Photoassisted Double Alkyne Addition to a Coordinated Cyclohexadienyl Ring. Synthesis of Tricyclo[5.2.1.0^{4,8}]deca-2,5-dien-10-yl Derivatives

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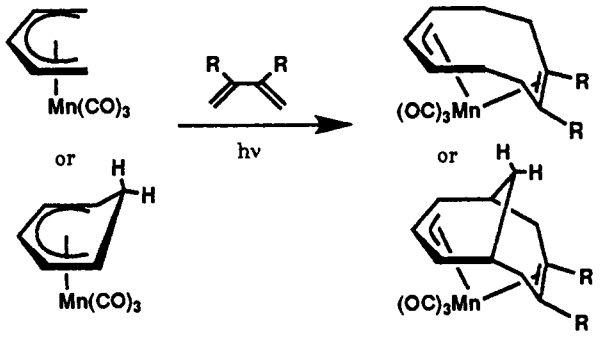
Abstract: Irradiation of the cyclohexadienyl complexes [(η^5-$C_6H_6R^1$)Mn(CO)$_3$] (**1**) (R^1 = *exo*-H, Me, Tol) and 2 equiv of the alkynes (RC≡CR, R = Ph, Me, Et) with UV light in toluene or *n*-hexane gives the new tricyclic complexes **2**. These complexes arise from sequential [5 + 2] and [3 + 2] cycloadditions of two alkyne molecules to the η^5-coordinated six-membered ring forming a tricyclo[5.2.1.0^{4,8}]deca-2,5-dien-10-yl ligand. An X-ray crystallographic study on the adduct from [(η^5-C_6H_7)Mn(CO)$_3$] and two molecules of 1-phenyl-1-propyne has been performed: monoclinic, $P2_1/c$, a = 8.859(2) Å, b = 16.318(3) Å, c = 15.358(3) Å, β = 105.79(3)°, R = 0.043 for 2672 independent reflections. The tetramethyl and tetraethyl complexes **2a,b** react with [CPh_3]$^+$ to give the cations **3**. The X-ray structure of the methylene species **3a** is reported: monoclinic, $P2_1/c$, a = 8.585(2) Å, b = 13.960(3) Å, c = 15.286(3) Å, β = 96.00(3)°, R = 0.047 for 2382 independent reflections. The tricyclo[5.2.1.0^{4,8}]deca-2,5-dienes containing an exocyclic double bond at C(10) can be decomplexed from the metal in **3** by refluxing in acetonitrile.

Introduction

Transition metal mediated cycloaddition reactions of alkynes have been studied for many years[1] and have found applications in the formation of many different ring systems. Noteworthy among these are the cyclotrimerization of alkynes to arenes,[2] the coupling of alkynes with carbene ligands in the Dötz reaction,[3] and the Pauson–Khand reaction for the formation of cyclopentenones from an alkyne, an alkene, and carbon monoxide.[4] Another emerging area of synthesis is the use of transition metal complexes to facilitate higher order cycloaddition processes.[5] Much progress in this area has been achieved by Rigby and coworkers and includes synthetic applications of [6 + 2] as well as [6 + 4] cycloadditions of alkenes and other trienophiles to a variety of cyclic trienes.[5]

In the course of our own studies on the intramolecular coupling of coordinated polyenes and carbon based ligands,[6] we have reported the photoinduced [6 + 2] cycloaddition of alkynes to tricarbonyl(cycloheptatriene)chromium(0) that leads to good yields of bicyclo[4.2.1]nona-2,4,7-trienes.[6c] At present, there are few examples of [6 + 2] cycloadditions involving alkynes,[7] but a general feature of these processes is that the triene is η^6- or η^4-coordinated to a metal. Indeed, it is believed that the metal promotes the higher order process over the more common [4 + 2] addition by holding the triene and trienophile in close proximity to one another, i.e. in the metal coordination sphere.[7b]

Scheme 1. Metal-Mediated [5 + 4] Cycloadditions



In view of this, we felt that a polyene that is η^5-bonded to a metal such as a cyclohexa- or cycloheptadienyl group would be a good manifold for new higher order cycloadditions involving 5 carbon atoms. Thus, [5 + 2] and [5 + 4] cycloadditions could be developed with the appropriate *dienylophile*. Previous to our studies, a few [5 + 4] cycloadditions had been reported by Kreiter and Lehr[8] in which various dienes were added to [(η^5-dienyl)-Mn(CO)3] complexes (Scheme 1). However, to our knowledge these remain the only examples of metal-mediated cycloadditions

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(1) Schore, N. E. *Chem. Rev.* **1988**, *88*, 1081–1119 and references therein.
(2) (a) Negishi, E.; Ay, M.; Sugihara, T. *Tetrahedron* **1993**, *49*, 5471. (b) Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539.
(3) (a) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 644. (b) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587. (c) Wulff, W. D. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press plc: New York, 1991; Vol. *5*, pp 1065–1113.
(4) (a) Khand, I. U.; Knox, G. R.; Pauson, P. L.; Watts, W. E.; Foreman, M. I. *J. Chem. Soc., Perkin Trans. 1* **1973**, 977. (b) Pauson, P. L. *Tetrahedron* **1985**, *41*, 5855.
(5) (a) Rigby, J. H. *Acc. Chem. Res.* **1993**, *26*, 579–585 and references therein. (b) Rigby, J. H.; Ateeq, H. S.; Charles, N. R.; Henshilwood, J. A.; Short, K. M.; Sugathapala, P. M. *Tetrahedron* **1993**, *49*, 5495. (c) Rigby, J. H.; Ateeq, H. S.; Charles, N. R.; Cuisiat, S. V.; Ferguson, M. D.; Henshilwood, J. A.; Krueger, A. C.; Ogbu, C. O.; Short, K. M.; Heeg, M. J. *J. Am. Chem. Soc.* **1993**, *115*, 1382. (d) Rigby, J. H.; Ahmed, G.; Ferguson, M. D. *Tetrahedron Lett.* **1993**, *34*, 5397.
(6) (a) Wang, C.; Sheridan, J. B.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 3603. (b) Sheridan, J. B.; Padda, R. S.; Chaffee, K.; Huang, Y.; Wang, C.; Lalancette, R. *J. Chem. Soc., Dalton Trans.* **1992**, 1539. (c) Chaffee, K.; Sheridan, J. B.; Aistars, A. *Organometallics* **1992**, *11*, 18.
(7) (a) Fischler, I.; Grevels, F.-W.; Leitich, J.; Özkar, S. *Chem. Ber.* **1991**, *124*, 2857. (b) Davis, R. E.; Dodds, T. A.; Hseu, T.-H.; Wagnon, J. C.; Devon, T.; Tancrede, J.; Mckennis, J. S.; Pettit, R. *J. Am. Chem. Soc.* **1974**, *96*, 7562. (c) Mach, K.; Antropiusova, H.; Petrusova, L.; Hanus, V.; Turecek, F.; Sedmera, P. *Tetrahedron* **1984**, *40*, 3295. (d) Klein, R.; Sedmera, P.; Cejka, J.; Mach, K. *J. Organomet. Chem.* **1992**, *436*, 143. (e) Bourner, D. G.; Brammer, L.; Green, M.; Moran, G.; Orpen, A. G.; Reeve, C.; Schaverien, C. J. *J. Chem. Soc., Chem. Commun.* **1985**, 1409. (f) Nagashima, H.; Matsuda, H.; Itoh, K. *J. Organomet. Chem.* **1983**, *258*, C15.
(8) (a) Kreiter, C. G.; Lehr, K. *J. Organomet. Chem.* **1993**, *454*, 199. (b) Kreiter, C. G.; Lehr, K. *Z. Naturforsch.* **1991**, *46b*, 1377. (c) Kreiter, C. G.; Lehr, K.; Exner, R. *J. Organomet. Chem.* **1991**, *411*, 225. (d) Kreiter, C. G.; Lehr, K. *J. Organomet. Chem.* **1991**, *406*, 159. (e) Kreiter, C. G.; Lehr, K.; Leyendecker, M.; Sheldrick, W. S.; Exner, R. *Chem. Ber.* **1991**, *124*, 3. (f) Kreiter, C. G.; Lehr, K.; Heeb, G. *Z. Naturforsch.* **1991**, *46b*, 941.

