Photoreactions of Chromium Cyclodienyl Complexes with Alkynes: Double [5 + 2],*homo*[5 + 2] Cycloaddition Reactions

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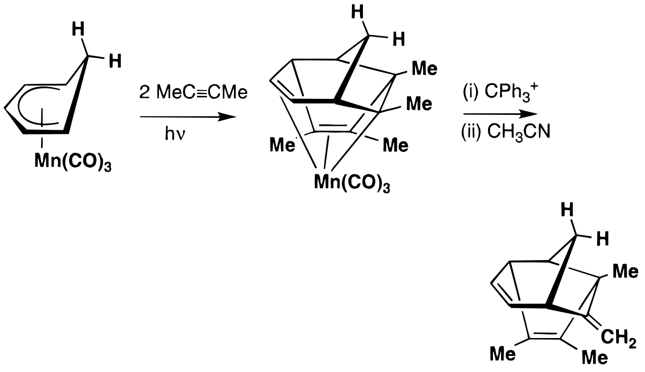
UV irradiation of the cycloheptadienyl complexes [(η^5-C_7H_8R)Cr(CO)$_3$SnPh$_3$] (**1a**, R = H; **1b**, R = $\overline{\mathrm{C(Me)S(CH_2)_3S}}$; **1c**, R = CHPh$_2$) or cyclohexadienyl complexes [(η^5-C_6H_6R)Cr(CO)$_2$(NO)] (**7**, R = $\overline{\mathrm{C(Me)S(CH_2)_3S}}$) and 2 equiv of 2-butyne or 3-hexyne in toluene or *n*-hexane gave new tricyclic complexes **2**, **5**, and **8**. These complexes arise from sequential [5 + 2] and *homo*[5 + 2] cycloadditions of two alkyne molecules to the η^5-dienyl manifold forming 11-alkylidenetricyclo[5.3.1.0^{4,10}]undeca-2,5-diene or tricyclo[5.2.1.0^{4,9}]deca-2,5-dien-10-yl ligands, respectively. Heating **2** in acetonitrile gave [Cr(CO)$_3$(CH$_3$CN)$_3$] and the tricyclic organic compounds **3**. UV irradiation of **1a** and 1-phenyl-1-propyne or **1c** and 2-butyne directly gave the organic compounds **4a**,**b** and **5c**, **6a**,**b**, respectively, as mixtures of isomers. The adduct resulting from **1a** and two molecules of 3-hexyne has been characterized by an X-ray diffraction study.

Introduction

Transition metal-mediated cycloaddition reactions continue to attract interest as a means of generating a variety of ring systems both efficiently and stereoselectively.[1] Within this field, significant advances have been made in the construction of medium-size carbo- and heterocyclic rings through transition metal-mediated higher-order cycloaddition processes.[2−4] For example, Rigby and co-workers have extensively investigated photoinduced [6 + 2] and [6 + 4] cycloadditions using [(η^6-triene)Cr(CO)$_3$] complexes and olefins,[4] dienes,[5,6] heterocumulenes,[7] or even transition metal carbene complexes.[8] Likewise, we[9,10] and others[11] have demonstrated the related chromium-mediated [6 + 2] cycloadditions of alkynes to trienes.

Photoassisted higher-order cycloadditions of alkynes to η^5-dienyl ligands have also been reported by us,[12] as well as by Kreiter and co-workers,[13] using tricarbonyl(η^5-cyclohexadienyl)manganese(0). In these studies, sequential [5 + 2],*homo*[5 + 2] double alkyne additions to the dienyl ligand gave new tricyclic species, (Scheme 1).

Scheme 1. [5 + 2],*homo*[5 + 2] Double Alkyne Addition to [Mn(CO)$_3$(η^5-C_6H_7)]



More recently, Kreiter has reported a [5 + 2] coupling of alkynes and pentadienylmanganese complexes,[14,15] as well as [5 + 2],*homo*[5 + 2] double alkyne addition to tricarbonyl(η^5-cycloheptadienyl)manganese(0),[16] again promoted by UV light. The [5 + 4] coupling of dienyl ligands and dienes at a manganese center is also known,[17−21] and it appears [5 + 2] or [5 + 4] cycloadditions of dienyl ligands to appropriate *dienylophiles*

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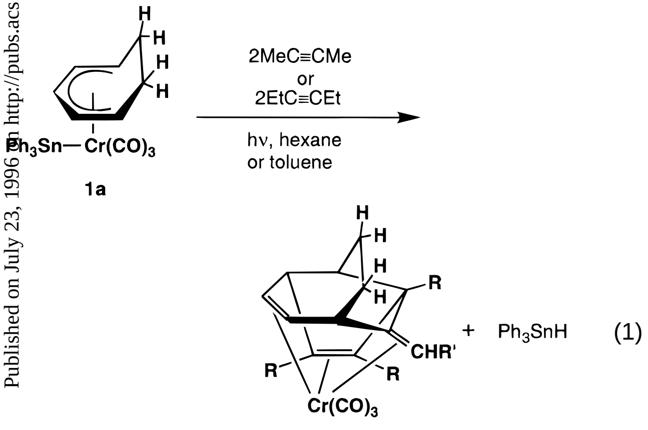
may be quite general. The potential of metal-mediated higher-order cycloaddition reactions is further exemplified by a complementary catalytic [5 + 2] cycloaddition protocol between alkynes and vinylcyclopropanes that has recently been reported by Wender and associates.[22]

In continuing our studies on the photoreactions of dienyl complexes with alkynes, we now present details of a [5 + 2],*homo*[5 + 2] double cycloaddition to both cycloheptadienyl(triarylstannyl)- and cyclohexadienyl(nitrosyl)*chromium* manifolds. A schematic representation of the coupling reaction for the seven-membered ring is shown in Scheme 2. The final products from the tin precursors contain an 11-alkylidene-tricyclo[5.3.1.0^{4,10}]undeca-2,5-diene ring coordinated to a $Cr(CO)_3$ group, with an exocyclic alkylidene that is generated by elimination of Ph_3SnH. Subsequent reaction of these species with acetonitrile gives the functionalized tricyclic compounds in good to excellent yields.

Results and Discussion

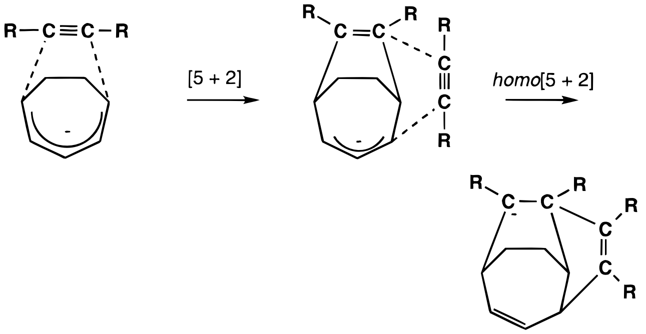
Chromium-Mediated Cycloheptadienyl−Alkyne Coupling. Irradiation of toluene or n-hexane solutions of tricarbonyl(η^5-cycloheptadienyl)(triphenylstannyl)-chromium(II) (**1a**) and 2-butyne or 3-hexyne (2 equiv) with UV light at room temperature for 0.5−4 h resulted in a gradual disappearance of **1a**, as monitored by IR spectroscopy, and the formation of new neutral tricarbonyl species **2a**,**b**, respectively (eq 1). Analysis of the reaction solutions by gas chromatography−mass spectrometry (GCMS) showed the presence of triphenyltin hydride as a byproduct of the reaction. Workup of the reaction by column chromatography allowed the isolation of pure **2a**,**b** as moderately air stable yellow solids in 75% and 88% yields (based on **1a**), respectively.



2a R = Me, R' = H. (75%)
2b R = Et, R' = Me. (88%)

Both **2a** and **2b** were fully characterized by elemental analysis, ^1H, ^{13}C, and $^1H-^1H$ (2D COSY) NMR, and IR spectroscopy (see Table 1 and Experimental Section).

