

Heterocumulenes as 2π Partners in Metal-Promoted [$6\pi+2\pi$] Cycloaddition Reactions

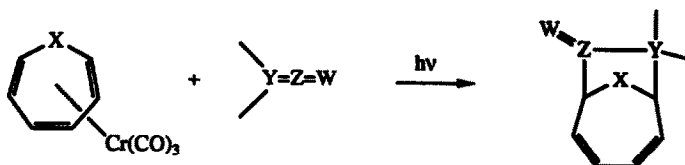
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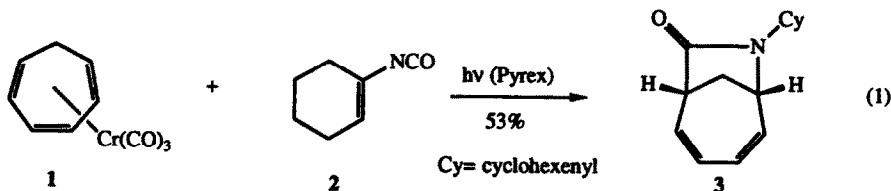
Summary: Alkyl and aryl substituted isocyanates and ketenes have been shown to be useful 2π partners in photoinitiated chromium(0)-promoted [$6\pi+2\pi$] cycloaddition reactions.

Transition metal intervention in higher-order cycloaddition processes has recently proven to be an effective tactic for enhancing the efficiency of these notoriously ill-behaved transformations.^{1,2} Among the more important examples of higher-order cycloadditions, the combination of 6π and 2π reactants to afford bicyclo[4.2.1]nonane type adducts has been particularly difficult to implement in a synthetically useful fashion.³ Typically, only small quantities of products derived from the higher-order pathway are isolated. An exception to this trend is the intramolecular, photoinduced [6+2] cycloaddition of protonated tropones, which is a synthetically viable reaction in a number of cases.⁴ Sporadic reports of reasonably efficient metal-mediated [$6\pi+2\pi$] cycloadditions have also appeared over the years, however, many of these have been of limited scope.⁵

Scheme I

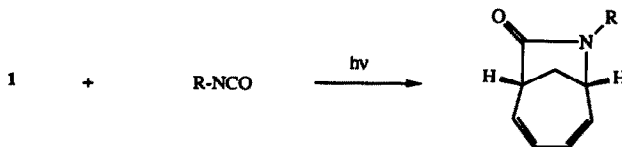


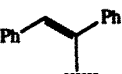
In this Letter we disclose an effective chromium(0) facilitated [$6\pi+2\pi$] cycloaddition reaction employing several types of heterocumulene species as 2π addends.^{6,7} The success of the metal promoted [6+2] cycloaddition of electron deficient alkenes reported previously from our laboratory^{2d} suggested that other potential candidates could be identified as effective participants in these processes, thereby extending the utility of the methodology. The well-known electrophilicity of isocyanates and ketenes recommended these species for examination in this context.



Irradiation (Canrad-Hanovia medium-pressure mercury vapor lamp, 450 W, Pyrex filter) of a mixture of (cycloheptatriene)tricarbonylchromium(0) (1)⁸ and excess cyclohexenyl isocyanate⁹ afforded the anticipated bicyclic lactam 3¹⁰ in 53% isolated yield. It is noteworthy that no adducts derived from the alternative [6+4] pathway were observed in this reaction. Other representative isocyanate-triene cycloaddition results are compiled in Table I. Of particular note is the result in entry 5 which involves the cycloaddition of an *isothiocyanate* addend. Although the yield of cycloadduct is modest in this instance, it is interesting that the sulfur analog is capable of undergoing cycloaddition to any extent under these reaction conditions.

Table I. [6+2] Cycloadditions of Isocyanates with Complex 1.



