figure 1. Tricarbonyl[bis-(η^2 -alkyne)]iron complexes (**RS-9** and **SS-9**) and the diyne **10**.

is expected to be slower than that of **RS-9**. As a result, the corresponding $\text{Fe}(\text{CO})_3$ complex **6c** is formed more slowly. The same reasoning also explains the observation that **10**, which has two additional methyl groups compared to the substrate **5**, did not undergo the cyclocarbonylation but was recovered unreacted. Diyne **11**, which was prepared by the same method as used for **5**, reacted with $\text{Fe}(\text{CO})_5$ to give the inseparable diastereomeric mixture **12**. The anticipated mixture of two diastereomers **13a,b** was obtained in ca. 1.1:1 ratio (Scheme 4). The ^1H NMR spectrum of the mixture **12** was not useful for determining the ratio of the diastereomers.



We did not examine the potential selectivity of this conversion for a shorter reaction time because of the poorer overall yield.

Since we found that the silyl acetal moiety is a good tether for $\text{Fe}(\text{CO})_5$ -promoted cyclocarbonylation, we prepared the diynes **16** and **17**, which have two different alkyne units tethered by the silyl acetal moiety, according to the route depicted in Scheme 5. Monoalkoxylation was accomplished by using a 5-fold excess of dichlorodiphenylsilane, the excess of which could be recovered by distillation of the resulting

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mixture.¹³ The addition of another alkynol (**8**¹⁴ or **15**¹⁵) to the obtained monochlorosilane **14** by using 2,6-lutidine as a base afforded the diynes **16** and **17**, which underwent cyclocarbonylation to give the mixture of two diastereomers **18a,b** and **19a,b**, respectively. Treatment of the diastereomeric mixtures of the Fe(CO)₃ complexes with Me₃NO gave single products **20** and **21**.

The diols **20** and **21** are equivalent to the products of an intermolecular version of this reaction that would give not

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only the cross-coupled product but also the homocoupled products and possibly their regioisomers.

In conclusion, we have demonstrated that "silicon-tethered" Fe(CO)₅-promoted cyclocarbonylation can provide an effective method for carbonylative cross-coupling of alkynes to furnish cyclopentadienones with variable substituents.

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Supporting Information Available: Experimental procedures, spectroscopic data, copies of ¹H NMR and ¹³C NMR spectra for new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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