Alkyne and CO Coupling Reactions in Dimanganese Carbonyl Complexes. The Reactions of Mn₂(CO)₉(NCMe) with HC≡CCO₂Me

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Four compounds Mn₂(CO)₈{μ-O=C[C(H)=C(CO₂Me)]₂}, 2, 35%, (OC)₄Mn[*trans*-μ-HC=C-(CO₂Me)]Mn(CO)₅, 3, 3%, (OC)₄Mn[C(CO₂Me)=C(H)C(=O)C(H)=C(CO₂Me)C(H)=C(CO₂-Me)]Mn(CO)₄, 4, 20%, and (OC)₄Mn[C(CO₂Me)=C(H)C(=O)C(H)=C(CO₂Me)C(H)=CH-(CO₂Me)], 5, 5% yield, were obtained from the reaction of Mn₂(CO)₉(MeCN), 1, with HC≡CCO₂Me in hexane solvent at 25 °C. Compounds 3–5 are new. Compound 3 is a dimetalated olefin complex formed by the insertion of the alkyne into the metal–metal bond of 1. Compounds 4 and 5 were characterized by a single-crystal X-ray diffraction analysis. Compound 4 contains two metallacyclic rings (one five membered and one six membered) formed by the coupling of three alkynes to one CO ligand. In the five membered ring the oxygen atom of the CO-derived carbonyl group is coordinated to one of the metal atoms. The six membered ring was formed by one of the alkynes and a coordinated carboxylate group from one of the alkynes coupled to it. Compound 4 was independently obtained from 2 by the addition of 1 equiv of HC≡CCO₂Me at 25 °C. Compound 5 is similar to 4, but only has one metal atom. A hydrogen atom has replaced the metal atom on the carbon of the six membered ring in 4. Compound 5 was obtained independently from the reaction of 4 with aqueous HCl. The metal atoms in 2 were removed sequentially in a series of reactions with aqueous HCl to yield Mn(CO)₄[C(CO₂Me)C(H)C-(=O)C(H)C(H)CO₂Me], 6, in 86% yield and the metal free organic compound MeO₂CC(H)C-(H)C(=O)C(H)C(H)CO₂Me, 7, 20% yield. Crystal Data: (for 4) space group = *Pbca*, a = 14.905(2) Å, b = 12.370(2) Å, c = 28.109(6) Å, Z = 8, 1642 reflections, R = 0.033; (for 5) space group = *P*1̄, a = 11.978(3) Å, b = 12.729(3) Å, c = 7.020(1) Å, α = 93.80(2)°, β = 95.93(2)°, γ = 70.86(2)°, Z = 2, 1396 reflections, R = 0.035.
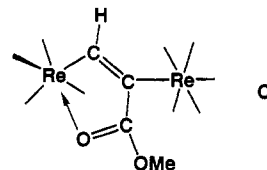
Introduction

Coupling reactions involving alkynes and CO have led to a wide variety of new organic ligands and organic molecules.[1] There are very few examples of the coupling of CO to alkynes by dimanganese complexes.[2–4] In recent studies we have shown that the reaction of HC≡COEt with Mn₂(CO)₉(NCMe), 1, produces a novel coupling of two alkynes at their unsubstituted end to the carbon atom of one CO ligand to yield the novel dimetalated ketone complex Mn₂(CO)₈{μ-O=C[C(H)=C(OEt)]₂}, A.[3] When treated with CO in the presence of AlCl₃, one of the metal—oxygen bonds was cleaved and the CO adduct B was obtained, eq 1.[3] Derunov et al. have obtained the
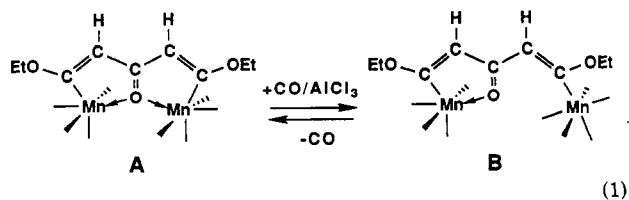
complex corresponding to A, Mn₂(CO)₈{μ-O=C[C(H)=C(CO₂Me)]₂}, 2,having carboxylate groups in place of the

OEt groups of A from the photoreaction of Mn₂(CO)₁₀ with HC≡CCO₂Me.[4]

We have recently shown that Re₂(CO)₉(NCMe) reacts with HC≡CCO₂Me by displacement of the NCMe ligand and insertion of the alkyne into the metal—metal bond to yield the dimetalated olefin complex, Re(CO)₄[*trans*-μ-HC=C(CO₂Me)]Re(CO)₅, C.[5] We have now investi-

gated the reaction of HC≡CCO₂Me with Mn₂(CO)₉-(NCMe). Although a small amount of the manganese homologue of C, (OC)₄Mn[*trans*-μ-HC=C(CO₂Me)]Mn-(CO)₅, 3, was formed, complex 2 obtained in a reasonable yield (35%) is the major product, but a new previously unreported complex (OC)₄Mn[C(CO₂Me)=C(H)C(=O)C-(H)=C(CO₂Me)C(H)=C(CO₂Me)]Mn(CO)₄, 4, formed by the combination of three alkynes with Mn₂(CO)₉(NCMe) was also obtained. The removal of the metal atoms from 2 and 4 was achieved by treatment with HCl. The results of this study are reported here.

