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Metal-Mediated Cycloaddition Reactions of the η^5-Cyclohexadienyl Ligand. Synthesis and Reactions of [5 + 2] Single and [5 + 2],*homo*[5 + 2] Double Cyclohexadienyl−Alkyne Adducts of Manganese

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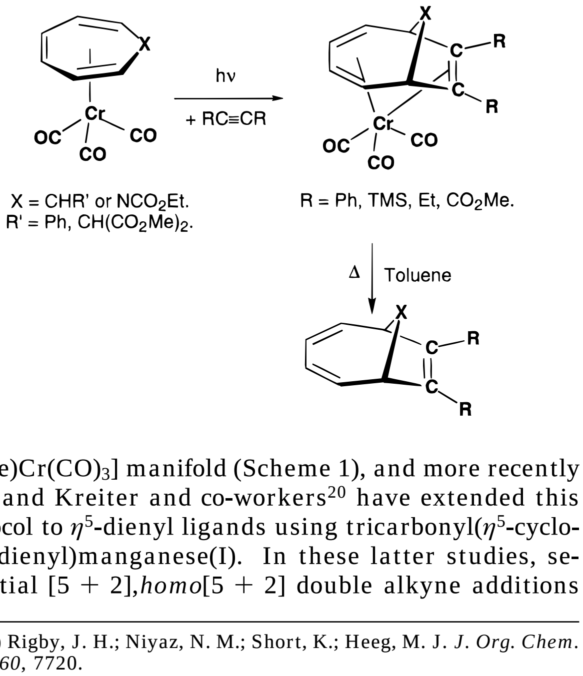
UV irradiation of the cyclohexadienyl complex $[(\eta^5\text{-}C_6H_7)Mn(CO)_3]$ (**1**) and 1 or 2 equiv of the alkynes PhC≡CR (R = H, Me, Ph) in toluene gave both the [5 + 2] adducts $[\{\eta^{2:3}\text{-}C_8H_7\text{-}Ph(R)\}Mn(CO)_3]$ (**2**) and the tricyclic [5 + 2],*homo*[5 + 2] double adducts $[(\eta^{1:2:2}\text{-}C_{10}H_7Ph_2R_2)\text{-}Mn(CO)_3]$ **3a**−**d**. The reactions involve sequential metal-mediated alkyne cycloadditions, first across the η^5-dienyl ligand and then across the resulting olefin−allyl manifolds. Reaction of the monoadducts **2** with an additional equivalent of 2-butyne or 1-phenyl-1-propyne gave the mixed double adducts **3e**−**j**. The THF complex $[(\eta^5\text{-}C_6H_7)Mn(CO)_2(THF)]$ (**4**) reacted thermally with 1-phenyl-1-propyne to form both types of adducts **2** and **3**, indicating the role of UV light is to generate a coordinatively unsaturated metal center by CO ejection. Photolysis of **1** and dimethyl acetylenedicarboxylate gave the organic double adduct 1,2,3,-10-tetrakis(methoxycarbonyl)tricyclo[5.2.1.0^{4,9}]deca-2,5-diene (**5a**), whereas protonation of **3a**,**c** using $HBF_4\cdot Et_2O$ gave the analogous organic tricyclodienes **5b**,**c**. Reaction of the adducts $[(\eta^{1:2:2}\text{-}C_{10}H_7R_4)Mn(CO)_3]$ (**3a**, **3k** R = Me; **3l** R = Et) with carbon monoxide (200 psi; 100 °C) gave new CO insertion products **6a**−**c**. The single addition product **2c**, the double adducts **3a** and **3j**, and the CO insertion products **6b**,**c** have been characterized by X-ray diffraction studies.

Introduction

Transition metal-mediated cycloaddition reactions continue to attract interest because they allow the efficient and stereoselective synthesis of a variety of ring systems.[1] In particular, medium-size carbo- and heterocyclic rings can be accessed via transition metal-mediated higher-order cycloadditions,[2,3] and Rigby and co-workers have shown that the [6 + 2] and [6 + 4] processes, originally discovered in the 1970s,[4,5]can be extended to a range of *trienophiles*[6−13] as well as to the syntheses of natural products.[14,15] We[16,17] and others[18] have reported the [6 + 2] addition of alkynes to the $[(\eta^6\text{-}triene)Cr(CO)_3]$ manifold (Scheme 1), and more recently we[19] and Kreiter and co-workers[20] have extended this protocol to η^5-dienyl ligands using tricarbonyl(η^5-cyclohexadienyl)manganese(I). In these latter studies, sequential [5 + 2],*homo*[5 + 2] double alkyne additions

Scheme 1. [6 + 2] Additions of Alkynes to Trienes Mediated by Chromium Complexes



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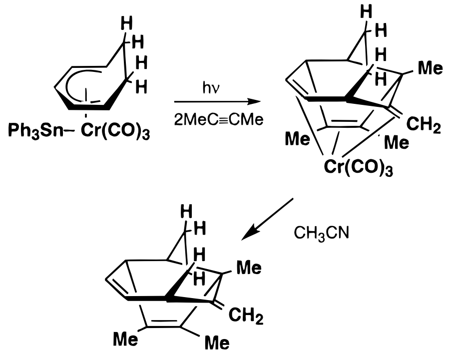
Scheme 2. Chromium Mediated Cycloheptadienyl−Alkyne Coupling

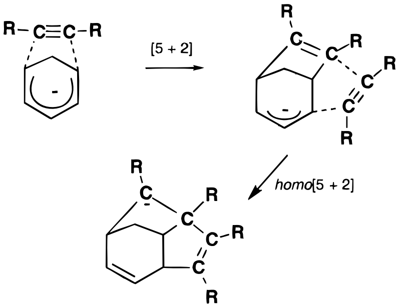


to the dienyl ligand gave tricyclo[5.2.1.0^{4,9}]deca-2,5-dien-10-yl derivatives, further studies on which are described herein. In related work, Kreiter has reported the [5 + 2] coupling of alkynes and pentadienylmanganese complexes,[21,22] a [5 + 2],*homo*[5 + 2] double alkyne addition to tricarbonyl(η^5-cycloheptadienyl)manganese(I),[23] and the [5 + 4] coupling of dienyl ligands with dienes,[24−28] all of which are promoted by UV light. In an earlier study, Ernst and co-workers reported the reaction of $PhC{\equiv}CSiMe_3$ with a dienyl titanium complex that also appears to proceed via an initial metal-promoted [5 + 2] cycloaddition.[29] Very recently, we reported the [5 + 2],*homo*[5 + 2] double addition of alkynes to both cycloheptadienyl(triarylstannyl)- and cyclohexadienyl(nitrosyl)*chromium* manifolds (Scheme 2).[30]

The metal-mediated [5 + 2] or [5 + 4] cycloaddition of appropriate *dienylophiles* to dienyl ligands therefore appears to be a general process for the construction of seven- and nine-membered rings and complements other metal-catalyzed [5 + 2] cycloadditions such as the intramolecular coupling of alkynes and vinylcyclopropanes recently reported by Wender.[31]

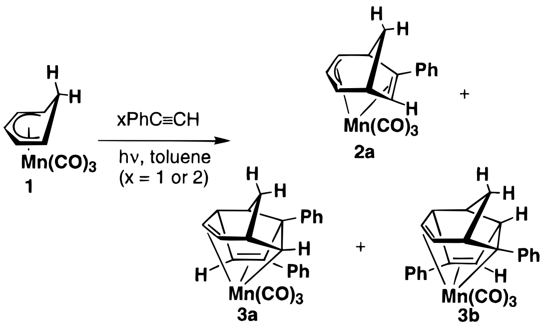
In this paper we present further studies on the photoinduced [5 + 2],*homo*[5 + 2] double cycloaddition of alkynes to tricarbonyl(η^5-cyclohexadienyl)manganese(I) (**1**) including the isolation of single [5 + 2] adducts and their subsequent reaction with additional alkynes leading to mixed [5 + 2],*homo*[5 + 2] double adducts. We also report the reactions of the double adducts with proton sources and carbon monoxide, which gives the decomplexed organic ligands and CO insertion products respectively, as well as studies on the mechanism of the coupling reactions in which dicarbonyl(tetrahydrofuran)(η^5-cyclohexadienyl)manganese(I) reacts with 1-phenyl-1-propyne in the dark to give both single [5 + 2] and double [5 + 2],*homo*[5 + 2] addition products. A schematic representation of the coupling reactions is shown in Scheme 3.

Scheme 3. [5 + 2] + *homo*[5 + 2] Double Alkyne Addition to a Cyclohexadienyl Ring



Results and Discussion

[5 + 2] Cyclohexadienyl−Alkyne Adducts. Irradiation of toluene solutions of tricarbonyl(η^5-cyclohexadienyl)manganese(I) (**1**) and 1 or 2 equivs of phenylacetylene at room temperature for 3.5 h gave a mixture of three isolable complexes **2a**, **3a**, and **3b**, in varying ratios dependent upon the amount of alkyne added, (eq 1). Complex **2a** was isolated as a yellow crystalline solid and characterized by ^1H, ^{13}C, $^1H-^1H$ 2D (COSY) NMR and IR spectroscopy (Table 1) and results from the [5 + 2] cycloaddition of a single alkyne molecule across the 1 and 5 carbons of the cyclohexadienyl ligand. The new bicyclo[3.2.1]octadienyl ligand is η^2-6,7-η^3-2−4-coordinated to a $Mn(CO)_3$ group.



(1)

The isolation of **2a** is significant since it resembles a proposed intermediate **X** in the [5 + 2],*homo*[5 + 2] double additions previously observed for **1** and other alkynes,[19,20] and we propose that **2a** forms from **X** and CO in the absence of excess alkyne (Scheme 4). This is supported by the observation that the yield of **2a** is doubled when photolyses of **1** and phenylacetylene are performed under a purge of CO (Table 2).

