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Novel Reactivity of Enynes in Presence of Cobalt (I) Complexes

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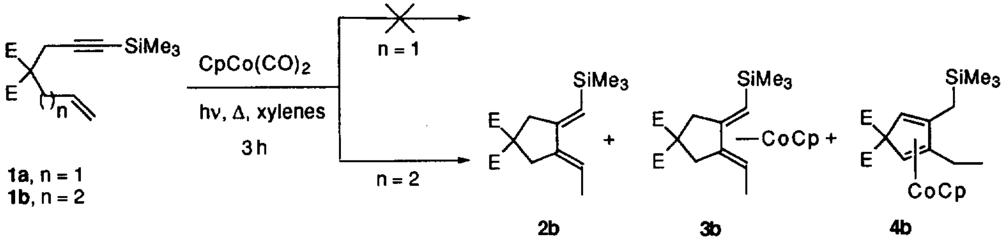
Abstract : 1,7- and 1,8-enynes led to five-membered carbocycles in presence of $CpCo(CO)_2$. Free ligands and η^4-cobalt complexes have been isolated and characterized. A mechanism for this new cobalt-mediated cycloisomerization involving selective cobalt allylic C-H activation is proposed.

The need of harsh reaction conditions or strict structural requirements has limited the applicability of the thermal Alder-ene reaction.[1] Transition-metal mediated versions have overcome such limitations and have enhanced the synthetic utility of this process. Cyclizations of enynes have been achieved with a wide range of transition metal complexes either in a catalytic or stoichiometric manner[2] and represent a versatile approach to a variety of products by simple manipulation of the catalyst.

Cobalt catalyst species are particularly precious mediators for effecting [2+2+2] cyclotrimerizations,[3] Pauson-Khand reactions,[4] homo Diels-Alder cyclizations,[5] ene type reactions[6] and more recently reductive carbocyclizations.[7] In connection with our studies on cobalt-catalyzed [2+2+2] cycloaddition reactions of allenediynes,[8] we recently disclosed a new cobalt-mediated formal Alder-ene reaction of allenynes.[9] While we focused on this reaction, we have found that (η^5-cyclopentadienyl)dicarbonyl cobalt [$CpCo(CO)_2$] is able to assist the cyclization of enynes to five-membered carbocycles *via* selective cobalt allylic C-H activation process.

The 1,6-, 1,7- and 1,8-enynes were readily prepared by successive alkylation of the dimethylmalonate with silylpropargyl bromide and the corresponding ω-ethylenic bromide.

