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Coupling of CO to HC≡COEt in Dimanganese Carbonyl Complexes

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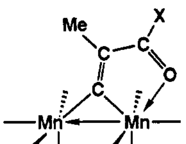
Three new compounds $(OC)_4Mn[C(OEt){=}C(H)C({=}O)]Mn(CO)_5$, **1**, $Mn_2(CO)_8[\mu\text{-}C{=}C(H)C(OEt){=}O]$, **2**, and $Mn_2(CO)_8\{\mu\text{-}O{=}C[C(H){=}C(OEt)]_2\}$, **3**, were obtained in low yields when solutions of $Mn_2(CO)_{10}$ and HC≡COEt were irradiated (UV). The yield of **3** was significantly larger in the thermal reaction of $Mn_2(CO)_9(NCMe)$ with HC≡COEt, but **1** was not formed. Compound **1** was characterized by a single-crystal X-ray diffraction analysis. The molecule contains a metallacyclic ring formed by the coupling of one molecule of HC≡COEt to one CO ligand. The oxygen atom of the CO group is coordinated to the metal atom. Compound **3** was converted to its bis-PMe_2Ph derivative $Mn_2(CO)_6(PMe_2Ph)_2\{\mu\text{-}O{=}C[C(H){=}C(OEt)]_2\}$, **4**, which was then characterized by a single-crystal X-ray diffraction analysis. Compound **4** contains two metallacyclic rings formed by the coupling of two HC≡COEt alkynes to one CO ligand. The oxygen atom of the carbonyl group is coordinated as a bridge between the two metal atoms. Compound **3** added 1 equiv of CO when exposed to a CO atmosphere in the presence of $AlCl_3$ to yield the compound $Mn_2(CO)_9\{\mu\text{-}O{=}C[C(H){=}C(OEt)]_2\}$, **5**, in 90% yield. An X-ray diffraction analysis of **5** showed that one of the metallacyclic rings had been opened by the cleavage of one of the Mn–O bonds and the addition of CO to one of the manganese atoms to form a $Mn(CO)_5$ grouping. In the absence of $AlCl_3$ and CO, **5** slowly converted back to **3** at 25 °C, 96% yield, in 24 h. When **3** was treated with HCl or $NaBH_4$, one of the manganese atoms was removed and the new compound $Mn(CO)_4[C(OEt){=}C(H)C(O)C(H){=}CH(OEt)]$, **6** was formed in 90% yield. Compound **6** was also characterized by a single-crystal X-ray diffraction analysis. This compound is structurally similar to **5** except that the $Mn(CO)_5$ grouping was replaced with a hydrogen atom. Crystal data: For **1**, space group = $P2_1/n$, a = 12.088(2) Å, b = 10.521(3) Å, c = 15.726(3) Å, β = 108.14(2)°, Z = 4, 1440 reflections, R = 0.027; for **4**, space group = $C2/c$, a = 26.271(7) Å, b = 9.130(2) Å, c = 15.616(5) Å, β = 113.90(2)°, Z = 4, 1226 reflections, R = 0.038; for **5**, space group = $P2_1/n$, a = 7.565(2) Å, b = 22.788(4) Å, c = 13.015(2) Å, β = 92.71(2)°, Z = 4, 1515 reflections, R = 0.032; for **6**, space group = $P\bar{1}$, a = 9.207(1) Å, b = 10.428(2) Å, c = 8.911(1) Å, α = 105.89(1)°, β = 93.40(1)°, γ = 70.34(1)°, Z = 2, 1826 reflections, R = 0.032.