Scheme 4

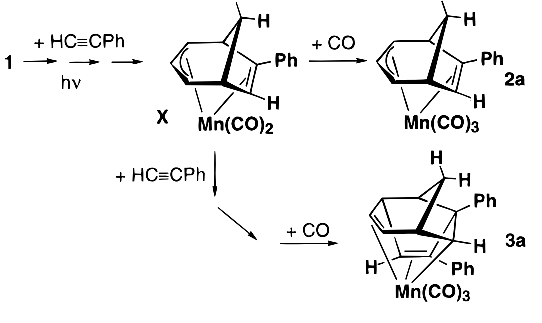


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Table 1. ^{1}H and ^{13}C NMR Spectral Data for Single Cyclohexadienyl−Alkyne Adducts 2a−c[a]

complex	^{1}H	^{13}C[b]
2a	0.81 (1H, d, $H_{8'}$), 1.28 (1H, m, H_8), 3.07 (1H, m, br, H_1), 3.45 (1H, t, H_2), 3.51 (1H, m, br, H_5), 3.76 (1H, t, H_4), 3.93 (1H, d, H_7), 4.23 (1H, t, H_3), 7.20-7.38 (5H, m, Ph)	36.0 (C8), 36.6 (C1), 37.7 (C5), 54.5 (C2,4), 77.8 (C7), 80.9 (C6), 92.3 (C3), 128.3, 126.5, 129.0, 134.5 (Ph), 224 (CO)
2b	0.80 (1H, d, $H_{8'}$), 1.28 (1H, m, H_8), 2.20 (3H, s, 7-Me), 2.86 (1H, m, br, H_1), 3.43 (1H, m, br, H_5), 3.70 (1H, t, H_2), 3.85 (1H, t, H_4), 4.34 (1H, t, H_3), 7.24 (1H, m, Ph), 7.36 (2H, t, Ph), 7.47 (2H, t, Ph)	18.3 (Me), 35.3 (C8), 38.0 (C1), 40.4 (C5), 42.0 (C4), 44.8 (C2), 80.0 (C7), 81.0 (C6), 92.9 (C3), 126.5, 128.0, 128.8, 134.9 (Ph), 223.8 (CO)
2c	0.83 (1H, d, $H_{8'}$), 1.40 (1H, m, H_8), 3.47 (2H, m, $H_{1,5}$), 3.92 (2H, t, $H_{2,4}$), 4.37 (1H, t, H_3), 7.18 (5H, m, Ph), 7.44 (5H, m, Ph)	35.4 (C8), 40.4 (C1,5), 44.7 (C2,4), 82.0 (C6,7), 93.6 (C3), 127.4, 130.0, 134.8 (Ph), 223.4 (CO)

[a] Labeling refers to Figure 1; in $CDCl_3$. [b] ^{1}H-Decoupled spectra.

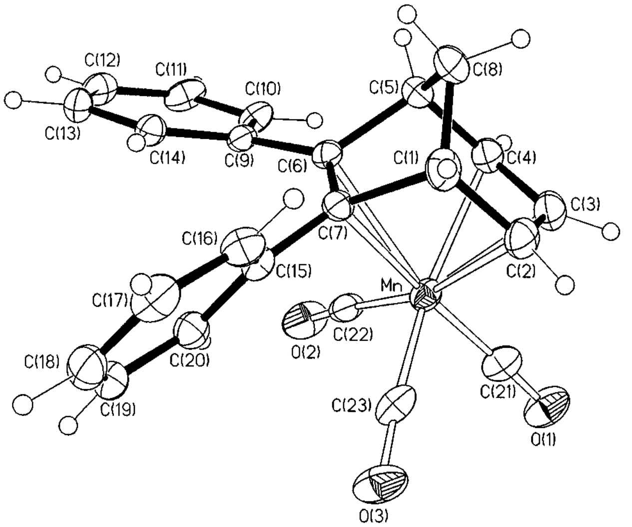
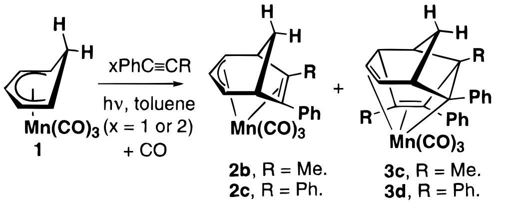


Figure 1. Molecular structure of **2c** showing the atom labeling and 30% thermal ellipsoids for all non-hydrogen atoms.

Table 2. Effect of CO Purge on Yields of Single Adducts

reaction	yield (%)	
	under CO	under N_2
1 + PhC≡CH → **2a**	16	8
1 + PhC≡CMe → **2b**	21	10
1 + PhC≡CPh → **2c**	39	18

A reinvestigation of our earlier studies with 1-phenyl-1-propyne and diphenylacetylene,[19] using a single equivalent of alkyne and a CO purge, also gave the monoadducts **2b**,**c** in up to 39% yield, as well as the previously reported double adducts **3c**,**d**, (Table 2, eq 2). Complexes **2b**,**c** were characterized by ^{1}H, ^{13}C, ^{1}H−^{1}H 2D (COSY) NMR and IR spectroscopy (Table 1 and Experimental Section), and the structure of **2c** was confirmed by an X-ray diffraction study (Figure 1, Tables 3 and 4). The structure shows **2c** is a typical "piano stool" complex with the three carbonyls virtually trans to C(2), C(4), and C(6)═C(7) of the bicyclo[3.2.1]octadienyl ligand. The geometry at the metal is octahedral with the Mn atom closer to the allyl fragment as evidenced by shorter Mn−allyl−carbon bond distances (average 2.159(6) Å) compared to Mn−C(6) and Mn−C(7) (average 2.414(4) Å). The molecule shows little strain, for example the C(2)−C(1)−C(7) and C(4)−C(5)−C(6) angles average 106.8(4)°, close to ideal tetrahedral geometry.



(2)

In contrast to the reactions of arylalkynes, reaction of 2-butyne with **1** under a CO purge did not yield an isolable [5 + 2] adduct, although IR analysis of the reaction mixtures showed a trace of a tricarbonyl-containing complex with CO absorptions similar to those of **2a**−**c**, (ν_{max} (CO)/cm^{-1} (hexane), 2009, 1924, 1912). This latter species could not be isolated due to its formation in small amounts and its facile conversion to the double adduct. As reported earlier, the use of a single equivalent of 2-butyne with **1** under a nitrogen atmosphere gave the double adduct (**3k**) as the only isolable species, (ν_{max} (CO)/cm^{-1} (hexane), 2000, 1920, 1913).[19]

[5 + 2],*homo*[5 + 2] Double Cyclohexadienyl−Alkyne Adducts. The major products from the reactions shown in eqs 1 and 2 are the double adducts **3a**−**d**, of which **3a** and **3b** are new and were isolated as orange solids in 21 and 24% yield, respectively (2 equiv of PhC≡CH) and spectroscopically characterized (Table 5). Complexes **3a**,**b** are two of four possible isomers, with **3a** being the 1,2-diphenyl- and **3b** the 3,10-diphenyltricylo[5.2.1.0^{4,9}]deca-2,5-dien-10-yl $Mn(CO)_3$ species.[32] The remaining two possible isomers, although equally as likely to form, were not observed, presumably due to alkyne insertion preferences during the bond-forming processes, (see mechanistic discussion). Compounds **3a**,**b** show notably different NMR spectral data. For example, a distinct signal in the ^{13}C NMR spectra of all the double adducts is that for C(10), which normally appears at high field, and allows for the identification of the type of isomer formed. Thus, for **3c** and **3d** this signal is seen at δ −4.0 and −4.6 respectively, indicative of phenyl substitution at this site. In **3a**, however, C(10) bears a hydrogen atom and this signal is observed at the furthest upfield position of any of the double adducts synthesized to date (δ −34.5), whereas for **3b**, C(10) appears at δ −18.6. Absolute assignments of these isomers was confirmed by an X-ray diffraction study on complex **3a** (Figure 2, Tables 3 and 6) and the ^{1}H NMR spectrum of **3b**, which shows that H(1) has a coupling of 8 Hz to H(2). The X-ray crystal structure of **3a** reveals a "piano stool" geometry with essentially octahedral geometry at Mn

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[32] The numbering scheme for the tricyclo[5.2.1.0^{4,9}]decadiene ligand is shown in Figures 2−5.

Table 3. X-ray Crystallographic Data for 2c, 3a, 3j, 6b and 6c

compound	**2c**	**3a**	**3j**	**6b**	**6c**
formula	$C_{23}H_{17}O_3Mn$	$C_{25}H_{19}O_3Mn$	$C_{26}H_{21}O_3Mn$	$C_{18}H_{19}O_4Mn$	$C_{22}H_{26}O_4Mn$
MW	396.33	422.37	436.39	354.29	409.39
a (Å)	10.416(3)	11.070(1)	8.901(2)	8.621(2)	15.176(3)
b (Å)	10.949(2)	14.096(2)	11.714(3)	14.760(3)	15.446(2)
c (Å)	16.793(2)	12.567(1)	19.961(4)	12.833(3)	16.819(3)
β (deg)	105.34(2)	94.68(1)	101.87(1)	98.07(3)	90.0
Vol (Å^3)	1846.9	1954.5	2036.8	1616.8	3942.5
Z	4	4	4	4	8
ρ (g cm^{-3})	1.425	1.435	1.423	1.456	1.379
no. of reflctns for centering	20	48	17	44	25
range for centering (min/max) (deg)	5.3/14.6	6.7/13.6	6.0/12.6	10.0/20.8	6.4/12.2
system	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic
space group	*P*2(1)/*c* (No. 14)	*P*2(1)/*c* (No. 14)	*P*2(1)/*n* (No. 14)	*P*2(1)/*n* (No. 14)	*Pbca* (No. 61)
cryst description	trapezoid	parallelepiped	plate	plate	hexagon
color	orange	orange	orange	orange-yellow	orange
F(000)	816	872	904	736	1728
μ (cm^{-1})	7.3	7.0	6.7	8.3	6.9
abs corr	ψ-scans	ψ-scans	face-indexed	ψ-scans	face-indexed
transm factor (min/max)	0.702/0.510	0.561/0.522	0.796/0.973	0.468/0.130	0.752/0.808
cryst dimens (mm)	0.48 × 0.32 × 0.20	0.40 × 0.40 × 0.30	0.52 × 0.40 × 0.04	0.52 × 0.30 × 0.12	0.48 × 0.40 × 0.34
Data Collection					
speed (deg/min)	10.0 constant	3.0−45.0	5.0−60.0	3.0−40.0	3.0−50.0
collection range (θ)	1.5−25.0	1.5−22.5	1.5−22.5	1.5−30.0	1.5−22.5
type collected	$\pm h,+k,+l$	$\pm h,+k,+l$	$\pm h,+k,+l$	$\pm$h,$+k,+l$	$+h,+k,+l$
data collected (θ−2θ)	4462	2840	3813	5149	2933
unique data	3231	2545	2642	4682	2581
$F > 4\sigma(F)$	1680	1652	1298	2742	1444
no. of params	247	265	275	211	248
max Δ/σ	0.013	0.038	0.009	0.002	0.074
largest diff peak (eÅ^{-3})	0.35	0.23	0.45	1.07	0.25
largest diff hole (eÅ^{-3})	−0.38	-0.23	-0.38	-0.75	-0.22
R	0.046	0.038	0.049	0.057	0.038
R′	0.044	0.043	0.045	0.056	0.037
goodness of fit	1.07	0.96	1.02	1.52	0.92