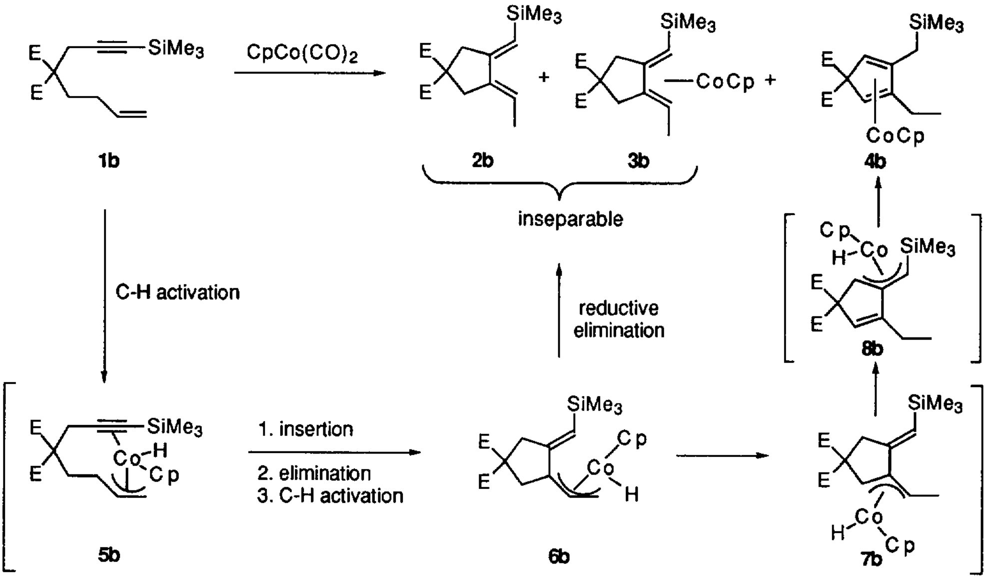


Scheme 1

When the 1,6-enyne **1a** was exposed to a stoichiometric amount of $CpCo(CO)_2$ in boiling xylenes under irradiation, the starting material was consumed after 3 h but untractable materials were obtained. On the contrary, under the same conditions, 1,7-enyne **1b** led to three compounds : the cobalt 1,2-dimethylidene cyclopentane **2b**, its complexed form **3b** and the (η^4-cyclopentadiene) cobalt complex **4b** in 12 %, 8 % and 16 % yields respectively (Scheme 1). Control experiments showed that enynes **1** were totally recovered in the absence of $CpCo(CO)_2$ in boiling xylenes with or without irradiation, indicating the crucial role of the cobalt mediator.

The behavior of **1a** and **1b** was quite surprising. Thus, 1,6-enyne **1a** apparently failed to cyclize and 1,7-enyne **1b** led to five-membered ring formation, under the above conditions, whereas in the presence of palladium catalysts these compounds cycloisomerize to 1,2-dialkylidene cycloalkanes either through a hydridopalladium or palladacyclopentene mechanism.[2a-c] These results suggest that the mechanism of this cyclization is totally different.

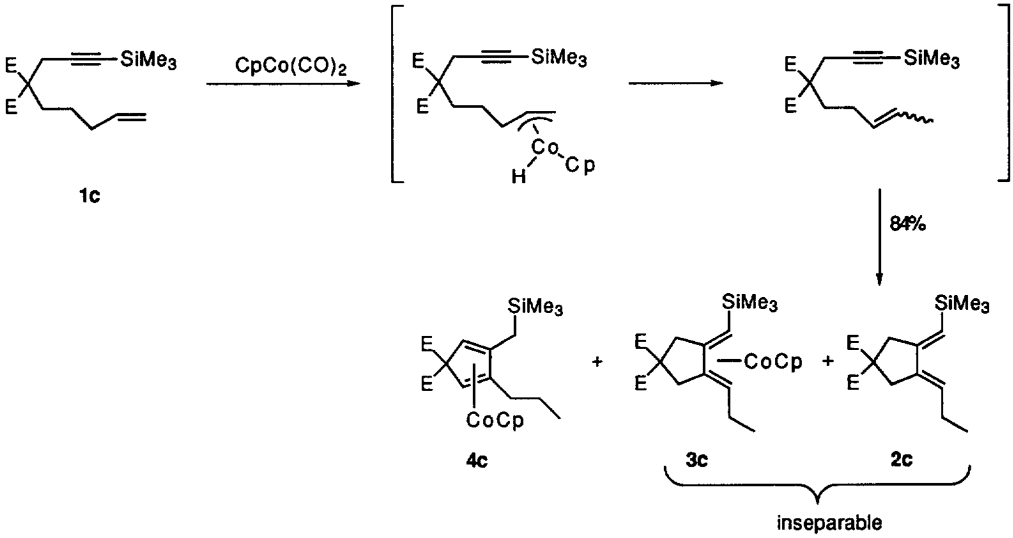
The most plausible mechanism for the formation of **2b**, **3b** and **4b** appears to involve η^3-allyl hydride complexes (scheme 2). Indeed, after coordination of the enyne with the cobalt complex, the next step is probably the oxidative formation of the η^3-allyl hydride complex **5b** through a C-H activation process. Successive alkyne insertion into the cobalt-hydride bond and reductive elimination would afford **2b** and its η^4-diene complex **3b**. We anticipated that the formation of the (η^4-cyclopentadiene) cobalt complex **4b** could be the result of a cobalt assisted migration of the double bond *via* the allyl hydrides **7b** and **8b**.