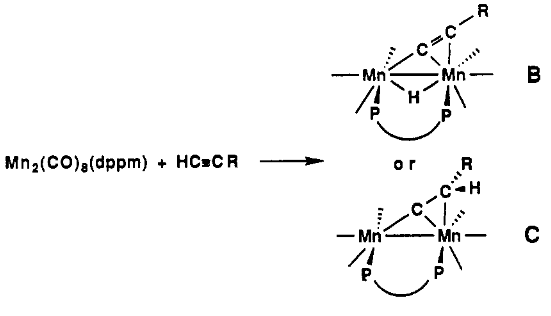
Introduction

In a recent report we have described the reactions of the electron-rich internal alkynes MeC≡CX, X = NMe_2 or OEt, with the dimanganese complex $Mn_2(CO)_9(NCMe)$. These reactions yielded the substituted vinylidene complexes $Mn_2(CO)_8[\mu\text{-}\eta^2\text{-}C{=}C(Me)C{=}O(X)]$, **A**, X = NMe_2, or OEt, respectively, by a rearrangement of the alkyne that included a CO insertion.[1]



A

Reactions of dimanganese carbonyl complexes with terminal alkynes have been shown to yield products containing bridging acetylide ligands **B** and vinylidene ligands **C**, eq 1, by cleavage or rearrangement of the acetylenic CH bond.[2-4]



(1)

We have now completed a study of the reactions of terminal alkyne HC≡COEt with $Mn_2(CO)_{10}$ and $Mn_2(CO)_9(NCMe)$. We have found that C–H activation is a minor reaction pathway for this alkyne. Instead, the dominant reaction involves coupling of the unsubstituted end of two alkynes to a CO ligand with a rearrangement

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[1] (a) Adams, R. D.; Chen, G.; Chen, L.; Yin, L. *Organometallics* **1993**, *12*, 2644. (b) Adams, R. D.; Chen, G.; Chen, L.; Pompeo, M. P.; Yin, J. *Organometallics* **1992**, *11*, 2541.

(2) García Alonso, F. J.; Riera, V.; Ruiz, M. A.; Tiripicchio, A.; Camellini, M. T. *Organometallics* **1992**, *11*, 370.

(3) (a) Horton, A. D.; Kemball, A. C.; Mays, M. J. *J. Chem. Soc., Dalton Trans.* **1988**, 2953. (b) Iggo, J. A.; Mays, M. J.; Raithby, P. R.; Hendrick, K. *J. Chem. Soc., Dalton Trans.* **1983**, 205.

(4) Adams, R. D.; Chen, G.; Chen, L.; Pompeo, M. P.; Wu, W. *J. Cluster Sci.* **1992**, *3*, 103.

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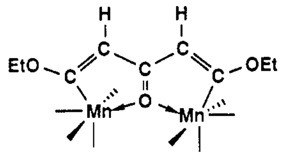
that leads to coordination of the oxygen atom of the carbonyl group as shown in **D**. The results of this study are reported here. A preliminary report of a portion of this work has been published.[5]



D

Experimental Section

All reactions were carried out under atmosphere of nitrogen. Hexane and THF were freshly distilled over sodium benzophenone ketyl before use. Other reagent grade solvents were stored over 4-Å molecular sieves. UV irradiation was performed by using an externally positioned 1000-W UV lamp on solutions in Pyrex glassware. $HC\equiv COEt$ (50 wt % solution in hexanes) was purchased from Aldrich and used without further purification. ^{13}CO (containing 99% ^{13}C) was from Cambridge Isotope Laboratories. All chromatographic separations were performed by TLC in air on silica gel (0.25-mm plates, F_{254}). 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. Mass spectra were run on a VG Model 70SQ mass spectrometer using electron-impact ionization. $Mn_2(CO)_9(MeCN)$ was prepared by the literature method.[6]