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

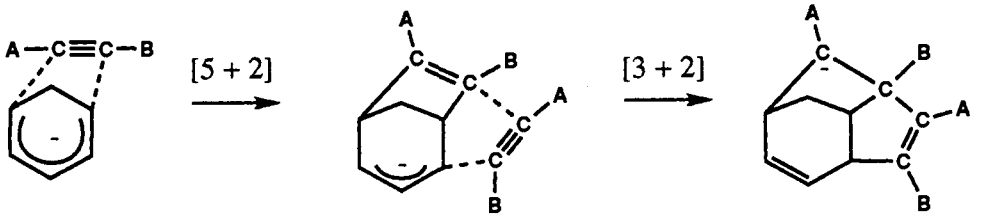


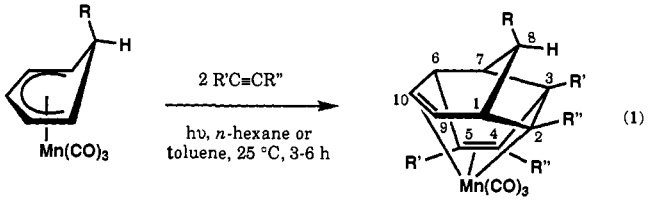
Table 1. ^{1}H and ^{13}C NMR Spectral Data[a] for Complexes **2a–f**

complex	(^{1}H)[b]	(^{13}C)[b,c]
2a	0.66 (3H, s, 3-Me), 0.68 (1H, d, H_8), 1.01 (1H, m, $H_{8'}$), 1.50 (3H, s, 2-Me), 1.53 (3H, s, 4-Me), 1.56 (3H, s, 5-Me), 1.69 (1H, dd, H_7), 2.10 (1H, dd, H_1), 3.03 (1H, dd, J = 7.0 Hz, H_6), 3.25 (1H, dd, J = 5.5, 6.8 Hz, H_{10}), 3.84 (1H, dd, J = 7.0, 7.4 Hz, H_9)	−19.2 (C_2), 13.4 (Me), 15.3 (Me), 19.7 (Me), 24.5 (Me), 30.9 (C_8), 46.9 (C_1), 47.0 (C_6), 53.8 (C_7), 60.3 (C_{10}), 60.6 (C_3), 75.9 (C_9), 77.0 (C_5), 97.0 (C_4), 211.5, 227.9, 229.0 (CO)
2b	0.48 (3H, t, J = 7.6 Hz, 3-Me), 0.74 (1H, d, J = 11.6 Hz, H_8), 0.79 (6H, t, J = 7.6 Hz, 4-Me, 5-Me), 0.96 (1H, m, $H_{8'}$), 1.25 (1H, m, 3-CH_2), 1.37 (4H, m, 3-CH_2, 2-Me), 1.60 (1H, m, CH_2), 1.80 (1H, m, CH_2), 2.05 (4H, m, H_7, CH_2), 2.25 (1H, m, CH_2), 2.41 (1H, t, H_1), 3.12 (1H, t, H_6), 3.22 (1H, t, H_{10}), 3.79 (1H, t, H_9)	−10.8 (C_2), 10.3 (Me), 13.1 (Me), 15.4 (Me), 15.7 (Me), 22.4 (CH_2), 22.6 (CH_2), 24.5 (CH_2), 29.4 (CH_2), 31.7 (C_8), 42.6 (C_1), 44.4 (C_6), 48.3 (C_7), 59.1 (C_{10}), 64.9 (C_3), 74.3 (C_9), 88.6 (C_5), 101.6 (C_4), 211.9, 226.8, 230.7 (CO)
2c	0.75 (1H, d, H_8), 1.44 (1H, m, $H_{8'}$), 2.37 (1H, d, H_7), 3.57 (1H, t, H_1), 3.72 (1H, t, H_6), 4.02 (1H, t, H_{10}), 4.16 (1H, t, H_9), 6.82 (6H, m, Ph), 6.95 (6H, m, Ph), 7.39 (3H, d, Ph), 7.53 (2H, d, Ph), 7.79 (3H, d, Ph)	−4.6 (C_2), 31.8 (C_8), 44.0 (C_1), 47.1 (C_6), 59.9 (C_7), 62.2 (C_{10}), 73.3 (C_3), 78.0 (C_9), 87.4 (C_5), 110.6 (C_4), 121.2, 126.6, 127.6, 129.4, 131.2, 134.0, 144.9, 152.9 (Ph), 211.0, 222.4, 227.0 (CO)
2d	0.58 (3H, s, 3-Me), 1.37 (1H, d, J = 12 Hz, H_8), 1.85 (1H, m, $H_{8'}$), 2.39 (3H, s, 5-Me), 2.51 (1H, s brd, H_7), 3.19 (1H, dd, J = 6.0 Hz, H_1), 4.08 (1H, dd, J = 5.1, 6.6 Hz, H_6), 4.21 (1H, t, J = 6 Hz, H_{10}), 4.33 (1H, t, J = 6 Hz, H_9), 7.20 (6H, m, Ph), 7.58 (2H, d, J = 7.5 Hz, Ph), 7.63 (2H, d, J = 7.5 Hz, Ph)[d]	−4.0 (C_2), 18.9 (3-Me), 27.0 (5-Me), 33.3 (C_8), 47.9 (C_1), 49.0 (C_6), 54.0 (C_7), 64.7 (C_{10}), 66.0 (C_3), 76.7 (C_5), 78.1 (C_9), 102.8 (C_4), 124.5, 127.4, 127.6, 127.7, 132.4, 132.6, 133.2, 148.7 (Ph), 211.4, 227.2, 228.3 (CO)[d]
2e	0.60 (3H, d, J = 6.6 Hz, 8-Me), 1.91 (1H, q, H_8), 2.11 (1H, dd, H_7), 3.45 (1H, dd, J = 5.1, 5.5 Hz, H_1), 3.71 (1H, dd, J = 7.0 Hz, H_6), 3.80 (1H, dd, J = 5.1, 7.0 Hz, H_{10}), 4.04 (1H, dd, J = 5.1, 6.6 Hz, H_9), 6.84 (6H, m, Ph), 6.97 (6H, m, Ph), 7.44 (6H, dt, Ph), 7.76 (2H, d, Ph)	−4.8 (C_2), 8.5 (8-Me), 33.1 (C_8), 45.4 (C_1), 48.0 (C_6), 61.7 (C_7), 64.4 (C_3), 64.5 (C_{10}), 73.5 (C_9), 89.8 (C_5), 107.5 (C_4), 121.1, 125.8, 126.6, 129.7, 131.3, 133.9, 145.2, 153.0 (Ph), 211.2, 221.9, 227.1 (CO)
2f	0.73 (3H, s, 2-Me), 1.53 (6H, 3-Me, 4-Me), 1.62 (3H, d, Tol-Me), 1.79 (1H, H_8), 2.15 (3H, s, 5-Me), 2.55 (1H, dd, H_7), 2.68 (1H, dd, H_1), 3.07 (1H, dd, H_6), 3.15 (1H, dd, H_{10}), 3.64 (1H, t, H_9), 6.80 (1H, d, Tol), 7.05 (2H, d, Tol), 7.44 (1H, d, Tol)	−19.4 (C_2), 13.3 (Me), 15.3 (Me), 19.9 (Me), 20.9 (Me), 24.8 (Me), 43.7 (C_8), 44.9 (C_1), 49.8 (C_6), 56.3 (C_7), 60.5 (C_{10}), 60.8 (C_3), 72.9 (C_9), 77.4 (C_5), 95.9 (C_4), 127.1, 127.5, 128.6, 128.7, 129.0, 129.7 (Tol), 211.4, 227.8, 228.9 (CO)

[a] Labeling refers to eqs 1. [b] In C_6D_6 unless stated otherwise. [c] ^{1}H-decoupled spectra. [d] In $CDCl_3$.

involving dienyl ligands and no reports of [5 + 2] cycloadditions involving alkynes are known.

Herein we describe a new photoassisted metal-mediated higher order cycloaddition reaction between two alkynes and a coordinated cyclohexadienyl group. The products derive from one alkyne adding to the dienyl ligand in a [5 + 2] fashion and the second adding via a [3 + 2] process. A schematic representation of this new coupling reaction is shown in Scheme 2. The double addition leads to a tricyclo[5.2.1.0^{4,8}]deca-2,5-dien-10-yl species[9] coordinated to a $Mn(CO)_3$ group. Reaction of this complex with $[CPh_3]^+$ followed by decomplexation with acetonitrile gives the functionalized tricyclic compounds.