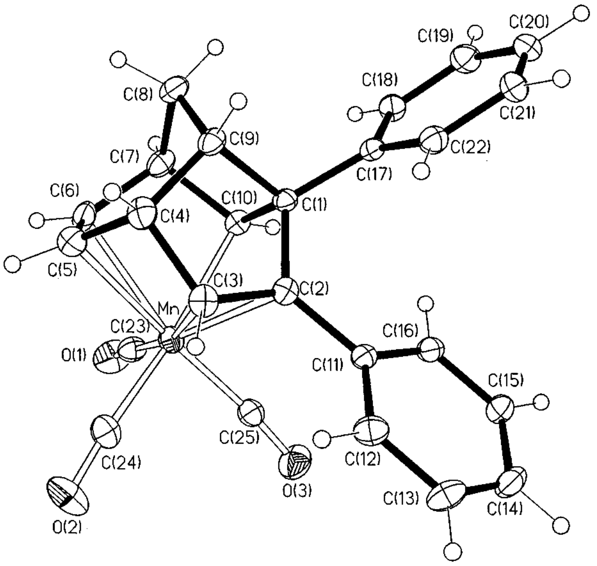
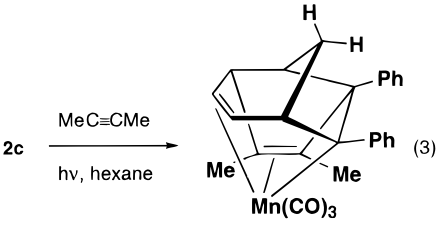


Figure 2. Molecular structure of **3a** showing the atom labeling and 30% thermal ellipsoids for all non-hydrogen atoms.

and carbonyls trans to C(10), C(2)=C(3), and C(5)=C(6). As expected the Mn−C(10) bond length of 2.134(4) Å is shorter than the Mn to C(2)=C(3) and Mn to C(5)=C(6) distances, which average 2.395(5) and 2.323(5) Å, respectively.

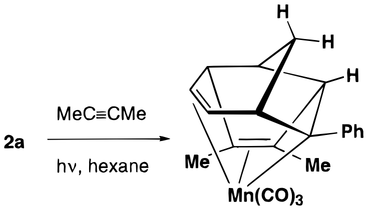
Mixed Double Adducts. It was previously proposed that the double alkyne additions proceed through an unsaturated single [5 + 2] adduct (**X**, Scheme 4), similar to **2a**−**c** but with one less CO ligand.[19,20] Thus, if a vacant coordination site can be generated in **2**, either by photoejection of CO or olefin decomplexation, the possibility exists for the addition of a second *different* alkyne to **2a**−**c**. Indeed this does occur, and the new *mixed* double adducts **3e**−**j** have been synthesized from **2a** or **2c** and the appropriate alkynes, (eqs 3−6).

UV irradiation of **2c** and 1.2 equivs of 2-butyne for 20 min gave **3e** as the only possible regioisomer in 59% yield, (eq 3). Similarly, **2a** and 2-butyne gave **3f** as the major isomer in 55% yield after only 5 min of photolysis, (eq 4). Complex **3f** results from addition of 2-butyne across C(2) and C(7) of **2a**, or in other words, via insertion into the Mn−CH bond of the monoadduct. Another minor isomer, presumably that in which butyne inserts into the Mn−CPh bond of **2a**, eluted from the



(3)

3e (59%)



(4)

3f (55%)

Table 4. Selected Bond Distances (Å) and Angles (deg) for 2c

Bond Distances

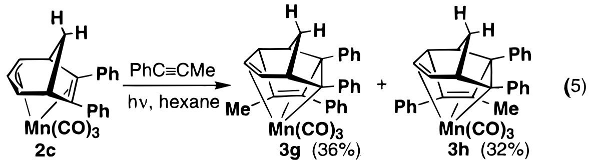
Mn−C(2)	2.188(6)	Mn−C(3)	2.095(6)	Mn−C(4)	2.194(6)
Mn−C(6)	2.434(4)	Mn−C(7)	2.393(4)	C(1)−C(2)	1.518(8)
C(1)−C(7)	1.554(8)	C(1)−C(8)	1.515(9)	C(2)−C(3)	1.385(9)
C(3)−C(4)	1.407(9)	C(4)−C(5)	1.499(7)	C(5)−C(8)	1.517(8)
C(5)−C(6)	1.539(8)	C(6)−C(7)	1.377(7)		

Bond Angles

C(7)−C(1)−C(2)	106.3(4)	C(8)−C(1)−C(2)	109.0(5)
C(8)−C(1)−C(7)	101.3(5)	C(1)−C(2)−C(3)	117.1(5)
C(2)−C(3)−C(4)	119.1(6)	C(3)−C(4)−C(5)	115.4(5)
C(4)−C(5)−C(6)	107.3(4)	C(4)−C(5)−C(8)	111.2(5)
C(8)−C(5)−C(6)	99.7(4)	C(5)−C(6)−C(7)	109.0(4)
C(5)−C(8)−C(1)	99.9(4)	C(1)−C(7)−C(6)	106.5(5)

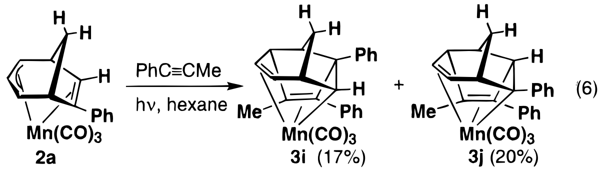
chromatography column before **3f** but was isolated in very low yield and could only be characterized by IR spectroscopy, (ν_{max} (CO)/cm^{-1} (hexane), 2003, 1936, 1927).

In contrast, irradiation of hexane solutions of **2c** and 1.2 equivs of 1-phenyl-1-propyne with UV light gave both possible isomers **3g** and **3h** in 36 and 32% isolated yield, respectively (eq 5). Complex **3g** results from insertion of the methyl-substituted alkyne carbon into the Mn−allyl bond of **2c,** with **3h** forming via insertion of this alkyne terminus into the Mn−olefin bond.



(5)

Likewise, photolysis of **2a** and 1.2 equivs of 1-phenyl-1-propyne in *n*-hexane or toluene for 0.2−4 h gave a mixture of three of the four possible double adducts of which two, **3i** and **3j**, could be isolated in 17 and 20% yield, respectively, with the third observed by IR only, (ν_{max} (CO)/cm^{-1} (hexane), 2012, 1937, 1929) (eq 6).



(6)

The structures of **3e**−**3j** were determined from ^{1}H, ^{1}H−^{1}H 2D (COSY), ^{13}C NMR and IR spectroscopy. In some cases the structures were confirmed by ^{1}H NMR NOE experiments. For **3g**, saturation of the 3-Me signal at δ 2.62 led to enhancement of H(4) (δ 4.09) as well as some of the phenyl signals (2-Ph); for **3i**, saturation of 3-Me (δ 2.55) increased the intensities of H(4) (δ 4.06) and the phenyl groups (2-Ph); whereas **3h** showed only enhancement of the phenyl signals (1-Ph and 3-Ph) when the 2-Me (δ 2.42) signal was irradiated.

Complex **3j** was further characterized by an X-ray diffraction study, (Figure 3, Tables 3 and 6). The structure confirms the assigned regiochemistry and shows remarkable similarities in almost all aspects with the structure of **3a**, except that the metal is slightly closer to C(5)═C(6) and hence the Mn to C(2)═C(3) distances are longer (average 2.449(8) Å) and the Mn to C(5)═C(6) lengths are marginally shorter (average 2.303(9) Å). The Mn−C(10) distance of 2.156(9) Å is comparable to that in **3a**.

Table 5. ^{1}H and ^{13}C NMR Spectral Data for Double Cyclohexadienyl−Alkyne Adducts 3[a]

