

Communications to the Editor

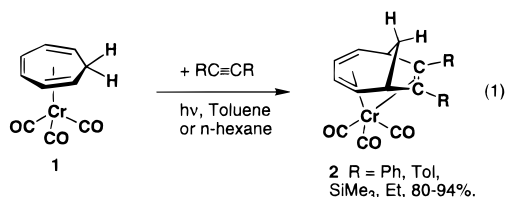
Metal-Mediated Tandem $[6 + 2]$, $\text{homo}[6 + 2]$ Cycloadditions of Alkynes to Cycloheptatriene. Generation of Novel Tetracycloundecadienes

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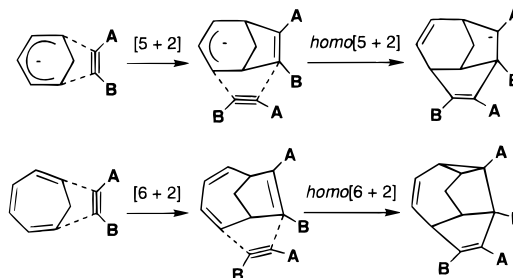
Transition metal-mediated cycloaddition reactions continue to attract interest for the efficient and stereoselective syntheses of a variety of ring systems.^{1,2} Metal-promoted higher-order processes that generate medium size rings (e.g., $[6 + 2]$ and $[6 + 4]$) were first reported in the 1970s,^{3,4} have been extensively studied by Rigby and co-workers, and used in a number of natural product syntheses.^{5–8} The $[6 + 2]$ cycloaddition of alkynes to coordinated polyene manifolds has been reported by a number of groups,^{3,9–13} and we have previously described a $[6 + 2]$ coupling of internal alkynes and $[(\eta^6\text{-triene})\text{Cr}(\text{CO})_3]$ complexes under photochemical conditions that gives bicyclo-[4.2.1]nonatriene derivatives (eq 1).^{14,15}



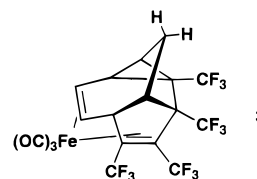
Higher-order cycloadditions have been extended to the η^5 -dienyl manifold,^{16–18} and we have recently reported novel $[5 + 2]$, $\text{homo}[5 + 2]$ double-alkyne cycloadditions to both

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Scheme 1. Tandem $[6\pi + 2\pi]$, $\text{homo}[6\pi + 2\pi]$ Alkyne Cycloadditions

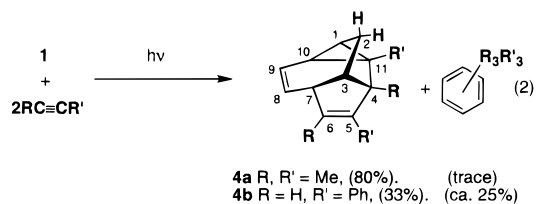


manganese^{19,20} and chromium²¹ cycloheptatriene species forming four new C–C bonds and two rings in a single step with high degrees of stereo- and regiocontrol. In early work, Green, Woodward, and co-workers briefly described a novel tetracyclic complex **3** derived from 2 equiv of hexafluorobut-2-yne and $[(\eta^6\text{-C}_7\text{H}_8)\text{-Fe}(\text{CO})_3]$,^{22,23} although no further details were reported. It is now clear that all of these double-addition reactions are variations of a general metal-assisted $[6\pi + 2\pi]$, $\text{homo}[6\pi + 2\pi]$ cycloaddition process, and a schematic representation for the dienyl and triene manifolds is shown in Scheme 1.



We now report that this double-addition protocol can be extended to the chromium complex **1** forming the decomplexed tetracyclic species **4**, in which five new C–C bonds are formed in a single step. The reaction proceeds in up to 80% yield with 2-butyne and can be performed in a tandem reaction sequence that couples two different alkyne partners with **1** allowing access to a range of new tetrasubstituted tetracycloundecadienes.

