Alkyne and CO Coupling Reactions with the Vinylidene Ligand in the Complex $Mn_2(CO)_7[\mu\text{-}\eta^2\text{-}C{=}CMe(CO_2Et)]$

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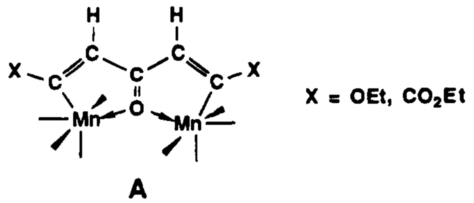
Reaction of the vinylidene complex $Mn_2(CO)_8[\mu\text{-}\eta^2\text{-}C{=}CMe(CO_2Et)]$ (**1a**) with CO (at 1000 psi) at 87 °C yielded the new compound $(OC)_4Mn[(EtO_2C)MeC{=}CC{=}OC{=}OC{=}CMe(CO_2Et)]Mn(CO)_4$ (**2**) in 59% yield and $Mn_2(CO)_{10}$. Compound **2** is believed to have been formed by the carbonylation of the vinylidene ligand, cleavage of a $Mn(CO)_5$ fragment, and a coupling of two metal groupings containing carbonylated vinylidene ligands. The reaction of **1a** with a combination of $MeC{\equiv}COEt$ and CO yielded only the compound $(OC)_4Mn[(EtO_2C)MeC{=}CC{=}CMe(CO_2Et)]Mn(CO)_4$ (**3**) in 72% yield. Compound **3** contains a 3,4-dimetallo-2,5-bis(ethoxycarbonyl)-2,4-hexadiene group formed by the coupling of two vinylidene ligands at the vinylidene carbon atoms. When the reaction of **1a** with $MeC{\equiv}COEt$ was performed in the absence of CO, the three isomeric products $Mn_2(CO)_7\{C(Me)C(OEt)C[{=}CMe(CO_2Et)]C(Me)C(OEt)\}$ (**4a**), $Mn_2(CO)_7\{C(Me)C(OEt)C[{=}CMe(CO_2Et)]C(OEt)C(Me)\}$ (**4b**), and $Mn_2(CO)_7\{C(OEt)C(Me)C[{=}CMe(CO_2Et)]C(Me)C(OEt)\}$ (**4c**) were formed in low yields. All three products contain a metallacyclohexadiene grouping that was formed by the addition and coupling of two $MeC{\equiv}COEt$ molecules to the carbon atom of the vinylidene ligand in **1a**. Compounds **2**, **3**, and **4a–c** were characterized by single-crystal X-ray diffraction analyses. Crystal data: for **2**, space group $P\bar{1}$, $a = 12.056(2)$ Å, $b = 18.016(3)$ Å, $c = 9.729(2)$ Å, $\alpha = 91.96(1)°$, $\beta = 111.82(1)°$, $\gamma = 85.13(2)°$, $Z = 3$, 4273 reflections, $R = 0.029$; for **3**, space group $P2_1/n$, $a = 8.532(2)$ Å, $b = 19.431(4)$ Å, $c = 14.331(3)$ Å, $\beta = 92.34(2)°$, $Z = 4$, 1562 reflections, $R = 0.036$; for **4a**, space group $P\bar{1}$, $a = 10.570(1)$ Å, $b = 13.930(6)$ Å, $c = 9.497(3)$ Å, $\alpha = 91.57(3)°$, $\beta = 98.48(3)°$, $\gamma = 72.63(4)°$, $Z = 2$, 1556 reflections, $R = 0.042$; for **4b**, space group = $P2_1/c$, $a = 12.080(3)$ Å, $b = 12.929(5)$ Å, $c = 16.723(4)$ Å, $\beta = 99.22(2)°$, $Z = 4$, 1473 reflections, $R = 0.040$; for **4c**, space group $P2_12_12_1$, $a = 13.876(3)$ Å, $b = 17.443(3)$ Å, $c = 10.871(2)$ Å, $Z = 4$, 1574 reflections, $R = 0.035$.

Introduction

It has recently been shown that $Mn_2(CO)_{10}$ and $Mn_2(CO)_9(NCMe)$ will react with terminal alkynes both with electron-donating groups[1] (e.g. $HC{\equiv}COEt$) and with electron-withdrawing groups (e.g. $HC{\equiv}CCO_2Et$)[2] to yield dimetalated ketone complexes **A**, formed by the coupling of the unsubstituted ends of two alkyne molecules to a CO ligand and the coordination of the oxygen atom of the carbonyl group to the two metal atoms. In contrast, the electron-rich internal alkynes $MeC{\equiv}CX$ (X = OEt, NMe_2) react with $Mn_2(CO)_9(NCMe)$ in a very different manner to yield the substituted vinylidene complexes $Mn_2(CO)_8[\mu\text{-}\eta^2\text{-}C{=}C(Me)C{=}O(X)]$ (**1a**, X = OEt, or **1b**, X = NMe_2, respectively) by an addition and rearrangement of the alkyne that includes a cleavage of the carbon–heteroatom bond, coupling of the heteroatom to a CO ligand, and a shift of the CO-coupled heteroatomic grouping to the methyl-substituted carbon atom.[3] There has been much recent interest in the chemistry of vinylidene ligands in polynuclear metal complexes.[4] The compounds **1** will react with MeC_2NMe_2 by 2 + 2 cycloaddition to yield the complexes $Mn_2(CO)_7[\mu\text{-}\eta^2\text{-}CC(Me)C(NMe_2)C(Me)C{=}O(X)]$ (X = OEt, NMe_2) that contain a substituted cyclobutenylidene ligand (eq 1).[3]



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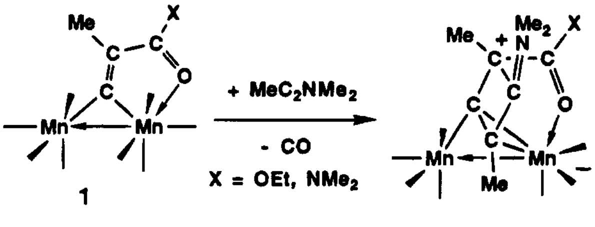

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[⊗] Abstract published in *Advance ACS Abstracts,* July 1, 1994.

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We have now investigated the reaction of **1a** with CO and with $MeC{\equiv}COEt$ in both the presence and absence of CO. The reaction of **1a** with CO proceeds by carbonylation of the vinylidene ligand and a subsequent coupling of two carbonylated vinylidene groupings to yield the new complex $(OC)_4Mn[(EtO_2C)MeC{=}CC{=}OC{=}OC{=}CMe(CO_2Et)]Mn(CO)_4$ (**2**) in good yield. In the presence of the alkyne this reaction with CO is suppressed and an alkyne addition occurs that is accompanied by a combination with CO to yield the complex $(OC)_4Mn[(EtO_2C)MeC{=}CC{=}CMe(CO_2Et)]Mn(CO)_4$ (**3**), containing a dimetalated 2,4-hexadiene grouping that can be viewed as a combination of two coupled vinylidene ligands. In the absence of CO, two alkynes will add to **1a**. They couple to the vinylidene ligand in three different ways to yield the three isomeric complexes $Mn_2(CO)_7\{C(Me)C(OEt)C[{=}CMe(CO_2Et)]C(Me)C(OEt)\}$ (**4a**), $Mn_2(CO)_7\{C(Me)C(OEt)C[{=}CMe(CO_2Et)]C(OEt)C(Me)\}$ (**4b**), and $Mn_2(CO)_7\{C(OEt)C(Me)C[{=}CMe(CO_2Et)]C(Me)C(OEt)\}$ (**4c**) containing metallacyclohexadiene groupings. The results of this study are reported here.

Experimental Section

Unless specified otherwise, all reactions were carried out under an atmosphere of nitrogen. Hexane solvent was freshly distilled from sodium before use. Water was removed from commercially supplied CO by passing the gas through a copper coil cooled to −116 °C in a slush of ethanol. TLC separations were performed in air by using silica gel (60 Å, F_{254}) on plates (Whatman, 0.25 mm). IR spectra were recorded on a Nicolet 5DXB FT-IR spectrophotometer. ^1H NMR spectra were taken at 300 MHz on a Bruker AM-300 spectrometer. Elemental analyses were performed by Desert Analytics, Tucson, AZ. $MeC{\equiv}COEt$[5] and $Mn_2(CO)_7[\mu\text{-}\eta^2\text{-}C{=}C(Me)C(OEt){=}O]$ (**1a**)[3] were prepared by reported methods.

Reaction of 1a with CO. A solution of 30.0 mg (0.067 mmol) of **1a** in 8.0 mL of hexane was placed in a Parr high-pressure reaction vessel. The vessel was pressurized to 1000 psi with CO and stirred at 87 °C for 12 h. After the mixture was cooled to room temperature and the system vented, the solvent was evaporated in vacuo, and the residue was separated by TLC using a hexane/CH_2Cl_2 (2/1) solvent mixture to give 16.7 mg of $Mn_2(CO)_{10}$ (128% yield) and 12.2 mg of orange $(OC)_4Mn[(EtO_2C)MeC{=}CC{=}OC{=}OC{=}CMe(CO_2Et)]Mn(CO)_4$ (**2**; 59% yield). IR (ν_{co} in hexane, cm^{-1}) for **2**: 2097 (m), 2094 (m), 2020 (vs), 2015 (sh, m), 2003 (s), 1954 (s), 1950 (sh), 1729 (w, br), 1666 (w, br), 1602 (w, br). ^1H NMR (δ in C_6D_6, ppm) for **2**: 3.53 (q, $^3J_{H-H}$ = 7.1 Hz, 4H, CH_2), 1.99 (s, 6H, CCH_3), 0.64 (t, $^3J_{H-H}$ = 7.1 Hz, 6H, CH_2CH_3). Anal. Calcd (found) for **2**: C, 43.00 (42.45); H, 2.61 (2.29).