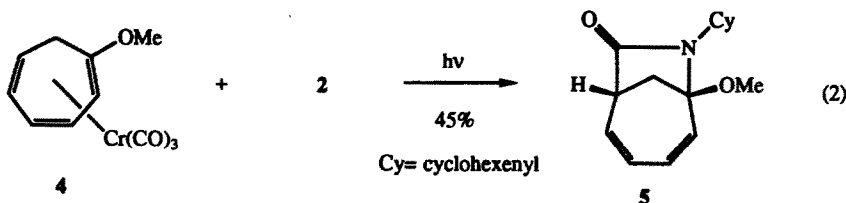
Entry	2 π addend	Yield (%) ^{a,b}
1	R = PhCH ₂	42 ^{d,e}
2	R = 	43 ^{d,e}
3	R = Cyclohexyl	41 ^{d,e}
4	R = PhCH ₂ CH ₂ CH ₂	43 ^{d,e}
5 ^c	CH ₃ CH ₂ NCS	18 ^{d,e}
6	R = 2-(p-nitrophenyl)ethenyl	0

^a All reactions were performed by irradiation through a Pyrex filter. ^b Reported yields are for isolated, purified products. ^c Reaction involves an *isothiocyanate* partner.

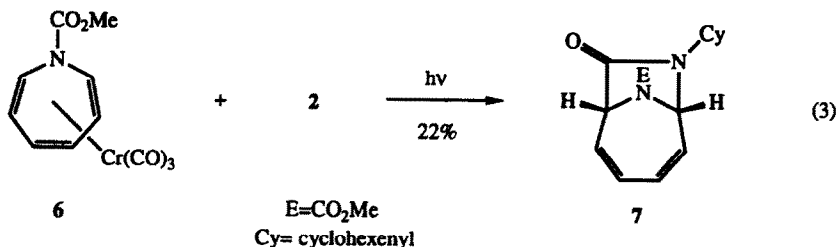
^d Ref. 10. ^e All adducts were isolated metal-free.

Chromium complexes involving substituted cycloheptatriene ligands also participate in this cycloaddition to afford adducts in a highly regioselective fashion. Irradiation of complex 4¹¹ with isocyanate 2 provided bicyclic lactam 5¹⁰ as a single regioisomer, the structure of which was supported by extensive decoupling

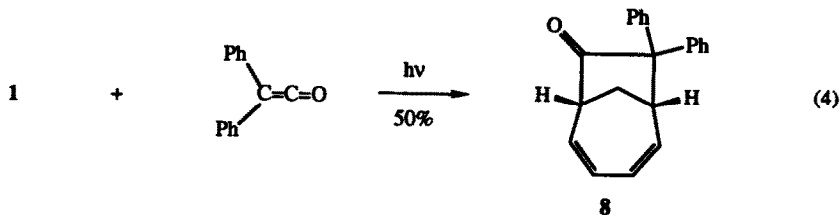
experiments. The regiochemical course of this transformation appears to closely resemble other metal-promoted [6+2] cycloaddition reactions.^{2d}



The [6+2] cycloaddition of heterocumulenes can also be executed in combination with heterocyclic triene complexes. For example, the readily available azepine complex **6**¹² undergoes photoinduced cycloaddition with isocyanate **2** to give a modest quantity of the corresponding diazabicyclic adduct **7**.¹⁰ In contrast, the corresponding (thiepin dioxide)tricarbonylchromium(0) complex¹³ afforded no adducts of any kind under these conditions. This lack of reactivity with electron deficient partners is reminiscent of the behavior of this complex when reacted with α,β -unsaturated carbonyl compounds.



A particularly intriguing version of this cycloaddition protocol would employ ketenes as electron deficient 2π partners. Ketenes normally engage most alkenes via a [2+2] pathway, but the observations made in conjunction with isocyanates as 2π partners in these cycloadditions suggested that metal intervention could overcome this predilection.⁶ Irradiation of complex **1** in the presence of excess diphenyl ketene¹⁴ afforded a 50% yield of the corresponding bicyclo[4.2.1]nonane product **8**.¹⁰ The relative efficiency of this particular process, in light of the considerable steric hindrance in the vicinity of one of the bond forming centers, is significant and bodes well for future applications of this transformation in organic synthesis. Unfortunately, *in situ* generated dichloroketene has not provided useful quantities of the corresponding cycloadduct and additional work on these potentially important reactions is currently underway, as is a search for other useful reaction partners.



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References and Notes

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