Photolysis of $Mn_2(CO)_{10}$ in the Presence of $HC\equiv COEt$. (1) Under CO. A 100-mg (0.256 mmol) amount of $Mn_2(CO)_{10}$ and a 60-μL (0.310 mmol) amount of $HC\equiv COEt$ were dissolved in 80 mL of hexane. After purging with CO at 25 °C for 10 min, the solution was exposed to UV at 25 °C for 1.5 h. After the solvent was removed, the residue was separated using a 1/4 CH_2Cl_2/hexane solvent mixture to give 21.2 mg of starting material, orange $Mn_2(CO)_8[\mu\text{-}C{=}C(H)C(OEt){=}O]$, **2** (2.8 mg, 3%), yellow $(OC)_4Mn[C(OEt){=}C(H)C({=}O)]Mn(CO)_5$, **1** (6.1 mg, 6%), and yellow $Mn_2(CO)_8\{\mu\text{-}O{=}C[C(H){=}C(OEt)]_2\}$, **3** (3.1 mg, 2% yield). These yields could not be improved, and most of the reaction material was consumed in the form of uncharacterizable "decomposition". IR (ν_{CO} in hexane, cm^{-1}) for **1**: 2122 (w), 2096 (w), 2083 (m), 2063 (w), 2026 (s), 2010 (m), 1994 (s), 1957 (m), 1944 (m), 1587 (w, br). ^1H NMR (δ, ppm in C_6D_6): 6.49 (s, 1H, CH), 3.56 (q, $^3J_{H-H}$ = 7.1 Hz, 2H, CH_2), 0.99 (t, $^3J_{H-H}$ = 7.1 Hz, 3H, CH_3). IR (ν_{co} in hexane, cm^{-1}) for **2**: 2100 (w), 2061 (m), 2020 (s), 2005 (m), 1984 (w), 1970 (m), 1934 (w), 1565 (w, br). ^1H NMR (δ, ppm in C_6D_6): 6.99 (s, 1H, CH), 3.50 (q, $^3J_{H-H}$ = 6.4 Hz, 2H, CH_2), 0.67 (t, $^3J_{H-H}$ = 6.6 Hz, 3H, CH_3). IR (ν_{co} in hexane, cm^{-1}) for **3**: 2096 (m), 2083 (w), 2012 (s), 1993 (m), 1969 (m), 1955 (s), 1498 (w, br in CCl_4). ^1H NMR (δ, ppm in $CDCl_3$): 5.90 (s, 2H, CH), 4.11 (q, $^3J_{H-H}$ = 7.1 Hz, 4H, CH_2), 1.45 (t, $^3J_{H-H}$ = 7.0 Hz, 6H, CH_3). The mass spectrum for **1** showed parent ion m/e = 460 and ions corresponding to the loss of each of the nine carbonyl ligands. The mass spectrum of **2** showed parent ion m/e = 432 and ions corresponding to the loss of each of the eight carbonyl ligands. The mass spectrum of **3** showed parent ion m/e = 502 and ions corresponding to the loss of each of the six carbonyl ligands. Anal. Calcd (found) for **1**: C, 36.52 (36.47); H, 1.30 (1.40). Calcd (found) for **3**: C, 40.66 (40.50); H, 2.39 (2.38). Note: Compound **2** is unstable in air at room temperature. Therefore, it should be separated and collected as quickly as possible.

(2) Under a Nitrogen Atmosphere. When the reaction was performed under a nitrogen atmosphere, $Mn_2(CO)_{10}$ (200 mg) with $HC\equiv COEt$ (120 μL), the yields of **1** and **2** were even lower. The yield of **3** was significantly higher but was still low: 92.7 mg of unreacted $Mn_2(CO)_{10}$, a trace of **2**, 1.9 mg of **1** (0.9% yield), and 19.2 mg of **3** (7% yield).

Reaction of $Mn_2(CO)_9(MeCN)$ with $HC\equiv COEt$. A 50-mg (0.124 mmol) amount of $Mn_2(CO)_9(MeCN)$ in 50 mL of hexane was allowed to react with a 60.5-μL (0.310 mmol) amount of $HC\equiv COEt$ at 35 °C for 3 h. After the reaction mixture was cooled and evaporated to dryness, the residue was separated using a 1/4 CH_2Cl_2/hexane solvent mixture to give the following compounds in order of elution: 0.4 mg of $Mn_2(CO)_{10}$; 1.2 mg of orange $Mn_2(CO)_8[\mu\text{-}C{=}C(H)C(OEt){=}O]$, **2**, 2% yield; 9.8 mg of yellow $Mn_2(CO)_8\{\mu\text{-}O{=}C[C(H){=}C(OEt)_2\}$, **3**, 16% yield; 4.8 mg of starting material. No **1** was formed.