• Abstract published in *Advance ACS Abstracts*, September 15, 1993.
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Experimental Section

All reactions were carried out under an atmosphere of nitrogen. Hexane was freshly distilled over sodium/benzophenone before use. CH_2Cl_2 was dried by calcium hydride and distilled before use. Other reagent grade solvents were dried by storage over 4-Å molecular sieves. CO was dehydrated by passing through a column of P_2O_5. $HC≡CCO_2Me$ was purchased from Aldrich and was used without further purification. 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 Brüker AM-300 spectrometer. Elemental analyses were performed by Desert Analytics, Tucson, AZ. Mass spectra were run on a VG Model 70SQ mass spectrometer using electron impact ionization. $Mn_2(CO)_9(MeCN)$, 1, was prepared by the literature method.[6]

Reaction of $Mn_2(CO)_9(MeCN)$, 1, with $HC≡CCO_2Me$. A 50.0-mg amount (0.124 mmol) of $Mn_2(CO)_9(MeCN)$, 1, in 50 mL of hexane was allowed to react with a 110-μL (1.241-mmol) amount of $HC≡CCO_2Me$ at 25 °C for 15 h. After the solvent was evaporated in vacuum, the residue was separated by TLC using a CH_2Cl_2/hexane 1/1 solvent mixture to give the following compounds in order of elution: 1.1 mg of $Mn_2(CO)_{10}$, 1.5 mg of pale yellow $(OC)_4Mn[trans-\mu-HC≡C(CO_2Me)]Mn(CO)_5$, 3, 3% yield, 1.0 mg of starting material, 23.0 mg of orange $Mn_2(CO)_8\{\mu-O≡C[C(H)≡C(CO_2Me)]_2\}$,[4] 2, 35% yield, 15.0 mg of deep red $(OC)_4Mn[C(CO_2Me)≡C(H)C(≡O)C(H)≡C(CO_2Me)C(H)≡C(CO_2Me)]Mn(CO)_4$, 4, 20% yield, and 3.0 mg of orange $(OC)_4Mn[C(CO_2Me)≡C(H)C(≡O)C(H)≡C(CO_2Me)C(H)≡CH(CO_2Me)]$, 5, 5% yield. IR ($\nu_{co}$ in hexane, cm^{-1}) for 2: 2104 (w), 2090 (w), 2029 (s), 2021 (s), 2004 (w), 1979 (w), 1965 (s), 1941 (w), 1721 (w, br), 1527 (w, br, in CH_2Cl_2). ^1H NMR (δ in C_6D_6, ppm): 6.63 (s, 2H, CH), 3.48 (s, 6H, OMe). Anal. Calcd (found) for 2 ($Mn_2C_{17}H_8O_{13}$): C, 38.49 (38.47); H, 1.51 (1.40). IR (ν_{co} in hexane, cm^{-1}) for 3: 2117 (w), 2078 (m), 2025 (s), 1999 (m, sh), 1992 (s), 1947 (s), 1554 (w, br). ^1H NMR (δ in C_6D_6, ppm) for 3: 10.16 (s, 1H, CH), 3.10 (s, 3H, OMe). The mass spectrum for 3 showed parent ion m/e = 446 and ions corresponding to the loss of each of the nine carbonyl ligands. IR (ν_{co} in hexane, cm^{-1}) for 4: 2089 (w), 2016 (s), 2002 (w, sh), 1966 (m), 1701 (w, br, in CH_2Cl_2), 1658 (w, br, in CH_2Cl_2), 1577 (w, br, in CH_2Cl_2), 1523 (w, br, in CH_2Cl_2). ^1H NMR (δ in C_6D_6, ppm): 8.74 (s, 1H, CH), 7.02 (s, 1H, CH), 6.30 (s, 1H, CH), 3.66 (s, 3H, OMe), 3.55 (s, 3H, OMe), 2.66 (s, 3H, OMe). Anal. Calcd (found) for 4 ($Mn_2C_{21}H_{12}O_{15}$): C, 41.04 (40.91); H, 1.95 (1.82). IR (ν_{co} in hexane, cm^{-1}) for 5: 2093 (w), 2015 (s), 1970 (m), 1740 (w, br), 1735 (w, br), 1720 (w, br), 1590 (w, br, in CH_2Cl_2), 1548 (w, br, in CH_2Cl_2). ^1H NMR (δ in $CDCl_3$, ppm) for 5: 8.25 (d, $^3J_{H-H}$ = 16.2 Hz, 1H, CH), 7.37 (s, 1H, CH), 7.16 (s, 1H, CH), 6.71 (d, $^3J_{H-H}$ = 16.2 Hz, 1H, CH), 3.90 (s, 3H, OMe), 3.87 (s, 3H, OMe), 3.82 (s, 3H, OMe). Anal. Calcd (found) for 5 ($MnC_{17}H_{13}O_{11}$): C, 45.54 (45.77); 2.90 (2.85).

Reaction of $Mn_2(CO)_8\{\mu-O≡C[C(H)≡C(CO_2Me)]_2\}$, 2, with $HC≡CCO_2Me$. A 120-mg amount (0.226 mmol) of 2 was dissolved in 70 mL of hexane. A 120-μL amount (1.352 mmol) of $HC≡CCO_2Me$ was added to the solution. The solution was stirred at 25 °C for 24 h, and then the solvent was evaporated. The residue was separated by TLC using a CH_2Cl_2/hexane 3/1 solvent mixture to give 50.0 mg of starting material; 36.0 mg of 4, 26% yield; and 3.7 mg of 5 in 3% yield.