1a R = H.
1b R = Me.
1c R = Tol.

2a R = H, R' = R" = Me.
2b R = H, R' = R" = Et.
2c R = H, R' = R" = Ph.
2d R = H, R' = Me, R" = Ph.
2e R = Me, R' = R" = Ph.
2f R = Tol, R' = R" = Me.

Results and Discussion

Synthesis of Bis(alkyne)(cyclohexadienyl)manganese Adducts. Irradiation of toluene or *n*-hexane solutions of tricarbonyl(η^5-cyclohexadienyl)manganese(I) (**1a**) and 2-butyne (2 equiv) at room temperature for 0.5–3 h resulted in a gradual disappearance of **1a**, as monitored by IR spectroscopy, and the formation of a new neutral tricarbonyl species **2a** (eq 1).

Complex **2a** was isolated in 90% yield (based on **1a**) as a yellow powder and was fully characterized by elemental analysis, ^{1}H, ^{13}C, ^{1}H–^{1}H (2D COSY), and ^{1}H–^{13}C (2D COSY) NMR and IR spectroscopy (Table 1). The new ligand is a tricyclic system which results from the coupling of two alkynes and the cyclohexadienyl ring via sequential [5 + 2] and [3 + 2] cycloadditions. The new organic moiety consists of three fused rings (C_5, C_5, C_6) with four of the ring carbon atoms, C(2), C(3), C(4), and C(5), derived from added alkynes. The ligand is bonded to a manganese tricarbonyl group through C(2), C(4), C(5), C(9), and C(10) to give the complex **2a**.

The ^{1}H NMR spectrum of **2a** shows seven distinct resonances for the C_6 ring and four unique methyl resonances consistent with the asymmetric structure shown. No resonances above δ 3.90 are observed, indicating that the olefinic protons H(9) and H(10) are attached to coordinated carbon atoms. An alternative structure, $[(MeC{\equiv}CMe)_2(CO)_3Mn(\eta^1\text{-}C_6H_7)]$, with an η^1-cyclohexadienyl ring and two coordinated alkynes can therefore be eliminated proving the alkynes have coupled with the ring. All proton NMR assignments were confirmed by a ^{1}H–^{1}H 2D COSY NMR experiment. The $^{13}C\{^1H\}$ NMR spectrum is also consistent with the assigned structure and shows three distinct carbonyl signals at δ 211.5, 227.9, and 229, as well as five carbon signals between δ 60 and 97. Of these peaks, only two signals at δ 75.9 and 60.3 exhibit NOE and are therefore assigned to C(9) and

(9) An alternative nomenclature for the new ligand in **2a** is 3a,6,7,7a-tetrahydro-1,2,3,8-tetramethyl-1,6-methano-1*H*-indenyl. Ring system #RF 21120 from: *Ring Systems Handbook*; American Chemical Society: Washington, DC, 1988. For clarity and consistency throughout this manuscript the numbering shown in eqs 1–3 is adopted for all NMR assignments and atom labels in the X-ray structures.

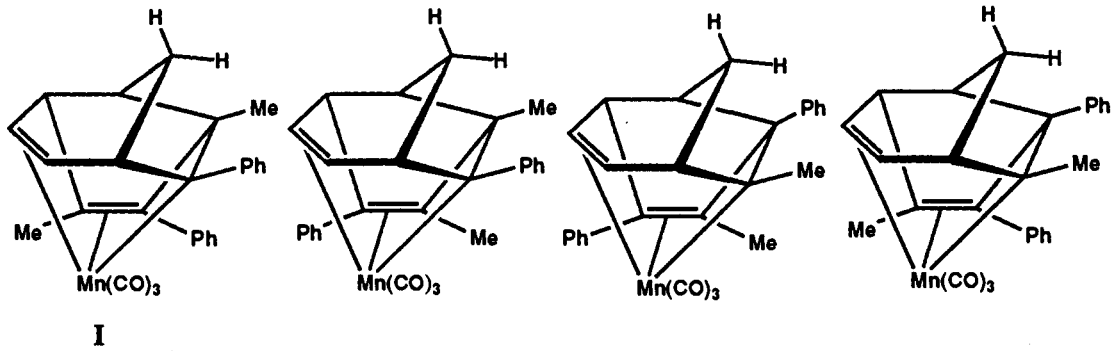


Figure 1. Four possible structures of **2d**.

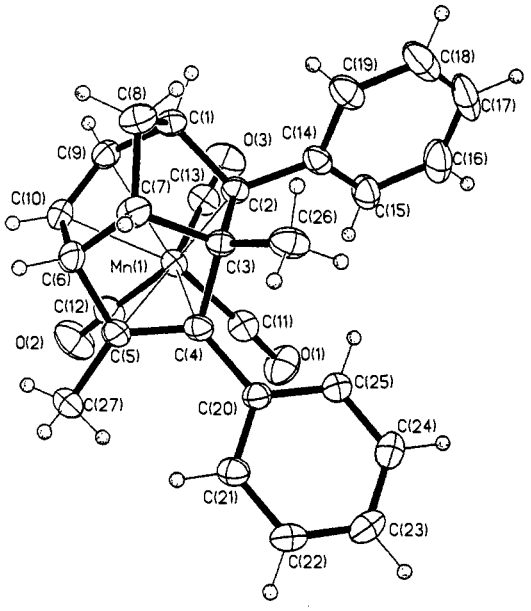


Figure 2. Molecular structure and labeling scheme for **2d**.

C(10), the remaining three being assigned to C(3)–C(5). A distinctive signal at −19.2 ppm is assigned to C(2); the upfield shift of this resonance is typical of a σ bonded Mn–*C* carbon atom.[10] Full ^{13}C NMR assignments were made from the ^{1}H–^{13}C 2D COSY NMR spectrum. The IR spectrum of **2a** (ν_{max}(CO)/cm^{-1}, 2000, 1920, and 1912) indicates three carbonyl ligands are present in the complex and eliminates any structure that might arise via alkyne/CO substitution, e.g. [(MeC≡CMe)$_2$(CO)Mn-(η^5-C$_6$H$_7$)]. An X-ray diffraction study on a derivative of **2a** as well as one on **2d**, both of which are described below, confirmed the structure as that shown.

Complex **1a** also reacts with 3-hexyne, diphenylacetylene, and 1-phenyl-1-propyne to form **2b,c,d**, respectively (eq 1). Complexes **2b–d** are isostructural with **2a** and were fully characterized by IR and ^{1}H, ^{13}C, and ^{1}H–^{1}H (2D COSY) NMR spectroscopy (Table 1). Noteworthy is that the chemical shift of C(2) in these products, {**2b**, δ −10.8; **2c**, δ −4.6; **2d**, δ −4.0} is diagnostic of the type of group attached to C(2) {C(2)-Me, δ −19; C(2)-Et, δ −11; C(2)-Ph, δ −4}. Thus in **2d**, the resonance for C(2) is at δ −4.0, and a phenyl substituent is predicted at this site rather than a methyl group. Surprisingly, **2d** forms as only one isomer, although four different species are possible (Figure 1). The isolated product (**I**) is that in which the two phenyl groups are at positions 2 and 4, and not that with the phenyl groups placed as far apart as possible, i.e. positions 2 and 5. The regioselectivity most likely arises from the orientation of the alkynes during coupling with the C6 ring and also gives an insight into how the overall coupling reaction proceeds (see mechanistic discussion below).

The molecular structure of **2d** was confirmed by an X-ray diffraction study (Figure 2, Tables 2 and 3). The structure is essentially octahedral at manganese with the σ-bonded carbon C(2) and the coordinated olefins C(4)=C(5) and C(9)=C(10) all *trans* to carbonyl ligands. The Mn–C distance for the carbonyl *trans* to C(2) (1.829(4) Å) is significantly longer than those *trans* to the olefins (average 1.792(3) Å). This indicates the stronger *trans* influence of the σ-bonded group C(2), compared to the coordinated olefins. The C(9)=C(10) bond is more tightly

(10) Mann, B. E.; Taylor, B. E. *^{13}C NMR Data for Organometallic Compounds*; Academic Press: New York, 1981; p 41.