Preparation of $Mn_2(^{13}CO)_8\{\mu\text{-}O{=}^{13}C[C(H){=}C(OEt)]_2\}$, 3*. A 350-mg amount of $Mn_2(CO)_{10}$ in 10 mL of octane was placed in a Parr reaction vessel under 1 atm of ^{13}CO and heated at 125 °C for 4 h. After cooling, the reaction mixture was filtered with a silica gel column. A 270-mg amount of $Mn_2(^{12}CO)_n(^{13}CO)_{10-n}$ was obtained after the solvent was removed. The mass spectrum showed about 45% of the carbonyl ligands were enriched with ^{13}CO. This $Mn_2(^{12}CO)_n(^{13}CO)_{10-n}$ was converted to $Mn_2(^{13}CO)_9(MeCN)$ and then $Mn_2(^{13}CO)_8\{\mu\text{-}O{=}^{13}C[C(H){=}C(OEt)]_2\}$, **3***, in the same way as described above. IR for **3*** in hexane showed the absorption at 1498 cm^{-1} due to the unlabeled bridging C=O grouping and a second absorption of approximately equal intensity at 1483 cm^{-1} that is attributed to the labeled bridging C=O grouping. ^1H NMR for **3*** (in C_6D_6): δ 5.68 (t, $^2J_{H-C}$ = 7.9 Hz, 2H, CH), 3.59 (q, $^3J_{H-H}$ = 7.1 Hz, 4H, CH_2), 0.99 (t, $^3J_{H-H}$ = 7.1 Hz, 6H, CH_3).

Reaction of $Mn_2(CO)_8\{\mu\text{-}O{=}C[C(H){=}C(OEt)]_2\}$, 3, with PMe_2Ph. A 30-mg (0.060 mmol) amount of **3** and a 20.0-μL amount (0.149 mmol) of PMe_2Ph were dissolved in 80 mL of hexane. The solution was heated to reflux for 1 h. After cooling, the solution was evaporated to dryness, and the residue was separated by TLC using a 1/1 CH_2Cl_2/hexane solvent mixture to give 41.1 mg of yellow $Mn_2(CO)_6(PMe_2Ph)_2\{\mu\text{-}O{=}C[C(H){=}C(OEt)]_2\}$, **4**, 95% yield. IR ($\nu_{CO}$ in hexane, cm^{-1}) for **4**: 2020 (s), 2007 (s), 1992 (w), 1940 (s), 1934 (m, sh), 1906 (s). ^1H NMR (δ in $CDCl_3$): 7.39 (m, 10H, Ph), 5.77 (d, 2H, $^4J_{P-H}$ = 2.3 Hz, CH), 3.84 (dq, $^1J_{H-H}$ = 9.4 Hz, $^3J_{H-H}$ = 7.0 Hz, 2H, CH*H*), 3.58 (dq, $^1J_{H-H}$ = 9.4 Hz, $^3J_{H-H}$ = 7.4 Hz, 2H, CH*H*), 1.63 (d, $^2J_{P-H}$ = 8.2 Hz, 6H, PMe), 1.45 (d, $^2J_{P-H}$ = 8.6 Hz, 6H, PMe), 1.23 (t, $^3J_{H-H}$ = 6.9 Hz, 6H, Me). Anal. Calcd. (found) for **4**: C, 51.54 (51.64); H, 4.74 (4.53).

Reaction of $(OC)_4Mn[C(OEt){=}C(H)C({=}O)]Mn(CO)_5$, 1, with $HC\equiv COEt$. A 10-mg (0.024 mmol) amount of **1** was allowed to react with a 25.0-μL (0.128 mmol) amount of $HC\equiv COEt$ in 20 mL of hexane at 40 °C for 24 h. After the solution was cooled to room temperature and evaporated to dryness, the residue was separated using a 1/4 CH_2Cl_2/hexane solvent mixture to give 3.2 mg of starting material and 3.5 mg of **3** in 29% yield.