Reaction of 2 with CO. The solution of 10.0 mg (0.016 mmol) of **2** in 6.0 mL of hexane was placed in a Parr high-pressure reaction vessel. The vessel was pressurized to 1100 psi with CO and stirred at 105 °C for 16 h. After the mixture was cooled to room temperature and the system vented, the solvent was removed, and the residue was separated by TLC using a hexane/CH_2Cl_2 (2/1) solvent mixture to give 2.1 mg of $Mn_2(CO)_{10}$ (33% yield) and 4.0 mg of unreacted **2**. The organic residue that was displaced was not recovered.

Reaction of 1a with $MeC{\equiv}COEt$ and under CO. A solution containing a 40.0-mg amount of **1a** (0.090 mmol) and a 40.0-μL amount of $MeC{\equiv}COEt$ (0.335 mmol) in 8 mL of hexane was placed in a Parr high-pressure reaction vessel and was pressurized to 1000 psi with CO and then heated to 90 °C and stirred for 12 h. After the mixture was cooled to room temperature and the system vented, the solvent was removed under vacuum and the residue separated by TLC using a CH_2Cl_2/hexane (1/3) solvent mixture to give 8.4 mg of unreacted starting material and 36.0 mg of orange $(OC)_4Mn[(EtO_2C)MeC{=}CC{=}CMe(CO_2Et)]Mn(CO)_4$ (**3**) in 72% yield. IR (ν_{co} in hexane, cm^{-1}) for **3**: 2090 (m), 2079 (m), 2069 (w), 2058 (w), 2023 (w), 2015 (w), 2006 (s), 1999 (s), 1975 (w), 1971 (w), 1961 (s), 1952 (s), 1596 (w, br), 1571 (w, br). ^1H NMR (δ in C_6D_6, ppm) for **3**: 3.76 (dq, $^2J_{H-H}$ = 10.8 Hz, $^3J_{H-H}$ = 7.2 Hz, 2H, CHH), 3.62 (dq, $^2J_{H-H}$ = 10.8 Hz, $^3J_{H-H}$ = 7.2 Hz, 2H, CHH), 2.01 (s, 6H), 0.74 (t, $^3J_{H-H}$ = 7.2 Hz, 6H, CH_3). Anal. Calcd (found) for **3**: C, 43.03 (43.10); H, 2.89 (3.11).

Reaction of 1a with $MeC{\equiv}COEt$ in the Absence of CO. A 20.0-mg amount (0.045 mmol) of **1a** and a 13.4-μL amount (0.113 mmol) of $MeC{\equiv}COEt$ were dissolved in 40 mL of hexane, and the solution was heated at 40 °C for 1 h. After the mixture was cooled to room temperature, the solvent was evaporated under vacuum. The residue was separated by TLC using a CH_2Cl_2/hexane (1/3) solvent mixture to give the following compounds in order of elution: 1.0 mg of unreacted starting material, 1.7 mg of orange $Mn_2(CO)_7\{C(Me)C(OEt)C[{=}CMe(CO_2Et)]C(Me)C(OEt)\}$ (**4a**; 5% yield), 3.2 mg of orange $Mn_2(CO)_7\{C(Me)C(OEt)C[{=}CMe(CO_2Et)]C(OEt)C(Me)\}$ (**4b**; 12% yield), and 2.6 mg of orange $Mn_2(CO)_7\{C(OEt)C(Me)C[{=}CMe(CO_2Et)]C(Me)C(OEt)\}$ (**4c**; 10% yield). IR (ν_{co} in hexane, cm^{-1}): for **4a**, 2069 (m), 2029 (s), 2006 (s), 1978 (s), 1970 (m, sh), 1959 (m), 1937 (m), 1728 (w, br); for **4b**, 2068 (m), 2025 (s), 2006 (s), 1973 (s), 1965 (m), 1953 (m), 1928 (m), 1727 (w, br); for **4c**, 2070 (m), 2025 (s), 2006 (s), 1978 (m), 1969 (s), 1961 (s), 1958 (sh), 1938 (m), 1726 (w, br). ^1H NMR (δ in C_6D_6, ppm): for **4a**, 3.93 (m, br, 4H, CH_2), 3.79 (q, $^3J_{H-H}$ = 7.0 Hz, 2H, CH_2), 2.39 (s, 3H, CCH_3), 2.06 (s, 3H, CCH_3), 1.86 (s, 3H, CCH_3), 1.23 (t, $^3J_{H-H}$ = 7.0 Hz, 3H, CH_2CH_3), 0.94 (t, $^3J_{H-H}$ = 7.0 Hz, 3H, CH_2CH_3), 0.93 (t, $^3J_{H-H}$ = 7.1 Hz, 3H, CH_2CH_3); for **4b**, 4.23 (q, $^3J_{H-H}$ = 7.0 Hz, 2H, CH_2), 4.07 (q, $^3J_{H-H}$ = 7.0 Hz, 2H, CH_2), 3.93 (q, $^3J_{H-H}$ = 7.1 Hz, 2H, CH_2), 2.42 (s, 3H, CCH_3), 2.39 (s, 3H, CCH_3), 1.89 (s, 3H, CCH_3), 1.08 (t, $^3J_{H-H}$ = 7.1 Hz, 3H, CH_2CH_3), 0.97 (t, $^3J_{H-H}$ = 7.1 Hz, 3H, CH_2CH_3), 0.91 (t, $^3J_{H-H}$ = 7.1 Hz, 3H, CH_2CH_3); for **4c**, 3.93 (q, $^3J_{H-H}$ = 7.1 Hz, 4H, CH_2), 3.76 (q, br, $^3J_{H-H}$ = 7.1 Hz, 2H, CH_2), 2.40 (s, 3H, CCH_3), 1.89 (s, 3H, CCH_3), 1.70 (s, 3H, CCH_3), 1.10 (t, $^3J_{H-H}$ = 6.9 Hz, 3H, CH_2CH_3), 1.05 (t, $^3J_{H-H}$ = 6.9 Hz, 3H, CH_2CH_3), 0.92 (t, $^3J_{H-H}$ = 7.1 Hz, 3H, CH_2CH_3). Anal. Calcd (found) for **4a**: C, 47.12 (47.85); H, 4.13 (4.91). Calcd (found) for **4b**: C, 47.12 (48.01); H, 4.13 (4.83). Calcd (found) for **3c**: C, 47.12 (47.54); H, 4.13 (4.34).

Crystallographic Analysis. Crystals of compounds **2** and **4a–c** suitable for X-ray diffraction analysis were grown from solutions in CH_2Cl_2/hexane (1/1) solvent mixtures by cooling to −3 °C. Crystals of compound **3** were grown from solutions in diethyl ether by cooling to −14 °C. All crystals that were used in diffraction intensity measurements were mounted in thin-walled glass capillaries. Diffraction measurements were made on a Rigaku AFC6S fully automated four-circle diffractometer by using graphite-monochromated Mo Kα radiation. Unit cells were determined and refined from 15 randomly selected reflections obtained by using the AFC6 automatic search, center, index, and least-squares routines. All data processing was performed on a Digital Equipment Corp. VAXstation 3520 computer by using the TEXSAN structure solving program library (version 5.0) obtained from Molecular Structure Corp., The Woodlands, TX. Neutral atom scattering factors were calculated by the standard procedures.[6a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[6b] Lorentz/polarization (Lp) and empirical absorption corrections based on three azimuthal scans were applied to the data for each structure. Full-matrix least-squares refinements minimized the function $\sum_{hkl} w(|F_o| - |F_c|)^2$, where $w = 1/\sigma(F_o)^2$, $\sigma(F_o) = \sigma(F_o^2)/2F_o$, and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (0.02I_{net})^2]^{1/2}/Lp$.

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[5] Brandsma, L. *Preparative Acetylenic Chemistry*; Elsevier: Barking, Essex, England, 1971.

[6] (a) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1975; Vol. IV, Table 2.2B, pp 99–101. (b) *Ibid.*, Table 2.3.1, pp 149–150.

Table 1. Crystallographic Data for Compounds 2, 3, and 4a−c

	2	**3**	**4a**	**4b**	**4c**
empirical formula	$Mn_2O_{14}C_{22}H_{16}$	$Mn_2O_{12}C_{20}H_{16}$	$Mn_2O_{11}C_{23}H_{24}$	$Mn_2O_{11}C_{23}H_{24}$	$Mn_2O_{11}C_{23}H_{24}$
fw	614.24	558.22	586.31	586.31	586.31
cryst syst	triclinic	monoclinic	triclinic	monoclinic	orthorhombic
lattice params					
a (Å)	12.056(2)	8.532(2)	10.570(4)	12.080(3)	13.876(3)
b (Å)	18.016(3)	19.431(4)	13.930(6)	12.929(5)	17.443(3)
c (Å)	9.729(2)	14.331(3)	9.497(3)	16.723(4)	10.871(2)
α (deg)	91.96(1)		91.57(3)		
β (deg)	111.82(1)	92.34(2)	98.48(3)	99.22(2)	
γ (deg)	85.13(2)		72.63(4)		
V (Å^3)	1955(1)	2372.9(8)	1319.8(9)	2578(1)	2631(2)
space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P2_12_12_1$ (No. 19)
Z	3	4	2	4	4
D_{calc} (g/cm^3)	1.56	1.56	1.48	1.51	1.48
μ(Mo Kα) cm^{-1}	9.95	10.79	9.71	9.94	9.74
temp (°C)	20	20	23	23	23
$2\theta_{max}$ (deg)	45.0	40.0	40.0	40.0	46.0
no. of obs rflns ($I > 3\sigma(I)$)	4273	1562	1556	1473	1574
no. of variables	514	307	325	325	325
residuals: R, R_w	0.029, 0.034	0.036, 0.036	0.042, 0.045	0.040, 0.041	0.035, 0.039
shift/err in final cycle	0.05	0.00	0.01	0.00	0.00
largest peak in final diff Fourier (e/Å^3)	0.31	0.27	0.24	0.27	0.25
abs Cor	empirical	none	empirical	none	empirical
transmissn coeff, max/min	1.0/0.86		1.0/0.87		1.0/0.86

Each structure was solved by a combination of direct methods (MITHRIL) and difference Fourier analyses. For all five structural analyses, all non-hydrogen atoms were refined with anisotropic thermal parameters. The positions of all hydrogen atoms were calculated by assuming idealized geometries: C−H = 0.95 Å. The scattering contributions of the hydrogen atoms were added to the structure factor calculations, but their positions were not refined. Crystal data and results of the analyses are listed in Table 1.