Table 2. Crystal Data for Compounds **2d** and **3a**

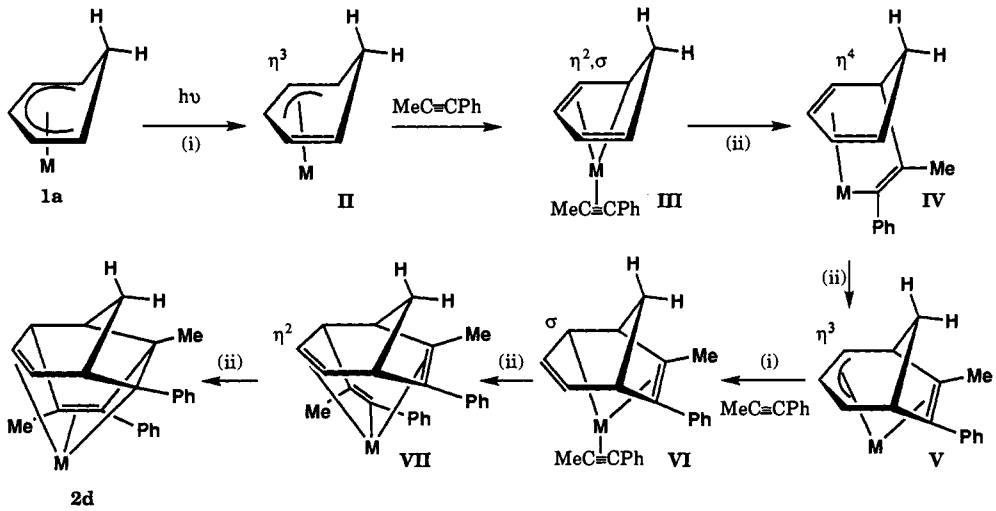
	2d	**3a**
formula	$C_{27}H_{23}MnO_3$	$C_{17}H_{18}F_6MnO_3P$
fw	450.4	470.2
space group	$P2_1/c$	$P2_1/c$
a, Å	8.859(2)	8.585(2)
b, Å	16.318(3)	13.960(3)
c, Å	15.358(3)	15.286(3)
β, deg	105.79(3)	96.00(3)
V, Å^3	2136.6(7)	1821.9(9)
Z	4	4
D(calc), g cm^{-3}	1.400	1.714
μ(Mo Kα), cm^{-1}	64.4	88.8
radiation	Mo Kα (λ = 0.71073 Å)	
$R(F)$,[a] %	4.3	4.7
$R_w(F)$,[a] %	4.9	5.3

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

Table 3. Selected Bond Distances and Angles for **2d**

(a) Bond Distances (Å)			
Mn(1)–C(2)	2.152(4)	Mn(1)–C(4)	2.402(3)
Mn(1)–C(5)	2.415(3)	Mn(1)–C(9)	2.294(3)
Mn(1)–C(10)	2.318(3)	Mn(1)–C(11)	1.787(3)
Mn(1)–C(12)	1.829(4)	Mn(1)–C(13)	1.795(4)
O(1)–C(11)	1.154(4)	O(2)–C(12)	1.142(6)
O(3)–C(13)	1.147(5)	C(1)–C(2)	1.559(4)
C(1)–C(8)	1.537(5)	C(1)–C(9)	1.513(5)
C(2)–C(3)	1.567(4)	C(2)–C(14)	1.508(5)
C(3)–C(4)	1.549(5)	C(3)–C(7)	1.551(4)
C(3)–C(26)	1.528(5)	C(4)–C(5)	1.373(5)
C(4)–C(20)	1.484(4)	C(5)–C(6)	1.515(4)
C(5)–C(27)	1.498(6)	C(6)–C(7)	1.547(6)
C(6)–C(10)	1.501(5)	C(7)–C(8)	1.519(5)
C(9)–C(10)	1.353(5)		
(b) Bond Angles (deg)			
C(2)–Mn(1)–C(4)	66.2(1)	C(2)–Mn(1)–C(9)	65.7(1)
C(5)–Mn(1)–C(10)	60.8(1)	C(9)–Mn(1)–C(11)	164.4(2)
C(10)–Mn(1)–C(11)	161.4(2)	C(2)–Mn(1)–C(12)	168.9(1)
C(11)–Mn(1)–C(12)	85.5(2)	C(5)–Mn(1)–C(13)	168.4(1)
C(4)–Mn(1)–C(13)	148.7(2)	C(12)–Mn(1)–C(13)	94.9(2)
C(11)–Mn(1)–C(13)	87.9(2)	C(2)–C(1)–C(9)	103.6(3)
C(2)–C(1)–C(8)	105.9(3)	C(1)–C(2)–C(3)	104.6(2)
C(8)–C(1)–C(9)	107.8(3)	C(2)–C(3)–C(4)	106.4(3)
C(2)–C(3)–C(7)	103.5(2)	C(4)–C(3)–C(7)	102.1(3)
C(5)–C(6)–C(10)	105.2(3)	C(3)–C(4)–C(5)	110.3(3)
C(3)–C(7)–C(6)	104.5(3)	C(4)–C(5)–C(6)	110.8(3)
C(6)–C(7)–C(8)	113.5(3)	C(5)–C(6)–C(7)	103.5(3)
C(1)–C(9)–C(10)	119.3(3)	C(7)–C(6)–C(10)	112.8(3)
Mn(1)–C(11)–O(1)	173.8(4)	C(3)–C(7)–C(8)	103.8(3)
Mn(1)–C(13)–O(3)	176.6(4)	C(1)–C(8)–C(7)	99.9(3)
Mn(1)–C(12)–O(2)	175.8(3)	C(6)–C(10)–C(9)	121.6(3)

Scheme 3. Proposed Mechanism for Dienyl–Alkyne Coupling in the Formation of **2d**



M = $Mn(CO)_3$; The hapticity of the C_6 ring in intermediates **II-VII** is shown for clarity.
(i) Ring Slip. (ii) Insertion.

bonded to the metal than C(4)=C(5) {average 2.306(3) Å for Mn–C(9), Mn–C(10), and 2.407(3) Å for Mn–C(4), Mn–C(5)}, suggesting the metal ligand bonding is somewhat strained. Selected bond distances and angles are presented in Table 3.

The substituted cyclohexadienyl complexes **1b,c** react cleanly with alkynes to give tricyclic complexes isostructural with **2a–d**. The products **2e** and **2f** are isolated from the reactions of **1b** with diphenylacetylene and **1c** with 2-butyne, respectively. Each was characterized as described in the Experimental Section and pertinent NMR data are given in Table 1. These products show ^{13}C NMR resonances for C(2) at δ –4.8 and –19.4, respectively, as expected for phenyl and methyl substitution at this site. No other unusual features are observed for **2e,f**, but their formation serves to demonstrate the photoreactions are possible with groups other than H at the *exo*-C_6 position of **1**.

Mechanism of Dienyl–Alkyne Coupling. The formation of **2** can be viewed as sequential [5 + 2] and [3 + 2] cycloadditions between a dienyl moiety and two alkynes. A proposed mechanism for this process for **2d** is shown in Scheme 3. 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. Two possibilities are the following: (i) irradiation generates a coordinatively unsaturated intermediate such as **II** through an η^5- to η^3-ring slip or (ii) UV light causes the ejection of a CO ligand. There is precedent for the latter since **1a–c** undergo photoinduced CO substitution.[11] Furthermore, a detailed study on the related [6 + 4] cycloaddition of dienes to tricarbonyl(η^6-cycloheptatriene)-chromium(0) concluded that CO loss was the primary photoprocess, although a photoinduced ring slip also occurred.[12] An earlier report had promoted a mechanism involving a photoinduced ring slip[13] and more recently Rigby has advocated this mechanism based upon his observations that purging the reaction solutions with an inert gas actually increased the yields of the [6 + 4] adducts.[5a]

If argon is vigorously bubbled through a toluene solution of **1a** and 2-butyne during the photoreaction, the yield and rate of formation of **2a** are the same as when no purge is conducted. This observation and the efficiency of the reaction suggest CO loss may not be involved, although the ejected CO could add sufficiently rapidly following dienyl–alkyne coupling that none is lost due to the purge. Notwithstanding this fact, Scheme 3 shows a mechanism involving a ring slip, but it should be stressed that a mechanism involving photoinduced CO loss is equally plausible, especially given the contrasting results for the [6 + 4] process. Numerous attempts to detect intermediates in the reaction failed, including the use of only 1 equiv of alkyne which gave an ca. 50% yield of the double addition product and no single alkyne cycloaddition.