Reaction of $Mn_2(CO)_8\{\mu\text{-}O{=}C[(H){=}C(OEt)]_2\}$, 3, with CO in the Presence of $AlCl_3$. A 50-mg (0.374 mmol) amount of $AlCl_3$ was added to 10-mg (0.020 mmol) of **3** in 50 mL of CH_2Cl_2 at 25 °C. After 20 min, this solution was purged with CO for 3 h at 25 °C and then filtered quickly over a 2-in. silica gel column to remove the $AlCl_3$. The solvent was evaporated at room temperature, and the residue was separated by TLC using hexane solvent to give 9.5 mg of $Mn_2(CO)_9\{\mu\text{-}O{=}C[C(H){=}C(OEt)]_2\}$, **5**, in 90% yield. IR (ν_{co} in hexane, cm^{-1}) for **5**: 2122 (w), 2084 (w), 2065 (w), 2032 (s), 2005 (s), 1995 (s), 1954 (s), 1553 (w, br). ^1H NMR (δ in C_6D_6): 6.31 (s, 1H, CH), 5.89 (s, 1H, CH), 3.75 (q, $^3J_{H-H}$ = 7.0 Hz, 2H, CH*H*), 3.43 (q, $^3J_{H-H}$ = 7.0 Hz, 2H, CH*H*), 1.12 (t, $^3J_{H-H}$ = 7.0 Hz, 3H, CH_3), 1.00 (t, $^3J_{H-H}$ = 6.9 Hz, 3H, CH_3). Anal. Calcd (found) for **5**: C, 40.75 (40.86); H, 2.26 (2.13).

Decarbonylation of $Mn_2(CO)_9\{\mu\text{-}O{=}C[C(H){=}C(OEt)]_2\}$, 5. A solution of 10.0-mg (0.020 mmol) of **5** in 50 mL of hexane was purged slowly with nitrogen at 25 °C for 24 h. After the solvent was removed, the residue was separated using hexane as elution solvent to give 9.0 mg of **4**, 96% yield.

Preparation of $Mn(CO)_4[C(OEt){=}C(H)C(O)C(H){=}CH(OEt)]$, 6. (1) Reaction of 3 with HCl under CO. A 10-mg (0.020 mmol) amount of **3** was dissolved in 20-mL of hexane. CO

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[5] (a) Adams, R. D.; Chen, G.; Chen, L.; Wu, W.; Yin, J. *J. Am. Chem. Soc.* **1991**, *113*, 9406.

[6] Koelle, U. *J. Organomet. Chem.* **1978**, *155*, 53.

Table I. Crystallographic Data for Compounds 1 and 4–6

	compd			
	1	**4**	**5**	**6**
empirical formula	$Mn_2O_{11}C_{14}H_6$	$Mn_2P_2O_9C_{31}H_{34}$	$Mn_2O_{12}C_{18}H_{12}$	$MnO_7C_{13}H_{13}$
fw	460.07	722.43	530.16	336.18
cryst system	monoclinic	monoclinic	monoclinic	triclinic
lattice params				
a (Å)	12.088(2)	26.271(7)	7.565(2)	9.207(1)
b (Å)	10.521(3)	9.130(2)	22.788(4)	10.428(2)
c (Å)	15.726(3)	15.616(5)	13.015(2)	8.911(1)
α (deg)				105.89(1)
β (deg)	108.14(2)	113.90(2)	92.71(2)	93.40(1)
γ (deg)				70.34(1)
V (Å^3)	1900.6(7)	3425(3)	2241.3(8)	774.4(2)
space group	$P2_1/n$ (No. 14)	$C2/c$ (No. 15)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
Z	4	4	4	2
D_{calc} (g/cm^3)	1.61	1.40	1.57	1.44
μ(Mo Kα) (cm^{-1})	13.26	8.47	11.38	8.44
temp (°C)	20	20	20	20
$2\theta_{max}$ (deg)	42.0	43.0	42.1	46.1
no. of observns ($I > 3\sigma(I)$)	1440	1226	1515	1826
no. of variables	268	200	337	229
residuals: R; R_w	0.027; 0.026	0.038; 0.036	0.032; 0.031	0.032; 0.040
goodness of fit indicator	129	1.34	1.41	1.79
max shift in final cycle	0.01	0.00	0.04	0.04
largest peak in final diff map (e/Å^3)	0.18	0.26	0.23	0.23
abs corr	empirical	empirical	empirical	empirical