Scheme 2. [5 + 2],*homo*[5 + 2] Double Alkyne Addition to a Cycloheptadienyl Ring



The new ligand is a tricyclic triene that results from the coupling of two alkynes with the cycloheptadienyl ring via sequential [5 + 2] and *homo*[5 + 2] cycloadditions. Elimination of a hydrogen atom adjacent to C(11) of the newly formed ring forms an exocyclic double bond at this site. The ligand consists of three fused rings (C_5, C_6, C_7) with four of the ring carbon atoms, C(1), C(2), C(3) and C(11), derived from added alkynes. It is bonded to a chromium tricarbonyl group through all three double bonds, i.e. C(2)═C(3), C(5)═C(6), and C(11)═C(12), each trans to a CO ligand.

The ^1H NMR spectrum of **2a** shows nine distinct resonances for the C_7 ring as well as two singlets at δ 3.94 and 3.87 assigned to the exocyclic methylene protons at C(12). Only three methyl group signals are observed at δ 1.18, 1.55, and 2.06 since one of the former alkyne methyl groups has been converted to the methylene moiety. Likewise, the $^{13}C\{^1H\}$ NMR spectrum shows a signals at δ 74.3 {C(12)} and δ 63.6 {C(11)} for the coordinated exocyclic methylene and a further 10 signals associated with the ring as well as three distinct CO resonances at δ 233.4, 234.8, and 235.6 (Table 1).

Complex **2b** is analogous to **2a** and was similarly characterized. However, for **2b** there exists the possibility of two isomers (*E*/*Z*) for the exocyclic alkylidene group, since either of the two disatereoselective methylene hydrogens adjacent to the ring can be eliminated with the Ph_3Sn moiety. Remarkably, a single isomer is formed as observed by NMR spectroscopy, which contrasts with the related manganese complexes generated by hydride abstraction with $[CPh_3]^+$. In those species both *E* and *Z* isomers were formed.[12] The molecular structure of **2b** was confirmed by an X-ray diffraction study (Figure 1; Tables 2 and 3). The structure is essentially octahedral at chromium with the three coordinated olefins of the tricyclic ligand trans to carbonyls. The structure shows the stereochemistry of the C(11)═C(12) bond is *E*.

Double alkyne addition to **1a** includes the elimination of Ph_3SnH and thus necessitates the use of alkynes with hydrogen atoms adjacent to the C≡C bond. Consequently, attempts to induce coupling reactions with diphenylacetylene and bis(trimethylsilyl)acetylene failed to yield any tractable products. On the other hand, the efficiency of the coupling reaction is not affected by the nature of the stannyl substituent, with the trimethylstannyl derivative $[(\eta^5-C_7H_9)Cr(CO)_3SnMe_3]^{23}$ yielding

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Table 1. ^1H and $^{13}C\{^1H\}$ NMR Spectral Data[a]

