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DIENES FROM THE THERMOLYSIS OF DICOBALTHEXACARBONYL-COMPLEXED ENYNES: MECHANISTIC INSIGHT

Marie E. Krafft,* Anne M. Wilson,@ Olivier A. Dasse, Llorente V. R. Bonaga, Y. Y. Cheung,
Zice Fu, Bin Shao and Ian L. Scott
Department of Chemistry, The Florida State University, Tallahassee, FL 32306

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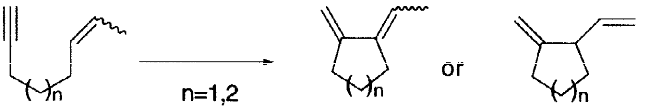
Abstract: Thermolysis of the hexacarbonyldicobalt complex of 1,6- or 1,7-enynes yields monocyclic 1,3-dienes. Deuterium labeling studies rule out an α-elimination as the mechanistic pathway for diene formation.

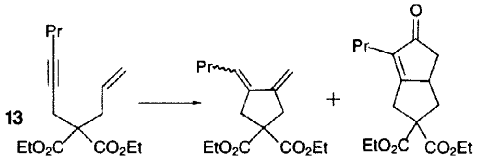
Keywords: Pauson-Khand reaction, dienes, mechanism.

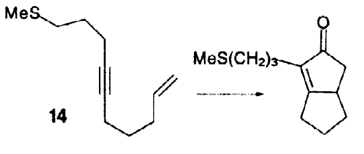
Cycloisomerization of 1,6 and 1,7-enynes to generate cyclic 1,3- and 1,4-dienes occurs in the presence of a number of transition metal catalysts (eq 1).[1-5] In the thermal Pauson-Khand reactions of dicobalthexacarbonyl-complexed 1,6- and 1,7-enynes, 1,3-dienes have been previously observed only as by-products when unactivated alkenes were used, or as major products in the reactions of electron deficient alkenes.[6,7] We have now found that conjugated dienes can be formed in good yield as a product of the thermolysis of the dicobalthexacarbonyl complex of unactivated 1,6- and 1,7-enynes.



(1)

Slow addition of a toluene solution of the hexacarbonyldicobalt complex of enyne **1** to refluxing toluene[8] followed by cooling and oxidative decomposition of the cobalt residue (N-methylmorpholine-N-oxide) yielded 1,3-diene **2**, which could be isolated after silica gel chromatography (Table). The E-alkene isomer is the predominant product formed, although, on prolonged heating, other diene isomers become more prevalent. In only one case, entry 4, was the Z-substituted diene the only stereoisomer found. Proton nOe experiments were used to determine the alkene geometry. Regardless of reaction conditions used the dicobalthexacarbonyl complex of enyne **13** gave a mixture of diene and Pauson-Khand bicyclic enone. Reaction of the dicobalthexacarbonyl complex of thioether **14** resulted in the formation of the Pauson-Khand bicycle only. This was not surprising in light of our previous results on heteroatom acceleration of the Pauson-Khand reaction.[9]





With the formation of 1,3-dienes now as the major product from the thermolysis of dicobalthexacarbonyl complexed 1,6-enynes, we considered the use of a deuterium labeled enyne as a potential mechanistic tool. The issue of 1,3-diene formation from a metallacyclic intermediate via an α- or β-elimination manifold could be addressed.[10,11] Using a dideuteriosubstituted terminal alkene, such as **15** (Scheme 1), reaction via metallacycle **16** would be expected to yield diene **18** (perhaps via the intermediacy of **17**) if a formal β-elimination or an equivalent process was operative. Deuterium migration, resulting in the formation of diene **20**, would be anticipated from thermolysis via a manifold involving an α-elimination to generate intermediate complex **19** followed by insertion of the metal carbene into the adjacent C-H bond and subsequent reductive C-D coupling to release the metal.