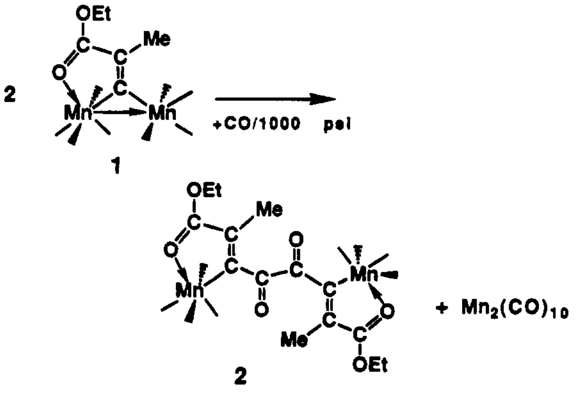
Compounds **2** and **4a** crystallized in a triclinic crystal system. The space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of the structure in each case. The crystal of **2** is somewhat unusual in that it contains three molecules in the unit cell and one and a half molecules in the asymmetric crystal unit (i.e., one of the molecules lies on a center of symmetry).

Compounds **3** and **4b** crystallized in the monoclinic crystal system. The space groups $P2_1/n$ and $P2_1/c$, respectively, were identified uniquely from the patterns of systematic absences observed in the data.

Compound **4c** crystallized in the orthorhombic crystal system. Its space group, $P2_12_12_1$, was identified uniquely from the patterns of systematic absences observed in the data.

Results and Discussion

The reaction of **1a** with CO at 1000 psi and 87 °C for 12 h gave the new compound $(OC)_4Mn[(EtO_2C)MeC{=}CC{=}OC{=}OC{=}CMe(CO_2Et)]Mn(CO)_4$ (**2**) in 59% yield and $Mn_2(CO)_{10}$ in 128% yield. The yields were calculated according to eq 2. The excess of $Mn_2(CO)_{10}$ can be explained by the transformation of some of compound **2** into $Mn_2(CO)_{10}$ by loss of the organic ligand. This was confirmed by an independent treatment of **2** with CO (1100 psi at 105 °C), which gave $Mn_2(CO)_{10}$ in 33% yield after 16 h. The ^{1}H NMR spectrum of **2** is very simple (δ 3.53 (q, $^3J_{H-H}$ = 7.1 Hz, 4H, CH_2), 1.99 (s, 6H, CCH_3), 0.64 (t, $^3J_{H-H}$ = 7.1 Hz, 6H, CH_2CH_3)) and does not reveal the true structural complexity of the molecule. Full details of the structure were provided by a single-crystal X-ray diffraction analysis. Curiously, compound **2** crystallizes in the triclinic space group with one and a half molecules in the unit cell. One molecule, **2A**, lies in a completely general position while the other, **2B**,



(2)

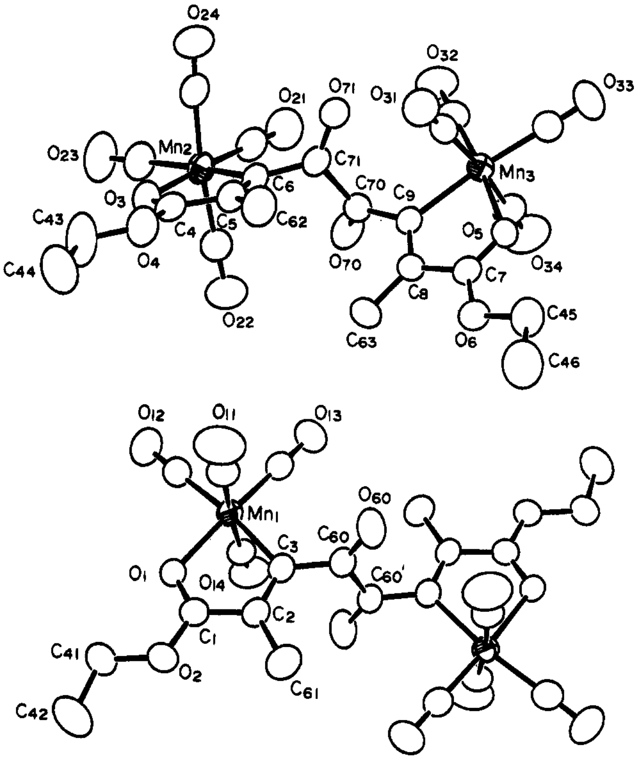


Figure 1. ORTEP diagrams of molecules **2A** (top) and **2B** (bottom) of $(OC)_4Mn[(EtO_2C)MeC{=}CC{=}OC{=}OC{=}CMe(CO_2Et)]Mn(CO)_4$ (**2**) showing 50% probability thermal ellipsoids.

Table 2. Positional Parameters and *B*(eq) Values for 2

atom	*x*	*y*	*z*	*B*(eq) (Å²)
Mn(1)	0.38842(04)	0.32221(02)	0.91425(05)	3.12(2)
Mn(2)	−0.03214(04)	0.35407(02)	0.26833(05)	3.40(2)
Mn(3)	0.19533(04)	−0.00420(02)	0.38627(05)	3.11(2)
O(1)	0.43751(17)	0.27622(10)	1.12323(20)	3.20(8)
O(2)	0.49832(18)	0.30455(11)	1.3645(02)	3.7(1)
O(3)	−0.09897(18)	0.38504(11)	0.0492(02)	4.1(1)
O(4)	−0.1411(02)	0.34160(13)	−0.1803(02)	5.3(1)
O(5)	0.26900(17)	−0.04757(10)	0.2365(02)	3.46(9)
O(6)	0.32392(18)	−0.01636(11)	0.0515(02)	4.0(1)
O(11)	0.1425(02)	0.36207(17)	0.9148(03)	7.0(1)
O(12)	0.3260(02)	0.17685(13)	0.7605(03)	6.2(1)
O(13)	0.3204(02)	0.39727(14)	0.6277(03)	5.8(1)
O(14)	0.6382(02)	0.30109(15)	0.9194(03)	6.2(1)
O(21)	0.0725(02)	0.30084(14)	0.5756(03)	6.0(1)
O(22)	0.2134(02)	0.37701(15)	0.2769(03)	6.3(1)
O(23)	−0.0890(03)	0.51069(14)	0.3431(03)	6.8(1)
O(24)	−0.2640(02)	0.30634(15)	0.2672(03)	5.9(1)
O(31)	−0.0461(02)	−0.01232(13)	0.1439(03)	5.1(1)
O(32)	0.0957(02)	0.07164(14)	0.5918(03)	5.6(1)
O(33)	0.1888(02)	−0.15463(14)	0.5005(03)	6.3(1)
O(34)	0.4354(02)	0.02102(17)	0.6137(03)	7.2(1)
O(60)	0.3493(02)	0.53016(12)	0.9311(03)	5.9(1)
O(70)	0.22392(19)	0.20972(12)	0.3913(03)	5.0(1)
O(71)	−0.04365(19)	0.14271(12)	0.2686(03)	5.0(1)
C(1)	0.4649(02)	0.32327(16)	1.2245(03)	3.2(1)
C(2)	0.4635(03)	0.40178(15)	1.1927(03)	3.3(1)
C(3)	0.4352(02)	0.41417(15)	1.0481(03)	3.2(1)
C(4)	−0.1018(03)	0.33256(19)	−0.0368(04)	3.9(1)
C(5)	−0.0594(03)	0.25690(16)	0.0178(03)	3.6(1)
C(6)	−0.0194(02)	0.25423(15)	0.1658(03)	3.1(1)
C(7)	0.2806(02)	0.00033(16)	0.1554(03)	3.2(1)
C(8)	0.2451(02)	0.07941(15)	0.1698(03)	3.1(1)
C(9)	0.2025(02)	0.09012(15)	0.2788(03)	2.9(1)
C(11)	0.2346(03)	0.34579(18)	0.9136(03)	4.2(2)
C(12)	0.3498(03)	0.23226(19)	0.8213(03)	4.1(1)
C(13)	0.3466(03)	0.36820(17)	0.7405(04)	3.9(1)
C(14)	0.5441(03)	0.30826(17)	0.9216(03)	3.8(1)
C(21)	0.0322(03)	0.32202(18)	0.4558(04)	4.1(1)
C(22)	0.1198(03)	0.36932(17)	0.2742(03)	4.1(1)
C(23)	−0.0656(03)	0.45028(20)	0.3171(04)	4.7(2)
C(24)	−0.1787(03)	0.32616(18)	0.2622(03)	3.9(1)
C(31)	0.0435(03)	−0.00970(15)	0.2377(04)	3.5(1)
C(32)	0.1327(03)	0.04175(18)	0.5105(03)	3.8(1)
C(33)	0.1923(03)	−0.09731(19)	0.4571(03)	4.2(2)
C(34)	0.3457(03)	0.01060(19)	0.5255(04)	4.4(2)
C(41)	0.5058(03)	0.22578(18)	1.3994(03)	4.3(1)
C(42)	0.5445(04)	0.2196(02)	1.5621(04)	6.3(2)
C(43)	−0.1786(04)	0.4185(02)	−0.2341(04)	8.1(2)
C(44)	−0.1987(05)	0.4217(03)	−0.3859(05)	8.8(3)
C(45)	0.3518(04)	−0.09517(19)	0.0277(04)	5.7(2)
C(46)	0.3811(05)	−0.1024(02)	−0.1031(05)	8.2(3)
C(60)	0.4372(03)	0.48860(16)	0.9927(03)	3.5(1)
C(61)	0.4938(03)	0.45805(18)	1.3161(04)	5.1(2)
C(62)	−0.0658(03)	0.19388(19)	−0.0899(04)	5.1(2)
C(63)	0.2572(03)	0.13531(17)	0.0660(03)	4.2(1)
C(70)	0.1596(03)	0.16478(16)	0.3129(03)	3.3(1)
C(71)	0.0229(03)	0.18373(16)	0.2470(03)	3.4(1)