complex	$\delta(^1H)$	$\delta(^{13}C\{^1H\})$
2a	1.18 (3H, s, Me), 1.55 (3H, s, Me), 1.62 (1H, m, H_9), 1.66 (1H, m, H_8), 1.72 (1H, m, $H_{8'}$), 1.90 (1H, m, $H_{9'}$), 2.06 (3H, s, Me), 2.07 (1H, dd, H_7), 2.36 (1H, dd, H_{10}), 3.11 (1H, dd, H_4), 3.45 (1H, dd, H_6), 3.87 (1H, s, H_{12}), 3.94 (1H, s, $H_{12'}$), 4.34 (1H, dd, H_5)[b]	13.0, 16.1, 16.7 (Me), 26.0, 26.4 (C8,9), 38.9 (C10), 46.8 (C7), 47.0 (C1), 52.4 (C4), 62.9 (C5), 63.6 (C11), 67.3 (C6), 71.9 (C12), 82.0 (C2), 105.5 (C3), 233.4, 234.8, 235.6 (CO)
2b	0.91 (3H, t, Me), 0.93 (3H, t, Me), 1.12 (3H, t, Me), 1.35 (2H, m, CH_2Me), 1.55 (2H, m, CH_2Me), 1.62 (2H, m, $H_{8,9}$), 1.90 (2H, m, $H_{7,8'}$), 2.08 (3H, d, Me), 2.17 (2H, m, $H_{9'}$, CH_2Me), 2.78 (1H, m, CH_2Me), 2.99 (1H, m, H_{10}), 3.29 (1H, t, H_4), 3.66 (1H, t, H_6), 4.08 (1H, t, H_5), 4.68 (1H, q, H_{12})	9.5, 13.7, 16.6, 17.2 (Me), 18.5, 22.7, 23.3 (CH_2Me), 26.3 (C9), 31.5 (C8), 33.6 (C10), 47.1 (C7), 50.2 (C4), 52.7 (C1), 65.7 (C11), 66.3 (C5), 69.1 (C6), 92.5 (C12), 93.7 (C2), 107.5 (C3), 232.0, 233.7, 233.8 (CO)
3a	1.28 (3H, s, Me), 1.61 (3H, s, Me), 1.65 (3H, s, Me), 1.87−2.00 (5H, m, $H_{8,8',9,9',10}$), 2.78 (2H, m, $H_{7,4}$), 4.67 (2H, s, $H_{12'}$), 5.72 (1H, dd, H_6), 5.74 (1H, dd, H_5)	9.1 (Me), 13.1 (Me), 18.2 (Me), 25.1 (C8), 27.8 (C9), 45.1 (C7), 48.2 (C10), 51.4 (C1), 56.2 (C4), 105.3 (C12), 130.4 (C6), 132.2 (C5), 135.0 (C2), 137.4 (C3), 157 (C11)
3b	0.86 (3H, t, Me), 0.98 (3H, t, Me), 0.99 (3H, t, Me), 1.49 (1H, m, H_8), 1.58 (3H, d, Me), 1.68−1.78 (2H, m, CH_2), 1.84 (1H, m, $H_{8'}$), 1.86 (1H, m, H_9), 1.94 (1H, m, $H_{9'}$), 2.0−2.2 (5H, m, CH_2, H_{10}), 2.94 (1H, t, H_4), 3.24 (1H, m, H_7), 5.20 (2H, q, H_{12}), 5.68 (1H, dd, H_6), 5.72(1H, dd, H_5)	9.7 (Me), 13.0 (Me), 13.1 (Me), 15.6 (Me), 17.9, 19.6, 20.7 (CH_2), 26.9 (C8), 30.3 (C9), 35.5 (C7), 43.5 (C10), 53.2 (C4), 55.8 (C1), 113.0 (C12), 129.4 (C6), 133.2 (C5), 141.8 (C2), 143.0 (C3), 146.5 (C11)
4a	1.64 (1H, m, H_8), 1.78 (3H, s, Me), 1.79 (1H, m, $H_{8'}$), 1.83 (1H, m, H_9), 1.97 (1H, m, $H_{9'}$), 2.42 (1H, t, H_{10}), 3.08 (1H, dd, H_7), 3.52 (1H, t, H_4), 4.68 (1H, s, H_{12}), 5.07 (1H, s, $H_{12'}$), 5.71 (1H, dd, H_6), 5.83 (1H, t, H_5), 7.20−7.44 (10H, m, Ph)	12.7 (Me), 18.0 (C8), 26.8 (C9), 45.1 (C7), 53.0 (C10), 56.0 (C4), 64.3 (C1), 110.7 (C12), 126.0, 127.0, 128.2, 128.5, 128.8, 129.0 (Ph), 131.5, 132.2 (C5,6), 138.0 (C2), 140.5, 142.0 (Ph), 147.0 (C3), 151.9 (C11)
4b	1.61 (1H, m, H_8), 1.71 (3H, s, Me), 1.76 (1H, m, $H_{8'}$), 1.82 (1H, m, H_9), 1.92 (1H, m, $H_{9'}$), 2.64 (1H, t, H_{10}), 3.06 (1H, dd, H_7), 3.11 (1H, t, H_4), 4.00 (1H, s, H_{12}), 5.00 (1H, s, $H_{12'}$), 5.84 (1H, dd, H_6), 5.88 (1H, t, H_5), 7.02−7.67 (10H, m, Ph)	
5a	1.11 (s, Me), 1.53 (s, Me), 1.77 (s, Me), 1.82 (t, H_9), 1.91 (m, $H_{9'}$), 2.06 (s, Me), 2.10 (m, $H_{7,10}$), 2.20, (m, H_{15}), 2.40 (m, $H_{15'}$), 2.65−3.00 (m, $H_{14,14',16,16',8}$), 3.04 (t, H_4), 3.78 (s, H_{12}), 3.81 (s, $H_{12'}$), 3.84 (d, H_6), 4.15 (t, H_5)	13.5, 13.7, 16.6, 16.7, 20.5, 20.6 (Me), 25.5−29.2 (C8, C9, C14−16, Me-13), 39.2, 41.5 (C10), 47, 47.3, 48.2, 48.7, 49.8 (C4, C7, C13), 52.3, 53.5, 54.1, (C13, C1), 61.0, 62.2 (C5), 63.7, 64.4 (C11), 66.3, 68.0 (C6), 71.5, 73.0 (C12), 83.5 (C2), 95, 98.2 (C3), 232.2, 234.4, 235.1, 236.0 (CO)[c]
5b	1.14 (s, Me), 1.48 (s, Me), 1.74 (s, Me), 1.81 (t, H_8), 1.93 (m, $H_{8'}$), 2.05 (s, Me), 2.10 (m, $H_{7,10}$), 2.20, (m, H_{15}), 2.40 (m, $H_{15'}$), 2.65−3.00 (m, $H_{14,14',16,16',4,9}$), 3.52 (d, H_6), 3.74 (s, H_{12}), 3.76 (s, $H_{12'}$), 4.09 (t, H_5)	
5c	1.11 (3H, s, Me), 1.18 (1H, m, H_8), 1.44 (3H, s, Me), 1.71 (1H, m, $H_{8'}$), 1.94 (1H, m, H_7), 2.03 (3H, s, Me), 2.07 (1H, dd, H_{10}), 2.58 (1H, dd, H_9), 3.29 (1H, t, H_4), 3.45 (1H, t, H_6), 3.63 (1H, s, H_{12}), 3.72 (1H, s, $H_{12'}$), 3.83 (1H, d, $CHPh_2$), 4.21 (1H, t, H_5), 7.18−7.35 (10H, m, Ph)	13.2, 17.0, 24.3 (Me), 26.5 (C8), 41.7, 42.0 (C9, C10), 47.2 (C1), 47.2 (C7), 52.5 (C4), 55.2 ($CHPh_2$), 61.0 (C5), 64.0 (C11), 68.5 (C6), 72.2 (C12), 82.2 (C2), 98.5 (C3), 126.2, 126.8, 127.5, 128.1, 128.7, 129.1, 143.1, 143.4 (Ph), 232.2, 234.0, 234.5 (CO)
6a,b	1.30, (s, Me), 1.31 (s, Me), 1.40 (m, $H_{9'}$), 1.44 (s, Me), 1.57 (s, Me), 1.58 (s, Me), 1.60 (s, Me), 1.72−2.00 (m, $H_{8,9,10,8'}$), 2.55 (dd, H_7), 2.68−2.78 (m, $H_{4,7}$), 3.17 (m, H_4), 3.75 (d, $CHPh_2$), 4.00 (d, $CHPh_2$), 4.50 (s, $H_{12'}$), 4.62 (s, $H_{12'}$), 4.74 (s, H_{12}), 4.76 (s, H_{12}), 5.50 (t, H_6), 5.78 (t, H_5), 5.88−5.91 (m, $H_{5,6}$), 7.1−7.4 (m, Ph)[d]	
8a	0.93 (3H, s, 10-Me), 1.18 (3H, s, 1-Me), 1.81 (1H, m, H_{13}), 1.88 (3H, s), 1.89, (3H, s), 1.93 (3H, s, 2-Me, 3-Me, 11-Me), 2.00 (2H, m, H_8, $H_{13'}$), 2.37 (1H, m, brd, H_7), 2.51 (1H, m, brd, H_9), 2.70 (2H, m, H_{12}, H_{14}), 2.96 (2H, m, $H_{12'}$, $H_{14'}$), 3.72 (1H, t, H_5), 4.20 (1H, t, H_4), 4.94 (1H, t, H_6)	−1.7 (C10), 13.7, 14.1 (1-Me, 10-Me), 20.4, 23.2, 25.3 (2-Me, 3-Me, 11-Me), 26.7, 26.8, 28.6 (C12, C13, C14), 46.2 (C9), 46.7 (C8), 49.9 (C7), 54.8 (C4), 60.7 (C1), 68.8 (C5), 79.3 (C6), 86.6 (C3), 99.9 (C2), 236.2, 239.6 (CO)
8b	0.71 (3H, t), 0.95 (3H, t), 1.04 (3H, t), 1.16 (3H, t, 1-Me, 2-Me, 3-Me, 10-Me), 1.47, 1.55 (4H, m, CH_2), 1.77 (1H, m, H_{13}), 1.86 (3H, s, 11-Me), 1.94 (2H, m, brd, H_8, $H_{13'}$), 2.32, 2.40 (4H, m, CH_2), 2.55 (1H, s, brd, H_7), 2.67 (2H, m, H_{12}, H_{14}), 2.75 (1H, s, brd, H_9), 2.92 (2H, m, $H_{12'}$, $H_{14'}$), 3.63 (1H, t, H_5), 4.27 (1H, t, H_4), 4.88 (1H, t, H_6)	7.1 (C10), 10.3, 12.9, 14.7, 15.9 (Me), 21.2, 22.3, 22.5 (CH_2), 25.3 (Me), 26.6, 26.8 (C12, C14), 28.3, 28.5 (CH_2, C13), 42.0 (C9), 43.4 (C8), 47.6 (C7), 49.8 (C11), 51.0 (C4), 65.8 (C1), 71.5 (C5), 81.1 (C6), 96.2 (C3), 105.4 (C2), 235.8, 240.4 (CO)

[a] See eqs 2, 4, and 6 for labeling; in $CDCl_3$ unless stated otherwise. [b] In CD_3NO_2. [c] Spectrum of the mixture of **5a,b**. [d] Spectrum of the mixture of **6a,b**.

2a in yield similar to that obtained from **1a**[24] along with trimethyltin hydride as the byproduct.[25]

Decomplexation of the Organic Ligand from 2a,b. When acetonitrile solutions of **2a**,**b** are heated to reflux for 15−30 min, the tricyclic organic ligands are cleanly decomplexed from the metal with concomitant formation of $[Cr(CO)_3(CH_3CN)_3]$ (eq 2). Evaporation of the solvent in vacuo and extraction of the residue with hexane gave crude **3a,b** as colorless oils. Pure samples were isolated in good yield following chromatography on silica gel. The new organic compound **3a** is 1,2,3-trimethyl-11-methylenetricyclo[5.3.1.0^{4,10}]undeca-2,5-diene, whereas **3b** is 1,2,3-triethyl-11-(*E*-ethylidene)-tricyclo[5.3.1.0^{4,10}]undeca-2,5-diene.

The isolation of the bis(alkyne)−dienyl cycloadducts as $Cr(CO)_3$ complexes rather than the free organic species is dependent upon the alkyne used as well as the nature of the substituents on the C_7 ring. In some

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(24) Wang, C. Ph.D. Thesis, Rutgers University, 1993.

(25) GCMS analysis of the reaction mixture showed Me_3SnH was present as well as species of molecular mass consistent with products derived from the insertion of excess 2-butyne into the SnH bond, e.g. $Me_3SnC(Me){=}CHMe$.