As shown, one molecule of alkyne adds to the metal to form an 18e species **III**, followed by dienyl–alkyne coupling to give **IV**. Insertion of an alkyne ligand into an η^3-dienyl species has not been reported, but if the η^3 group is considered an η^2-, σ-bonded species then the alkyne simply inserts into the Mn–C σ bond. This type of insertion has been invoked in most coupling reactions of alkynes.[2,14] Following insertion, the former alkyne is shown as a vinyl ligand and may be η^1-coordinated to the metal with the ring as an η^4-bonded species. Alternatively an η^2-vinyl-η^2-diene structure is also possible. Either way an alkyl–olefin insertion of the vinyl group into the metal olefin bond would give the [5 + 2] cycloadduct **V**. The last three steps of the mechanism involve the [3 + 2] cycloaddition of a second alkyne across the coordinated allyl and olefin groups in **V**. This alkyne can coordinate to **V** if the η^3-allyl moiety slips to η^1-bonding. Subsequent insertion into the Mn–C σ bond in **VI**, as for **III** to **IV**, would form **VII**, and a final olefin–vinyl insertion would then give **2**.

The regiochemistry observed in the formation of **2d** must be dictated in these last steps. We propose that for 1-phenyl-1-propyne the second alkyne insertion proceeds exclusively through the methyl-substituted carbon giving an α-phenylvinyl group (shown in intermediates **IV** and **VII**) and that the subsequent ring closure (**VII** to **2**) occurs only to the methyl-substituted carbon of the coordinated olefin. This last requirement may be forced by the ring slip in **V** to **VI** which must favor the carbon closest to the methyl substituent of **V**. Many variations on this mechanism in which different groups insert into one another are possible. However, the essential features shown [i.e. (i) alkynes insert into a metal–carbon σ bond rather than a metal–η^2-olefin bond; (ii) alkynes initially insert through a methyl-substituted carbon rather than a phenyl-substituted terminus; and (iii) the vinyl species ring close to the methyl-substituted coordinated olefin carbon] adequately explain the regioselectivity found for **2d**.

Reaction of Ph_3C^+ with Tricyclic Complexes 2a,b. The reaction of $[Ph_3C][PF_6]$ with **2a,b** in CH_2Cl_2 at 0 °C resulted in the

(11) Connelly, N. G.; Freeman, M. J.; Orpen, A. G.; Sheehan, A. R.; Sheridan, J. B.; Sweigart, D. A. *J. Chem. Soc., Dalton Trans.* **1985**, 1019–1026.
(12) van Houwelingen, T.; Stufkens, D. J.; Oskam, A. *Organometallics* **1992**, *11*, 1146.
(13) (a) Kreiter, C. G. *Adv. Organomet. Chem.* **1986**, *26*, 297. (b) Michels, E.; Sheldrick, W. S.; Kreiter, C. G. *Chem. Ber.* **1985**, *118*, 964.
(14) See for example: Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; Chapter 18.

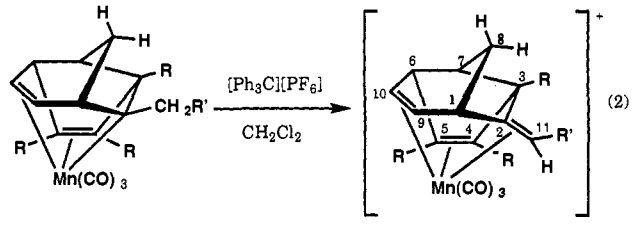
Table 4. ^{1}H and ^{13}C NMR Spectral Data for Complexes **3a,b**[a]

complex	(^{1}H)[b]	(^{13}C)[c]
3a	1.24 (3H, s, 3-Me), 1.69 (3H, s, 4-Me), 1.82 (1H, d, J = 12.9 Hz, H_8), 1.99 (1H, m, $H_{8'}$), 2.26 (3H, s, 5-Me), 2.75 (1H, d, H_1), 3.28 (1H, dd, J = 5.9, 6.3 Hz, H_7), 3.83 (1H, dd, J = 7, 7.8 Hz, H_6), 4.18 (1H, dd, J = 5.5, 6.6 Hz, H_9), 4.62 (1H, s, H_{11}), 4.64 (1H, s, $H_{11'}$), 4.98 (1H, dd, J = 5.9, 6.3 Hz, H_{10})	13.3 (3-Me), 16.6 (5-Me), 23.4 (4-Me), 31.4 (C_8), 36.9 (C_1), 48.7 (C_7), 53.6 (C_6), 57.4 (C_3), 66.8 (C_{10}), 67.8 (C_2), 69.8 (C_9), 72.8 (C_{11}), 93.2 (C_5), 101.2 (C_4), 218.6 (CO)[d]
		14.9 (q, J = 129 Hz, 3-Me), 16.9 (q, J = 129 Hz, 5-Me), 23.5 (q, J = 133 Hz, 4-Me), 31.8 (t, J = 135 Hz, C_8), 37.6 (d, J = 151 Hz, C_1), 49.3 (d, J = 145 Hz, C_7), 54.9 (d, J = 145 Hz, C_6), 58.2 (s, C_3), 66.9 (d, J = 174 Hz, C_{10}), 68.7 (s, C_2), 69.9 (d, J = 170 Hz, C_9), 72.9 (t, J = 164 Hz, C_{11}), 93.5 (s, C_5), 101.5 (s, C_4), 219.6 (CO)[b]
3b (major isomer)	0.96 (3H, t, J = 7.6 Hz, 3-Me), 1.20 (3H, t, J = 7.6 Hz, 5-Me), 1.40 (3H, t, J = 7.6 Hz, 4-Me), 1.68 (1H, d, J = 12.5 Hz, H_8), 1.84 (1H, m, 3-CH_2), 1.96 (1H, m, $H_{8'}$), 2.06 (1H, m, 3-$CH_{2'}$), 2.18 and 2.24 (2H, m, 5-CH_2), 2.32 (3H, d, J = 7.0 Hz, 11-Me), 2.56 (1H, m, 4-CH_2), 2.84 (1H, m, 4-$CH_{2'}$), 2.98 (1H, m brd, H_1), 3.08 (1H, t, J = 6.3 Hz, H_7), 4.25 (1H, dd, J = 7.0, 7.6 Hz, H_6), 4.53 (1H, dd, J = 5.1, 6.3 Hz, H_9), 4.76 (1H, dd, J = 5.7, 6.3 Hz, H_{10}), 5.86 (1H, q, J = 7.0 Hz, H_{11})	9.5, 13.8, 17.7, 18.2 (Me), 23.8, 24.0, 30.0 (CH_2), 33.4 (C_8), 41.2 (C_1), 47.1 (C_7), 55.6 (C_6), 61.0 (C_3), 71.9 (C_9), 73.0 (C_{10}), 103.5 (C_5), 106.6 (C_4), 107.8 (C_{11}), 219.8 (CO)[b,e]
3b' (minor isomer)	0.90 (t, 3-Me), 1.14 (t, 5-Me), 1.33 (t, 4-Me), 1.74 (d, H_8), 1.98 (m, $H_{8'}$), 1.8 and 2.0 (3-CH_2), 2.2 and 2.25 (5-CH_2), 2.24 (d, 11-Me), 2.5 and 2.78 (4-CH_2), 2.88 (m brd, H_1), 3.58 (t, H_7), 4.2 (dd, H_6), 4.37 (dd, H_9), 4.92 (dd, H_{10}), 5.64 (q, H_{11})	9.3, 13.5, 17.3, 18.7 (Me), 23.5, 24.0, 32.1 (CH_2), 32.6 (C_8), 34.6 (C_1), 47.3 (C_7), 52.6 (C_6), 70.1 (C_9), 70.4 (C_{10}), 99.5 (C_{11}), 219.8 (CO)[b,f]

[a] Labeling refers to eq 2. [b] In CD_3NO_2. [c] ^{1}H-decoupled spectra unless J_{CH} given. [d] In acetone-d_6. [e] Signal for C_2 obscured by solvent. [f] Signals for C_2–C_5 could not be distinguished from spectral noise.

formation of the tricyclic complexes **3a,b** (eq 2). These species arise via the abstraction of hydride from the methyl or methylene groups at C(2) of **2a** and **2b**, respectively, forming an exocyclic double bond that coordinates to the metal center.