complex	^{1}H	^{13}C[b]
3a	0.88 (1H, m, H$_{10}$), 1.02 (1H, d, H$_{8'}$), 1.34 (1H, m, H$_{8}$), 2.61 (1H, s, br, H$_{9}$), 3.23 (1H, m, H$_{7}$), 3.82 (1H, t, H$_{5}$), 4.08 (1H, m, H$_{4}$), 4.20 (1H, t, H$_{6}$), 4.58 (1H, d, H$_{3}$), 6.67−7.56 (10H, Ph)	−34.5 (C10), 33.7 (C8), 36.9 (C7), 41.0 (C4), 54.7 (C9), 57.5 (C3), 62.9 (C5), 64.4 (C1), 78.2 (C6), 106.6 (C2), 125.6−145.3 (Ph), 211.6, 224.3, 228.5 (CO)
3b	1.09 (1H, m, H$_{8'}$), 1.39 (1H, m, H$_{8}$), 3.12 (1H, s, br, H$_{9}$), 3.36 (1H, t, H$_{7}$), 4.10 (1H, m, H$_{5}$), 4.16 (1H, d, H$_{1}$), 4.18 (1H, d, H$_{2}$), 4.26 (1H, m, H$_{4}$), 4.45 (1H, t, H$_{6}$), 6.91−7.51 (10H, Ph)	−18.6 (C10), 29.7 (C8), 33.3 (C1), 42.2 (C4), 43.2 (C7), 47.4 (C9), 54.7 (C5), 62.9 (C6), 65.9 (C2), 98.0 (C3), 121.6−153.9 (Ph), 212.4, 223.4, 227.5 (CO)
3e	1.09 (1H, d, H$_{8'}$), 1.48 (1H, m, H$_{8}$), 2.15 (3H, s, 3-Me), 2.26 (3H, s, 2-Me), 2.46 (1H, t, H$_{9}$), 3.78 (1H, t, H$_{7}$), 3.92 (1H, t, H$_{4}$), 3.99 (1H, t, H$_{5}$), 4.40 (1H, t, H$_{6}$), 6.81, 7.15 (10H, Ph)	−9.6 (C10), 16.1, 16.6 (Me), 30.4 (C8), 41.4 (C7), 47.3 (C9), 58.9 (C4), 59.2 (C5), 69.5 (C1), 75.2 (C6), 80.6 (C3), 98.4 (C2), 120.1, 125.4, 126.9, 128.2, 144.0, 152.2 (Ph), 213.2, 223.3, 225.8 (CO)
3f	0.92 (1H, m, H$_{8'}$), 1.26 (1H, m, H$_{8}$), 2.02 (3H, s, 2-Me), 2.06 (3H, s, 3-Me), 3.02 (1H, m, H$_{9}$), 3.36 1H, t, H$_{7}$), 3.43 (1H, d, H$_{1}$), 3.94 (1H, t, H$_{4}$), 4.07 (1H, t, H$_{5}$), 4.56 (1H, t, H$_{6}$), 7.00−7.71 (5H, m, Ph)	−12.0 (C10), 16.0, 16.7 (Me), 33.4 (C8), 43.9 (C7), 46.7 (C4), 48.7 (C9), 60.0 (C5), 62.1 (C1), 77.5 (C6), 82.8 (C2), 94.1 (C3), 121.5−155.6 (Ph), 212.0, 225.3, 227.3 (CO)
3g	1.15 (1H, d, H$_{8'}$), 1.64 (1H, m, H$_{8}$), 2.51 (1H, s, br, H$_{9}$), 2.62 (3H, s, 3-Me), 3.85 (1H, s, br, H$_{7}$), 4.09 (1H, t, H$_{4}$), 4.15 (1H, t, H$_{5}$), 4.62 (1H, t, H$_{6}$), 6.70, 6.85, 6.93, 7.19, 7.29, 7.80 (15H, Ph)	−6.3 (C10), 20.5 (3-Me), 30.8 (C8), 44.5 (C7), 49.3 (C4) 60.0 (C9), 60.1 (C5), 71.9 (C1), 76.8 (C6), 85.6 (C3), 105.8 (C2), 120.3−152.8 (Ph), 212.0, 221.8, 226.0 (CO)
3h	1.25 (1H, d, H$_{8'}$), 1.57 (1H, s, H$_{8}$), 2.50 (3H, s, 2-Me) 2.63 (1H, s, H$_{9}$), 3.90 (1H, t, H$_{7}$), 4.18 (1H, t, H$_{5}$), 4.50 (1H, t, H$_{6}$), 4.81 (1H, t, H$_{4}$), 6.75−7.79 (15H, Ph)	−7.9 (C10), 18.3 (2-Me), 30.7 (C8), 41.5 (C7), 46.4 (C4) 58.7 (C9), 61.6 (C5), 72.2 (C1), 76.6 (C6), 82.6 (C3), 102.0 (C2), 120.3−152.0 (Ph), 211.8, 223.2, 226.0 (CO)
3i	0.90 (1H, m, br, H$_{8'}$), 1.10 (1H, d, H$_{10}$), 1.31 (m, H$_{8}$), 2.58 (1H, s, br, H$_{9}$), 2.63 (3H, s, 3-Me), 3.30 (1H, m, br, H$_{7}$), 4.14 (2H, m, H$_{4}$, H$_{5}$), 4.48 (1H, t, H$_{6}$), 7.01−7.48 (10H, m, Ph)	−24.7 (C10), 19.2 (Me), 29.7 (C8), 40.0 (C7), 48.8 (C4) 56.6 (C9), 63.5 (C5), 68.9 (C1), 80.7 (C6), 88.0 (C3), 106.7 (C2), 125.4−146.3 (Ph), 211.5, 225.2, 228.6 (CO)
3j	0.89 (1H, m, H$_{8'}$), 1.28 (1H, s, br, H$_{8}$), 2.22 (3H, s, 3-Me), 3.14 (1H, s, br, H$_{9}$), 3.45 (1H, s, br, H$_{7}$), 4.08 (1H, t, H$_{4}$), 4.25 (1H, d, H$_{1}$), 4.33 (1H, t, H$_{5}$), 4.68 (1H, t, H$_{6}$), 6.88−7.58 (10H, m, Ph)	−10.3 (C10), 16.6 (Me), 33.2 (C8), 43.2 (C7), 46.4 (C4), 51.3 (C9), 60.0 (C1), 62.7 (C5), 77.4 (C6), 90.1 (C3), 95.9 (C2), 121.2, 124.8, 127.6, 128.2, 129.3, 134.2, 154.1 (Ph), 210.9, 223.9, 227.5 (CO)

[a] Labeling refers to Figures 2 and 3; in CDCl$_3$. [b] ^{1}H-Decoupled spectra.

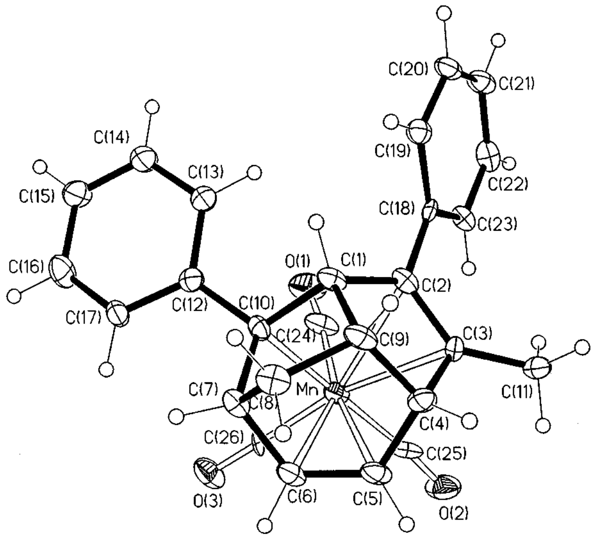
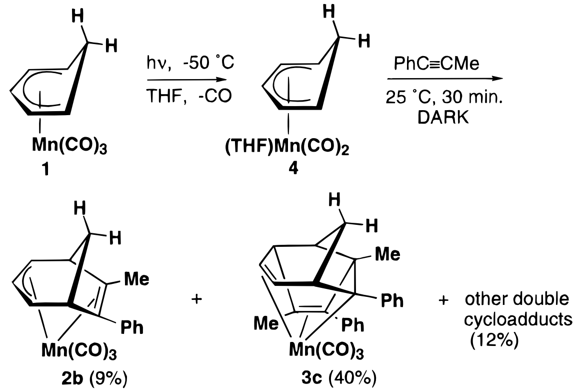


Figure 3. Molecular structure of **3j** showing the atom labeling and 30% thermal ellipsoids for all non-hydrogen atoms.

Table 6. Selected Bond Distances (Å) and Angles (deg) for 3a and 3j

	Bond Distances for **3a**		
Mn−C(2)	2.420(4)	Mn−C(5)	2.326(5)
Mn−C(10)	2.134(4)	C(1)−C(10)	1.529(6)
C(1)−C(9)	1.560(6)	C(2)−C(11)	1.485(6)
C(4)−C(5)	1.501(7)	C(5)−C(6)	1.361(7)
C(7)−C(8)	1.528(7)	C(8)−C(9)	1.516(6)
Mn−C(3)	2.361(5)	Mn−C(6)	2.320(5)
C(1)−C(2)	1.536(6)	C(1)−C(17)	1.517(6)
C(2)−C(3)	1.362(6)	C(3)−C(4)	1.516(6)
C(4)−C(9)	1.542(6)	C(6)−C(7)	1.510(6)
C(7)−C(10)	1.534(6)		
	Bond Angles for **3a**		
C(10)−C(1)−C(2)	104.7(3)	C(3)−C(4)−C(5)	105.4(4)
C(17)−C(1)−C(9)	110.1(3)	C(5)−C(6)−C(7)	119.5(4)
C(1)−C(2)−C(11)	125.1(3)	C(8)−C(7)−C(10)	104.6(4)
C(3)−C(4)−C(9)	102.8(3)	C(10)−C(1)−C(9)	101.4(3)
C(4)−C(9)−C(8)	113.9(4)	C(1)−C(2)−C(3)	109.5(4)
C(6)−C(7)−C(10)	103.8(3)	C(2)−C(3)−C(4)	112.3(4)
C(4)−C(9)−C(1)	104.5(3)	C(4)−C(5)−C(6)	120.5(4)
C(17)−C(1)−C(2)	117.7(4)	C(6)−C(7)−C(8)	107.3(4)
C(9)−C(1)−C(2)	102.5(3)	C(7)−C(8)−C(9)	100.2(4)
C(3)−C(2)−C(11)	125.1(4)		
	Bond Distances for **3j**		
Mn−C(2)	2.425(8)	Mn−C(5)	2.325(8)
Mn−C(10)	2.156(9)	C(1)−C(10)	1.548(10)
C(2)−C(3)	1.376(11)	C(3)−C(4)	1.517(13)
C(4)−C(5)	1.518(11)	C(5)−C(6)	1.348(13)
C(7)−C(8)	1.536(11)	C(8)−C(9)	1.524(13)
Mn−C(3)	2.473(8)	Mn−C(6)	2.281(9)
C(1)−C(2)	1.518(13)	C(1)−C(9)	1.538(10)
C(2)−C(18)	1.486(11)	C(3)−C(11)	1.506(13)
C(4)−C(9)	1.532(13)	C(6)−C(7)	1.534(12)
C(7)−C(10)	1.548(11)	C(10)−C(12)	1.485(10)
	Bond Angles for **3j**		
C(9)−C(1)−C(2)	104.9(6)	C(6)−C(7)−C(10)	103.3(7)
C(1)−C(2)−C(3)	108.8(7)	C(8)−C(9)−C(1)	104.4(6)
C(4)−C(3)−C(11)	120.4(7)	C(12)−C(10)−C(7)	118.2(7)
C(9)−C(4)−C(5)	113.0(7)	C(10)−C(1)−C(9)	104.2(6)
C(6)−C(7)−C(8)	107.1(6)	C(2)−C(3)−C(11)	128.5(8)
C(8)−C(7)−C(10)	105.3(6)	C(3)−C(4)−C(9)	104.5(6)
C(1)−C(10)−C(7)	105.5(6)	C(5)−C(6)−C(7)	120.1(7)
C(10)−C(1)−C(2)	109.7(6)	C(7)−C(8)−C(9)	100.3(7)
C(2)−C(3)−C(4)	110.2(8)	C(8)−C(9)−C(4)	114.2(7)
C(3)−C(4)−C(5)	105.1(7)	C(1)−C(10)−C(12)	118.5(6)
C(4)−C(5)−C(6)	120.8(8)		

Scheme 5



Mechanism for Manganese-Mediated Cyclohexadienyl−Alkyne Coupling. The formation of complexes **2** and **3** as well as the organic species **5a** described below can be viewed as occurring through an initial [5 + 2] cycloaddition of one alkyne molecule to the cyclohexadienyl manifold followed by a second *homo*[5 + 2] addition to this initial adduct. Carbon−carbon bond formation does not occur via a traditional concerted cycloaddition but through a cascade of insertion reactions at the metal center. We previously proposed that the role of UV light was to provide a vacant coordination site at the metal via an η^5- to η^3-"ring slip" of the dienyl ligand.[19] However, in related chromium-mediated reactions, we have proposed that the vacant coordination site is generated by photoinduced CO loss and we now provide evidence for a similar process in the formation of **2** and **3**. Specifically, addition of alkyne to the reactive complex [(η^5-C_6H_7)-$Mn(CO)_2$(THF)] (**4**, THF = tetrahydrofuran) *in the dark* yields the single and double adducts **2** and **3**, proving the bond-forming process does not require UV light and that a "ring slip" is not necessary (Scheme 5).[33]

Thus, a deep red solution of [(η^5-C_6H_7)$Mn(CO)_2$(THF)] (**4**, ν_{max} (CO)/cm^{-1} (THF), 1930, 1857), prepared by UV irradiation of **1** in THF at −50 °C for 5 h, was treated with 1 equiv of 1-phenyl-1-propyne at −50 °C in the dark and warmed to room temperature over 30 min. The products isolated from the resulting brown solution were identified as **2b** (9%), **3c** (40%), and traces of other double cycloadducts (GC/MS) (12%). Negligible amounts of **2b**, **3c**, or other products were observed (GC/MS) if THF solutions of **1** and 1-phenyl-1-propyne were refluxed for prolonged periods.