Preparation of $(OC)_4Mn[C(CO_2Me)≡C(H)C(≡O)(H)≡C(CO_2Me)C(H)≡CH(CO_2Me)]$, 5. An 11.0-mg amount (0.018 mmol) of 4 was dissolved in 20 mL of hexane. After the solution was purged with CO at 25 °C for 30 min, a 1.5-mL amount of aqueous 12 M HCl was added. The reaction mixture was stirred with slow CO purging at 25 °C for 4 h. The hexane solution was separated from the aqueous solution. The aqueous portion was extracted with 4 × 1.5 mL of CH_2Cl_2. The extract was combined with the hexane solution and evaporated in vacuum to dryness. The residue was separated by TLC using a CH_2-

Cl_2/hexane 2/1 mixture solvent to give 5.7 mg of 5, 71% yield, and 3.2 mg of $Mn(CO)_5Cl$.[7]

Preparation of $Mn(CO)_4[C(CO_2Me)C(H)C(≡O)C(H)C(H)CO_2Me]$, 6. To a 100.0-mg (0.189 mmol) amount of 2 in 100 mL of hexane was added a 2.0-mL amount of aqueous 12 M HCl. The reaction mixture was heated to reflux for 3 h. After cooling to room temperature, a TLC separation as described above gave the following result: 59.1 mg of orange $Mn(CO)_4[C(CO_2Me)C-(H)C(O)C(H)C(H)CO_2Me]$, 6, 86% yield, and 12.5 mg of $Mn(CO)_5Cl$. IR (ν_{co} in hexane, cm^{-1}) for 6: 2095 (w), 2016 (s), 1969 (m), 1739 (w, br), 1720 (w, br), 1559 (w, br). ^1H NMR (δ in C_6D_6, ppm): 6.85 (s, 1H, CH), 6.75 (d, $^3J_{H-H}$ = 15.9 Hz, 1H, CH), 6.24 (d, $^3J_{H-H}$ = 15.9 Hz, 1H, CH), 3.56 (s, 3H, OMe), 3.25 (s, 3H, OMe). The mass spectrum for 6 showed parent ion m/e = 364.

Preparation of $MeO_2CC(H)C(H)C(≡O)C(H)C(H)CO_2Me$, 7. To a 50.0-mg amount (0.137 mmol) of 6 in 50 mL of heptane was added a 2.0-mL amount of aqueous 12 M HCl. After the reaction mixture was purged with CO at 25 °C for 15 min, it was heated to reflux for 2 h with CO bubbling. After cooling to room temperature, workup in the same way as described above gave the following result: 5.4 mg of colorless 7, 20% yield, and 5.0 mg of $Mn(CO)_5Cl$.[7] IR (ν_{co} in hexane, cm^{-1}) for 7: 1715. ^1H NMR (δ in C_6D_6, ppm) for 7: 6.95 (d, $^3J_{H-H}$ = 15.9 Hz, 2H, CH), 6.53 (d, $^3J_{H-H}$ = 15.9 Hz, 2H, CH), 3.27 (s, 6H, OMe). The mass spectrum of 7 showed parent ion m/e = 198.

Crystallographic Analysis. Crystals of compounds 4 and 5 suitable for X-ray diffraction analysis were grown by slow evaporation of solvent from solutions in hexane solvent at -3 °C. The 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 $K\alpha$ 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.[8a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[9b] Lorentz/polarization (Lp) corrections were applied to the data for each structure. Full-matrix least-squares refinements minimized the function: $\Sigma_{hkl} w(|F_o| - |F_c|)^2$, where $w = 1/\sigma(F_o)^2$, $\sigma(F_o) = \sigma(F_o^2)/2F_o$, and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (0.02I_{net})^2]^{1/2}/Lp$. Both structures were solved by a combination of direct methods (MITHRIL) and difference Fourier analyses. Crystal data and results of the analyses are listed in Table I.

Compounds 4 crystallized in the orthorhombic crystal system. The space group $Pbca$ was identified uniquely from the systematic absences in the data. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms H(1), H(4), and H(7) were located and refined on their positional parameters with fixed isotropic thermal parameters, B = 6.0 Å². The positions of all hydrogen atoms on the methyl groups were calculated by assuming idealized geometries with C-H = 0.95 Å.

Compound 5 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. All non-hydrogen atoms were refined with anisotropic thermal parameters. The positions of all hydrogen atoms H(1), H(4), H(7), and H(8) were located and refined on their positional parameters and isotropic thermal parameters. The positions of all hydrogen atoms on the methyl

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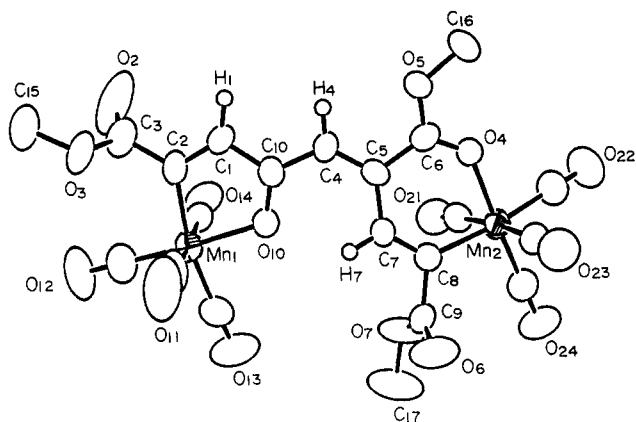
Figure 1. ORTEP diagram of (OC)₄Mn[C(CO₂Me)=C(H)C-(=O)C(H)=C(CO₂Me)C(H)=C(CO₂Me)]Mn(CO)₄, **4**, showing 50% probability thermal ellipsoids.