was purged slowly through the solution for 10 min at 25 °C, and a 1-mL amount of aqueous 12 M HCl was then added. The reaction mixture was heated to 50 °C for 30 min while the CO purge was maintained. After the solution was cooled to room temperature, the solvent was removed under vacuum. The residue was separated by TLC using a 2/1 hexane/CH_2Cl_2 solvent mixture to give 6.0 mg of yellow $Mn(CO)_4[C(OEt){=}C(H)C(O)C(H){=}CH(OEt)]$, **6**, 90% yield, and 3.2 mg of the known compound $Mn(CO)_5Cl$ that was characterized by IR analysis.[7] IR (ν_{co} in hexane, cm^{-1}) for **6**: 2085 (m), 1998 (s), 1956 (s), 1940 (w), 1919 (w), 1647 (m), 1627 (m), 1512 (m). ^{1}H NMR (δ in C_6D_6, ppm): 7.42 (d, $^3J_{H-H}$ = 12.4 Hz, 1H, COEt*H*), 5.82 (s, 1H, C*H*), 5.60 (d, $^3J_{H-H}$ = 12.4 Hz, 1H, C*H*), 3.65 (q, $^3J_{H-H}$ = 7.1 Hz, 2H, OCH_2), 3.18 (q, $^3J_{H-H}$ = 7.1 Hz, 2H, OCH_2), 1.06 (t, $^3J_{H-H}$ = 7.1 Hz, 3H, CH_3), 0.76 (t, $^3J_{H-H}$ = 7.1 Hz, 3H, CH_3). Anal. Calcd (found) for **6** ($MnO_7C_{13}H_{13}$): C, 46.40 (47.02); H, 3.87 (3.92).

(2) Reaction of 3 with $NaBH_4$ under CO. CO was purged through a solution containing a 10.0-mg (0.020 mmol) amount of **3** in 20.0 mL of THF at 25 °C for 10 min. A 1.5-mg (0.040 mmol) amount of $NaBH_4$ was added, and the solution was stirred at 25 °C for 3 h in the presence of the CO purge. A 1.0-mL amount of H_2O was added to the solution, and the mixture was stirred at 25 °C for another 3 h. The solution was then evaporated to dryness under vacuum. The residue was separated by TLC using a 3/1 hexane/CH_2Cl_2 solvent mixture to give 1.0 mg of starting material and 5.0 mg of **6**, 75% yield. The eliminated manganese grouping was not located in this reaction.

Crystallographic Analysis. Crystals of compounds **1** and **5** suitable for X-ray diffraction analysis were grown by slow evaporation of solvent from solutions in 3/1 hexane/CH_2Cl_2 solvent mixtures at −3 °C. Crystals of compound **4** were grown by slow evaporation of solvent from 1/1 hexane/CH_2Cl_2 solvent mixtures at 25 °C. Crystals of compound **6** were grown by slow evaporation of solvent from a solution in Et_2O 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.[8a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[8b] 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

$$\sum\nolimits_{hkl} w(|F_o| - |F_c|)^2$$

where $w = 1/\sigma(F_o)^2$, $\sigma(F_o) = \sigma(F_o^2)/2F_o$, and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (0.02I_{net})^2]^{1/2}/Lp$. Each structure was 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 **1** and **5** crystallized in the monoclinic crystal system. The space group $P2_1/n$ was identified uniquely from the systematic absences in the data. For both compounds all non-hydrogen atoms were refined with anisotropic thermal parameters, and the positions of all hydrogen atoms were located and refined with isotropic thermal parameters.