A proposed mechanism for the formation of **2** and **3** is shown in Scheme 6 and is similar to the previously suggested mechanism, except that CO loss is invoked as the initial step. For the formation of the mixed adducts, we propose that **2** loses CO giving intermediate **X**, which proceeds to **3** as for the double additions. It should be noted that the photoreaction between **2** and alkynes proceeds very rapidly, indicating **2** is more sensitive to UV light than **1**. One further alternative route to **3** from **2** might involve an η^3- to η^1-allyl slip or decomplexation of the olefin of **2** prior to alkyne coordination and coupling. However, thermal reaction of **2** and alkynes in the dark did not give double addition products and suggests that photoejection of CO is involved.

As shown in Scheme 6, the photogenerated unsaturated intermediate captures one molecule of alkyne

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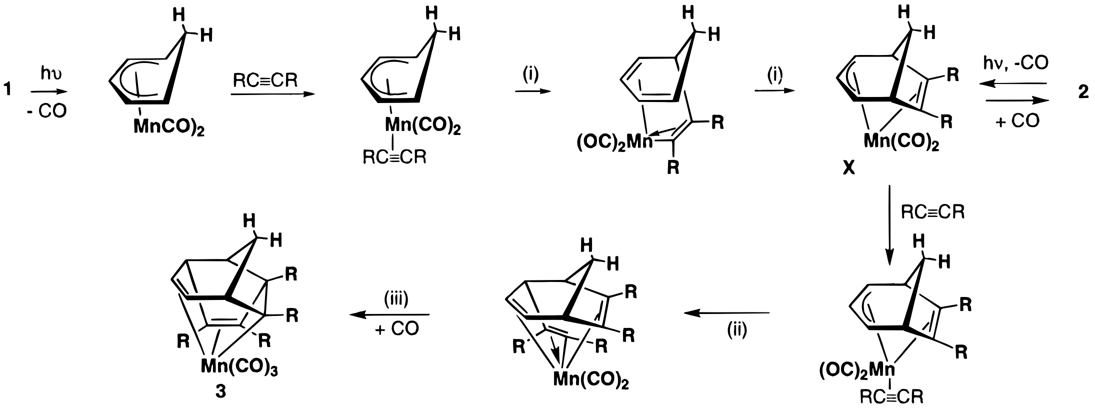
(33) In an earlier report, Kreiter showed that **4** leads to double adducts **3d**, **3k**, and **3l** when reacted with excess 2-butyne, 3-hexyne, and diphenylacetylene, respectively; see ref 20.

Scheme 6. A Proposed Mechanism for Dienyl−Alkyne Coupling[a]



[a] (i) Insertion. (ii) Insertion into Mn-allyl. (iii) Insertion into Mn−olefin.

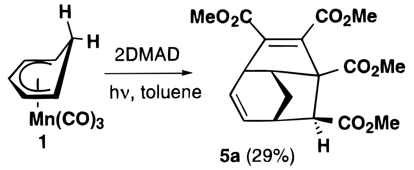
Table 7. ^{1}H and ^{13}C NMR Spectral Data for Compounds 5a−c[a]

complex	^{1}H	^{13}C[b]
5a	1.71 (1H, d, $H_{8'}$), 2.33 (1H, m, H_8), 2.96 (1H, s, br, H_7), 3.22 (1H, s, H_{10}), 3.34 (1H, s, br, H_9), 3.62, 3.74, 3.78 (12H, Me), 3.63 (1H, m, H_4), 5.72 (1H, m, H_5), 6.14 (1H, t, H_6)	34.0 (C8), 40.6 (C7), 48.5 (C9), 50.7 (C4), 52.1, 52.2, 52.3, 52.4 (Me), 54.9 (C10), 70.9 (C1), 128.8, 136.1 (C5, C6), 142.3, 143.3 (C2, C3), 163.7, 166.0, 171.4 172.6 (CO_2Me)
5b	1.60 (1H, m, $H_{8'}$), 1.89 (1H, m, H_8), 2.63 (1H, s, br, H_9), 2.72 (2H, m, br, H_{10}, $H_{10'}$), 2.86 (1H, m, br, H_7), 3.42 (1H, s br, H_4), 5.70 (1H, m, H_5), 6.12 (1H, t, H_6), 6.39 (1H, s, H_3), 7.08−7.33 (10H, m, Ph)	33.2 (C8), 37.1 (C7), 37.3 (C10), 47.7 (C4), 58.9 (C9), 63.0 (C1), 129.6, 132.2 (C5,6), 136.4 (C3), 125.4, 126.4, 126.7, 127.8, 127.9 (Ph), 147.4, 149.4, 159.2 (C2, Ph)
5c	1.13 (3H, s, 1-Me), 1.71 (1H, d, $H_{8'}$), 1.78 (3H, s, 3-Me), 1.98 (1H, m, H_8), 2.62 (1H, s, br, H_9), 2.72 (1H, s, br, H_7), 2.93 (1H, d, H_{10}), 3.26 (1H, m, H_4), 5.93 (1H, dd, H_5), 6.04 (1H, t, H_6), 6.23 (2H, d, Ph), 6.98 (3H, m, Ph), 7.15 (3H, m, Ph), 7.34 (2H, m, Ph)	15.1 (1-Me), 28.2 (3-Me), 34.1 (C8), 44.7 (C7), 53.2 (C9), 56.1 (C4), 60.4 (C10), 61.1 (C1), 129.3 (C6), 125.7, 126.3, 127.0, 127.4, 127.5, 130.3 (Ph), 129.3, 134.1 (C5,6), 137.5, 139.5, 142.1, 142.3 (C2,3, Ph)

[a] Labeling as for Tables 1 and 5; in $CDCl_3$. [b] ^{1}H-Decoupled spectra.

which then inserts into the dienyl−manganese bond. Following this step, the former alkyne is a vinyl ligand which can further insert into the metal−diene bond to give the [5 + 2] cycloadduct **X**. The second *homo*[5 + 2] addition follows in like fashion as a series of stepwise insertions, and it is during these steps that the regiochemistry of the final adducts is directed. From the observed results it is clear that many factors are involved in determining the regiochemistry of **3**, from the preference of particular alkyne termini for insertion over others, to insertions into allyl− or olefin−Mn bonds, or to the likelihood of alkyne insertions into hydrogen-, methyl-, or phenyl-substituted olefin carbons. Few clear trends can be seen in the formation of **3a**−**j**, except that 1-phenyl-1-propyne appears to prefer additions that give 3-methyl-2-phenyl derivatives (**3c**, **3g**, **3i**, **3j**), indicating a preference for insertion of the methyl substituted alkyne terminus into the allyl moiety of intermediate **X**. Surprisingly, the additon of two phenylacetylene molecules to **1** favors isomers **3a** and **3b** despite the fact that the other two possible isomers appear equally as likely. This unsusual selectivity may be due to unfavorable steric interactions between phenyl groups during the second addition. The study of a wider range of alkyne substrates is required to more fully understand the regiochemistry of these complex multiple cycloadditions.

Reaction of 1 with Dimethyl Acetylenedicarboxylate. UV irradiation of **1** and dimethyl acetylenedicarboxylate (DMAD, $MeO_2CC{\equiv}CCO_2Me$) in toluene led to the organic diene **5a** as a single diastereomer, (eq 7). The reaction was monitored by IR spectroscopy and terminated when all of **1** had been consumed. The IR spectrum of the reaction solution showed no absorptions in the metal carbonyl region, indicating no species akin to **2** or **3** were formed. Compound **5a** forms from the [5 + 2],*homo*[5 + 2] addition of 2 equivs of DMAD to the cyclohexadienyl ligand followed by protonation at C(10) and decomplexation from the metal. The source of the proton was not determined although it likely derives from traces of water in the DMAD reagent. The new species **5a** was identified by GC/MS, ^{1}H, ^{1}H−^{1}H 2D (COSY), and ^{13}C NMR spectroscopy (Table 7).



(7)

The formation of an organic product rather than a complex is typical of photoassisted metal-mediated cycloadditions of DMAD[8,16] and presumably arises from the instability of DMAD adduct complexes or from the reductive elimination of the ligands in the ultimate step of the cycloaddition process. The fact that a single diastereoisomer is formed suggests a complex of the ligand does form prior to decomplexation, since protonation of metal−alkyls typically occurs at the metal leading to retention of configuration at the formally metal-bonded carbon.[34]

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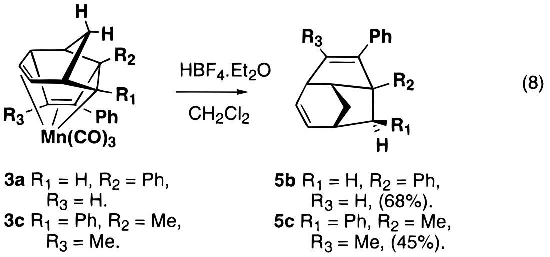
(34) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*, 2nd ed.; University Science Books: Mill Valley, CA, 1987; p 434.