Table I. Crystallographic Data for Compounds 4 and 5

compd	4	5
empirical formula	Mn₂O₁₅C₂₁H₁₂	MnO₁₁C₁₇H₁₃
fw	614.19	448.22
cryst syst	orthorhombic	triclinic
lattice params		
a (Å)	14.905(2)	11.978(3)
b (Å)	12.370(2)	12.729(3)
c (Å)	28.109(6)	7.020(1)
α (deg)	90.0	93.80(2)
β (deg)	90.0	95.93(2)
γ (deg)	90.0	70.86(2)
V (Å³)	5183(4)	1005.1(9)
space group	*Pbca* (No. 61)	$P\bar{1}$ (No. 2)
Z	8	2
D_{calc} (g/cm³)	1.57	1.48
$\mu_{Mo\,K\alpha}$ (cm⁻¹)	10.03	6.83
temp (°C)	20	20
$2\theta_{max}$ (deg)	40.0	40.0
no. of observations ($I > 3\sigma(I)$)	1642	1396
no. of variables	352	278
residuals: R, R_w	0.033; 0.033	0.035; 0.036
goodness of fit indicator	1.58	1.63
max shift in final cycle	0.05	0.06
largest peak in final diff map (e/Å³)	0.29	0.18
abs corr	empirical	none

groups were calculated by assuming idealized geometries with C–H = 0.95 Å.

Results and Discussion

Four compounds Mn₂(CO)₈{μ-O=C[C(H)=C(CO₂-Me)]₂}, **2**, 35% yield, (OC)₄Mn[*trans*-μ-HC=C(CO₂Me)]-Mn(CO)₅, **3**, 3% yield, (OC)₄Mn[C(CO₂Me)=C(H)C-(=O)C(H)=C(CO₂Me)C(H)=C(CO₂Me)]Mn(CO)₄, **4**, 20% yield, and (OC)₄Mn[C(CO₂Me)=C(H)C(=O)C(H)=C(CO₂Me)C(H)=CH(CO₂Me)], **5**, 5% yield, were obtained when a solution of Mn₂(CO)₉(MeCN), **1**, was allowed to react with HC≡CCO₂Me in 50 mL of hexane at 25 °C for 15 h. Compound **2** has been obtained previously in a slightly lower yield from the photoreaction of Mn₂(CO)₁₀ with HC≡CCO₂Me.[4] Compound **3** is spectroscopically very similar to C and thus is believed to be a structurally similar dimetalated olefin complex formed by the insertion of the alkyne into the metal—metal bond of **1**. Compound **3** is unstable to treatment by TLC on silica gel, and therefore only small amounts of it could be obtained in a pure form. It exhibits the characteristic deshielded resonance for the olefin hydrogen atom, 10.16 (s) ppm, and the low energy IR absorption 1554 (w) for the coordinated ester grouping as found in C.
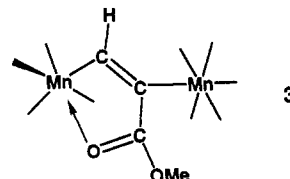
Table II. Positional Parameters and B(eq) for 4