Table 3. Intramolecular Distances for the Two Independent Molecules of 2[a]

Mn(1)—O(1)	2.076(2)	C(2)—C(3)	1.340(4)
Mn(1)—C(3)	2.055(3)	C(2)—C(61)	1.502(4)
Mn(2)—O(3)	2.057(2)	C(3)—C(60)	1.468(4)
Mn(2)—C(6)	2.049(3)	C(4)—C(5)	1.460(4)
Mn(3)—O(5)	2.071(2)	C(5)—C(6)	1.339(4)
Mn(3)—C(9)	2.050(3)	C(5)—C(62)	1.505(4)
O(1)—C(1)	1.244(3)	C(6)—C(71)	1.469(4)
O(2)—C(1)	1.316(3)	C(7)—C(8)	1.470(4)
O(2)—C(41)	1.458(4)	C(8)—C(9)	1.342(4)
O(3)—C(4)	1.235(4)	C(8)—C(63)	1.503(4)
O(4)—C(4)	1.308(4)	C(9)—C(70)	1.471(4)
O(4)—C(43)	1.471(5)	C(41)—C(42)	1.479(5)
O(5)—C(7)	1.239(3)	C(43)—C(44)	1.407(6)
O(6)—C(7)	1.316(3)	C(45)—C(46)	1.441(5)
O(6)—C(45)	1.462(4)	C(60)—C(60′)	1.556(6)
O(60)—C(60)	1.211(3)	C(70)—C(71)	1.542(4)
O(70)—C(70)	1.210(3)	Mn—C (av)	1.837(4)
O(71)—C(71)	1.213(3)	O—C (av)	1.140(4)
C(1)—C(2)	1.456(4)		

[a] Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Table 4. Intramolecular Bond Angles for the Two Independent Molecules of 2[a]

O(1)—Mn(1)—C(3)	78.3(1)	Mn(2)—C(6)—C(71)	122.8(2)
O(3)—Mn(2)—C(6)	78.5(1)	C(5)—C(6)—C(71)	121.9(3)
O(5)—Mn(3)—C(9)	78.5(1)	O(5)—C(7)—O(6)	122.4(3)
Mn(1)—O(1)—C(1)	113.2(2)	O(5)—C(7)—C(8)	121.3(3)
C(1)—O(2)—C(41)	118.0(2)	O(6)—C(7)—C(8)	116.3(3)
Mn(2)—O(3)—C(4)	113.6(2)	C(7)—C(8)—C(9)	111.3(2)
C(4)—O(4)—C(43)	116.2(3)	C(7)—C(8)—C(63)	119.6(2)
Mn(3)—O(5)—C(7)	113.3(2)	C(9)—C(8)—C(63)	129.1(3)
C(7)—O(6)—C(45)	117.4(2)	Mn(3)—C(9)—C(8)	115.6(2)
O(1)—C(1)—O(2)	121.9(3)	Mn(3)—C(9)—C(70)	123.1(2)
O(1)—C(1)—C(2)	121.0(3)	C(8)—C(9)—C(70)	121.3(3)
O(2)—C(1)—C(2)	117.1(3)	O(2)—C(41)—C(42)	107.5(3)
C(1)—C(2)—C(3)	112.2(3)	O(4)—C(43)—C(44)	110.0(4)
C(1)—C(2)—C(61)	120.2(3)	O(6)—C(45)—C(46)	108.7(3)
C(3)—C(2)—C(61)	127.5(3)	O(60)—C(60)—C(3)	124.9(3)
Mn(1)—C(3)—C(2)	114.9(2)	O(60)—C(60)—C(60′)	119.4(3)
Mn(1)—C(3)—C(60)	123.7(2)	C(3)—C(60)—C(60′)	115.6(3)
C(2)—C(3)—C(60)	121.4(3)	O(70)—C(70)—C(9)	124.2(3)
O(3)—C(4)—O(4)	122.3(3)	O(70)—C(70)—C(71)	119.6(3)
O(3)—C(4)—C(5)	121.2(3)	C(9)—C(70)—C(71)	116.2(2)
O(4)—C(4)—C(5)	116.5(3)	O(71)—C(71)—C(6)	123.2(3)
C(4)—C(5)—C(6)	111.5(3)	O(71)—C(71)—C(70)	120.0(3)
C(4)—C(5)—C(62)	120.0(3)	C(6)—C(71)—C(70)	116.8(3)
C(6)—C(5)—C(62)	128.5(3)	Mn—C—O (av)	178.0 (3)
Mn(2)—C(6)—C(5)	115.2(2)		

[a] Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

lies on a center of symmetry. Although both molecules have the same exact formula, they are conformational isomers. ORTEP diagrams of the molecular structures of **2A** and **2B** are shown in Figure 1. Final atomic positional parameters are listed in Table 2. Selected bond distances and angles are listed in Tables 3 and 4, respectively. Both molecules contain two $Mn(CO)_4$ groups. Each manganese group contains a carboxylate-substituted alkenyl group in which the carboxylate group is coordinated to the manganese atom as found in **1**. The Mn—O and Mn—C distances (Mn(2)—O(3) = 2.057(2) Å, Mn(3)—O(5) = 2.071(2) Å, Mn(1)—O(1) = 2.076(2) Å; Mn(2)—C(6) = 2.049(3) Å, Mn(3)—C(9) = 2.050(3) Å, Mn(1)—C(3) = 2.055(3) Å) are similar to those found in **1a** and **1b** (Mn—O = 2.068(2) and 2.024(2) Å and Mn—C = 2.125(2) and 2.105(3) Å, respectively).[3a] There is a methyl group on the β-carbon and a CO group on the α-carbon. The halves of the molecule are joined by a C—C single bond between the two CO groups. The C—C bond distance between the two C=O groups is C(70)—C(71) = 1.542(4) Å in **2A** and C(60)—C(60′) = 1.556(6) Å in **2B**. These distances are similar to those found for coupled CO groups in other organometallic complexes: Cp′(CO)(NO)Mn—C(O)C(O)Tol, 1.527(7) Å;[7] $Ru(dmpm)(CO)[\mu\text{-}C_2(CO_2Me)_2][COCOC(CO_2Me)_2]$, 1.57(1) Å;[8] $Pt(PPh_3)_2Cl(COCOPh)$, 1.560 and 1.667 Å (the positions of these CO groups were not refined).[9] The distance between the two carbonyl carbon atoms in the molecule dibenzyl, $(PhC{=}O)_2$, is 1.523(7) Å.[10] Molecule **2B** is completely centrosymmetric, with

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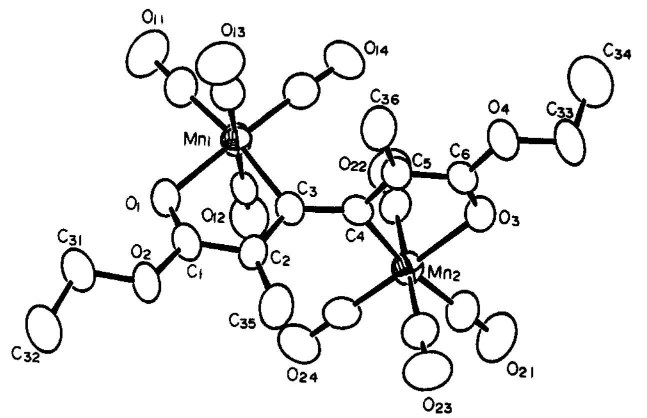


Figure 2. ORTEP diagram of $(OC)_4Mn[(EtO_2C)MeC{=}CC{=}CMe(CO_2Et)]Mn(CO)_4$ (**3**) showing 50% probability thermal ellipsoids.

Table 5. Positional Parameters and *B*(eq) Values for 3

atom	*x*	*y*	*z*	*B*(eq) (Å^2)
Mn(1)	0.70978(11)	0.41455(05)	0.16839(08)	3.46(5)
Mn(2)	0.82349(11)	0.21668(05)	0.32544(07)	3.29(5)
O(1)	0.8705(05)	0.4859(02)	0.2188(03)	3.7(2)
O(2)	1.1190(05)	0.4978(02)	0.2723(03)	4.3(3)
O(3)	0.8223(05)	0.1429(02)	0.2231(03)	3.5(2)
O(4)	0.8757(05)	0.1254(02)	0.0736(03)	4.6(3)
O(11)	0.4683(06)	0.5208(03)	0.1193(04)	7.3(4)
O(12)	0.5688(06)	0.3955(03)	0.3536(04)	5.5(3)
O(13)	0.8626(06)	0.4362(03)	−0.0141(04)	6.5(3)
O(14)	0.5171(06)	0.3031(03)	0.0867(04)	6.0(3)
O(21)	0.7399(06)	0.1121(03)	0.4664(04)	6.3(3)
O(22)	0.4827(06)	0.2434(03)	0.2856(04)	5.8(3)
O(23)	1.1622(06)	0.1876(03)	0.3696(04)	6.0(3)
O(24)	0.8535(06)	0.3297(03)	0.4605(04)	6.2(3)
C(1)	0.9978(09)	0.4585(03)	0.2437(05)	3.5(4)
C(2)	1.0224(08)	0.3857(03)	0.2430(05)	3.2(4)
C(3)	0.8939(07)	0.3499(03)	0.2118(04)	2.8(4)
C(4)	0.8822(06)	0.2764(03)	0.2108(05)	2.7(3)
C(5)	0.9021(07)	0.2371(03)	0.1340(05)	3.0(4)
C(6)	0.8651(07)	0.1657(04)	0.1471(06)	3.1(4)
C(11)	0.5635(09)	0.4805(04)	0.1383(05)	4.7(4)
C(12)	0.6252(08)	0.4028(03)	0.2830(06)	3.5(4)
C(13)	0.8054(08)	0.4262(04)	0.0554(06)	4.5(4)
C(14)	0.5903(08)	0.3477(04)	0.1193(05)	4.1(4)
C(21)	0.7727(08)	0.1523(04)	0.4125(06)	4.3(4)
C(22)	0.6127(09)	0.2349(03)	0.2982(05)	3.8(4)
C(23)	1.0365(09)	0.1986(04)	0.3512(05)	4.1(4)
C(24)	0.8377(08)	0.2851(04)	0.4073(05)	4.0(4)
C(31)	1.1002(08)	0.5719(04)	0.2672(05)	5.1(4)
C(32)	1.2336(10)	0.6026(04)	0.3202(06)	6.2(5)
C(33)	0.8371(10)	0.0539(04)	0.0837(06)	5.6(5)
C(34)	0.7101(14)	0.0358(05)	0.0233(08)	10.4(7)
C(35)	1.1790(08)	0.3560(04)	0.2729(06)	5.5(4)
C(36)	0.9558(09)	0.2609(03)	0.0411(05)	4.9(4)

the crystallographic center of symmetry lying at the midpoint of the C(60)—C(60′) bond. Molecule **2B** has approximate C_2 symmetry, but this is not crystallographically required. The presence of only one set of resonances in the ^1H NMR spectrum in solution indicates that the two isomers are in rapid equilibrium on the NMR time scale at room temperature.