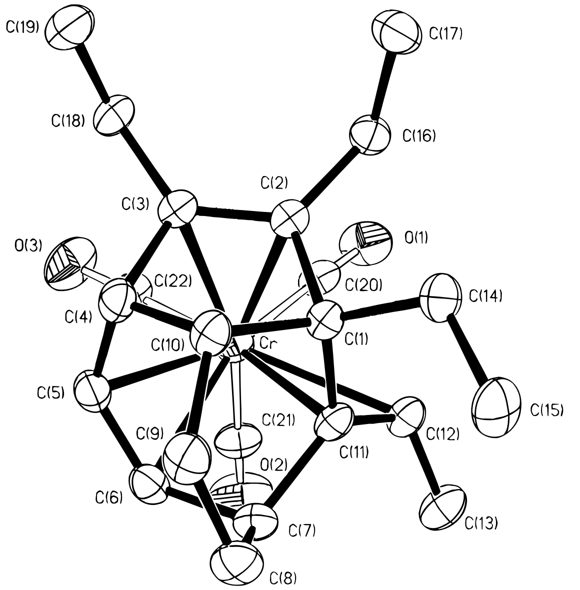
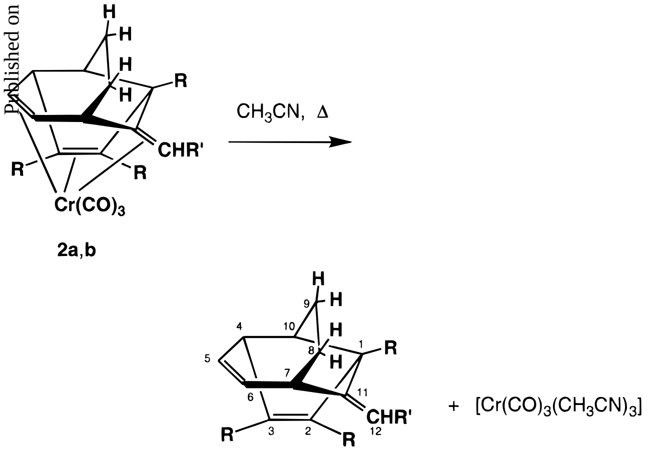


Figure 1. Molecular structure of **2b** showing the atom labeling and 30% thermal ellipsoids for all non-hydrogen atoms. Hydrogen atoms have been omitted for clarity.

Table 2. Crystal Data for Compound 2b

formula	$C_{22}H_{28}CrO_3$
fw	392.46
space group	$P\bar{1}$ (No. 2)
a, Å	7.615(2)
b, Å	9.094(1)
c, Å	14.816(2)
α, deg	92.86(1)
β, deg	97.64(1)
γ, deg	109.565(9)
V, Å^3	953.4(4)
Z	2
D(calc), g cm^{-3}	1.367
μ(Mo Kα), cm^{-1}	6.2
radiation	Mo Kα (λ = 0.710 73 Å)
$R(F)$, %^{a}	5.35
$R_w(F)$, %^{a}	6.36

[a] $R(F) = \sum(|F_o| - |F_c|)/\sum|F_o|$; $R_w(F) = \sum(w^{1/2}(|F_o| - |F_c|))/w^{1/2}(|F_o|)$.



3a R = Me, R' = H. (92%)
3b R = Et, R' = Me. (98%) (2)

Table 3. Selected Bond Distances and Angles for 2b

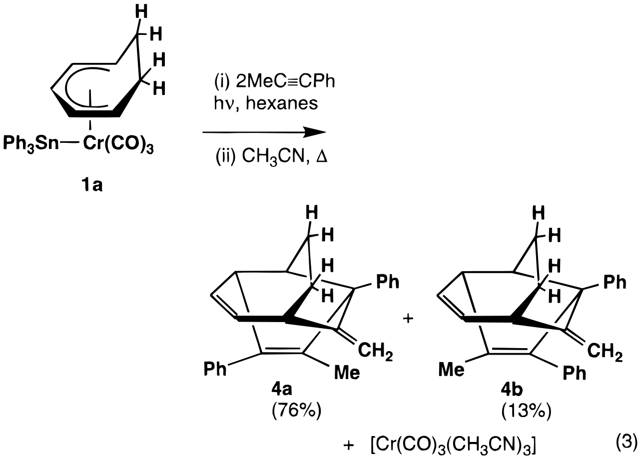
(a) Bond Distances (Å)

Cr−C(2)	2.447(3)	Cr−C(3)	2.466 (4)
Cr−C(5)	2.374(4)	Cr−C(6)	2.368(4)
Cr−C(11)	2.322(3)	Cr−C(12)	2.445(3)
Cr−C(20)	1.830(4)	Cr−C(21)	1.817(4)
Cr−C(22)	1.824(4)	C(20)−O(1)	1.155(5)
C(21)−O(2)	1.164(5)	C(22)−O(3)	1.160(4)
C(1)−C(2)	1.552(4)	C(1)−C(10)	1.556(5)
C(1)−C(11)	1.540(5)	C(1)−C(14)	1.532(5)
C(2)−C(3)	1.352(5)	C(2)−C(16)	1.515(5)
C(3)−C(4)	1.531(5)	C(3)−C(18)	1.512(4)
C(4)−C(5)	1.498(5)	C(4)−C(10)	1.543(4)
C(5)−C(6)	1.352(5)	C(6)−C(7)	1.514(5)
C(7)−C(8)	1.534(5)	C(7)−C(11)	1.514(5)
C(8)−C(9)	1.514(5)	C(9)−C(10)	1.540(5)
C(11)−C(12)	1.360(5)		

(b) Bond Angles (deg)

Cr−C(20)−O(1)	174.6(3)	Cr−C(21)−O(2)	174.7(3)
Cr−C(22)−O(3)	177.4(4)	C(5)−Cr−C(22)	83.4(2)
C(6)−Cr−C(22)	103.2(2)	C(3)−Cr−C(22)	84.7(1)
C(2)−Cr−C(22)	111.3(1)	C(11)−Cr−C(22)	160.8(2)
C(5)−Cr−C(21)	107.9(2)	C(6)−Cr−C(21)	83.4(2)
C(11)−Cr−C(21)	103.8(1)	C(3)−Cr−C(21)	165.2(2)
C(2)−Cr−C(21)	162.1(2)	C(2)−Cr−C(20)	89.4(1)
C(3)−Cr−C(20)	106.1(1)	C(5)−Cr−C(20)	164.1(1)
C(6)−Cr−C(20)	162.7(1)	C(1)−Cr−C(20)	110.1(1)
C(2)−Cr−C(3)	31.9(1)	C(2)−Cr−C(5)	81.9(1)
C(2)−Cr−C(6)	98.9(1)	C(2)−Cr−C(11)	62.9(1)
C(2)−Cr−C(12)	75.8(1)	C(3)−Cr−C(5)	60.2(1)
C(3)−Cr−C(6)	88.5(1)	C(3)−Cr−C(11)	82.9(1)
C(3)−Cr−C(12)	105.2(1)	C(5)−Cr−C(6)	33.1(1)
C(5)−Cr−C(11)	77.7(1)	C(6)−Cr−C(11)	61.8(1)
C(6)−Cr−C(12)	86.9(1)	C(11)−Cr−C(12)	33.0(1)
C(7)−C(11)−C(12)	123.3(3)	C(1)−C(11)−C(12)	119.4(3)
C(1)−C(11)−C(7)	117.3(3)	C(1)−C(2)−C(3)	111.1(3)
C(1)−C(2)−C(16)	123.5(3)	C(1)−C(10)−C(9)	117.6(3)
C(2)−C(3)−C(4)	109.5(3)	C(2)−C(3)−C(18)	128.5(3)
C(3)−C(4)−C(5)	106.5(3)	C(3)−C(4)−C(10)	102.1(3)
C(4)−C(5)−C(6)	127.3(3)	C(5)−C(6)−C(7)	124.3(3)
C(6)−C(7)−C(8)	112.0(3)	C(7)−C(8)−C(9)	111.8(3)
C(8)−C(7)−C(11)	112.9(3)	C(8)−C(9)−C(10)	114.1(3)

cases, decomposition of the organometallic adducts to the organic compounds prevented isolation of the pure complexes. In these instances, a one-pot strategy was employed involving irradiation of the alkynes and **1** until all of **1** had been consumed, followed by heating in acetonitrile. Thus, **1a** and 2 equiv of 1-phenyl-1-propyne gave the organic material as two isomers **4a**,**b** in a 4:1 ratio (eq 3). Compounds **4a**,**b** were separated by TLC and spectroscopically characterized (Table 1). The major product (**4a**) is the 1,3-diphenyl-substituted isomer with the minor product (**4b**) that with phenyl groups at C(1) and C(2). This regioselectivity is similar to that observed for the manganese-mediated cyclohexadienyl−alkyne coupling mentioned earlier and arises because of insertion preferences of the alkyne during the *homo*[5 + 2] addition (see mechanistic discussion). Compounds **4a**,**b** show distinctly different ^{1}H NMR