atom	x	y	z	B(eq) (Å²)
Mn(1)	0.25108(07)	−0.13902(07)	−0.00856(03)	3.77(4)
Mn(2)	0.37382(06)	0.20647(08)	0.21067(03)	3.85(5)
O(2)	0.4608(05)	−0.2173(05)	−0.0893(02)	11.7(5)
O(3)	0.3780(03)	−0.3483(04)	−0.06655(17)	7.6(3)
O(4)	0.4851(02)	0.1238(03)	0.18744(14)	3.7(2)
O(5)	0.5760(03)	0.0080(04)	0.15202(14)	5.1(3)
O(6)	0.1624(03)	0.0426(05)	0.20561(19)	8.5(4)
O(7)	0.1640(03)	0.1600(04)	0.14746(20)	7.1(3)
O(10)	0.3140(03)	−0.0860(03)	0.05126(13)	3.8(2)
O(11)	0.2085(05)	−0.3471(04)	0.04070(17)	9.4(4)
O(12)	0.1696(04)	−0.2164(04)	−0.09811(17)	8.1(3)
O(13)	0.0845(04)	−0.0309(05)	0.02601(20)	8.9(4)
O(14)	0.3148(03)	0.0527(04)	−0.06300(18)	6.3(3)
O(21)	0.3549(03)	0.3390(04)	0.12256(17)	6.7(3)
O(22)	0.4930(04)	0.3679(04)	0.2580(02)	7.8(3)
O(23)	0.3652(04)	0.0569(04)	0.29410(17)	7.0(3)
O(24)	0.2166(04)	0.3172(04)	0.25026(20)	8.0(4)
C(1)	0.4353(04)	−0.1662(05)	0.0149(02)	4.0(4)
C(2)	0.3769(04)	−0.1953(05)	−0.0188(02)	3.7(3)
C(3)	0.4095(05)	−0.2532(06)	−0.0617(03)	5.0(4)
C(4)	0.4528(04)	−0.0588(05)	0.0909(02)	3.8(3)
C(5)	0.4259(04)	0.0012(05)	0.1283(02)	3.4(4)
C(6)	0.4965(05)	0.0499(06)	0.1584(02)	3.7(4)
C(7)	0.3334(05)	0.0215(06)	0.1412(02)	3.9(4)
C(8)	0.3035(04)	0.0949(05)	0.1726(02)	3.4(4)
C(9)	0.2030(05)	0.0955(06)	0.1775(02)	4.3(4)
C(10)	0.3978(05)	−0.1037(05)	0.0530(02)	3.6(4)
C(11)	0.2238(05)	−0.2678(06)	0.0226(02)	5.5(4)
C(12)	0.2007(05)	−0.1872(05)	−0.0632(03)	5.2(4)
C(13)	0.1472(05)	−0.0741(06)	0.0123(02)	5.3(4)
C(14)	0.2890(04)	−0.0183(06)	−0.0419(02)	4.3(4)
C(15)	0.4012(05)	−0.4057(07)	−0.1092(03)	9.3(6)
C(16)	0.6502(04)	0.0534(07)	0.1781(02)	7.0(5)
C(17)	0.0686(05)	0.1650(07)	0.1490(03)	10.1(6)
C(21)	0.3657(05)	0.2897(06)	0.1558(02)	4.7(4)
C(22)	0.4489(05)	0.3047(06)	0.2402(02)	5.2(4)
C(23)	0.3701(04)	0.1137(06)	0.2623(02)	4.5(4)
C(24)	0.2775(05)	0.2746(06)	0.2344(02)	5.0(4)

Table III. Intramolecular Distances for 4[a]

Mn(1)–O(10)	2.034(4)	O(7)–C(17)	1.424(8)
Mn(1)–C(2)	2.021(6)	O(10)–C(10)	1.270(6)
Mn(2)–O(4)	2.055(4)	C(1)–C(2)	1.336(8)
Mn(2)–C(8)	2.037(6)	C(1)–C(10)	1.435(8)
O(2)–C(3)	1.177(7)	C(2)–C(3)	1.483(8)
O(3)–C(3)	1.274(7)	C(4)–C(5)	1.348(8)
O(3)–C(15)	1.435(8)	C(4)–C(10)	1.453(8)
O(4)–C(6)	1.239(7)	C(5)–C(6)	1.479(8)
O(5)–C(6)	1.306(7)	C(5)–C(7)	1.448(8)
O(5)–C(16)	1.441(7)	C(7)–C(8)	1.343(8)
O(6)–C(9)	1.190(7)	C(8)–C(9)	1.505(8)
O(7)–C(9)	1.300(7)	C–O(av)	1.35(1)

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

Compound **4** is stable and was analyzed by a single-crystal X-ray diffraction analysis. An ORTEP diagram of the molecular structure of **4** is shown in Figure 1. Final atomic positional parameters are listed in Table II. Selected bond distances and angles are listed in Tables III and IV, respectively. The molecule contains two metal-lacyclic rings. One contains five atoms Mn(1)–C(2)–C(1)–C(10)–O(10) and the other contains six Mn(2)–C(8)–C(7)–C(5)–C(6)–O(4). In the first ring the C(1)–C(2) and C(10)–O(10) distances are short 1.336 (8) and 1.270 (6) Å and are indicative of carbon–carbon and carbon–oxygen double

Table IV. Intramolecular Bond Angles for 4[a]

O(10)–Mn(1)–C(2)	78.6(2)	C(4)–C(5)–C(7)	125.1(6)
O(4)–Mn(2)–C(8)	84.9(2)	C(6)–C(5)–C(7)	117.6(6)
C(3)–O(3)–C(15)	117.2(6)	O(4)–C(6)–O(5)	120.6(6)
Mn(2)–O(4)–C(6)	133.5(4)	O(4)–C(6)–C(5)	125.5(6)
C(6)–O(5)–C(16)	118.1(5)	O(5)–C(6)–C(5)	113.9(6)
C(9)–O(7)–C(17)	116.9(6)	C(5)–C(7)–C(8)	126.8(6)
Mn(1)–O(10)–C(10)	115.5(4)	Mn(2)–C(8)–C(7)	129.3(5)
C(2)–C(1)–C(10)	115.0(6)	Mn(2)–C(8)–C(9)	117.4(5)
Mn(1)–C(2)–C(1)	114.2(5)	C(7)–C(8)–C(9)	113.2(6)
Mn(1)–C(2)–C(3)	125.9(5)	O(6)–C(9)–O(7)	122.8(7)
C(1)–C(2)–C(3)	119.5(6)	O(6)–C(9)–C(8)	124.3(7)
O(2)–C(3)–O(3)	121.1(7)	O(7)–C(9)–C(8)	112.8(6)
O(2)–C(3)–C(2)	124.5(7)	O(10)–C(10)–C(1)	116.5(6)
O(3)–C(3)–C(2)	114.4(7)	O(10)–C(10)–C(4)	121.2(6)
C(5)–C(4)–C(10)	127.8(6)	C(1)–C(10)–C(4)	122.2(6)
C(4)–C(5)–C(6)	117.3(6)	Mn–C(av)–O	178(1)