Table 6. Intramolecular Distances for 3[a]

Mn(1)—O(1)	2.059(4)	C(2)—C(3)	1.358(8)
Mn(1)—C(3)	2.086(6)	C(2)—C(35)	1.501(9)
Mn(2)—O(3)	2.051(5)	C(3)—C(4)	1.432(8)
Mn(2)—C(4)	2.090(6)	C(4)—C(5)	1.355(8)
O(1)—C(1)	1.249(7)	C(5)—C(6)	1.437(9)
O(2)—C(1)	1.336(7)	C(5)—C(36)	1.499(9)
O(2)—C(31)	1.450(8)	C(31)—C(32)	1.47(1)
O(3)—C(6)	1.244(7)	C(33)—C(34)	1.40(1)
O(4)—C(6)	1.319(7)	Mn—C (av)	1.852(9)
O(4)—C(33)	1.436(8)	O—C (av)	1.144(8)
C(1)—C(2)	1.429(9)		

[a] Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Table 7. Intramolecular Bond Angles for 3[a]

O(1)—Mn(1)—C(3)	79.5(2)	C(2)—C(3)—C(4)	124.7(6)
O(3)—Mn(2)—C(4)	79.6(2)	Mn(2)—C(4)—C(3)	124.4(5)
Mn(1)—O(1)—C(1)	111.9(4)	Mn(2)—C(4)—C(5)	111.6(5)
C(1)—O(2)—C(31)	118.0(5)	C(3)—C(4)—C(5)	124.0(6)
Mn(2)—O(3)—C(6)	112.6(4)	C(4)—C(5)—C(6)	113.8(6)
C(6)—O(4)—C(33)	118.1(6)	C(4)—C(5)—C(36)	126.9(6)
O(1)—C(1)—O(2)	119.8(6)	C(6)—C(5)—C(36)	119.3(6)
O(1)—C(1)—C(2)	123.1(6)	O(3)—C(6)—O(4)	121.2(6)
O(2)—C(1)—C(2)	117.1(7)	O(3)—C(6)—C(5)	122.1(7)
C(1)—C(2)—C(3)	113.1(6)	O(4)—C(6)—C(5)	116.6(7)
C(1)—C(2)—C(35)	120.5(6)	O(2)—C(31)—C(32)	107.2(6)
C(3)—C(2)—C(35)	126.4(6)	O(4)—C(33)—C(34)	110.8(7)
Mn(1)—C(3)—C(2)	112.2(5)	Mn—C—O (av)	177.7(7)
Mn(1)—C(3)—C(4)	123.1(5)		

[a] Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

When complex **1a** was allowed to react with MeC≡COEt in the presence of CO (1000 psi), the new compound $(OC)_4Mn[(EtO_2C)MeC{=}CC{=}CMe(CO_2Et)]Mn(CO)_4$ (**3**; 72% yield) was obtained as the only isolable product. Compound **3** was characterized by a combination of IR, ^1H NMR, and single-crystal X-ray diffraction analyses. An ORTEP diagram of the molecular structure of **3** is shown in Figure 2. Final atomic positional parameters are listed in Table 5. Selected bond distances and angles are listed in Tables 6 and 7, respectively. The molecule contains a six-carbon chain consisting of the atoms C(35), C(2), C(3), C(4), C(5), and C(36). There are C—C double bonds between C(2) and C(3) (1.358(8) Å) and C(4) and C(5) (1.355(8) Å). Metal substituents are σ-bonded to atoms C(3) and C(4), and CO_2Et groups are located on C(2) and C(5). Thus, the six-carbon chain could be viewed as a 3,4-dimetallo-2,5-bis(ethoxycarbonyl)-2,4-hexadiene. The C(3)—C(4) bond (1.432(8) Å) is slightly shorter than a C—C single bond. The carbonyl groups of both carboxylate groups are coordinated to the manganese atoms to form five-membered metallacyclic rings. The Mn—O and Mn—C distances (Mn(1)—O(1) = 2.059(4) Å, Mn(2)—O(3) = 2.051(5) Å; Mn(1)—C(3) = 2.086(6) Å, Mn(2)—C(4) = 2.090(6) Å) are similar to those found in **1a,b** and **2** (see above). The planes of the two metallacyclic rings are not coplanar, and the dihedral angle between them is 81.09°. Each manganese atom also contains four linear terminal carbonyl ligands. Overall, the molecule possesses C_2 symmetry, with the C_2 axis bisecting the C(3)—C(4) bond, but this symmetry is not crystallographically imposed. As a result, the ^1H NMR spectrum shows only one resonance for the equivalent methyl groups C(35) and C(36) (δ 2.01 (s, 6H)) and one triplet for the methyl groups C(32) and C(34) (δ 0.74). The protons on the methylene groups C(31) and C(33) are diastereotopic, as expected for a chiral molecule such as this (δ =3.76 (dq, 2H), 3.62 (dq, 2H) with $^2J_{H-H}$ = 10.8 Hz, $^3J_{H-H}$ = 7.2 Hz). This indicates that there is also a hindered rotation about the C(3)—C(4) bond that is slow on the NMR timescale at 25 °C, since a facile rotation about this bond would lead to an interchange of the environments of these protons.

When compound **1a** was allowed to react with MeC≡COEt at 40 °C in the absence of CO, three

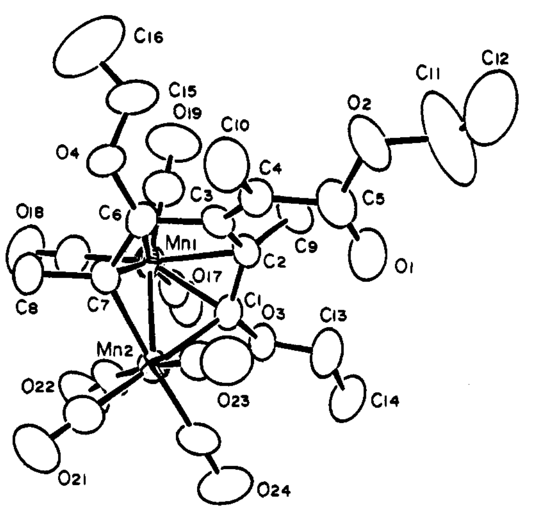


Figure 3. ORTEP diagram of $Mn_2(CO)_7$\{C(Me)C(OEt)C[=C(Me)(CO_2Et)]C(Me)C(OEt)\} (**4a**) showing 50% probability thermal ellipsoids.

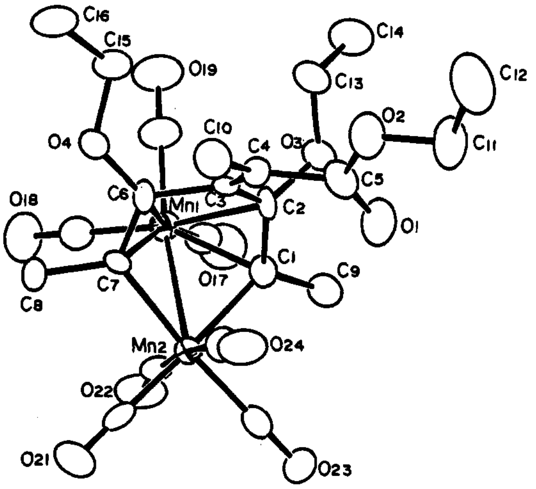


Figure 4. ORTEP diagram of $Mn_2(CO)_7$\{C(Me)C(OEt)C[=C(Me)(CO_2Et)]C(OEt)C(Me)\} (**4b**) showing 50% probability thermal ellipsoids.

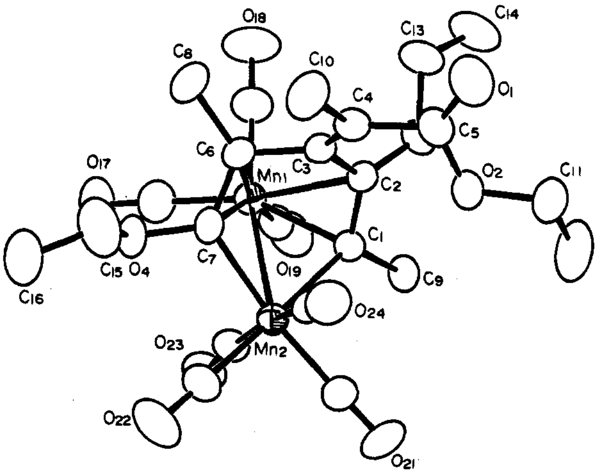


Figure 5. ORTEP diagram of $Mn_2(CO)_7$\{C(OEt)C(Me)C[=C(Me)(CO_2Et)]C(Me)C(OEt)\} (**4c**) showing 50% probability thermal ellipsoids.

isomeric products were formed in low yields: $Mn_2(CO)_7$\{C(Me)C(OEt)C[=C(Me)(CO_2Et)]C(Me)C(OEt)\} (**4a**; 5% yield), $Mn_2(CO)_7$\{C(Me)C(OEt)C[=C(Me)(CO_2Et)]C(OEt)C(Me)\} (**4b**; 12% yield), and $Mn_2(CO)_7$\{C(OEt)C(Me)C[=C(Me)(CO_2Et)]C(Me)C(OEt)\} (**4c**; 10% yield).