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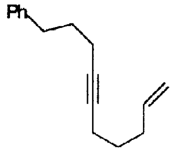
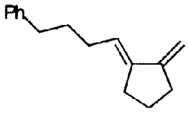
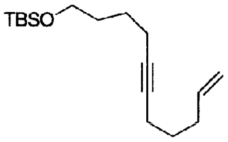
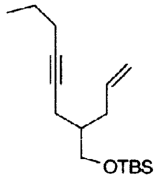
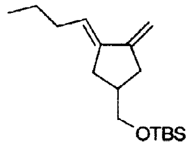
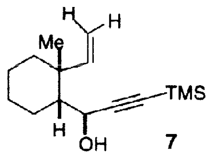
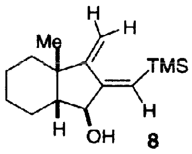
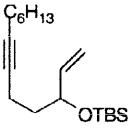
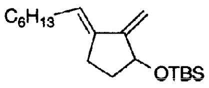
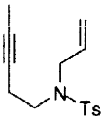
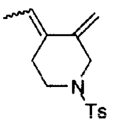
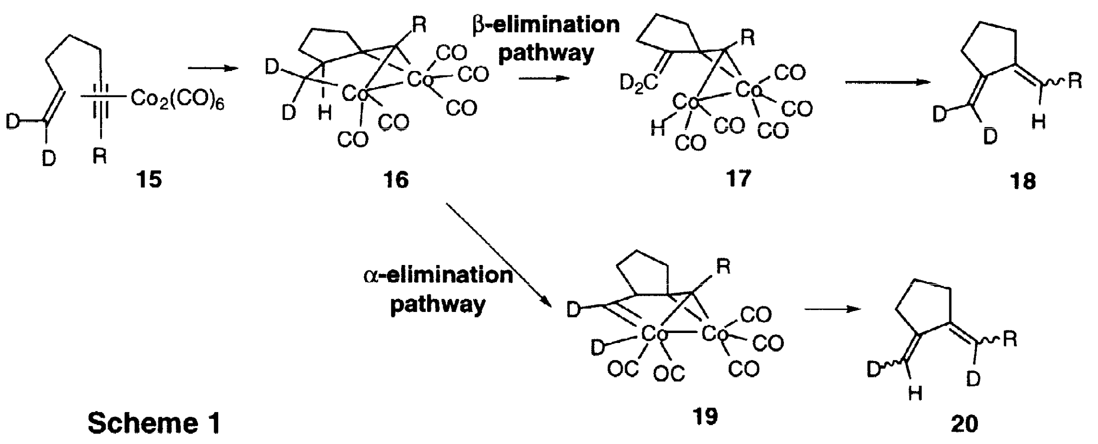
TABLE

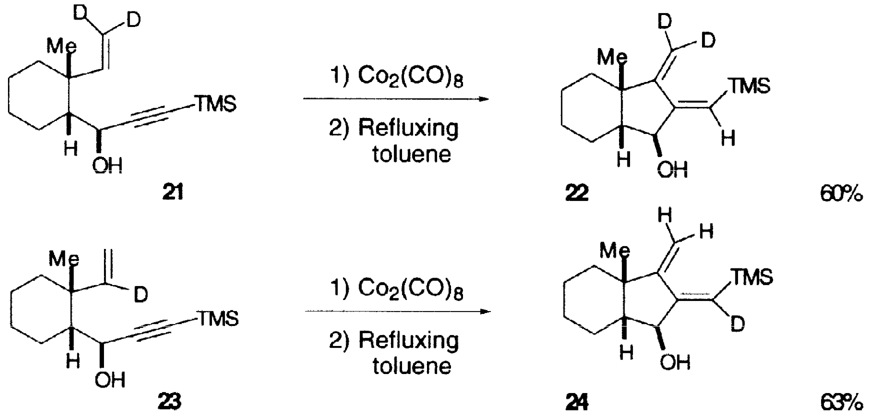
Entry	Enyne[a]	1,3-Diene	Yield[b,c]
1	 **1**	 **2**	55%[d]
2	 **3**	 **4**	60%[d]
3	 **5**	 **6**	67%[d]
4	 **7**	 **8**	69%
5	 **9**	 **10**	60%[d]
6	 **11**	 **12**	41%

a) The corresponding $Co_2(CO)_6$ complexed alkyne was used. b) Isolated, chromatographed yields. c) see ref. 8 for typical experimental conditions. d) 5-8% of other diene isomers were observed.