Complex **3a** was isolated as an analytically pure yellow solid in 76% yield (based on **2a**) and characterized by elemental analysis, IR, and ^{1}H, ^{13}C, and ^{1}H–^{1}H (2D COSY) NMR spectroscopy (Table 4) as well as by an X-ray diffraction study. The proton



2a R = Me, R'= H
2b R = Et, R'= Me

3a R = Me, R'= H
3b R = Et, R'= Me

NMR spectrum of **3a** shows only three signals due to the methyl groups attached to C(3), C(4), and C(5). Two singlets at δ 4.62 and 4.64 are observed for the exocyclic methylene at C(2). The remaining seven proton signals are similar to those for **2a**. The ^{13}C{1H} NMR spectrum shows signals at δ 72.8 {C(11)} and 67.8 {C(2)} for the coordinated exocyclic olefin, as well as high field peaks assigned to the three methyl groups. The remaining ^{13}C{1H} NMR signals are consistent with the assigned structure. Assignments were made from the proton coupled ^{13}C NMR spectrum (Table 4), including C(2) through C(5) which were assigned on the basis of their $^2J_{CH}$ couplings. Thus, the signal for C(2) appears as a vague triplet {coupling to H(11) and H(11)'} and is the broadest of the four. The line width is greater because the $^2J_{CH}$ coupling through the double bond is larger than the $^2J_{CH}$ couplings to C(3), C(4), and C(5) which are through single bonds. The line widths of all four signals are in agreement with the expected multiplicities and $^2J_{CH}$ couplings of ca. 8 Hz for $C{=}CH_2$ and 4 Hz for $C{-}CH_3$.[15] The structure of **3a** was confirmed by an X-ray diffraction study (Figure 3, Tables 2 and 5). Yellow

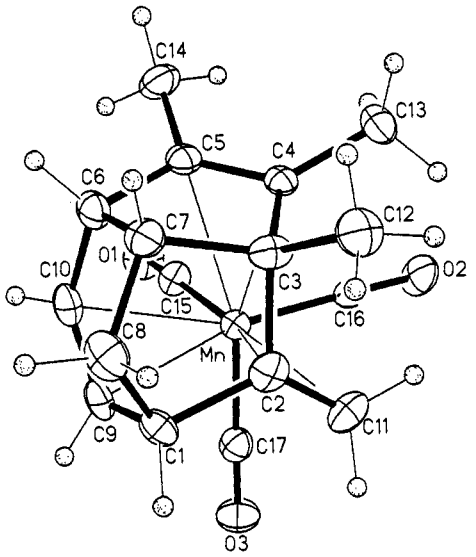


Figure 3. Molecular structure and labeling scheme for **3a**.

prisms of **3a** were obtained from the slow diffusion of diethyl ether into a nitromethane solution of the salt over a week. A drawing of the structure of **3a** is shown in Figure 3 and shows a piano stool type geometry similar to that of **2d** with three carbonyl ligands *trans* to the coordinated double bonds of the tricyclic ligand. The metal center is η^2-bonded to all three olefins of the ligand {C(2)=C(11), C(4)=C(5) and C(9)=C(10)}. Unlike complex **2d**, the three carbonyl ligands are equidistant from the metal with a mean Mn–C distance of 1.821(6) Å. As was found for **2d**, the C(9)=C(10) bond is closer to the metal {average 2.335 Å of Mn–C(9) and Mn–C(10)} than the C(4)=C(5) double bond (average 2.440 Å). The difference (0.005 Å for **3a** vs 0.01 Å in **2d**) is less for the cation suggesting the ligand in **3a** is less strained. Selected bond distances and angles are shown in Table 5.

Complex **3a** results from hydride abstraction from an atom adjacent to the σ-bonded carbon C(2). Consequently, **2c–e** do not react with Ph_3C^+ to give cationic complexes. On the other hand, the reaction between Ph_3C^+ and **2b** gave **3b** which is isostructural with **3a**. Complex **3b** was isolated as a pure yellow solid in 70% yield (based on **2b**) as a mixture of E/Z isomers and

(15) Levy, G. C.; Lichter, R. L.; Nelson, G. L. *Carbon-13 Nuclear Magnetic Resonance Spectroscopy*; Wiley: New York, 1980.

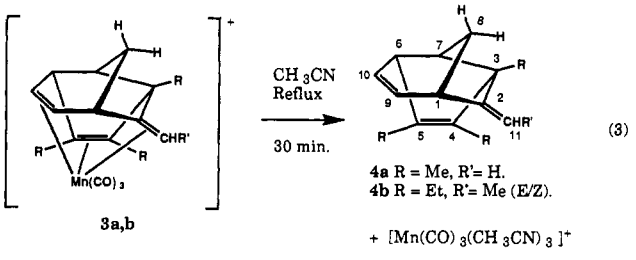
(16) (a) Winkhaus, G.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1961**, 3807. (b) Chung, Y. K.; Williard, P. G.; Sweigart, D. A. *Organometallics* **1982**, *1*, 1053.

Table 5. Selected Bond Distances and Angles for **3a**

(a) Bond Distances (Å)			
Mn–C(2)	2.283(6)	Mn–C(4)	2.421(5)
Mn–C(5)	2.458(5)	Mn–C(9)	2.316(7)
Mn–C(10)	2.355(6)	Mn–C(11)	2.325(7)
Mn–C(15)	1.823(7)	Mn–C(16)	1.820(6)
Mn–C(17)	1.821(6)	O(1)–C(15)	1.133(8)
O(2)–C(16)	1.145(8)	O(3)–C(17)	1.136(8)
C(1)–C(2)	1.516(9)	C(1)–C(8)	1.542(9)
C(1)–C(9)	1.517(9)	C(2)–C(3)	1.539(8)
C(2)–C(11)	1.330(9)	C(3)–C(4)	1.531(8)
C(3)–C(7)	1.543(9)	C(3)–C(12)	1.520(9)
C(4)–C(5)	1.360(8)	C(4)–C(13)	1.480(8)
C(5)–C(6)	1.523(9)	C(5)–C(14)	1.506(9)
C(6)–C(7)	1.516(9)	C(6)–C(10)	1.523(9)
C(7)–C(8)	1.537(9)	C(9)–C(10)	1.314(10)
(b) Bond Angles (deg)			
C(2)–Mn–C(4)	63.9(2)	C(2)–Mn–C(9)	61.8(2)
C(5)–Mn–C(10)	59.7(2)	C(2)–Mn–C(15)	160.6(3)
C(11)–Mn–C(15)	165.4(3)	C(10)–Mn–C(16)	159.9(2)
C(9)–Mn–C(16)	166.6(2)	C(15)–Mn–C(16)	88.1(3)
C(5)–Mn–C(17)	164.4(2)	C(4)–Mn–C(17)	160.7(2)
C(15)–Mn–C(17)	88.0(3)	C(16)–Mn–C(17)	91.3(3)
C(2)–C(1)–C(8)	101.9(5)	C(2)–C(1)–C(9)	102.3(5)
C(8)–C(1)–C(9)	108.0(5)	C(1)–C(2)–C(3)	110.9(5)
C(3)–C(2)–C(11)	122.7(6)	C(1)–C(2)–C(11)	126.3(6)
C(2)–C(3)–C(7)	100.3(5)	C(2)–C(3)–C(4)	108.4(5)
C(5)–C(6)–C(10)	103.9(5)	C(4)–C(3)–C(7)	103.6(5)
C(3)–C(7)–C(6)	104.3(5)	C(3)–C(4)–C(5)	109.1(5)
C(6)–C(7)–C(8)	113.0(5)	C(4)–C(5)–C(6)	111.3(5)
C(1)–C(9)–C(10)	121.5(6)	C(5)–C(6)–C(7)	103.3(5)
Mn–C(16)–O(2)	178.1(6)	C(7)–C(6)–C(10)	113.8(5)
F(2)–P–F(4)	175.3(3)	C(3)–C(7)–C(8)	104.6(5)
F(3)–P–F(5)	179.7(3)	C(1)–C(8)–C(7)	100.5(5)
F(1)–P–F(6)	178.3(3)	C(6)–C(10)–C(9)	120.5(6)
Mn–C(17)–O(3)	178.2(6)	Mn–C(15)–O(1)	174.7(6)

characterized by IR and ^{1}H, ^{13}C, and ^{1}H–^{1}H (2D COSY) NMR spectroscopy (Table 4). The two isomers are formed in a 1:4 ratio (from integration of the proton NMR signals); however it is not known which predominates. Two isomers arise because the intermolecular reaction with trityl cation leads to abstraction of either of the two methylene hydrogens adjacent to C(2). There is restricted rotation about the Et–C(2) bond that renders these hydrogens inequivalent. This is supported by the ^{1}H NMR spectra of both **2b** and **3b**, in which the methylene protons of all the ethyl groups appear as complex 1H multiplets, rather than quartets.