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

Scheme I
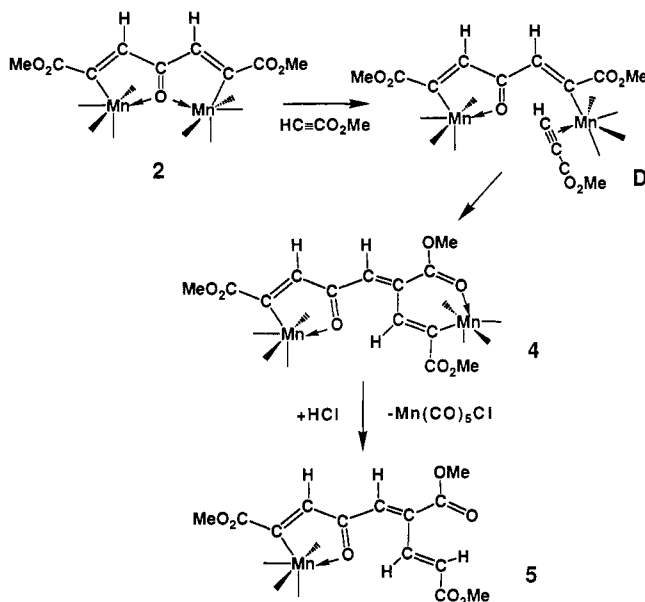
bonds, respectively. The C(1)–C(10) distance is much longer 1.435 (8) Å and has only slight multiple bond character. In the second ring the C(7)–C(8) and C(6)–O(4) distances are short 1.343 (8) and 1.239 (7) Å and indicative of carbon–carbon and carbon–oxygen double bonds, while the C(5)–C(6) and C(5)–C(7) distances are longer 1.479(8) and 1.448 (8) Å and have only slight multiple bond character. The bonds C(4)–C(5) and C(4)–C(10) that join the two metallacycles are 1.348 (8) and 1.453 (8) Å. The former is double and the latter is largely single. Thus, the structure shown below would best represent the bonding in 4.

4
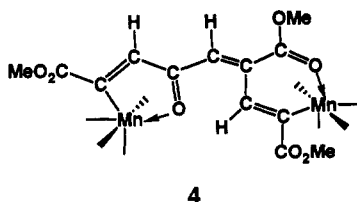
It appeared that 4 was a product of the addition of HC≡CCO₂Me to 2, and this was confirmed by an independent experiment. The reaction of 2 with HC≡CCO₂Me at 25 °C produced a 26% yield of 4 after 24 h at 25 °C. Thus, the formation of 4 appears to be that of
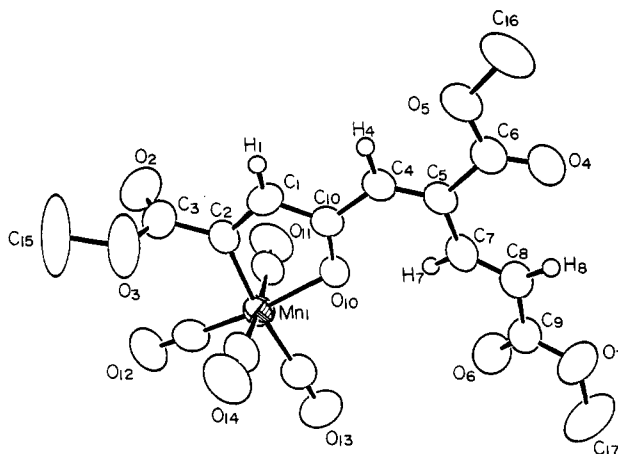
Figure 2. ORTEP diagram of (OC)₄Mn[C(CO₂Me)=C(H)-C(=O)C(H)=C(CO₂Me)C(H)=CH(CO₂Me)], 5, showing 50% probability thermal ellipsoids.