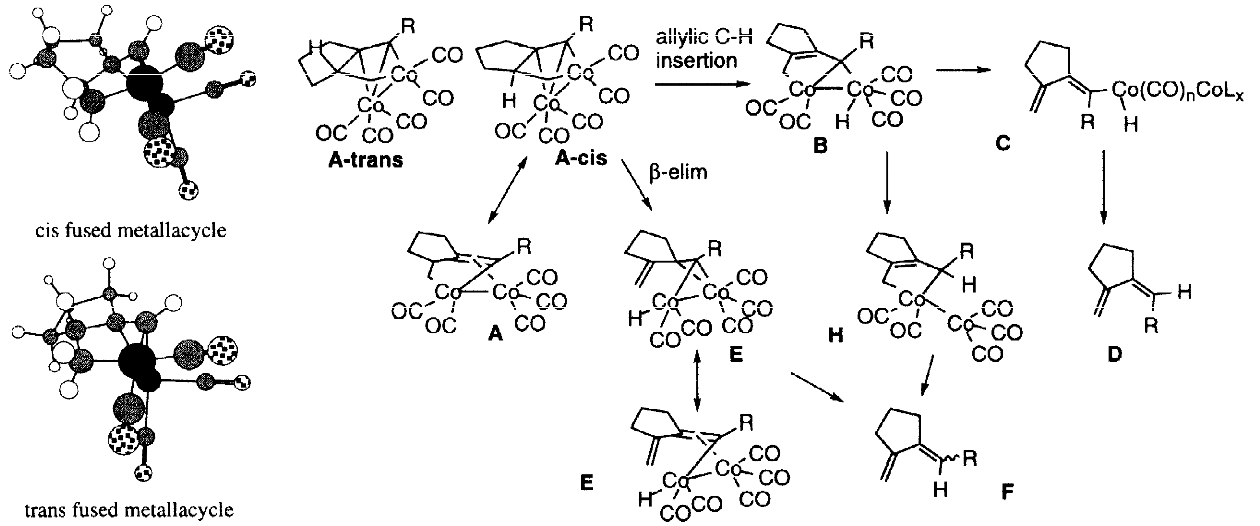


Scheme 1

Reaction of the dicobalthexacarbonyl complex of enyne **21** gave rise to diene **22** in 60% yield. Under similar conditions, the dicobalthexacarbonyl complex of monodeuterio enyne **23** gave monodeuterio diene **24**, in 63% yield, with complete migration of the deuterium. The lack of deuterium scrambling in the cycloaddition of enyne **21** and the exclusive migration of deuterium in the reaction of enyne **23** strongly suggest that the α-elimination pathway is not the preferred pathway for elimination.



It is generally accepted that the Pauson-Khand cycloadduct and the corresponding diene arise from the same metallacyclic intermediate (Scheme 2, **A**). A formal β-elimination from **16** to **17** (Scheme 1) should prefer a transition state in which the M-C and C-H bonds are approximately syn and parallel.[10,11] Since the relevant metal center is in the five-membered metallacyclic ring, this alignment would be expected to be difficult to achieve with that metal. Consequently, we propose an alternate pathway which more closely fits the observed data (Scheme 2). Insertion of the π-bound metal center into the allylic C-H bond[12] of **A-cis** generates metallacycle **B** which then undergoes a retrocycloaddition generating vinyl cobalt complex **C**. The direction of cycloreversion is determined by the steric bulk of the two substituents, (Co_2L_n) and R. Subsequent direct reductive C-H coupling gives **D**, the observed diene product. Reversing the order of the last two steps, i.e., reductive elimination of **B** to form **H** followed by cycloreversion would be expected to give either of the alkene stereoisomers with the ratio determined by steric interactions generated by R and H upon ring opening.



cis fused metallacycle

trans fused metallacycle

Scheme 2

The proposed mechanism assumes the formation of a cis-fused metallacyclic intermediate **A-cis** from the initial cycloaddition. Recent molecular mechanics calculations reported by Moyano and Pericas[13] suggest that, in a Pauson-Khand reaction, a trans-fused metallacyclic intermediate cannot be ruled out as unreasonable based on energy differences between the cis- and trans-fused metallacycles. However, a trans-fused metallacyclic intermediate would not be expected to undergo the insertion into the allylic C-H bond which is necessary in our mechanistic proposal to rationalize the results from reactions of deuterated enynes **21** and **23**. Perhaps our results now provide direct experimental evidence for a cis-fused cycloadduct.[14,15]

We have demonstrated that 1,3-dienes can be formed from the thermolysis of hexacarbonyl-complexed 1,6- or 1,7-enynes. More importantly, our results rule out the α-elimination pathway and strongly implicate an allylic C-H insertion pathway, rather than the formal β-elimination route, for the formation of 1,3-dienes.

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@ Present Address: Department of Chemistry, Butler University, 4600 Sunset Ave, Indianapolis, IN, 46208.

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