Table 8. Positional Parameters and *B*(eq) for 4a

atom	*x*	*y*	*z*	*B*(eq) (Å^2)
Mn(1)	0.63356(13)	0.63653(10)	0.75260(13)	4.1(1)
Mn(2)	0.47033(13)	0.82620(10)	0.72369(13)	3.8(1)
O(1)	0.7363(08)	0.8612(06)	1.1789(07)	7.6(6)
O(2)	0.9546(08)	0.8255(08)	1.1957(08)	11.5(8)
O(3)	0.4633(05)	0.7168(04)	0.9833(06)	4.3(4)
O(4)	0.8894(06)	0.7177(05)	0.6877(06)	5.5(4)
O(17)	0.4684(08)	0.5153(05)	0.8354(07)	7.1(6)
O(18)	0.6245(08)	0.5427(06)	0.4693(08)	8.9(6)
O(19)	0.8667(09)	0.4653(07)	0.8533(10)	10.4(7)
O(21)	0.3659(07)	0.9597(06)	0.4682(08)	7.6(6)
O(22)	0.3245(07)	0.6987(06)	0.5580(08)	8.8(6)
O(23)	0.5745(07)	0.9898(05)	0.8586(08)	6.9(5)
O(24)	0.2180(08)	0.9087(06)	0.8436(09)	8.6(6)
C(1)	0.5520(09)	0.7406(06)	0.9074(08)	3.5(5)
C(2)	0.6873(09)	0.7111(06)	0.9619(08)	3.9(6)
C(3)	0.7724(08)	0.7609(06)	0.8983(09)	3.8(6)
C(4)	0.8419(09)	0.8168(07)	0.9703(10)	4.6(6)
C(5)	0.8352(12)	0.8373(09)	1.1250(11)	6.3(8)
C(6)	0.7697(09)	0.7429(06)	0.7432(09)	4.1(6)
C(7)	0.6528(08)	0.7655(06)	0.6509(08)	3.7(5)
C(8)	0.6631(09)	0.7694(07)	0.4947(09)	5.3(7)
C(9)	0.7480(09)	0.6434(07)	1.0917(09)	5.6(6)
C(10)	0.9236(10)	0.8724(09)	0.9073(10)	7.4(8)
C(11)	0.967(02)	0.833(03)	1.3476(19)	24(3)
C(12)	1.032(02)	0.8750(17)	1.4064(20)	17(2)
C(13)	0.4530(11)	0.7548(09)	1.1212(11)	7.5(9)
C(14)	0.3318(12)	0.7557(10)	1.1684(11)	9(1)
C(15)	1.0037(12)	0.6462(10)	0.7613(13)	9(1)
C(16)	1.0939(19)	0.6025(17)	0.685(02)	25(2)
C(17)	0.5310(10)	0.5628(07)	0.8059(09)	5.1(7)
C(18)	0.6270(10)	0.5819(07)	0.5786(11)	5.8(7)
C(19)	0.7746(11)	0.5348(08)	0.8119(11)	6.2(7)
C(21)	0.4084(09)	0.9081(08)	0.5679(11)	5.2(7)
C(22)	0.3917(10)	0.7392(07)	0.6266(10)	5.2(7)
C(23)	0.5390(09)	0.9251(08)	0.8118(10)	4.9(7)
C(24)	0.3179(10)	0.8767(07)	0.7987(11)	5.7(7)

Table 9. Intramolecular Distances for 4a[a]

Mn(1)—Mn(2)	2.674(2)	O(1)—C(5)	1.20(1)
Mn(1)—C(1)	2.146(8)	O(2)—C(5)	1.32(1)
Mn(1)—C(2)	2.367(7)	O(2)—C(11)	1.46(1)
Mn(1)—C(6)	2.413(8)	O(3)—C(2)	1.375(9)
Mn(1)—C(7)	2.107(8)	O(3)—C(13)	1.44(1)
Mn(1)—C(17)	1.79(1)	O(4)—C(6)	1.372(9)
Mn(1)—C(18)	1.81(1)	O(4)—C(15)	1.44(1)
Mn(1)—C(19)	1.76(1)	C(1)—C(2)	1.37(1)
Mn(2)—C(1)	2.086(8)	C(2)—C(3)	1.48(1)
Mn(2)—C(7)	2.087(8)	C(3)—C(4)	1.33(1)
Mn(2)—C(21)	1.81(1)	C(3)—C(6)	1.51(1)
Mn(2)—C(22)	1.86(1)	C(4)—C(5)	1.51(1)
Mn(2)—C(23)	1.83(1)	C(6)—C(7)	1.37(1)
Mn(2)—C(24)	1.84(1)	O—C (av)	1.15(1)
Mn(1)—C(3)	2.803(8)		

[a] Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

All three products were characterized by IR, ^{1}H NMR, and single-crystal X-ray diffraction analyses. ORTEP diagrams of the molecular structures of **4a–c** are shown in Figures 3–5, respectively. Final atomic positional parameters are listed in Tables 8–10. Selected bond distances are listed in Tables 11–13, respectively, and selected bond angles are listed in Tables 14–16, respectively. All three compounds have similar structures. Each molecule contains a $Mn_2(CO)_7$ group in which the manganese atoms are mutually bonded (Mn(1)—Mn(2) = 2.674(2), 2.685(2), and 2.677(2) Å for **4a–c**, respectively) and a metallacyclohexadiene group that includes the atoms Mn(2), C(1), C(2), C(3), C(6), and C(7). The ring was formed by the addition and coupling of two MeC≡COEt molecules to the vinylidene carbon atom of **1a**. The C—C double bonds lie at the sites C(1)—C(2) and C(6)—C(7) (1.37(1) and 1.37(1) Å for **4a**, 1.39(1)

Table 10. Intramolecular Bond Angles for 4a[a]

Mn(2)—Mn(1)—C(1)	49.8(2)	C(2)—C(3)—C(6)	109.5(7)
Mn(2)—Mn(1)—C(7)	50.1(2)	C(4)—C(3)—C(6)	124.7(7)
Mn(1)—Mn(2)—C(1)	51.8(2)	C(3)—C(4)—C(5)	118.9(8)
Mn(1)—Mn(2)—C(7)	50.7(2)	C(3)—C(4)—C(10)	125.2(8)
Mn(1)—Mn(2)—C(21)	126.7(3)	C(5)—C(4)—C(10)	115.3(8)
Mn(1)—Mn(2)—C(22)	69.2(3)	O(1)—C(5)—O(2)	124(1)
Mn(1)—Mn(2)—C(23)	129.5(3)	O(1)—C(5)—C(4)	124.6(9)
Mn(1)—Mn(2)—C(24)	118.0(3)	O(2)—C(5)—C(4)	111(1)
C(5)—O(2)—C(11)	115.5(8)	O(4)—C(6)—C(3)	118.9(7)
C(2)—O(3)—C(13)	119.3(6)	O(4)—C(6)—C(7)	118.7(7)
C(6)—O(4)—C(15)	120.0(6)	C(3)—C(6)—C(7)	121.4(8)
Mn(1)—C(1)—Mn(2)	78.4(3)	Mn(1)—C(7)—Mn(2)	79.2(3)
Mn(1)—C(1)—C(2)	81.3(5)	Mn(1)—C(7)—C(6)	85.2(5)
Mn(1)—C(1)—C(9)	123.0(6)	Mn(1)—C(7)—C(8)	122.2(6)
Mn(2)—C(1)—C(2)	120.1(6)	Mn(2)—C(7)—C(6)	121.0(6)
Mn(2)—C(1)—C(9)	121.9(6)	Mn(2)—C(7)—C(8)	121.1(6)
C(2)—C(1)—C(9)	116.5(7)	C(6)—C(7)—C(8)	115.3(7)
O(3)—C(2)—C(1)	117.7(7)	O(2)—C(11)—C(12)	108(1)
O(3)—C(2)—C(3)	119.2(7)	O(3)—C(13)—C(14)	107.6(8)
C(1)—C(2)—C(3)	122.2(7)	O(4)—C(15)—C(16)	107.8(7)
C(2)—C(3)—C(4)	125.2(7)	Mn—C—O (av)	175.4(9)