Decomplexation of the Organic Ligand from 3a,b. When acetonitrile solutions of **3a,b** are refluxed for 15–30 min, the tricyclic organic compounds are cleanly decomplexed from the metal with concomitant formation of $[Mn(CO)_3(NCCH_3)_3]^+$ (eq 3). Precipitation of the manganese species using diethyl ether and workup of the mother liquor by TLC gave good isolated yields of **4a,b** as colorless oils. The new organic compound **4a** is 10-methylene-5,6,7-trimethyltricyclo[5.2.1.0^{4,8}]deca-2,5-diene, whereas **4b** is the 10-(*E*/*Z*)-ethylidene-5,6,7-triethyl species.



(3)

Compounds **4a,b** were characterized by ^{1}H, ^{13}C, and ^{1}H–^{1}H (2D COSY) NMR spectroscopy (Table 6), as well as by high-resolution mass spectroscopy. No unusual features were observed in these spectra and **4b** was isolated as a mixture of *E*/*Z* isomers as expected since **3b** was a mixture. The signals for each of these isomers were assigned and are identified in Table 6. The clean decomplexation reaction using acetonitrile affords a stable manganese species $[Mn(CO)_3(NCCH_3)_3][PF_6]$, which was identified by its distinctive IR spectrum in CH_3CN [ν(CO) = 2065, 1975 cm^{-1}].

Conclusions

We have demonstrated a new higher order cycloaddition reaction between alkynes and a coordinated cyclohexadienyl ring that generates tricyclo[5.2.1.0^{4,8}]deca-2,5-dien-10-yl species. The reaction is mediated by the metal but also requires UV light to generate the unsaturated transition metal intermediates. In the case of an asymmetric alkyne, the reaction is regiospecific and forms one of four possible isomers. The new tricyclo complexes undergo β-hydride abstraction giving triene complexes from which the organic groups can be efficiently decomplexed. The coupling reaction shows potential for the synthesis of new fused ring systems employing η^5-coordinated groups and alkynes. Remarkably, four new carbon–carbon bonds are formed both regio- and stereoselectively in a one-pot reaction. The extension of this new coupling reaction to other alkynes and studies using the η^5-coordinated cycloheptadienyl ligand, in which the same methodology may be used to access other new tricyclic systems, are in progress. Given the wide range of bonding modes of polyenes to transition metals, it should be possible to generate many new fused ring structures via metal mediated higher order cycloaddition reactions similar to that described herein.

Experimental Section

General. 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_2Cl_2), or K_2CO_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(cyclohexadienyl)manganese(I) derivatives were prepared using the literature procedure.[6b,16] Photolyses were conducted through Pyrex or quartz glassware using broadband irradiation from a 450 W Hanovia medium-pressure Hg lamp.

General Procedure for the Syntheses of 2a–f. A solution of the appropriate cyclohexadienyl complex **1a–c** (ca. 1 mmol) and alkyne (ca. 2 equiv) in toluene or *n*-hexane (40 mL) was irradiated (quartz or Pyrex glassware) with UV light (0.5–6 h) at room temperature. Irradiation was continued until **1a–c** could no longer be detected in the IR spectrum of the reaction mixture. Subsequent removal of the solvent in vacuo and chromatography on an alumina (2.5 cm × 20 cm) column, loading in toluene (2 mL), and eluting with the appropriate solvent mixture (diethyl ether/*n*-hexane) gave the complexes as yellow or red solutions from which the yellow or red powder was obtained after evaporation to dryness.

Preparation of $[(\eta^{1:2:2}\text{-}C_{10}H_7Me_4)Mn(CO)_3]$ (2a). Using the general procedure above, complex **1a** (0.300 g, 1.4 mmol) and 2-butyne (0.22 mL, 2.8 mmol) in toluene were irradiated (Pyrex) with UV light for 6 h. Complex **2a** was isolated as a bright yellow powder following chromatography on alumina eluting with diethyl ether/n-hexane (1:4). Yield (based on **1a**): 0.404 g, 90%; ν_{max}(CO)/cm^{-1}, (hex), 2000 (vs), 1920 (vs), and 1912 (vs). Anal. Calcd for $C_{17}H_{19}MnO_3$: C, 62.58; H, 5.83. Found: C, 62.80; H, 6.16.

Preparation of $[(\eta^{1:2:2}\text{-}C_{10}H_7Et_4)Mn(CO)_3]$ (2b). Using the general procedure above, complex **1a** (0.300 g, 1.4 mmol) and 3-hexyne (0.32 mL, 2.8 mmol) in toluene were irradiated (Pyrex) with UV light for 4 h. Complex **2b** was isolated as a bright yellow powder following chromatography on alumina eluting with diethyl ether/*n*-hexane (1:1). Yield (based on **1a**): 0.400 g, 76%; ν_{max}(CO)/cm^{-1}, (hex), 2000 (vs), 1920 (vs), and 1913 (vs).

Table 6. ^{1}H and ^{13}C NMR Spectral Data for **4a,b**[a,b]

complex	(^{1}H)	(^{13}C)[c]
4a	1.16 (3H, s, 3-Me), 1.82 (1H, d, J = 13 Hz, H_8), 1.58 (3H, s, 4-Me), 1.60 (3H, s, 5-Me), 1.8 (1H, m, $H_{8'}$), 2.37 (1H, s brd, H_7), 2.75 (1H, s brd, H_1), 2.85 (1H, s brd, H_6), 4.62 (1H, s, H_{11}), 4.70 (1H, s, $H_{11'}$), 5.70 (1H, dd, J = 5, 8 Hz, H_{10}), 5.94 (1H, t, J = 6 Hz, H_9)	10.0, 13.6, 24.0 (Me), 32.6 (C_8), 46.0 (C_1), 52.0 (C_7), 52.7 (C_6), 58.3 (C_3), 102.2 (C_{11}), 129.5 (C_{10}), 133.1 (C_9), 135.3, 135.8 (C_4, C_5), 159.2 (C_2)
4b (major isomer)	0.78 (3H, t, J = 7.4 Hz, 3-Me), 0.96 (3H, t, J = 7.4 Hz, 5-Me), 1.01 (3H, t, J = 7.4 Hz, 4-Me), 1.43 (1H, d, J = 11 Hz, H_8), 1.6–1.7 (2H, m, 3-CH_2, $H_{8'}$), 1.63 (3H, d, J = 7.4 Hz, 11-Me), 1.8–2.2 (5H, m, CH_2), 2.56 (1H, m brd, H_7), 2.72 (1H, t brd, H_1), 3.06 (1H, m, H_6), 5.15 (1H, q, J = 7.4 Hz, H_{11}), 5.59 (1H, dd, J = 5, 9 Hz, H_{10}), 5.89 (1H, t, J = 9 Hz, H_9)	10.0, 12.9, 14.3, 14.8 (Me), 19.6, 21.0, 26.6 (CH_2), 32.7 (C_8), 48.2 (C_1), 48.6 (C_7), 48.5 (C_6), 62.8 (C_3), 114.0 (C_{11}), 129.1 (C_{10}), 133.5 (C_9), 140.0, 144.2, 148.0 (C_2, C_4), C_5)
4b' (Minor isomer)	0.76 (t, 3-Me), 0.94 (t, 5-Me), 0.99 (t, 4-Me), 1.48 (d, H_8), 1.55 (d, 11-Me), 1.6 (m, 3-CH_2, $H_{8'}$), 1.8–2.2 (m, CH_2), 2.50 (m, H_7), 3.06 (m, H_1, H_6), 5.03 (q, H_{11}), 5.63 (dd, H_{10}), 5.94 (t, H_9)	10.1, 13.0, 14.6, 15.5 (Me), 18.4, 21.1, 28.3 (CH_2), 32.9 (C_8), 40.3 (C_1), 47.5 (C_7), 50.5 (C_6), 62.7 (C_3), 111.6 (C_{11}), 130.2 (C_{10}), 132.3 (C_9), 140.5, 142.7, 149.7 (C_2, C_4, C_5)

[a] Labeling refers to eq 3. [b] In $CDCl_3$. [c] ^{1}H-decoupled spectra.