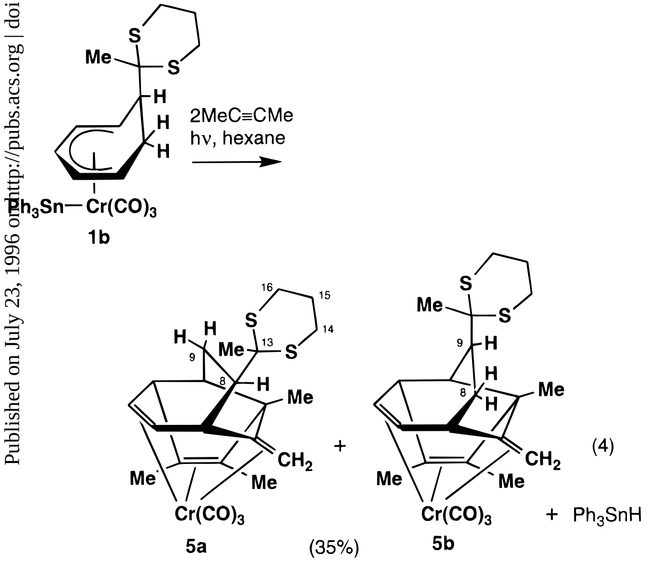


(3)

spectral data with the methylene signals (H_{12} and H_{12}') appearing as two singlets at δ 4.68 and 5.07 for **4a** and δ 4.00 and 5.00 for **4b**. We attribute this difference to the closer proximity of the phenyl substituent at C(2) in **4b** causing a greater chemical shift difference in the methylene protons. The facile decomplexation of **4a**,**b** from the metal precursors may be due to the formation of an η^6-phenyl-coordinated intermediate. Indeed, we have previously observed facile migration of $Cr(CO)_3$ from an $\eta^{2,4}$-coordinated bicyclic ring to a pendant phenyl group,[9] and the $\eta^{2,2,2}$- interaction in **2** might be expected to be weaker still.

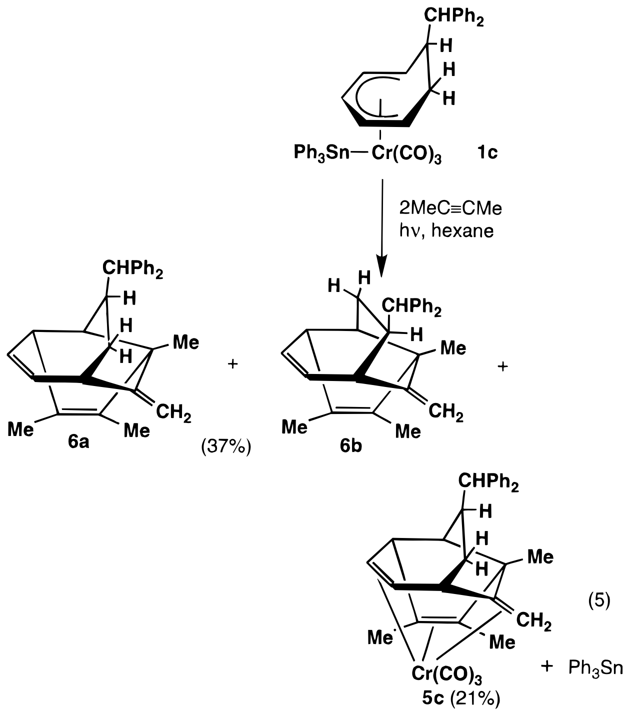
An important consideration in these double cycloaddition reactions is the regiochemistry of the second addition. As observed above (eq 3), unsymmetrical alkynes gave two regioisomers in which the groups at C(2) and C(3) of the organic ligand are different. An alternative probe into the regioselectivity of the double addition involves functionalization of the cycloheptadienyl ligand at C(6). In this case, the cycloheptadienyl complex is unsymmetrical and the second addition may occur either adjacent to, or remote from, the ring substituent. Thus, solutions of the complexes [(η^5-$C_7H_8R)Cr(CO)_3SnPh_3$] (**1b**, R = 6-*exo*-$\overline{C(Me)S(CH_2)_3S}$; **1c**, R = 6-*exo*-$CHPh_2$)[26] were irradiated with 2 equiv of 2-butyne and the products analyzed (eqs 4 and 5).

Complex **1b** gave two isomeric products **5a**,**b** in an approximate 2:1 ratio (eq 4). These species could not be separated by column chromatography but were characterized as a mixture by elemental analysis, ^1H, ^{13}C, and $^1H-^1H$ (2D COSY) NMR, and IR spectroscopy (Table 1 and Experimental Section). From these data the major isomer was determined to be that in which the 2-methyldithiane substituent is at C(8) of the tricyclic ring or furthest from the five-membered ring formed in the *homo*[5 + 2] coupling. The other isomer (**5b**) has this substituent at C(9). The ^1H NMR signals for the two isomers are very similar, and only those for the protons closest to the 2-methyldithiane moiety show significant differences in chemical shift.



(4)

In contrast to **1b**, the reaction of **1c** with 2-butyne gave three isolable products as well as Ph_3SnH (detected by GCMS) (eq 5). Two of these are the decomplexed 9- and 8-substituted tricyclic ligands **6a**,**b,** respectively, and are isolated as a mixture. The third is the 9-(diphenylmethyl)-substituted complex **5c** which elutes from the column after **6a,b**. No evidence for the 8-substituted complex was obtained, presumably due to its decomposition to **6b**. As was observed for **4a**,**b** decomplexation of the tricyclic ligand bearing phenyl substituents is quite facile, and this may be the reason why a mixture of decomplexed and complexed products is observed in this case. From the above results it appears that the 6-substituent on **1b**,**c** exerts little effect on the second cycloaddition, which is not surprising since this group is on the opposite side of the molecule from the metal center and hence on the opposite side to the bond-forming event.



(5)

Mechanism for Ph_3Sn-Cr-Mediated Cycloheptadienyl−Alkyne Coupling. The formation of complexes **2** and **5** as well as the organic species **4** and **6** can be viewed as occurring through sequential [5 + 2] and *homo*[5 + 2] cycloadditions of two alkyne molecules to a cycloheptadienyl manifold followed by elimination of Ph_3SnH. It should be stressed that C−C bond formation does not occur via a traditional concerted cycloaddition but rather through a series of stepwise insertions at the metal center. A proposed mechanism for the formation for **2a** is shown in Scheme 3 and is similar to the pathway by which other metal-mediated higher-order cycloadditions have been proposed to occur.[2,9,12,27] The reaction absolutely requires UV light since the products are not observed when solutions of **1** and alkynes are heated for prolonged periods. The exact role of the UV light is however unclear, but we propose that irradiation of **1** generates a coordinatively unsaturated intermediate by ejection of a CO ligand. As shown, one molecule of alkyne then adds to the metal prior to insertion into the dienyl−chromium bond. Following