Scheme 2

To our knowledge, no examples of cycloisomerization involving the formation of such hydrides have been reported, however this kind of intermediates has been invoked to explain the isomerization of double bonds in presence of cobalt complexes.[10] Therefore, the decomposition of **1a** could be explained by such a mechanism. If one considers from **1a** the initial formation of an η^3-allyl hydride intermediate **5a** having a *syn* configuration, a *6-endo-trig* cyclization process is forbidden because it would lead to a *E*-cyclohexene derivative. The competitive *4-exo-trig* cyclization process is totally disfavored in view of the formation of a highly constrained *exo*-methylene cyclobutane derivative.

In order to test the reactivity of 1,8-enyne and to reach possibly six-membered carbocycles, we checked the behavior of the enyne **1c**. Exposure of this latter to one equivalent of CpCo(CO)$_2$ furnished three five-membered ring compounds **2c**, **3c** and **4c** in 84 % yield (Scheme 3).[11]



Scheme 3

The assigned structure of **4c** was unambiguously confirmed by a single X-ray analysis.[12] The selective formation of cyclopentanes could be explained by the isomerization of the double bond in the first step followed by the same process as for **1b**.

In summary, these preliminary results showed the influence of the lenght of the tether on this new cobalt-mediated cycloisomerization of enynes. This C-H activation followed by insertion and migration processes should be of more synthetic importance if other kinds of unsaturated partners could be involved in this sequence. Studies devoted to this goal are under active investigation in our laboratory.

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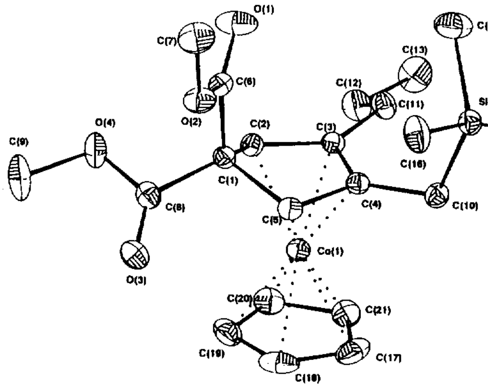
11. **Typical procedure for the cyclization of 1c.** $CpCo(CO)_2$ (1 mmol; 125 μL) was added to a refluxing solution of **1c** (1 mmol) in xylenes (10 mL) degassed by three freeze-pump-thaw cycles and was irradiated (light from a projector lamp; ELW, 300W, 70% of its power). The reaction was monitored by TLC and after the completion, the solvent was removed by vacuum transfer. The residue was purified by flash chromatography (petroleum ether : ether = 9 : 1) to afford the adducts **(2+3)c** and **4c** in 84% yield. **2c** (22%): ^{1}H-NMR (400MHz, C_6D_6) δ 5.87 (s, 1H), 5.23 (m, 1H), 3.34 (s, 6H), 2.90-2.42 (m, 6H), 1.23 (t, J = 7.2 Hz, 3H), 0.00 (s, 9H). **3c** (22%): ^{1}H-NMR (400MHz, C_6D_6) δ 4.55 (s, 5H), 3.55 (s, 3H), 3.20 (s, 3H), 2.90-2.42 (m, 6H), 1.43 (AB, 2H), 0.98 (t, J = 7.2 Hz, 3H), 0.19 (s, 9H). **4c** (40%): ^{1}H-NMR (400MHz, C_6D_6) δ 4.55 (s, 5H), 3.57 (s, 3H), 3.13 (s, 3H), 3.01 (AB, 2H), 2.64-2.28 (m, 2H), 2.20 (d, J = 14.1 Hz, 1H), 1.52-1.35 (m, 2H), 1.28 (d, J = 14.1 Hz, 1H), 0.95 (t, J = 7.3 Hz, 3H), 0.12 (s, 9H) ; ^{13}C-NMR (50 MHz, C_6D_6) δ 168.7, 166.8, 95.5, 94.3, 80.7 (5C), 67.7, 51.4, 50.9, 40.5, 38.3 , 22.9, 19.3, 14.4, -1.6 (3C).
12.



4c

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