Preparation of [($\eta^{1:2:2}$-$C_{10}H_7Ph_4$)Mn(CO)$_3$] (2c). Using the general procedure above, complex **1a** (0.200 g, 0.92 mmol) and diphenylacetylene (0.326 g, 1.84 mmol) in n-hexane were irradiated (Pyrex) with UV light for 5 h. Complex **2c** was isolated as a red powder following chromatography on alumina eluting with diethyl ether/n-hexane (1:1). Yield (based on **1a**): 0.395 g, 75%; ν_{max}(CO)/cm^{-1}, (hex), 2007 (vs), 1930 (vs), and 1918 (vs).

Preparation of [($\eta^{1:2:2}$-$C_{10}H_7Me_2Ph_2$)Mn(CO)$_3$] (2d). Using the general procedure above, complex **1a** (0.11 g, 0.51 mmol) and 1-phenyl-1-propyne (150 μL, 1.2 mmol) in toluene were irradiated (quartz) with UV light for 5 h. Complex **2d** was isolated as an orange powder following chromatography on alumina eluting with diethyl ether/n-hexane (1:9). The product was recrystallized from CH_2Cl_2/n-hexane. Yield (based on **1a**): 0.17g, 76%; ν_{max}(CO)/cm^{-1}, (hex), 2006 (vs), 1933 (vs), and 1917 (vs).

Preparation of [($\eta^{1:2:2}$-$C_{10}H_6MePh_4$)Mn(CO)$_3$] (2e). Using the general procedure above, complex **1b** (0.300 g, 1.30 mmol) and diphenylacetylene (0.46 g, 2.6 mmol) in toluene were irradiated (Pyrex) with UV light for 6 h. Complex **2e** was isolated as a red powder following chromatography on alumina eluting with diethyl ether/n-hexane (1:1). Yield (based on **1b**): 0.456 g, 60%. This reaction can also be done in n-hexane (4 h) and gives **2e** as a red precipitate. Yield (based on **1b**): 0.547 g, 72%; ν_{max}(CO)/cm^{-1}, (hex), 2008 (vs), 1930 (vs), and 1918 (vs).

Preparation of [($\eta^{1:2:2}$-$C_{10}H_6TolMe_4$)Mn(CO)$_3$] (2f). Using the general procedure above, complex **1c** (0.200 g, 0.65 mmol) and 2-butyne (0.11 mL, 1.3 mmol) in toluene were irradiated (Pyrex) with UV light for 6 h. Complex **2f** was isolated as a yellow powder following chromatography on alumina eluting with diethyl ether/n-hexane (1:4). Yield (based on **1c**): 0.228 g, 85%; ν_{max}(CO)/cm^{-1}, (hex), 2000 (vs), 1920 (vs), and 1913 (vs). Anal. Calcd for $C_{24}H_{23}MnO_3$: C, 69.23; H, 6.01. Found: C, 69.14; H, 6.39.

Preparation of [($\eta^{2:2:2}$-$C_{10}H_7$(=CH_2)Me_3)Mn(CO)$_3$][PF_6] (3a). Triphenylcarbenium hexafluorophosphate (0.237 g, 0.61 mmol) was added to a stirred yellow solution of **2a** (0.200 g, 0.61 mmol) in CH_2Cl_2 at 0 °C. The color quickly changed to deep yellow. Further stirring for 20 min at room temperature, removal of solvent in vacuo, and recrystalization of the residue from acetone/diethyl ether or nitromethane/diethyl ether gave **3a** as a yellow powder. Yield (based on **2a**): 0.218 g, 76%; ν_{max}(CO)/cm^{-1}, (CH_2Cl_2), 2061 (vs), and 1995 (vs). Anal. Calcd for $C_{17}H_{18}MnO_3PF_6$: C, 43.40; H, 3.83. Found: C, 43.05; H, 3.44. Crystals for an X-ray diffraction study were grown as follows: Diethyl ether (20 mL) was carefully layered on top of a solution of **3a** (0.025 g) in nitromethane (1 mL). Slow diffusion (1 week) of the two layers at room temperature gave yellow prisms of **3a** on the side of the tube.

Preparation of (E/Z)-[($\eta^{2:2:2}$-$C_{10}H_7$(=CHMe)Et_3)Mn(CO)$_3$][PF_6] (3b). Triphenylcarbenium hexafluorophosphate (0.306 g, 0.79 mmol) was added to a stirred yellow solution of **2b** (0.300 g, 0.79 mmol) in CH_2Cl_2 at 0 °C. The color quickly changed to deep yellow. Further stirring for 30 min at room temperature, removal of solvent in vacuo, and recrystalization of the residue from acetone/diethyl ether or nitromethane/diethyl ether gave **3b** as a yellow powder. Yield (based on **2b**): 0.291 g, 70%; ν_{max}(CO)/cm^{-1}, (CH_2Cl_2), 2058 (vs), and 1990 (vs).

10-Methylene-5,6,7-trimethyltricyclo[5.2.1.0^{4,8}]deca-2,5-diene (4a). A solution of **3a** (0.31 g, 0.65 mmol) in acetonitrile (70 mL) was stirred under reflux for 20 min. Evaporation of the solvent in vacuo and extraction of the residue with diethyl ether gave crude **4a** as a pale yellow oil. Pure **4a** was isolated following chromatography on silica (TLC, Fisher Scientific Redi/plate) eluting with CH_2Cl_2/hexane (1:3). Yield 0.10 g (82%); m/z 186.1409 (M^+), calcd for $C_{14}H_{18}$ = 186.1407.

10-(E/Z)-Ethylidene-5,6,7-triethyltricyclo[5.2.1.0^{4,8}]deca-2,5-diene (4b). Compound **4b** was prepared from **3b** as described above for **4a**. The product was obtained as a mixture of E and Z isomers. Yield 0.10 g, (63%); m/z 242.2034 (M^+), calcd for $C_{18}H_{26}$ = 242.2035.

X-ray Diffraction Study of 2d (Rutgers University). Crystallographic data are collected in Table 2. A crystal (orange pentagon) of dimensions 0.32 × 0.45 × 0.52 mm was selected from a sample grown from a CH_2Cl_2/hexane solution at −10 °C for 3 days and mounted inside a glass capillary under nitrogen. Fifteen high-angle reflections were used to calculate the orientation matrix and best cell dimensions. The assigned crystal system and space group were uniquely determined by systematic absences in the diffraction data. Data were collected on a Siemens P4 diffractometer at 297 K with a graphite monochromator using Mo Kα radiation with three check reflections recorded every 47 reflections. A total of 4853 unique reflections were measured in the θ–2θ scan mode ($3.0 < 2\theta < 55.0°$), of which 2672 had $F > 4\sigma(F)$ which were used in the refinement. Empirical absorption corrections (ψ-scans) were made. Autointerpreted Patterson synthesis was used to locate the heavy atom. All non-hydrogen atoms were found in difference electron density maps and were anisotropically refined. Hydrogen atoms were calculated and treated as idealized riding model contributions. Final difference electron density maps showed no features outside the range 0.26 to −0.28 e Å^{-3}. All computations used the PC SHELXTL program library (Version 4.21, G. Sheldrick, Siemens, Madison, WI).

X-ray Diffraction Study of 3a (University of Delaware). Crystallographic data are collected in Table 2. A crystal (yellow block) of dimensions 0.10 × 0.10 × 0.50 mm was selected from a sample grown by the slow diffusion of diethyl ether (20 mL) into a nitromethane solution (1 mL) of **3a** (0.025 g) at room temperature over 1 week. The assigned crystal system was confirmed by photographic methods, and the space group was uniquely determined by systematic absences in the diffraction data. Data were collected on a Siemens R3m/V diffractometer at 233 K. Of 2488 data collected ($4° < 2\theta < 45°$), 2382 were independent and 1743 were observed with $F \geq 5\sigma(F)$. Azimuthal scans about the diffraction vector showed a variation of less than 10%; accordingly, no correction for absorption was applied. Autointerpreted Patterson synthesis was used to locate the heavy atom. All non-hydrogen atoms were anisotropically refined and hydrogen atoms were treated as idealized contributions. All computations used the SHELXTL program library (PC Version 4.2, G. Sheldrick, Siemens, Madison, WI).

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Supplementary Material Available: Tables of X-ray structural data, positional parameters, anisotropic thermal parameters, bond lengths, and bond angles for compounds **2d** and **3a** (17 pages); tables of observed and calculated structure factors (17 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.