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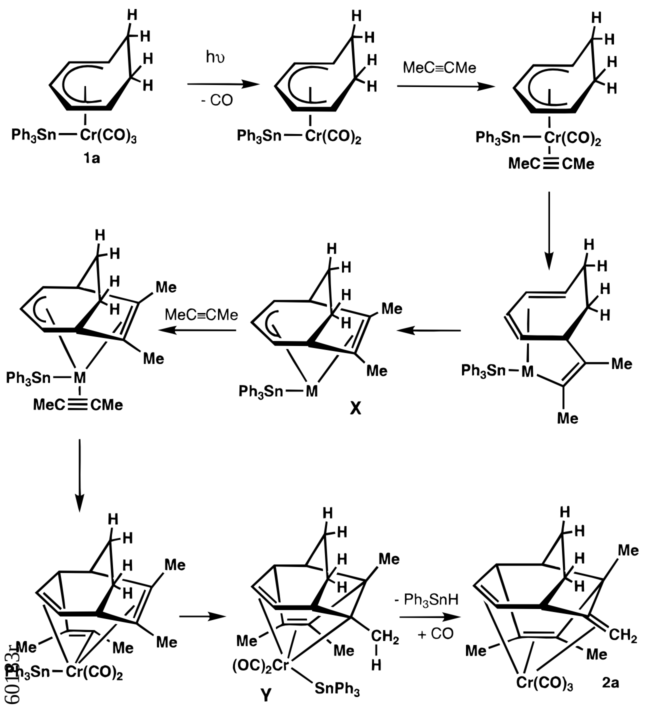
[26] Chen, W.; Sheridan, J. B.; Coté, M. L.; Lalancette, R. A. *Organometallics* **1996**, *15*, 2700.

[27] van Houwelingen, T.; Stufkens, D. J.; Oskam, A. *Organometallics* **1992**, *11*, 1146.

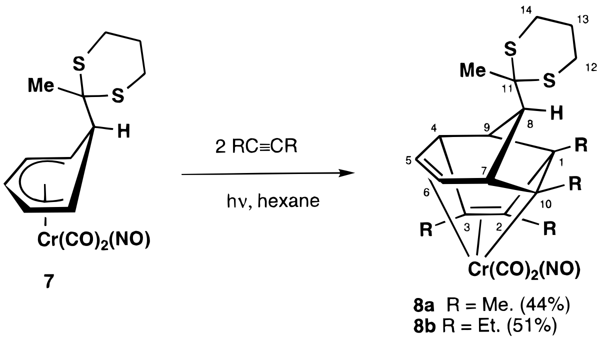
Scheme 3



this step, the former alkyne is now a vinyl ligand which can undergo further insertion into the metal–diene bond to give a [5 + 2] cycloadduct **X**. A second *homo*[5 + 2] addition follows in like fashion as a series of stepwise alkyne–olefin or alkyne–allyl insertions giving the penultimate intermediate **Y**.[28] This species is similar to those isolated for the related manganese-mediated cyclohexadienyl–alkyne [5 + 2],*homo*[5 + 2] double additions,[12,13] but unlike those complexes it is coordinatively unsaturated and eliminates a hydrogen atom adjacent to C(11) with the $SnPh_3$ ligand giving the $Cr(CO)_3$ triene complexes and Ph_3SnH. This latter step most probably occurs via β-elimination of hydride from the methyl group at C(11) to the metal followed by reductive elimination of Ph_3SnH and coordination of a molecule of CO from the reaction medium. There is precedent for abstraction of hydride by trityl cation from this position in the related manganese complexes,[12] as well as in a recent report by Kreiter in which irradiation of 2 equiv of 3-hexyne and $[(\eta^5\text{-cyclohexadienyl})Mn(CO)_3]$ with UV light gave a product containing an exocyclic alkylidene at C(10) of the related tricyclic ring. This latter species arose via a 1–5 shift of a hydrogen atom from a methylene group to C(5).[13] One interesting aspect of the Cr system is that the stereochemistry of the newly formed double bond is exclusively *E* as a result of the intramolecular elimination of Ph_3SnH. If this process were to involve the homolytic cleavage of the Cr–Sn bond and elimination of $Ph_3Sn^{\bullet}$, followed by abstraction of $H^{\bullet}$ from the remaining organometallic fragment, both *E* and *Z* isomers might be expected. The 1–5 shift described in ref 13 is stereoselective and presumably also proceeds via a metal–hydride intermediate. No stable tin-containing double cycloadducts are observed, probably because this would involve intermediate **Y** accepting a CO ligand and forming a 7-coordinate Cr center.

In the case of unsymmetrical alkynes (e.g. PhC≡CMe), the formation of the two isomers **4a**,**b** arises because the second alkyne insertion can occur in a number of ways as outlined in Scheme 4. The four possible routes shown involve insertion of either methyl- or phenyl-substituted alkyne termini into the Cr–allyl or Cr–alkene bonds of intermediate **Z**. The isolation of both **4a**,**b** indicates either (a) both the phenyl and methyl alkyne termini insert into either of the allyl– or olefin–chromium bonds of **Z** (shown as (i) in Scheme 4) or (b) if one alkyne terminus preferentially inserts over the other, it must occur into both the allyl or olefin bound groups. Some combination of (a) and (b) would also give **4a**,**b**. However, insertion into the Cr–allyl bond is considered more likely and since there is a preference for formation of **4a,** it appears that the phenyl- rather than methyl-substituted alkyne carbon initially inserts into the bicyclic ligand of **Z**. As mentioned above, substitution at the methylene carbons of the C_7 ring does not greatly affect the regiochemistry of **5a**–**c** or **6a**,**b**, although few conclusions can be drawn from these latter results given the rather low yields and instability of the organometallic adducts.

Chromium-Mediated Cyclohexadienyl–Alkyne Coupling. Irradiation of toluene or *n*-hexane solutions of dicarbonyl(nitrosyl)(η^5-cyclohexadienyl)chromium(0) (**7**) and 2-butyne or 3-hexyne (2 equiv) at room temperature for 2–6 h resulted in a gradual disappearance of **7**, as monitored by IR spectroscopy, and the formation of the neutral dicarbonyl–nitrosyl species **8a**,**b** (eq 6).



(6)

Complexes **8a**,**b** were isolated in 44 and 51% yield, respectively (based on **7**), as red-orange powders and were characterized using elemental analysis, ^1H, ^{13}C, and ^1H–^1H (2D COSY) NMR, and IR spectroscopy (Table 1). The polycyclic ligand in **8** is a tricyclic system that results from sequential [5 + 2] and *homo*[5 + 2] cycloadditions of two alkyne molecules to a cyclohexadienyl ring. As was observed for the related $Mn(CO)_3$ system,[12,13] the ligand has three fused rings, in this case (C_5, C_5, C_6), with C(1), C(2), C(3), and C(10) derived from added alkynes and C(2), C(3), C(5), C(6), and C(10) coordinated to chromium. The $^{13}C\{^1H\}$ NMR spectrum of **8a** is particularly diagnostic of the structure and shows two distinct carbonyl signals at δ 236 and 240, as well as a distinctive signal at −1.7 ppm assigned to C(10). The upfield shift of this resonance is typical of σ-bonded carbon atoms in these types of complexes.[12,13] Interestingly, the ^{13}C NMR shifts of most signals of **8a** are further downfield than those for the $Mn(CO)_3$ counterpart shown in Scheme 1 (C(10) is at δ −19.2),[12] indicating the $Cr(CO)_2(NO)$ group is more electrophilic. The IR spectrum of **8a** (ν_{max}(CO) 2000, 1944 and ν_{max}-

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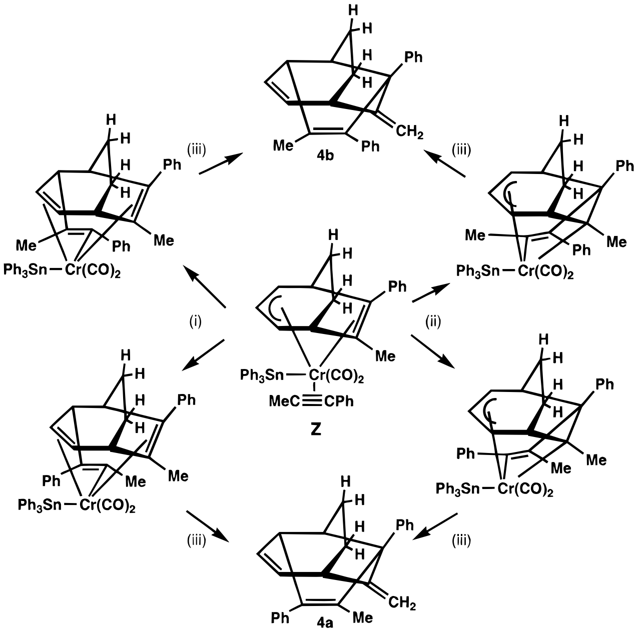
[28] In Scheme 3, initial insertion of the second alkyne into the allyl fragment is depicted. However, the alternative insertion into the Cr–olefin bond is also possible (see Scheme 4).