Table 8. ^{1}H and ^{13}C NMR Spectral Data for Compounds 6a–c[a]

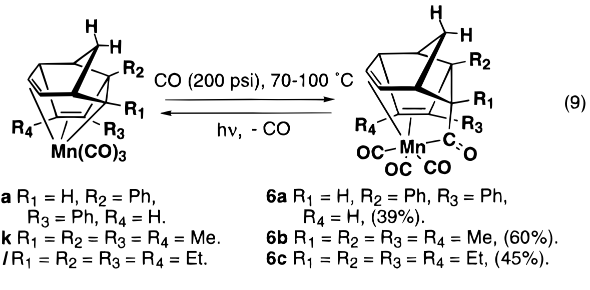
complex	^{1}H	^{13}C[b]
6a	1.54 (1H, d, $H_{8'}$), 1.70 (1H, m, H_8), 2.94 (1H, s, br, H_9), 3.03 (1H, s, br , H_7), 4.18 (1H, m, H_4), 4.55 (1H, t, H_5), 5.03 (1H, d, H_{10}), 5.36 (1H, t, H_6), 5.57 (1H, d, H_3), 6.97–7.28 (10H, m, Ph)	32.0 (C8), 37.7 (C7), 45.0 (C4), 62.9 (C9), 64.1 (C5), 64.4 (C1), 64.5 (C10), 108.4 (C6), 113.5 (C3), 134.0 (C2), 126.4, 128.6, 128.8, 140.8, 143.6 (Ph), 216.0 217.2, 222.9 (CO), 264.9 (C═O)
6b	0.93 (6H, 1-Me, 10-Me), 1.43 (1H, d, $H_{8'}$), 1.55 (3H, s, 2-Me), 1.68 (1H, tt, H_8), 2.19 (4H, s br, 3-Me, H_7), 2.37 (1H, m, H_9), 3.81 (1H, t, H_4), 4.44 (1H, t, H_5), 5.34 (1H, t, H_6)[c]	16.0, 18.3, 19.9, 22.0 (Me), 31.1 (C8), 45.4 (C7), 51.0 (C4), 57.0 (C9), 58.2 (C10), 61.9 (C5), 81.4 (C1), 108.6 (C3), 110.0 (C6), 130.6 (C2), 218.9, 221.8, 224.8 (CO), 261.0 (C═O)[c]
6c	0.83, 1.02, 1.06, 1.16 (12H, Me), 1.21 (2H, m, CH_2), 1.36 (2H, m, H_8, $H_{8'}$), 1.69, 1.82, 1.92, 2.24 (5H, m, CH_2), 2.54 (2H, m, br, H_7, H_9), 2.81 (1H, m, CH_2), 3.73 (1H, t, H_4), 4.14 (1H, t, H_5), 5.09 (1H, t, H_6)	10.6, 12.0, 12.1, 13.4 (Me), 24.1, 24.3, 24.6, 28.3 (CH_2), 31.0 (C8), 38.6 (C7), 48.5 (C4), 50.1 (C9), 60.1 (C5), 63.3 (C10), 84.2 (C1), 109.6 (C6), 114.5 (C3), 136.0 (C2), 218.0, 219.7, 223.0 (CO), 262.8 (C═O)

[a] Labeling refers to Figures 4 and 5; in $CDCl_3$ unless stated otherwise. [b] ^{1}H-Decoupled spectra. [c] In [$^2H_6$]Acetone.

Decomplexation of the Tricyclic Ligand Using HBF_4. Addition of $HBF_4 \cdot Et_2O$ to methylene chloride solutions of **3a**,**c** at −78 °C followed by warming to room temperature gave the new tricyclic organic compounds **5b**,**c** in 68 and 45% yield, respectively, as colorless oils following TLC on silica gel (eq 8). Compounds **5b**,**c** were characterized by GC/MS and ^{1}H, ^{1}H–^{1}H 2D (COSY), and ^{13}C NMR spectroscopy (Table 7). Like **5a**, diene **5c** is formed as a single diastereomer due to protonation of **3c** at the metal prior to formation of the C(10)–H(10) bond. The formation **5b**,**c** further supports the existence of a transient organometallic species in the preparation of **5a**.



Insertion of Carbon Monoxide into the Tricyclic Complexes. Manganese alkyl complexes such as $Mn(CO)_5Me$ are well known to insert carbon monoxide giving acyl derivatives.[35] The bis(alkyne) adducts **3** also possess a Mn–C σ bond, and CO insertion into this bond is also possible. Thus, when solutions of **3a**, **3k** (R = Me), and **3l** (R = Et) were heated in toluene or THF under a CO atmosphere (200 psi) for 1.5–5 h the insertion products **6a–c** were formed, respectively (eq 9). Complexes **6a–c** were isolated in moderate yields as yellow powders and fully characterized by elemental analysis, ^{1}H, ^{1}H–^{1}H 2D (COSY), ^{13}C NMR and IR spectroscopy (Table 8). The IR spectra of each shows a distinct acyl signal at ca. 1660 cm^{-1} (hexane) and the ^{13}C NMR spectra show a C═O signal between δ 261–265 assigned to the acyl carbon atom as well as three carbonyl resonances between δ 216–225. The molecular structures of complexes **6b** and **6c** were confirmed by X-ray diffraction studies, (Figures 4 and 5, Tables 3 and 9). The two structures are identical with the exception



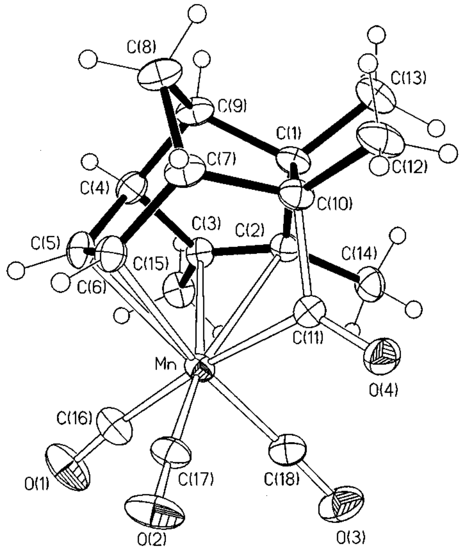


Figure 4. Molecular structure of **6b** showing the atom labeling and 30% thermal ellipsoids for all non-hydrogen atoms.

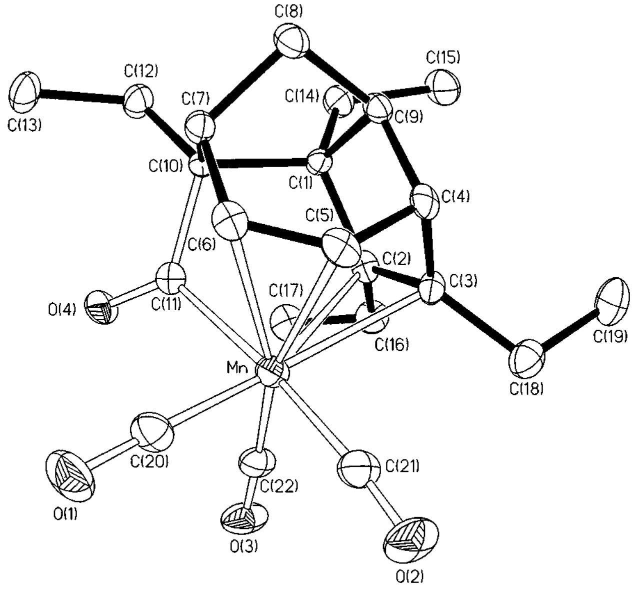


Figure 5. Molecular structure of **6c** showing the atom labeling and 30% thermal ellipsoids for all non-hydrogen atoms. Hydrogen atoms are omitted for clarity.

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(35) Reference 34, pp 355–376.

Table 9. Selected Bond Distances (Å) and Angles (deg) for 6b and 6c

Bond Distances for **6b**			
Mn−C(2)	2.364(4)	C(11)−O(4)	1.204(5)
Mn−C(11)	2.067(4)	Mn−C(5)	2.289(4)
C(1)−C(2)	1.548(6)	Mn−C(17)	1.788(5)
C(2)−C(3)	1.354(5)	C(1)−C(10)	1.588(6)
C(4)−C(5)	1.496(6)	C(3)−C(4)	1.516(5)
C(7)−C(8)	1.526(7)	C(5)−C(6)	1.365(6)
C(10)−C(11)	1.521(6)	C(8)−C(9)	1.522(6)
Mn−C(3)	2.357(4)	Mn−C(6)	2.305(4)
Mn−C(16)	1.823(4)	Mn−C(18)	1.784(4)
C(1)−C(9)	1.544(5)	C(1)−C(13)	1.524(6)
C(2)−C(14)	1.510(6)	C(3)−C(15)	1.514(5)
C(4)−C(9)	1.531(6)	C(6)−C(7)	1.514(6)
C(7)−C(10)	1.536(6)	C(10)−C(12)	1.529(6)
Bond Angles for **6b**			
C(9)−C(1)−C(2)	102.8(3)	C(4)−C(5)−C(6)	120.6(4)
C(2)−C(1)−C(10)	111.5(3)	C(6)−C(7)−C(10)	112.5(3)
C(1)−C(2)−C(3)	111.2(3)	C(8)−C(9)−C(4)	113.3(4)
C(2)−C(3)−C(15)	127.3(3)	C(1)−C(10)−C(12)	115.7(4)
C(3)−C(4)−C(5)	104.2(3)	C(7)−C(10)−C(11)	108.3(3)
C(6)−C(7)−C(8)	106.9(3)	C(10)−C(1)−C(9)	104.6(3)
C(8)−C(9)−C(1)	104.9(3)	C(10)−C(1)−C(13)	114.4(3)
C(1)−C(10)−C(7)	102.5(3)	C(1)−C(2)−C(14)	119.7(3)
C(1)−C(10)−C(11)	105.2(3)	C(4)−C(3)−C(15)	120.4(3)
C(10)−C(11)−O(4)	112.6(3)	C(5)−C(6)−C(7)	120.3(4)
C(13)−C(1)−C(9)	111.9(4)	C(7)−C(8)−C(9)	99.1(3)
C(2)−C(1)−C(13)	111.0(3)	C(4)−C(9)−C(1)	105.7(3)
C(3)−C(2)−C(14)	124.3(4)	C(7)−C(10)−C(12)	111.8(3)
C(2)−C(3)−C(4)	110.1(3)	C(11)−C(10)−C(12)	120.4(3)
Bond Distances for **6c**			
Mn−C(2)	2.405(5)	C(11)−O(4)	1.198(6)
Mn−C(11)	2.092(5)	Mn−C(5)	2.268(5)
C(1)−C(2)	1.535(7)	Mn−C(21)	1.810(6)
C(2)−C(3)	1.364(7)	C(1)−C(14)	1.534(7)
C(4)−C(5)	1.518(7)	C(3)−C(4)	1.514(7)
C(7)−C(8)	1.527(7)	C(5)−C(6)	1.352(7)
C(10)−C(12)	1.510(7)	C(8)−C(9)	1.505(7)
Mn−C(3)	2.347(5)	Mn−C(6)	2.295(5)
Mn−C(20)	1.782(6)	Mn−C(22)	1.785(6)
C(1)−C(9)	1.585(7)	C(1)−C(10)	1.590(6)
C(2)−C(16)	1.521(7)	C(3)−C(18)	1.521(7)
C(4)−C(9)	1.522(7)	C(6)−C(7)	1.515(7)
C(7)−C(10)	1.558(7)	C(10)−C(11)	1.545(7)
Bond Angles for **6c**			
C(2)−C(1)−C(9)	102.1(4)	C(6)−C(7)−C(8)	107.1(4)
C(9)−C(1)−C(14)	108.9(4)	C(1)−C(9)−C(8)	104.3(4)
C(1)−C(2)−C(16)	121.3(4)	C(1)−C(10)−C(11)	106.7(3)
C(4)−C(3)−C(18)	120.2(4)	C(1)−C(10)−C(7)	102.1(4)
C(3)−C(4)−C(9)	104.0(4)	C(2)−C(1)−C(14)	114.1(4)
C(5)−C(6)−C(7)	121.1(5)	C(1)−C(2)−C(3)	111.6(4)
C(7)−C(8)−C(9)	99.6(4)	C(2)−C(3)−C(4)	110.4(4)
C(1)−C(9)−C(4)	105.3(4)	C(3)−C(4)−C(5)	105.0(4)
C(7)−C(10)−C(12)	113.7(4)	C(4)−C(5)−C(6)	119.3(5)
C(2)−C(1)−C(10)	112.3(4)	C(6)−C(7)−C(10)	113.1(4)
C(10)−C(1)−C(14)	113.9(4)	C(4)−C(9)−C(8)	114.4(4)
C(3)−C(2)−C(16)	122.6(4)	C(7)−C(10)−C(11)	103.9(4)
C(2)−C(3)−C(18)	126.6(4)	C(10)−C(11)−O(4)	122.2(5)
C(5)−C(4)−C(9)	111.1(4)		