UV irradiation of toluene or *n*-hexane solutions of $[(\eta^6\text{-C}_7\text{H}_8)\text{-Cr}(\text{CO})_3]$ (**1**) and 2 equiv or more of 2-butyne at room temperature for 4–8 h followed by chromatographic workup gave an 80% isolated yield of 4,5,6,11-tetramethyltetracyclo-[8.1.0.0^{3,7}0^{4,11}]undeca-5,8-diene (**4a**) as a colorless oil (eq 2).^{24,25}



A trace of hexamethylbenzene (GC/MS) is also formed via cyclotrimerization of the alkyne substrate, but this contrasts with the previously reported titanium-mediated triene–alkyne cy-

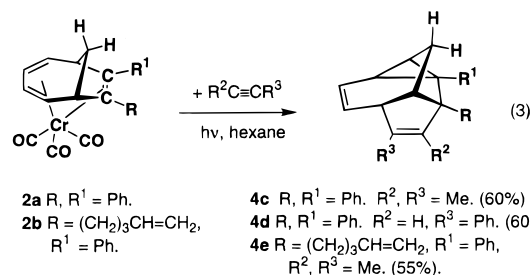
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cloadditions^{12,26} which almost exclusively gave arene products with nonsterically demanding alkynes. Compound **4a** consists of four rings, cyclopropane, -pentane, -pentene, and -heptene, and possesses six chiral centers. A single diastereomer is isolated since bond formation occurs at the metal face of the triene precursor.

The reaction is not confined to 2-butyne and can be extended to terminal alkynes. Thus, reaction of phenylacetylene and **1** under identical conditions to those used for 2-butyne gave moderate yields of **4b** as well as some triphenylbenzene (ca. 25%). Significantly, **4b** is a single regioisomer of the four possibilities that can form from the addition of two unsymmetrical alkynes to **1** and presumably arises from the various insertion preferences of particular alkyne termini during the stepwise coupling reaction. Similar regioselectivity has been observed in the related alkyne insertions into diene ligands.^{19–21}

The synthetic potential of the new double-cycloaddition reaction is highlighted by the fact that the tandem addition of two *different* alkynes to **1** is possible. Thus, reaction of **1** with diphenylacetylene gives the bicyclo[4.2.1]nonatriene complex **2a**,^{14,15} which can then be reacted with either 2-butyne or phenylacetylene to give single regioisomers of the mixed double adducts **4c** and **4d**, respectively (eq 3). More elaborate functionality can be introduced into the tetracyclic species by reaction of **1** with the eneyne $\text{PhC}\equiv\text{C}(\text{CH}_2)_3\text{CH}=\text{CH}_2$ giving bicyclic **2b** in 55% yield. Noteworthy is the fact that only the

alkyne group of the eneyne adds to **1**, although [6 + 2] cycloadditions of both alkynes^{14,15} and olefins²⁷ to **1** have been previously reported by us and Rigby et al., respectively. Subsequent UV irradiation of **2b** and 2-butyne results in a single regioisomer of the highly functionalized tetracyclic product **4e**.



In summary we have demonstrated the facile construction of complex tetracyclic species via the tandem addition two alkynes to cycloheptatriene utilizing Cr(CO)₃ derivatives and UV light. The [6 + 2],*homo*[6 + 2] cycloadditions described herein complement the [5 + 2],*homo*[5 + 2] processes we have discovered for Mn and Cr diene species and appear to be general for the reactions of alkynes with coordinated noncyclically conjugated 6π-polyene and 6π-polyenyl manifolds. Thus, through the use of different organometallic precursors, access to novel fused C₅,C₅,C₆;^{19,20} C₅,C₆,C₇;²¹ or C₃,C₅,C₅,C₇ ring systems is possible. Further studies to fully discern the synthetic potential of the new cycloadditions are planned.

Acknowledgment. We are grateful to the Rutgers Research Council for financial support.

Supporting Information Available: Characterization data for **4a–e** and the 1D and 2D COSY ¹H NMR spectra of **4c** (3 pages). See any current masthead page for ordering and Internet access instructions.

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(24) Satisfactory spectroscopic data (¹H, ¹³C, and ¹H–¹H 2D (COSY) NMR spectra and high-resolution MS) were obtained for all new compounds reported (see supporting information).

(25) General Procedure for the Preparation of **4a–e**. A solution of [(η⁶-C₇H₈)Cr(CO)₃] (**1**, 1–2 mmol) or **2** (1–2 mmol) and the appropriate alkyne (3–5 mmol) in *n*-hexane (100–200 mL) was irradiated with UV light from a 450 W Hanovia Hg vapor lamp through Pyrex at a distance of ca. 5 cm until all of **1** or **2** had been consumed (IR, 4–48 h). Removal of the solvent in vacuo and purification of the residue on a silica gel column or by TLC gave the products **4a–e** as clear colorless oils or white solids. The reactions proceed in good yields when higher concentrations of substrates are used, however the more intense color of these solutions necessitates longer reaction times.

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