Scheme 4. Possible Pathways to Isomers 4a,b[a]



[a] Key: (i) alkyne insertion into the Cr−allyl bond; (ii) alkyne insertion into the Cr−alkene bond; (iii) ring closure, −Ph$_3$SnH, −Cr(CO)$_x$.

(NO) 1677 cm^{-1}) indicates one nitrosyl and two carbonyl ligands are present in the complex and rules out any structure that might arise via alkyne/CO substitution, e.g. [(MeC≡CMe)$_2$(NO)Cr(η^5-C$_6$H$_6$R)]. In comparison to the isostructural and isoelectronic Mn(CO)$_3$ derivatives, the chromium species **8a**,**b** are less stable, again presumably due to the more electrophilic Cr(CO)$_2$(NO) fragment.

Conclusions

We have demonstrated that chromium cycloheptaand cyclohexadienyl complexes undergo photoassisted double [5 + 2],*homo*[5 + 2] cycloadditions with alkynes giving tricyclo[5.3.1.0^{4,10}]undeca-2,5,-diene and tricyclo[5.2.1.0^{4,9}]deca-2,5-dien-10-yl species, respectively. When the triphenyltin−cycloheptadienyl precursor complexes were used, elimination of Ph$_3$SnH led to an exocyclic alkylidene in the organic ligand which had exclusively *E* stereochemistry. In contrast, the nitrosyl−cyclohexadienyl species gave adducts in which no hydrogen atom abstraction occurred. The role of UV light in these reactions is to generate an unsaturated transition-metal intermediate which initiates a cascade of insertion processes leading to the final adducts. The organic products were isolated following reflux of the tricarbonyl complexes in acetonitrile. An identical coupling reaction has been described for the related manganese system,[12] and it appears that metal-mediated [5 + 2],*homo*[5 + 2] double additions may be quite general for metal−η^5-dienyl manifolds, allowing the generation of four new carbon−carbon bonds with a high degree of regio- and stereocontrol. The development of this multiple cycloaddition methodology for other coordinated polyene manifolds, in order to access new polycyclic systems, is in progress and will be reported in due course.

Experimental Section

General Methods. The preparation, purification, and reactions of all complexes described were performed under an atmosphere of dry nitrogen using standard Schlenk techniques. Manipulations of air-sensitive solids were performed inside a Braun MB 150 inert-atmosphere glovebox containing a nitrogen atmosphere. Solvents were dried over Na/benzophenone (toluene, benzene, THF, diethyl ether), CaH$_2$ (*n*-hexane, *n*-pentane, CH$_2$Cl$_2$) or K$_2$CO$_3$ (acetone) and were freshly distilled prior to use. Reagents were used as supplied by either the Aldrich Chemical Co. (Milwaukee, WI) or Farchan Laboratories (Gainesville, FL). Infrared spectra were recorded on a Nicolet 5ZDX FT instrument operated in the transmittance mode, and all NMR spectra were recorded on a Varian VXR-400S NMR Fourier transform spectrometer. Gas chromatography−mass spectrometry (GCMS) was performed using a Hewlett Packard HP5890 gas chromatograph connected to a Finnegan Mat Incos 50 mass spectrometer (70 eV). High-resolution mass spectra were obtained at Hoffman La Roche (Nutley, NJ). Microanalyses were carried out by Robertson Microlit Laboratories (Madison, NJ). Chromatography was performed on Alumina (150 mesh, standard grade, activated, neutral, purchased from Aldrich) or silica gel (230−425 mesh, purchased from Fisher Scientific). Tricarbonyl(triphenylstannyl)(η^5-cycloheptadienyl)chromium(II) derivatives (**1a**−**c**) and dicarbonyl(nitrosyl)(η^5-cyclohexadienyl)chromium(0) (**7**) were prepared using the literature procedures.[23,26] Photolyses were conducted through Pyrex or quartz glassware placed approx 5 cm from a 450 W Hanovia medium-pressure Hg broadband UV lamp.

Tricarbonyl(η^2,η^2,η^2-1,2,3-trimethyl-11-methylenetricyclo[5.3.1.0^{4,10}]undeca-2,5-diene)chromium(0) (2a). 2-Butyne (0.12 mL, 1.52 mmol, 2 equiv) was added to a stirred orange solution of [Ph$_3$SnCr(CO)$_3$(η^5-C$_7$H$_9$)] (0.300 g, 0.76 mmol) in *n*-hexane (40 mL) at room temperature. The mixture was photolyzed for 2 h at room temperature and monitored by IR spectroscopy until completion. Removal of the solvent in vacuo and chromatography of the residue on alumina (30 cm × 2.5 cm), loading with CH$_2$Cl$_2$ (3 mL), and eluting with *n*-hexane first and then CH$_2$Cl$_2$/*n*-hexane (1:1), followed by evaporation to dryness, gave **2a** as an orange powder. Yield: 0.192 g, 75%. ν_{max}(CO)/cm^{-1} (hex): 1959 (vs), 1878 (vs), and 1874 (vs). Anal. Calcd for C$_{18}$H$_{20}$CrO$_3$: C, 64.29; H, 5.95. Found: C, 64.41; H, 5.95.

Tricarbonyl(η^2,η^2,η^2-1,2,3-triethyl-11-(*E*)-ethylidenetricyclo[5.3.1.0^{4,10}]undeca-2,5-diene)chromium(0) (2b). 3-Hexyne (0.039 mL, 0.345 mmol, 2 equiv) was added to a stirred orange solution of [Ph$_3$SnCr(CO)$_3$(η^5-C$_7$H$_9$)] (0.10 g, 0.173 mmol) in *n*-hexane (150 mL) at room temperature. The mixture was photolyzed for 2 h at room temperature and monitored by IR spectroscopy until completion. Removal of the solvent in vacuo and chromatography of the residue on alumina (30 cm × 2.5 cm), loading with CH$_2$Cl$_2$ (2 mL), and eluting with CH$_2$Cl$_2$−*n*-hexane (1:1), followed by evaporation to dryness, gave **2b** as an orange powder. Yield: 0.060 g, 88%. ν_{max}(CO)/cm^{-1} (hex): 1954 (vs), 1872 (vs), and 1864 (vs). Anal. Calcd for C$_{22}$H$_{28}$CrO$_3$: C, 67.35; H, 7.14. Found: C, 67.10; H, 7.22.

1,2,3-Trimethyl-11-methylenetricyclo[5.3.1.0^{4,10}]undeca-2,5-diene (3a). A solution of complex **2a** (0.10 g, 0.30 mmol) in acetonitrile (20 mL) was stirred under reflux for 30 min. Evaporation of the solvent in vacuo and extraction of the residue with *n*-hexane gave crude **3a** as a pale yellow oil. Pure **3a** was isolated following TLC on silica gel eluting with *n*-hexane. Yield: 0.055 g (92%). GCMS (*m/z* for **3a**): 200 (M$^+$), 185 (M$^+$ − Me), 171, 157, 143, 129, 115, 105, 91, 77. The presence of [Cr(CO)$_3$(CH$_3$CN)$_3$] was confirmed by IR spectroscopy of the reaction solution, ν_{max}(CO)/cm^{-1} (CH$_3$CN), 2074 (vs), 1950 (vs), and 1927 (vs), but this complex was not isolated.