[a] Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Table 11. Positional Parameters and *B*(eq) Values for 4b

atom	*x*	*y*	*z*	*B*(eq) (Å^2)
Mn(1)	0.82457(11)	0.29453(10)	0.35230(08)	2.88(6)
Mn(2)	0.83193(10)	0.14782(10)	0.24057(08)	2.55(6)
O(1)	0.4547(05)	0.1925(06)	0.1801(04)	5.3(4)
O(2)	0.3720(05)	0.3215(05)	0.1041(04)	4.8(3)
O(3)	0.5514(05)	0.2802(04)	0.3329(03)	3.6(3)
O(4)	0.7759(04)	0.4735(05)	0.2017(03)	3.2(3)
O(17)	0.8417(06)	0.1920(06)	0.5106(04)	6.3(4)
O(18)	1.0551(06)	0.3699(06)	0.4044(04)	6.4(4)
O(19)	0.7526(06)	0.4775(06)	0.4329(04)	6.2(4)
O(21)	1.0130(06)	0.1142(05)	0.1426(05)	6.6(4)
O(22)	1.0063(06)	0.0924(06)	0.3816(04)	6.1(4)
O(23)	0.7745(05)	−0.0753(05)	0.2439(04)	4.8(4)
O(24)	0.6757(06)	0.1652(05)	0.0841(04)	5.1(4)
C(1)	0.7032(06)	0.1790(06)	0.3066(05)	2.4(4)
C(2)	0.6374(06)	0.2651(07)	0.2894(05)	2.4(4)
C(3)	0.6436(06)	0.3310(06)	0.2175(05)	2.0(4)
C(4)	0.5626(07)	0.3410(06)	0.1538(05)	2.6(4)
C(5)	0.4579(08)	0.2764(09)	0.1501(06)	3.5(5)
C(6)	0.7612(07)	0.3721(07)	0.2218(05)	2.6(5)
C(7)	0.8517(07)	0.3075(06)	0.2314(05)	2.3(4)
C(8)	0.9592(06)	0.3538(07)	0.2092(05)	3.0(4)
C(9)	0.6610(07)	0.0981(07)	0.3601(05)	4.0(5)
C(10)	0.5721(07)	0.4009(07)	0.0786(05)	3.9(5)
C(11)	0.2674(08)	0.2623(08)	0.0919(07)	6.2(6)
C(12)	0.1800(09)	0.3264(10)	0.0481(07)	7.7(7)
C(13)	0.5011(07)	0.3811(07)	0.3338(06)	4.1(5)
C(14)	0.4519(08)	0.3899(08)	0.4107(06)	5.4(6)
C(15)	0.7031(08)	0.5525(07)	0.2254(06)	4.1(5)
C(16)	0.7234(09)	0.6490(08)	0.1821(06)	6.1(6)
C(17)	0.8303(07)	0.2308(07)	0.4480(06)	3.6(5)
C(18)	0.9665(08)	0.3410(07)	0.3821(06)	3.9(5)
C(19)	0.7796(08)	0.4065(08)	0.3976(05)	4.0(5)
C(21)	0.9425(08)	0.1278(06)	1.805(06)	3.7(5)
C(22)	0.9386(08)	0.1235(07)	0.3315(06)	3.4(5)
C(23)	0.7976(07)	0.0102(08)	0.2437(05)	3.1(5)
C(24)	0.7316(07)	0.1565(07)	0.1453(06)	3.5(5)

Table 12. Intramolecular Distances for 4b[a]

Mn(1)—Mn(2)	2.685(2)	O(2)—C(11)	1.43(2)
Mn(1)—C(1)	2.125(8)	O(3)—C(1)	1.380(8)
Mn(1)—C(2)	2.293(8)	O(3)—C(13)	1.41(1)
Mn(1)—C(6)	2.365(8)	O(4)—C(6)	1.39(1)
Mn(1)—C(7)	2.139(8)	O(4)—C(15)	1.42(1)
Mn(1)—C(17)	1.83(1)	C(1)—C(2)	1.39(1)
Mn(1)—C(18)	1.80(1)	C(2)—C(3)	1.49(1)
Mn(1)—C(19)	1.76(1)	C(2)—C(9)	1.51(1)
Mn(2)—C(1)	2.066(8)	C(3)—C(4)	1.33(1)
Mn(2)—C(7)	2.074(8)	C(3)—C(6)	1.48(1)
Mn(2)—C(21)	1.81(1)	C(4)—C(5)	1.50(1)
Mn(2)—C(22)	1.82(1)	C(4)—C(10)	1.51(1)
Mn(2)—C(23)	1.87(1)	C(6)—C(7)	1.36(1)
Mn(2)—C(24)	1.80(1)	C(7)—C(8)	1.51(1)
O(1)—C(5)	1.19(1)	C—O (av)	1.17(1)
O(2)—C(5)	1.30(1)	Mn(1)—C(3)	2.916(8)

[a] Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Table 13. Intramolecular Bond Angles for 4b[a]

C(1)—Mn(1)—C(2)	36.3(3)	C(2)—C(3)—C(4)	124.5(8)
C(1)—Mn(1)—C(7)	84.5(3)	C(2)—C(3)—C(6)	112.2(8)
C(2)—Mn(1)—C(7)	85.6(3)	C(4)—C(3)—C(6)	123(1)
C(1)—Mn(2)—C(7)	87.7(3)	C(3)—C(4)—C(5)	121(1)
C(5)—O(2)—C(11)	118(1)	C(3)—C(4)—C(10)	125.7(9)
C(1)—O(3)—C(13)	118.5(8)	C(5)—C(4)—C(10)	113(1)
C(6)—O(4)—C(15)	119.3(8)	O(1)—C(5)—O(2)	123(1)
Mn(1)—C(1)—Mn(2)	79.7(3)	O(1)—C(5)—C(4)	126(1)
Mn(1)—C(1)—O(3)	117.3(6)	O(2)—C(5)—C(4)	111(1)
Mn(1)—C(1)—C(2)	78.4(5)	O(4)—C(6)—C(3)	118.8(7)
Mn(2)—C(1)—O(3)	116.7(5)	O(4)—C(6)—C(7)	118.4(8)
Mn(2)—C(1)—C(2)	124.3(7)	C(3)—C(6)—C(7)	122.0(8)
O(3)—C(1)—C(2)	118.9(7)	Mn(1)—C(7)—Mn(2)	79.2(3)
Mn(1)—C(2)—C(1)	65.2(4)	Mn(1)—C(7)—C(6)	81.7(6)
Mn(1)—C(2)—C(3)	93.2(5)	Mn(1)—C(7)—C(8)	122.9(6)
Mn(1)—C(2)—C(9)	117.5(6)	Mn(2)—C(7)—C(6)	120.7(6)
C(1)—C(2)—C(3)	116.3(7)	Mn(2)—C(7)—C(8)	120.7(5)
C(1)—C(2)—C(9)	124.2(9)	C(6)—C(7)—C(8)	117.0(8)
C(3)—C(2)—C(9)	118.9(8)	Mn—C—O (av)	176(1)

[a] Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

and 1.36(1) Å for **4b**, and 1.37(1) and 1.39(1) Å for **4c**). All four of these carbon atoms are bonded to the metal Mn(1) (Mn(1)—C(1) = 2.146(8) Å, Mn(1)—C(2) = 2.367(7) Å, Mn(1)—C(6) = 2.413(8) Å, Mn(1)—C(7) = 2.107(8) Å for **4a**; Mn(1)—C(1) = 2.125(8) Å, Mn(1)—C(2) = 2.293(7) Å, Mn(1)—C(6) = 2.365(8) Å, Mn(1)—C(7) = 2.139(8) Å for **4b**; Mn(1)—C(1) = 2.137(8) Å, Mn(1)—C(2) = 2.421(8) Å, Mn(1)—C(6) = 2.275(7) Å, Mn(1)—C(7) = 2.129(7) Å for **4c**), but the distances to C(2) and C(6) are much longer than those to C(1) and C(7). Carbons C(1) and C(7) are actually bridges between Mn(1) and Mn(2). There is an exocyclic double bond between the atoms C(3) and C(4) at 1.33(1), 1.33(1), and 1.34(1) Å for **4a–c**, respectively. There seems to be no significant bonding interaction between Mn(1) and C(3) in any of the complexes (Mn(1)–C(3) = 2.803(8), 2.916(8), and 2.838(8) Å for **4a–c**, respectively). Carbons C(3) and C(4) were the vinylidene carbon atoms in **1a**, and these atoms have been completely removed from bonding to the metal atoms in these products. Carbons C(1) and C(2), and C(6) and C(7), are the alkyne carbons of the two MeC≡COEt molecules that were added to **1a**. Compounds **4a,c** were both formed by an unsymmetric addition of the two MeC≡COEt molecules to carbon C(3). They differ in that carbon C(2), which lies cis to the carboxylate group on C(4), contains a methyl group in **4a** and an OEt group in **4c**. Compound **4b** was formed by the symmetric addition of the two MeC≡COEt molecules to C(3). Of the two possible ways in which this could happen, the one in which both OEt-substituted carbons are bonded to C(3) is the one that has occurred. We have found no evidence of formation of the other possible isomer.

Discussion

A summary of the results of this study are shown in Scheme 1. The carbonylation of **1a** leads to the formation of **2** and $Mn_2(CO)_{10}$. The mechanism of this reaction was not established, but the reaction could be explained by a series of CO additions to **1a**. The first

Table 14. Positional Parameters and *B*(eq) Values for 4c

atom	*x*	*y*	*z*	*B*(eq) (Å^2)
Mn(1)	0.43846(09)	0.80079(06)	0.80540(10)	3.99(5)
Mn(2)	0.44775(09)	0.94291(06)	0.71321(10)	4.12(5)
O(1)	0.6826(05)	0.9860(05)	1.1880(07)	11.2(5)
O(2)	0.5508(05)	1.0163(03)	1.0882(04)	5.9(3)
O(3)	0.4451(04)	0.8744(03)	1.0920(04)	5.0(2)
O(4)	0.5886(04)	0.8322(03)	0.6100(05)	4.8(3)
O(17)	0.4541(06)	0.6963(03)	0.5917(06)	8.3(4)
O(18)	0.4860(05)	0.6715(04)	0.9656(07)	9.4(5)
O(19)	0.2337(05)	0.7591(04)	0.8321(06)	7.5(4)
O(21)	0.3120(05)	1.0734(03)	0.7412(07)	8.9(4)
O(22)	0.5070(06)	0.9873(04)	0.4612(06)	9.6(5)
O(23)	0.2952(04)	0.8642(04)	0.5680(06)	7.1(4)
O(24)	0.6043(04)	1.0482(03)	0.7972(06)	6.7(3)
C(1)	0.4059(05)	0.9080(04)	0.8909(07)	3.9(4)
C(2)	0.4743(05)	0.8861(04)	0.9750(07)	3.8(4)
C(3)	0.5790(05)	0.8829(04)	0.9417(07)	3.9(4)
C(4)	0.6482(05)	0.9220(04)	1.0008(07)	4.4(4)
C(5)	0.6290(06)	0.9749(05)	1.1040(08)	5.4(5)
C(6)	0.5954(05)	0.8349(04)	0.8310(07)	3.9(4)
C(7)	0.5549(06)	0.8606(03)	0.7213(06)	3.9(3)
C(8)	0.6686(06)	0.7695(05)	0.8348(09)	6.1(5)
C(9)	0.3074(05)	0.9264(05)	0.9405(07)	5.2(4)
C(10)	0.7534(05)	0.9197(05)	0.9651(09)	6.4(5)
C(11)	0.5276(07)	1.0733(05)	1.1822(09)	7.2(5)
C(12)	0.4319(08)	1.0916(07)	1.1724(11)	10.6(8)
C(13)	0.4982(07)	0.8265(06)	1.1749(08)	7.4(6)
C(14)	0.4401(08)	0.8099(06)	1.2806(08)	8.7(6)
C(15)	0.6848(08)	0.8539(07)	0.5780(10)	9.3(7)
C(16)	0.7059(07)	0.8387(07)	0.4536(10)	9.2(7)
C(17)	0.4480(07)	0.7366(04)	0.6758(08)	5.8(4)
C(18)	0.4662(06)	0.7229(05)	0.9050(08)	5.7(5)
C(19)	0.3123(06)	0.7773(04)	0.8208(07)	5.1(4)
C(21)	0.3630(06)	1.0222(05)	0.7291(08)	6.0(5)
C(22)	0.4840(07)	0.9703(05)	0.5581(08)	6.0(5)
C(23)	0.3537(06)	0.8891(05)	0.6312(08)	4.8(4)
C(24)	0.5439(06)	1.0069(05)	0.7726(08)	4.9(4)