Table V. Positional Parameters and B(eq) for 5

atom	x	y	z	B(eq) (Å²)
Mn(1)	0.67606(07)	0.28565(07)	0.78490(12)	3.69(5)
O(2)	0.8217(04)	−0.0314(04)	0.8375(08)	7.7(4)
O(3)	0.8655(04)	0.0277(04)	0.5731(08)	8.7(4)
O(4)	1.0862(03)	0.5360(04)	1.3475(06)	5.9(3)
O(5)	1.1730(03)	0.3554(04)	1.2904(05)	5.3(3)
O(6)	0.6378(04)	0.6972(03)	1.1263(06)	6.4(3)
O(7)	0.7405(04)	0.8141(04)	1.1424(07)	6.8(3)
O(10)	0.7841(03)	0.3563(03)	0.9562(05)	3.7(2)
O(11)	0.5978(04)	0.2200(04)	1.1369(06)	7.0(3)
O(12)	0.5459(04)	0.1556(04)	0.5512(06)	6.7(3)
O(13)	0.4756(04)	0.4992(04)	0.7477(07)	7.6(3)
O(14)	0.7771(04)	0.3148(04)	0.4273(06)	6.9(3)
C(1)	0.9113(06)	0.1766(05)	0.9391(09)	4.3(4)
C(2)	0.8229(05)	0.1541(05)	0.8278(08)	3.9(4)
C(3)	0.8377(05)	0.0393(06)	0.7512(11)	5.3(5)
C(4)	0.9761(05)	0.3263(05)	1.1220(07)	3.7(4)
C(5)	0.9693(04)	0.4286(05)	1.1959(07)	3.4(4)
C(6)	1.0801(05)	0.4473(06)	1.2869(08)	4.2(4)
C(7)	0.8591(05)	0.5233(06)	1.1782(07)	3.9(4)
C(8)	0.8467(05)	0.6310(06)	1.1970(08)	4.1(4)
C(9)	0.7294(06)	0.7144(05)	1.1533(08)	4.4(4)
C(10)	0.8856(05)	0.2903(05)	1.0057(07)	3.5(4)
C(11)	0.6253(05)	0.2475(05)	1.0050(09)	4.5(4)
C(12)	0.5949(05)	0.2080(05)	0.6413(08)	4.6(4)
C(13)	0.5521(06)	0.4184(06)	0.7647(09)	5.1(4)
C(14)	0.7386(05)	0.3072(05)	0.5640(09)	4.5(4)
C(15)	0.8750(08)	−0.0781(07)	0.4769(13)	12.7(8)
C(16)	1.2870(05)	0.3691(06)	1.3543(09)	6.7(5)
C(17)	0.6343(07)	0.9036(06)	1.0898(13)	9.7(6)

a simple insertion of one alkyne into one of the metal—carbon bonds of 2 with a carbon—carbon bond formation occurring at the unsubstituted end of the alkyne and a subsequent coordination of the carboxylate ketonic grouping, Scheme I. This may, in fact, proceed through an alkyne containing intermediate D formed by the opening of one of the Mn—O bonds. We showed previously that one of the Mn—O bonds in the related complex A could be opened by the addition of CO, eq 1.[3] The olefin hydrogen atoms in 4 exhibit characteristic deshielded resonance shifts in the ¹H NMR spectrum, δ = 8.74 (s), 7.02 (s), 6.30 (s) ppm. Specific assignments cannot be made with this data alone.

Compound 5 was analyzed by a single-crystal X-ray diffraction analysis. An ORTEP diagram of the molecular structure of 5 is shown in Figure 2. Final atomic positional parameters are listed in Table V. Selected bond distances and angles are listed in Tables VI and VII, respectively. The molecule contains only one metal atom and it is part

Table VI. Intramolecular Distances for 5[a]

Mn(1)–O(10)	2.056(3)	C(1)–C(2)	1.347(7)
Mn(1)–C(2)	2.003(5)	C(1)–C(10)	1.434(7)
O(2)–C(3)	1.193(7)	C(2)–C(3)	1.484(8)
O(3)–C(3)	1.313(7)	C(4)–C(5)	1.349(7)
O(3)–C(15)	1.442(8)	C(4)–C(10)	1.465(7)
O(4)–C(6)	1.202(6)	C(5)–C(6)	1.496(7)
O(5)–C(6)	1.323(6)	C(5)–C(7)	1.467(7)
O(5)–C(16)	1.455(6)	C(7)–C(8)	1.329(8)
O(6)–C(9)	1.183(6)	C(8)–C(9)	1.473(8)
O(7)–C(9)	1.326(7)	Mn(1)–C(av)	1.85(1)
O(7)–C(17)	1.436(7)	O–C(av)	1.13(1)
O(10)–C(10)	1.259(5)		

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

Table VII. Intramolecular Bond Angles for 5[a]

O(10)–Mn(1)–C(2)	78.8(2)	C(4)–C(5)–C(7)	122.2(5)
C(3)–O(3)–C(15)	116.6(6)	C(6)–C(5)–C(7)	119.1(5)
C(6)–O(5)–C(16)	116.0(5)	O(4)–C(6)–O(5)	122.9(6)
C(9)–O(7)–C(17)	116.8(5)	O(4)–C(6)–C(5)	124.4(6)
Mn(1)–O(10)–C(10)	114.8(3)	O(5)–C(6)–C(5)	112.7(5)
C(2)–C(1)–C(10)	115.0(5)	C(5)–C(7)–C(8)	127.8(6)
Mn(1)–C(2)–C(1)	114.3(4)	C(7)–C(8)–C(9)	119.8(6)
Mn(1)–C(2)–C(3)	125.3(4)	O(6)–C(9)–O(7)	123.6(6)
C(1)–C(2)–C(3)	120.4(5)	O(6)–C(9)–C(8)	126.4(6)
O(2)–C(3)–O(3)	124.7(7)	O(7)–C(9)–C(8)	110.0(6)
O(2)–C(3)–C(2)	124.4(7)	O(10)–C(10)–C(1)	117.0(5)
O(3)–C(3)–C(2)	110.8(6)	O(10)–C(10)–C(4)	122.6(5)
C(5)–C(4)–C(10)	129.0(6)	C(1)–C(10)–C(4)	120.3(5)
C(4)–C(5)–C(6)	118.5(5)	Mn(1)–C(av)–O	177(1)