1,2,3-Triethyl-11-(*E*)-ethylidenetricyclo[5.3.1.0^{4,10}]undeca-2,5-diene (3b). A solution of complex **2b** (0.07 g, 0.179 mmol) in acetonitrile (20 mL) was stirred under reflux for 30 min. Evaporation of the solvent in vacuo and extraction of the residue with hexane gave crude **3b** as a pale yellow oil. Pure **3b** was isolated following TLC on silica gel eluting with *n*-hexane. Yield: 0.045 g (98%). GCMS (*m*/*z* for **3b**): 256 (M^+), 227 ($M^+ - Et$), 199, 185, 171, 157, 143, 128, 115, 105, 91, 79.

2-Methyl-1,3-diphenyl-11-methylenetricyclo[5.3.1.0^{4,10}]undeca-2,5-diene (4a) and 3-Methyl-2,3-diphenyl-11-methylenetricyclo[5.3.1.0^{4,10}]undeca-2,5-diene (4b). 1-Phenyl-1-propyne (0.087 mL, 0.69 mmol) was added to a stirred orange solution of [$Ph_3SnCr(CO)_3(\eta^5\text{-}C_7H_9)$] (**1a**, 0.200 g, 0.345 mmol) in *n*-hexane (100 mL) at room temperature. The mixture was photolyzed for 4 h at room temperature and monitored by IR spectroscopy until **1a** had been completely consumed. The solvent was removed in vacuo, acetonitrile (20 mL) was added, and the solution was heated to reflux for 30 min. Filtration through Celite, removal of the acetonitrile in vacuo, and purification (TLC, silica, eluate 1:3 hexane/CH_2Cl_2) gave **4a** (0.085 g, 76%) and **4b** (0.015 g, 13%) as colorless oils, combined yield 0.100 g, 89%. **4a**: $m/z = 324.1882$. **4b**: $m/z = 324.1892$; calcd for $C_{25}H_{24}$, $m/z = 324.1878$.

5a,b. 2-Butyne (0.02 g, 0.37 mmol) was added to a stirred orange solution of [$Ph_3SnCr(CO)_3(\eta^5\text{-}C_7H_8R)$] (**1b**, R = 2-methyldithiane, 0.130 g, 0.183 mmol) in *n*-hexane (150 mL) at room temperature. The mixture was photolyzed for 4 h at room temperature and monitored by IR spectroscopy until all of **1b** had been consumed. Removal of the solvent in vacuo, chromatography of the residue on an alumina column (30 cm × 2.5 cm), loading with CH_2Cl_2 (2 mL), and eluting initially with *n*-hexane and then CH_2Cl_2/*n*-hexane (1:1), followed by evaporation to dryness, gave the mixture of isomers **5a**,**b** as an orange powder. Yield: 0.03 g, 35%. $\nu_{max}(CO)/cm^{-1}$ (hex): 1959 (vs), 1876 (vs), and 1875 (vs). Anal. Calcd for $C_{23}H_{28}CrO_3S_2$: C, 58.97; H, 5.98. Found: C, 59.07; H, 6.04.

5c and 6a,b. 2-Butyne (0.036 g, 0.672 mmol) was added to a stirred orange solution of [$Ph_3SnCr(CO)_3(\eta^5\text{-}C_7H_8CHPh_2)$] (**1c**, 0.250 g, 0.336 mmol) in *n*-hexane (200 mL) at room temperature. The mixture was photolyzed for 3 h at room temperature and monitored by IR spectroscopy until all of **1c** had been consumed. Removal of the solvent in vacuo, chromatography of the residue on alumina (30 cm × 2.5 cm), loading with CH_2Cl_2 (2 mL), and eluting with *n*-hexane gave a mixture of the two organic isomeric products **6a**,**b**, 0.044 g, yield 37%, following evaporation of solvent. Subsequent elution with 1:1 *n*-hexane/CH_2Cl_2 and evaporation to dryness gave a small amount of complex **5c** as an orange powder. Yield: 0.035 g, 21%. $\nu_{max}(CO)/cm^{-1}$ (hex): 1959 (vs), 1876 (vs), and 1874 (vs).

8a. 2-Butyne (47 μL, 0.6 mmol) was added to a solution of **7** (0.105 g, 0.30 mmol) in toluene (50 mL) and the mixture irradiated (quartz) with UV light for 2 h. Complex **8a** was isolated as a red-orange powder following chromatography on silica gel eluting with diethyl ether/*n*-hexane (1:40). Yield (based on **7**): 60 mg, 44%. $\nu_{max}(CO)$ (hex): 2000 (vs), 1944 (vs) cm^{-1}. $\nu_{max}(NO)$: 1677 (vs) cm^{-1}. Anal. Calcd for $C_{21}H_{27}CrNS_2O_3$: C, 55.14; H, 5.95; N, 3.06. Found: C, 55.39; H, 6.07; N, 2.93.

8b. 3-Hexyne (64 μL, 0.58 mmol) was added to a solution of **7** (0.100 g, 0.29 mmol) in toluene (50 mL) and the mixture irradiated (quartz) with UV light for 6 h. Complex **8b** was isolated as a red orange powder following chromatography on silica gel eluting with diethyl ether/*n*-hexane (1:49) for 2−3 min, followed by *n*-hexane. Yield (based on **7**): 75 mg, 51%. $\nu_{max}(CO)$ (hex): 1998 (vs), 1942 (vs). $\nu_{max}(NO)$: 1677 (vs) cm^{-1}. Anal. Calcd for $C_{25}H_{35}CrNS_2O_3$: C, 58.46; H, 6.87; N, 2.73. Found: C, 58.71; H, 6.96; N, 2.66.

X-ray Diffraction Study. Crystallographic data are collected in Table 2. An orange-red parallelepiped (0.48 × 0.28 × 0.24 mm) of **2b** was mounted on a glass fiber with epoxy. Twenty-nine automatically centered reflections ($8.0 < \theta < 19.7°$) were used to refine the cell parameters using graphite-monochromated Mo Kα (0.710 73 Å) radiation on a Siemens P4 diffractometer. Data were collected using the θ-2θ mode with θ scan width = 0.76° + Kα separation and θ scan speed 3−60° min^{-1}. A total of 4663 reflections were measured ($1.5 < \theta < 30°$, $\pm h, \pm k, +l$), of which 4334 were unique (merging $R = 0.046$) after absorption correction (face-indexed numerical) (max, min transmission factors = 0.870, 0.830)], giving 2890 with $F > 4\sigma(F)$. The selected crystal had a linear absorption coefficient μ(Mo Kα) = 6.2 cm^{-1}. A Patterson map was used to find the Cr and some of the light atoms, followed by difference maps to find all other non-hydrogen atoms. Full-matrix least-squares refinement proceeded with all non-hydrogen atoms anisotropic and hydrogens in calculated positions and riding on the atoms to which they are bound, with U_{iso} for the exocyclic methine H (0.045 Å^2), U_{iso} for the ethyl-group methylene H's (0.055 Å^2), U_{iso} for the four methyl groups' H's (0.076 Å^2), and U_{iso} for the H's on the cyclic ring system (0.08 Å^2). The weighting scheme $w = 1/[\sigma^2(F) + 0.0007F^2]$, with $\sigma(F_o)$ from counting statistics gave satisfactory agreement analyses. Final R and R' values are 0.0535 and 0.0636, respectively, goodness of fit = 1.13, maximum $\Delta/\sigma = 0.032$, largest difference peak = 0.37 e Å^3, and largest difference hole = −0.44 e Å^3. Data collection, cell refinement, data reduction, structure solution, structure refinement, molecular graphics, and preparation of material for publication used SHELXTL/PC.[29,30]

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Supporting Information Available: Complete tables of X-ray structural data, including positional and *U* parameters, anisotropic thermal parameters, and bond lengths and angles for **2b** (5 pages). Ordering information is given on any current masthead page.

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