Table 15. Intramolecular Distances for 4c[a]

Mn(1)–Mn(2)	2.677(2)	O(1)–C(5)	1.193(9)
Mn(1)–C(1)	2.137(7)	O(2)–C(5)	1.31(1)
Mn(1)–C(2)	2.421(8)	O(2)–C(11)	1.46(1)
Mn(1)–C(6)	2.275(7)	O(3)–C(2)	1.350(9)
Mn(1)–C(7)	2.129(7)	O(3)–C(13)	1.43(1)
Mn(1)–C(17)	1.805(9)	O(4)–C(7)	1.389(8)
Mn(1)–C(18)	1.78(1)	O(4)–C(15)	1.43(1)
Mn(1)–C(19)	1.806(8)	C(1)–C(2)	1.37(1)
Mn(2)–C(1)	2.107(7)	C(2)–C(3)	1.50(1)
Mn(2)–C(7)	2.068(7)	C(3)–C(4)	1.34(1)
Mn(2)–C(21)	1.824(9)	C(3)–C(6)	1.48(1)
Mn(2)–C(22)	1.824(9)	C(4)–C(5)	1.48(1)
Mn(2)–C(23)	1.839(9)	C(6)–C(7)	1.39(1)
Mn(2)–C(24)	1.856(9)	O–C (av)	1.145(9)
Mn(1)–C(3)	2.838(8)		

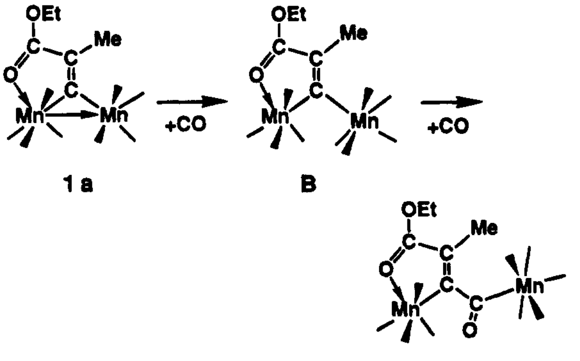
[a] Distances are in angstroms. Estimates standard deviations in the least significant figure are given in parentheses.

Table 16. Intramolecular Bond Angles for 4c[a]

Mn(2)–Mn(1)–C(1)	50.4(2)	C(5)–C(4)–C(10)	112.7(7)
Mn(2)–Mn(1)–C(6)	76.0(2)	O(1)–C(5)–O(2)	121.7(8)
Mn(2)–Mn(1)–C(7)	49.4(2)	O(1)–C(5)–C(4)	124.8(8)
Mn(1)–Mn(2)–C(1)	51.4(2)	O(2)–C(5)–C(4)	113.1(7)
Mn(1)–Mn(2)–C(7)	51.4(2)	Mn(1)–C(6)–C(3)	95.7(4)
Mn(1)–C(1)–Mn(2)	78.2(2)	Mn(1)–C(6)–C(7)	66.0(4)
Mn(1)–C(1)–C(2)	84.2(5)	C(3)–C(6)–C(7)	116.8(6)
Mn(2)–C(1)–C(2)	120.1(5)	C(3)–C(6)–C(8)	120.1(7)
C(2)–C(1)–C(9)	116.7(6)	C(7)–C(6)–C(8)	122.2(7)
O(3)–C(2)–C(1)	117.6(6)	Mn(1)–C(7)–Mn(2)	79.2(3)
O(3)–C(2)–C(3)	120.8(6)	Mn(1)–C(7)–O(4)	117.1(4)
C(1)–C(2)–C(3)	121.3(6)	Mn(1)–C(7)–C(6)	77.4(4)
C(2)–C(3)–C(4)	124.1(7)	Mn(2)–C(7)–O(4)	117.0(5)
C(2)–C(3)–C(6)	111.4(6)	Mn(2)–C(7)–C(6)	123.4(5)
C(4)–C(3)–C(6)	124.4(7)	O(4)–C(7)–C(6)	119.6(6)
C(3)–C(4)–C(5)	123.5(7)	Mn–C–O (av)	176.3(9)
C(3)–C(4)–C(10)	123.7(7)		

[a] Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

CO addition would lead to cleavage of the heteropolar metal–metal bond in **1a** and formation of a $Mn(CO)_5$ grouping (see intermediate **B** in eq 3). A second CO addition could occur, and in combination with an insertion into a metal–carbon bond, a species such as **C** could be formed. Products analogous to **B** and **C** were formed, isolated, and structurally characterized in the reactions of the related vinylidene complex $Re_2(CO)_8[\mu\text{-}\eta^2\text{-}C{=}CH(CO_2Me)]$ with CO.[11] A disproportionation of **C** could then lead directly to **2** and $Mn_2(CO)_{10}$ (eq 2).

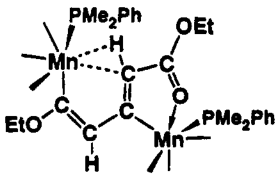


(3)

The formation of compound **3** appears to be the result of the coupling of two vinylidene ligands as found in **1a**. It is possible that a disproportionation of the species **B** could lead to **3** and $Mn_2(CO)_{10}$, but we consider this process unlikely, since no $Mn_2(CO)_{10}$ was observed in this reaction. Instead, we believe that **1a** has combined with 1 equiv of the added MeC≡COEt, and the MeC≡COEt ligand was transformed into a second vinylidene-like grouping by carbonylation and rearrangement in a manner that might be similar to the way the vinylidene ligand in **1a** was formed.[3] This vinylidene-like grouping is then coupled to the first vinylidene ligand, and compound **3** is formed. Further details of the formation of **3** have not been established.

In the absence of added CO the carbonylation of the MeC≡COEt that led to the formation of **3** does not occur. Instead, two MeC≡COEt molecules are added and coupled to the vinylidene ligand leading, to the isomers **4a–c** by coupling of the different ends of the alkynes to the vinylidene carbon atom.

In a related study we have recently obtained the complex $Mn_2(CO)_6(PMe_2Ph)_2[\mu\text{-}C(OEt){=}C(H)C{=}C(H)\text{-}C{=}O(OEt)]$ (**5**) from the reaction of HC≡COEt with $Mn_2(CO)_8(PMe_2Ph)_2$.[12] The formation of this compound appears to have involved the addition of *one* HC≡COEt molecule to a carboxylate-substituted vinylidene ligand that was formed in situ.



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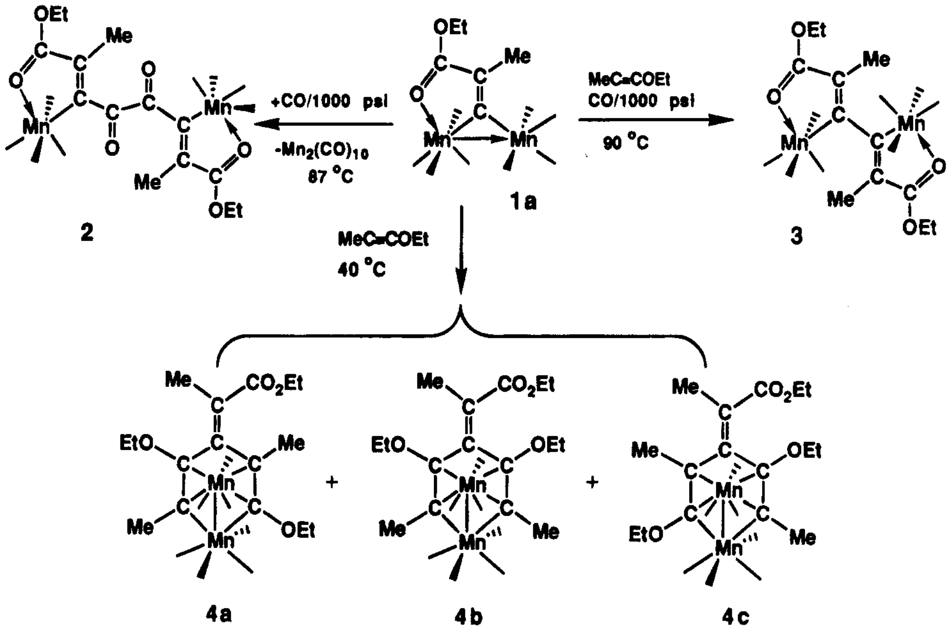
[11] Adams, R. D.; Chen, L.; Wu, W. *Organometallics* **1993**, *12*, 1257.

[12] Adams, R. D.; Chen, G.; Chen, L.; Pompeo, M. P.; Wu, W. *J. Cluster Sci.* **1992**, *3*, 103.

Scheme 1



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Supplementary Material Available: Tables of hydrogen atom positional parameters and anisotropic thermal parameters for all of the structural analyses (17 pages). Ordering information is given on any current masthead page.

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