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

of a metallacyclic ring of five atoms Mn(1)–C(2)–C(1)–C(10)–O(10) as in 4. The distances in this ring are similar to those in 4: C(1)–C(2) = 1.347(7) Å, C(10)–O(10) = 1.259-(5) Å, and C(1)–C(10) = 1.434(7) Å. Of the remaining distances, the short distances in 4 are all shorter than in 2, C(7)–C(8) = 1.329(8) Å and C(6)–O(4) = 1.202 (6) Å, and the long distances are all longer, C(5)–C(6) = 1.496(7) Å, C(5)–C(7) = 1.467(7) Å, and C(4)–C(10) = 1.465(7) Å, except for C(4)–C(5) which is essentially the same at 1.349-(7) Å. This is probably a result of less delocalization in the absence of the second metal atom. Instead of the metal atom C(8) contains a hydrogen atom. The ^{1}H NMR spectrum shows four highly deshielded resonances at 8.25 (d, $^3J_{H-H}$ = 16.2 Hz), 7.37 (s), 7.16 (s), and 6.71 (d, $^3J_{H-H}$ = 16.2 Hz), and two of them have strong coupling, J_{H-H} = 16.2 Hz, which is consistent with an olefin having trans stereochemistry, as found at carbons C(7) and C(8) in the structural analysis. The source of the hydrogen atom at C(8) in the original reaction has not been established; however, we were able to produce 5 from 4 in good yield (71%) by treatment of hexane solutions of 4 with aqueous 12 M HCl at 25 °C for 4 h; see Scheme I. From this reaction the coproduct Mn(CO)₅Cl was also obtained, which explains the fate of the manganese group that was removed.

In an attempt to cleave the metal atoms from 2, we have also investigated its reaction with HCl. Indeed, the metal atoms are sequentially removed in series to give the monometallic compound Mn(CO)₄[C(CO₂Me)C(H)C-(=O)C(H)C(H)CO₂Me], 6, in 86% yield and the metal free organic compound MeO₂CC(H)C(H)C(=O)C(H)C-(H)CO₂Me, 7, in 20% yield from 6. The ^{1}H NMR spectrum of 6 shows resonances at 6.85 (s, 1H, C*H*), 6.75 (d, $^3J_{H-H}$ = 15.9 Hz, 1H, C*H*), 6.24 (d, $^3J_{H-H}$ = 15.9 Hz), and 3.56

Scheme II
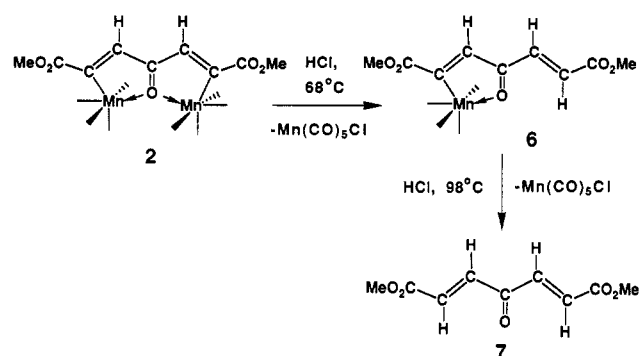
(s, 3H, O*Me*), 3.25 (s, 3H, O*Me*) ppm and the appropriate parent ion in the mass spectrum, m/e = 364. Compound 7 shows only the ketone stretch 1715 cm⁻¹ in its IR spectrum and doublets at 6.95 (d, $^3J_{H-H}$ = 15.9 Hz, 2H) and 6.53 (d, $^3J_{H-H}$ = 15.9 Hz) and a singlet at 3.27 ppm in the ^{1}H NMR spectrum for the olefin hydrogen atoms and for the carboxylate methyl groups, respectively. The mass spectrum of 7 showed the expected parent ion at m/e = 198. The large coupling constants between the olefin hydrogen atoms indicates that the stereochemistry at the double bonds is trans both in 6 and 7. In both reactions Mn-(CO)₅Cl was also obtained; see Scheme II.

In conclusion the reactions of 1 with HC≡CCO₂Me more closely resemble those of 1 with an HC≡COEt than that of Re₂(CO)₉(NCMe) with HC≡CCO₂Me and indicate that the reactions are more metal dependent than alkyne dependent in character. Interestingly, we have observed that ketone complex 2 will react with additional alkyne to produce a more extended organic framework, and the metal atoms of 2 and 4 can be partially and fully removed by reaction with HCl.

It is interesting to compare the reactions of 1 with alkynes with those of Fe₂(CO)₉ with alkynes. The coupling of two alkynes to a CO ligand by the diiron complex yields the well-known "flyover" bridged complexes **E** where each
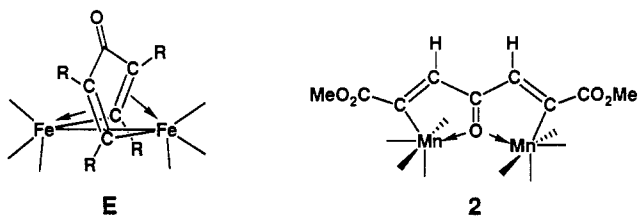
double bond of the two olefin groups is coordinated and they donate two electrons to the metal atoms.[9] In contrast the olefin double bonds in the molecules **A** and 2 are uncoordinated and the oxygen atoms of the ketones are coordinated to the metal atoms by using both lone pairs of electrons to donate two electrons to each metal atom.

Supplementary Material Available: Tables of hydrogen atom positional parameters and anisotropic thermal parameters for both of the structural analyses (8 pages). Ordering information is given on any current masthead page.

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