of the alkyl substituents, although they crystallize in different space groups (**6b** *P*2(1)/*n*; **6c** *Pbca*). They have typical "piano stool" structures with octahedral geometries at the metal centers. Two CO ligands in each are trans to olefins with the third trans to the acyl group. As expected, the Mn−C(acyl) bond distances are 2.067(4) and 2.092(5) Å, respectively, and are slightly shorter than the Mn−C(10) bonds in **3a** and **3j**. In general the acyl complexes have shorter Mn−C(olefin) bond lengths than **3a**,**j**, indicating a reduction of strain in the ligand when bonded to the metal. This is reflected in the C(6)−C(7)−C(10) angles of 112.5(3)° for **6b** and 113.1(4)° for **6c** compared to 103.8(3)° for **3a** and 103.3(7)° for **3j**.

Like $[Mn(CO)_5(COMe)]$, the insertion is reversible and photolysis of hexane solutions of **6c** for 30 min led to formation of complex **3l** as observed by IR spectroscopy.

Conclusions

We have shown that irradiation of the manganese−cyclohexadienyl complex **1** with 1 equiv of alkyne gave a single [5 + 2] cycloadduct **2** as well as the previously reported double [5 + 2],*homo*[5 + 2] adducts **3**, ideally under a CO atmosphere. The stepwise addition of two different alkynes to the dienyl manifold has been achieved giving tetrasubstituted tricyclo[5.2.1.0^{4,9}]deca-2,5-dien-10-yl complexes. The formation of tricyclo[5.2.1.0^{4,9}]deca-2,5-dienes **5**, either by using 2 equivs of dimethyl acetylenedicarboxylate with **1** or through protonation of the tricyclic complexes with $HBF_4{\cdot}Et_2O$, has been demonstrated. We have performed mechanistic studies and shown that $[(\eta^5\text{-}C_6H_7)Mn(CO)_2(THF)]$ reacts with a single equivalent of 1-phenyl-1-propyne in the dark to give the single and double alkyne adducts. We have proposed that carbon−carbon bond formation is a thermally driven process and that the role of light is to eject a CO molecule from **1** providing a vacant coordination site at the metal. We have also investigated the CO insertion reactions of **3** and prepared tricyclic acyl complexes **6**. The X-ray crystal structures of the single addition product **2c**, the double adducts **3a** and **3j**, and two of the acyl complexes **6b** and **6c** have been determined. The results described herein extend the scope of metal-mediated [5 + 2],*homo*[5 + 2] double additions at metal−η^5-dienyl manifolds, demonstrating the generation of four new carbon−carbon bonds with a high degree of regio- and stereocontrol. The development of this multiple cycloaddition methodology using different polyene manifolds and metal centers, and the design of catalytic cycloaddition processes that access new polycyclic systems, is in progress and will be reported in due course.

Experimental Section

General experimental details are described elsewhere.[30] Tricarbonyl(cyclohexadienyl)manganese(I) (**1**)[36] and complexes **3k** and **3l**[19] were prepared using the literature procedures. Microanalyses were attempted for most products; however, in many cases small yields and insufficient analytically pure material prevented the acquisition of satisfactory elemental analyses. All new compounds were pure based upon ^1H and ^{13}C NMR spectral data, and X-ray crystallographic studies were performed on representative samples of each of the major classes of compounds described.

Tricarbonyl(6-phenyl-η^2-6,7-η^3-2−4-bicyclo[3.2.1]octa-dien-2−4,6−7-yl)manganese(I) (2a). A solution of tricarbonyl(cyclohexadienyl)manganese(I) (**1**, 0.200 g, 0.92 mmol) and phenylacetylene (100 μL, 0.92 mmol) in toluene (70 mL) was irradiated (quartz) with UV light for 9.5 h under a constant purge of CO. Evaporation of the solvent in vacuo and chromatography on an alumina/*n*-hexane column (40 × 1 cm), loading with toluene (2 mL), and eluting with diethyl ether/*n*-hexane (1:15) removed any $Mn_2(CO)_{10}$ and unreacted **1**. Elution with diethyl ether/*n*-hexane (2:5) gave complex **2a** as a bright yellow powder after removal of solvents: yield 36 mg, 12% (based on **1**); ν_{max} (CO)/ cm^{-1} (hexane), 2012 (vs), 1937 (vs), 1929 (vs). The double cycloaddition products (**3a** and **3b**) could be eluted subsequently using a (2:3) mixture of diethyl ether/*n*-hexane, (see below).

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(36) Winkhaus, G.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1961**, 3807.

Tricarbonyl(6-phenyl-7-methyl-η^2-6,7-η^3-2−4-bicyclo[3.2.1]octadien-2−4,6−7-yl)manganese(I) (2b). A solution of **1** (0.113 g, 0.52 mmol) and 1-phenyl-1-propyne (65 μL, 0.52 mmol) in toluene (50 mL) was irradiated (quartz) with UV light for 2.5 h under a constant purge of CO. Evaporation of the solvent in vacuo and chromatography on an alumina/*n*-hexane column (40 × 1 cm), loading with toluene (2 mL), and eluting with diethyl ether/*n*-hexane (1:100) removed any $Mn_2(CO)_{10}$ and unreacted **1**. Elution with diethyl ether/*n*-hexane (1:25) gave complex **2b** as a bright yellow powder after removal of solvents: yield 36 mg, 21% (based on **1**); ν_{max} (CO)/ cm^{-1} (hexane), 2010 (vs), 1933 (vs), 1924 (vs). The double adduct **3c** was eluted subsequently using a (1:9) mixture of diethyl ether/*n*-hexane.

Tricarbonyl(6,7-diphenyl-η^2-6,7-η^3-2−4-bicyclo[3.2.1]octadien-2−4,6−7-yl)manganese(I) (2c). A solution of **1** (0.111 g, 0.51 mmol) and diphenylacetylene (91 mg, 0.51 mmol) in toluene (70 mL) was irradiated (quartz) with UV light for 1.5 h. under a constant purge of CO. Evaporation of the solvent in vacuo and chromatography on an alumina/*n*-hexane column (40 × 1 cm), loading with toluene (2 mL) and eluting with diethyl ether/*n*-hexane (1:4), gave complex **2c** as a yellow powder after removal of solvents: yield 78 mg, 39% (based on **1**); ν_{max} (CO)/ cm^{-1} (hexane), 2011 (vs), 1936 (vs), 1927 (vs). Anal. Calcd for $C_{23}H_{17}O_3Mn$: C, 69.70; H, 4.32. Found: C, 69.52; H, 4.43. The double adduct **3d** was subsequently eluted using a (1:1) mixture of diethyl ether/*n*-hexane. Crystals of **2c** for an X-ray diffraction study were grown from CH_2Cl_2 by evaporation at room temperature.

Tricarbonyl(1,2-diphenyl-$\eta^{1:2:2}$-tricyclo[5.2.1.0^{4,9}]deca-2,5-dien-10-yl)manganese(I) (3a) and Tricarbonyl(3,10-diphenyl-$\eta^{1:2:2}$-tricyclo[5.2.1.0^{4,9}]deca-2,5-dien-10-yl)manganese(I) (3b). A solution of **1** (0.100 g, 0.46 mmol) and phenylacetylene (100 μL, 0.92 mmol) in toluene (50 mL) was irradiated (quartz) with UV light for 3.5 h under nitrogen. Evaporation of the solvent in vacuo and chromatography on an alumina/*n*-hexane column (40 × 1 cm), loading with toluene (2 mL), and eluting with diethyl ether/*n*-hexane (2:5) removed $Mn_2(CO)_{10}$, unreacted **1** and **2a**. Elution with diethyl ether/*n*-hexane (2:3) gave **3a** and **3b** as a bright yellow powders after removal of the solvents. **3a:** yield 40 mg, 21% (based on **1**); ν_{max} (CO)/cm^{-1} (hexane) 2009 (vs), 1934 (vs), 1920 (vs). Anal. Calcd for $C_{25}H_{19}O_3Mn$: C, 71.10; H, 4.53. Found: C, 70.84; H, 4.58. Crystals of **3a** for the X-ray diffraction study were grown from *n*-hexane at −20 °C. **3b:** yield 45 mg, 24% (based on **1**); ν_{max} (CO)/cm^{-1} (hexane), 2011 (vs), 1944 (vs), 1920 (vs). Anal. Found: C, 70.86; H, 4.62.

Tricarbonyl(2,3-dimethyl-1,10-diphenyl-$\eta^{1:2:2}$-tricyclo[5.2.1.0^{4,9}]deca-2,5-dien-10-yl)manganese(I) (3e). A solution of **2c** (30 mg, 0.08 mmol) and 2-butyne (7 μL, 0.09 mmol) in hexane (20 mL) was irradiated (quartz) with UV light for 20 min. Evaporation of the solvent in vacuo, dissolution in CH_2Cl_2, and filtration through alumina gave **3e** as a yellow powder after removal of the solvent: yield 20 mg, 59% (based on **2c**); ν_{max}(CO)/cm^{-1} (hexane), 2009 (vs), 1938 (vs), 1922 (vs). Anal. Calcd for $C_{27}H_{23}O_3Mn$: C, 72.00; H, 5.15. Found: C, 70.96; H, 5.44.

