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Transition Metal Promoted Higher-Order Cycloaddition Reactions. [6+2] Cycloaddition of a Fischer Carbene Complex with Tricarbonyl(cycloheptatriene) Chromium(0)

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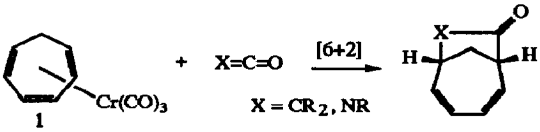
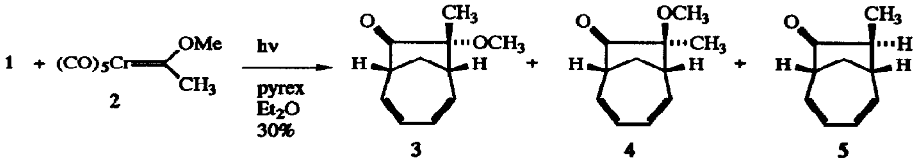
Summary: Photolytic reaction of pentacarbonyl [(methoxy)(methyl)carbene] chromium(0) with tricarbonyl(cycloheptatriene) chromium(0) afforded an isomeric mixture of bicyclo[4.2.1]nonanone products.

Group 6 transition metals have emerged as effective mediators of a variety of higher-order cycloaddition processes; and reactions involving [6π+4π][1] and [6π+2π][2] combinations have been notable beneficiaries of metal-intervention. Recently, a number of heterocumulenes, including ketenes, have been shown to participate as 2π partners in chromium(0) promoted [6π+2π] cycloaddition reactions with tricarbonyl(cycloheptatriene)chromium(0) (1)[3] (Scheme I).



Scheme I

In light of the well-established propensity for certain Fischer carbene complexes to behave as ketene equivalents under photolytic conditions,[4] a study of the reaction of these species with complex **1** was undertaken. It was reasoned that improved reaction efficiencies might be obtained with metal-bound ketene intermediates since many of the side reactions typical of free ketenes are absent in reactions involving these species. The projected reaction was also regarded as a possible probe for further understanding the scope and limitations of the metal-mediated higher-order cycloaddition process.



(1)

We wish to report that the Fischer carbene complex **2** does indeed undergo [6+2] cycloaddition, but with only modest efficiency. In a typical reaction, a mixture of complex **1** and excess (6 equiv.) carbene complex **2** was irradiated in a Pyrex immersion well to afford a 30% yield of three [6+2] adducts, **3**, **4** and **5** in a ratio of 3:1:1, respectively.[5] Minor quantities of numerous other species were also formed during this reaction, but none were characterized further. Cyclobutanones,[4a] if present at all, were only very minor components of the product mix. This result qualitatively parallels the [6+2] pathway observed in a related *intra*-molecular cycloaddition recently reported by Aumann.[6]

Interestingly, tricarbonyl(cycloheptatriene)chromium(0) (**1**) was the major product when cycloheptatriene itself was reacted with carbene complex **2** under these conditions. High CO pressures are known to improve Fischer carbene cycloadditions.[4a] However, performing the above reaction under an atmosphere of CO completely suppressed cycloaddition, which is consistent with our previous observations in a number of higher-order processes.[1b] Other Fischer carbenes, such as pentacarbonyl[(methoxy)(phenyl) carbene] chromium(0), failed to produce any [6+2] adducts.

It is noteworthy that executing the reaction in freshly distilled THF (from Na-benzophenone ketyl) afforded adducts **3** and **4** in approximately the same yields and ratios as in equation (1), however, none of compound **5** was detected. A similar result was obtained when freshly distilled ether was employed as solvent. These observations suggest that **5** is an artifact derived from an event occurring subsequent to cycloaddition, perhaps via a hydrogen atom abstraction-fragmentation process[7] promoted by small amounts of hydroperoxide species present in undistilled diethyl ether.

Although of only modest efficiency, the reaction described herein reinforces the notion that Fischer carbene derived metal-bound ketenes behave very much like their metal-free counterparts. Additional studies employing two transition metal complexes as participants in several other cycloaddition reactions are currently underway.

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