Tricarbonyl(2,3-dimethyl-10-phenyl-$\eta^{1:2:2}$-tricyclo[5.2.1.0^{4,9}]deca-2,5-dien-10-yl)manganese(I) (3f). A solution of **2a** (0.100 g, 0.31 mmol) and 2-butyne (29 μL, 0.37 mmol) in hexane (50 mL) was irradiated (quartz) with UV light for 10 min. Evaporation of the solvent in vacuo and chromatography on alumina eluting with diethyl ether/*n*-hexane (1:11) gave **3f** as a yellow powder after removal of solvents: yield 40 mg, 55% (based on **2a**); ν_{max} (CO)/cm^{-1} (hexane), 2007 (vs), 1936 (vs), 1918 (vs). Anal. Calcd for $C_{21}H_{19}O_3Mn$: C, 67.38; H, 5.12. Found: C, 67.59; H, 5.11.

Tricarbonyl(3-methyl-1,2,10-triphenyl-$\eta^{1:2:2}$-tricyclo[5.2.1.0^{4,9}]deca-2,5-dien-10-yl)manganese(I) (3g) and Tricarbonyl(2-methyl-1,3,10-triphenyl-$\eta^{1:2:2}$-tricyclo[5.2.1.0^{4,9}]deca-2,5-dien-10-yl)manganese(I) (3h). A solution of **2c** (83 mg, 0.21 mmol) and 1-phenyl-1-propyne (32 μL, 0.25 mmol) in toluene (20 mL) was irradiated (pyrex or quartz) with UV light for 4 h. Evaporation of the solvent in vacuo and chromatography on silica eluting with diethyl ether/*n*-hexane (1:20) gave **3g** and **3h** as yellow powders after removal of solvents. **3g:** yield 39 mg, 36% (based on **2c**); ν_{max} (CO)/cm^{-1} (hexane), 2010 (vs), 1938 (vs), 1922 (vs). **3h:** yield 35 mg, 32%; ν_{max} (CO)/cm^{-1} (hexane), 2010 (vs), 1936 (vs), 1930 (vs).

Tricarbonyl(3-methyl-1,2,-diphenyl-$\eta^{1:2:2}$-tricyclo[5.2.1.0^{4,9}]deca-2,5-dien-10-yl)manganese(I) (3i) and Tricarbonyl(3-methyl-2,10-diphenyl-$\eta^{1:2:2}$-tricyclo[5.2.1.0^{4,9}]deca-2,5-dien-10-yl)manganese(I) (3j). A solution of **2a** (0.130 g, 0.41 mmol) and 1-phenyl-1-propyne (62 μL, 0.49 mmol) in hexane (20 mL) was irradiated (pyrex or quartz) with UV light for 30 min. Evaporation of the solvent in vacuo and chromatography on alumina eluting with diethyl ether/*n*-hexane (1:15) gave **3i** and **3j** as yellow powders after removal of solvents. **3i:** yield 30 mg, 17% (based on **2a**); ν_{max} (CO)/cm^{-1} (hexane), 2006 (vs), 1931 (vs), 1917 (vs). **3j:** yield 35 mg, 20% (based on **2a**); ν_{max} (CO)/cm^{-1} (hexane), 2010 (vs), 1942 (vs), 1915 (vs). Anal. Calcd for $C_{26}H_{21}O_3Mn$: C, 71.55; H, 4.82. Found: C, 71.08; H, 4.75. Crystals of **3j** for the X-ray diffraction study were grown from *n*-hexane at −20 °C.

Reaction of [(η^5-C_6H_7)(CO)$_2$Mn(THF)] with 1-Phenyl-1-propyne. A solution of **1** (60 mg, 0.28 mmol) in THF (40 mL) was irradiated with UV light (quartz) at −50 °C for 5 h. The yellow solution gradually changed to a red color and monitoring by IR showed the disappearance of **1** (ν_{max} (CO)/cm^{-1} (THF), 2013, 1930) and the formation of [(η^5-C_6H_7)(CO)$_2$Mn(THF)] (**4**) (ν_{max} (CO)/cm^{-1} (THF), 1930, 1857). The flask was then covered in aluminum foil to exclude light and 1-phenyl-1-propyne (35 μL, 0.28 mmol) added, followed by warming to room temperature with stirring for 1 h. The resulting brown solution was evaporated to dryness in vacuo and the residue chromatographed on alumina as described above to give **2c** (**8** mg, 9%), **3c** (48 mg, 40%), and traces of other unidentified double adducts (GC/MS) (15 mg, 12%).

1,2,3,10-Tetrakis(methoxycarbonyl)tricyclo[5.2.1.0^{4,9}]deca-2,5-diene (5a). A solution of **1** (0.083 g, 0.38 mmol) and dimethyl acetylenedicarboxylate (94 μL, 0.76 mmol) in toluene (20 mL) was irradiated (pyrex) with UV light for 4 h. The resulting solution was filtered through alumina and Celite. Removal of the solvent in vacuo and chromatography on silica (TLC, Fisher Scientific Redi/plate), developing with CH_2Cl_2/*n*-hexane (1:1), gave **5a** as a colorless oil: yield 40 mg, 29% (based on **1**), HRMS $m/z = 364.1162$ (M$^+$), calcd for $C_{18}H_{20}O_8$ 364.1158; MS 364 (M$^+$), 332 (M$^+$ − MeOH), 300, 272, 245, 213 (int 100), 186, 155, 128, 77, 59.

1,2-Diphenyltricyclo[5.2.1.0^{4,9}]deca-2,5-diene (5b). Three drops of $HBF_4 \cdot Et_2O$ (85% in diethyl ether) were added to a stirred yellow solution of **3a** (55 mg, 0.13 mmol) in CH_2Cl_2 (15 mL) at −78 °C. Further stirring of the red solution for 10 min at room temperature, removal of solvent in vacuo, and extraction of the residue with diethyl ether gave crude **5b.** Pure **5b** was isolated as a colorless oil following chromatography on silica (TLC, Fisher Scientific Redi/plate) developing with CH_2Cl_2/*n*-hexane (1:3): yield 25 mg, 68% (based on **3a**), HRMS $m/z = 284.1571$ (M$^+$), calcd for $C_{22}H_{20}$ 284.1565; MS 284 (M$^+$, int 100), 269, 255, 243, 230, 217, 202, 193, 178, 165, 115, 91.

1,3-Dimethyl-2,10-diphenyltricyclo[5.2.1.0^{4,9}]deca-2,5-diene (5c). Ten drops of $HBF_4 \cdot Et_2O$ (85% in diethyl ether) were added to a stirred yellow solution of **3c** (62 mg, 0.14 mmol) in CH_2Cl_2 (15 mL) at room temperature, causing a color change to red. Diene **5c** was subsequently isolated following the procedure described above for **5b**: yield 19 mg, 45% (based on **3c**); HRMS $m/z = 312.1884$ (M$^+$), calcd for $C_{24}H_{24}$ 312.1878; MS 312 (M$^+$, int 100), 297, 245, 221 (int 77), 205, 182, 165, 155, 143, 128, 115, 105, 91 (int 76).

6a. A solution of **3a** (0.071 g, 0.17 mmol) in toluene (50 mL) was placed in a Parr reactor and heated at 70−100 °C under CO pressure (200 psi) for 5 h. Evaporation of the solvent and chromatography of the residue on alumina, eluting with diethyl ether/*n*-hexane (3:2) to remove unreacted **3a** and (Mn$_2$-

(CO)$_{10}$), followed by elution with 100% diethyl ether gave **6a** as a yellow powder: yield 30 mg, 39% (based on **3a**); ν_{max} (CO)/cm^{-1} (CH$_2$Cl$_2$), 2023 (vs), 1950 (vs), 1637 (w).

6b. A solution of **3k** (0.100 g, 0.31 mmol) in THF (50 mL) was placed in a Parr reactor and heated at 100 °C under CO pressure (200 psi) for 1.5 h. Evaporation of the solvent and chromatography of the residue on alumina, eluting with *n*-hexane to remove Mn$_2$(CO)$_{10}$, followed by elution with CH$_2$Cl$_2$/*n*-pentane (1:1) gave **6b** as a yellow-orange powder: yield 65 mg, 60% (based on **3k**); ν_{max} (CO)/cm^{-1} (hexane), 2022 (vs), 1955 (vs), 1941 (vs), 1663 (w). Anal. Calcd for C$_{18}$H$_{19}$O$_4$Mn: C, 61.02; H, 5.41. Found: C, 60.89; H, 5.39. Crystals for the X-ray diffraction study were grown from *n*-hexane at −20° C.

6c. A solution of **3l** (0.100 g, 0.26 mmol) in toluene (50 mL) was placed in a Parr reactor and heated at 70 °C under CO pressure (200 psi) for 5 h. Evaporation of the solvent and chromatography of the residue on alumina, eluting with *n*-hexane to remove Mn$_2$(CO)$_{10}$, followed by elution with diethyl ether/*n*-hexane (1:5) gave **6c** as a yellow-orange powder: yield 48 mg, 45% (based on **3l**); ν_{max} (CO)/cm^{-1} (hexane), 2019 (vs), 1950 (vs), 1939 (vs), 1659 (w). Crystals for the X-ray diffraction study were grown from *n*-hexane at −20° C.

X-Ray Diffraction Studies. Crystallographic data are collected in Table 3. All data were collected at 295 K on a Siemens P4 diffractometer using graphite-monochromated Mo Kα (0.710 73 Å) radiation.

Structure Analysis and Refinement. A Patterson map was used to find the Mn and some of the light atoms in each of the structures, followed by difference maps to find the remaining 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} (Å^2) for the methine Hs and the phenyl Hs (0.065 for **2c**, 0.046 for **3a**, 0.054 for **3j**, 0.069 for **6b**, 0.041 for **6c**), U_{iso} (Å^2) for the methylene Hs (0.054 for **2c**, 0.038 for **3a**, 0.041 for **3j**, 0.063 for **6b**, 0.039 for **6c**), and U_{iso} (Å^2) for the methyl groups Hs (0.094 for **3j**, 0.083 for **6b**, 0.101 for **6c**). The weighting scheme for all five structures, $w = 1/[\sigma^2(F) + 0.0006F^2]$, with $\sigma(F_o)$ from counting statistics gave satisfactory agreement analyses. Data collection, cell refinement, data reduction, structure solution, structure refinement, molecular graphics, and preparation of material for publication used SHELXTL/PC.[37,38]

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Supporting Information Available: Complete tables of X-ray structural data, positional parameters, anisotropic thermal parameters, bond lengths and angles, and additional thermal ellipsoid plots of **2c**, **3a**, **3j**, **6b**, and **6c** as well as ^{1}H NMR spectra of all new complexes (41 pages). Ordering information is given on any current masthead page.

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(38) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. 4.