Compound **4** crystallized in the monoclinic crystal system. The systematic absences in the data were consistent with either of the space groups $C2/c$ or Cc. The centrosymmetrical space group $C2/c$ 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 were calculated by assuming idealized geometries, C–H = 0.95 Å, and using located positions whenever possible.

Compound **6** 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 were calculated by assuming idealized geometries, C–H = 0.95 Å, and using located positions whenever possible.

Results and Discussion

Three new compounds $(OC)_4Mn[C(OEt){=}C(H)C({=}O)]Mn(CO)_5$, **1**, 6% yield, $Mn_2(CO)_8[\mu\text{-}C{=}C(H)C\text{-}$

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[7] Kaesz, H. D.; Bau, R.; Hendrickson, D.; Smith, J. M. *J. Am. Chem. Soc.* **1967**, *89*, 2844.

[8] (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.

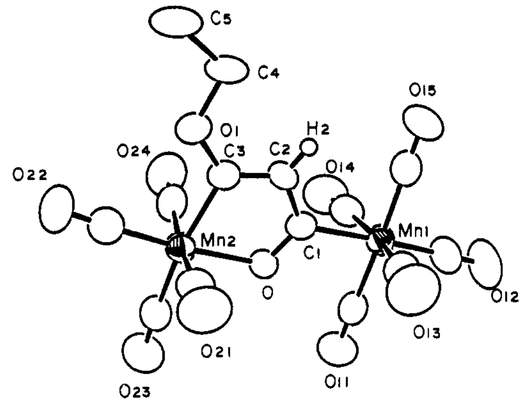


Figure 1. ORTEP diagram of $(OC)_4Mn[C(OEt){=}C(H)C({=}O)]Mn(CO)_5$. 1, showing 50% probability thermal ellipsoids.

Table II. Positional Parameters and *B*(eq) Values (Å²) for 1

atom	*x*	*y*	*z*	*B*(eq)
Mn(1)	0.33295(05)	0.05088(06)	0.64103(04)	3.81(3)
Mn(2)	0.22860(05)	–0.34955(06)	0.49123(04)	3.87(3)
O	0.2863(02)	–0.2079(03)	0.58289(18)	3.9(1)
O(1)	0.1440(02)	–0.2070(03)	0.32470(19)	4.4(1)
O(11)	0.3831(03)	–0.1439(04)	0.7864(02)	6.7(2)
O(12)	0.4212(04)	0.2546(04)	0.7776(03)	9.8(2)
O(13)	0.0844(03)	0.0588(04)	0.6333(03)	8.7(2)
O(14)	0.5580(03)	–0.0156(04)	0.6131(03)	7.9(2)
O(15)	0.2839(03)	0.2403(03)	0.4923(02)	6.9(2)
O(21)	–0.0112(04)	–0.3250(04)	0.5052(03)	7.9(2)
O(22)	0.1354(03)	–0.5303(03)	0.3431(02)	6.7(2)
O(23)	0.3090(04)	–0.5411(04)	0.6363(03)	8.4(2)
O(24)	0.4475(03)	–0.3363(04)	0.4436(03)	7.5(2)
C(1)	0.2731(03)	–0.0957(04)	0.5510(03)	3.4(2)
C(2)	0.2201(04)	–0.0839(05)	0.4580(03)	3.7(2)
C(3)	0.1911(03)	–0.1954(04	0.4134(03)	3.5(2)
C(4)	0.1281(05)	–0.0941(05)	0.2686(03)	5.0(3)
C(5)	0.0825(06)	–0.1427(07)	0.1747(04)	7.3(4)
C(11)	0.3638(04)	–0.0712(05)	0.7314(03)	4.5(2)
C(12)	0.3877(05)	0.1766(05)	0.7253(03)	6.1(3)
C(13)	0.1798(04)	0.0587(05)	0.6387(03)	5.2(2)
C(14)	0.4732(04)	0.0132(05)	0.6251(03)	4.9(2)
C(15)	0.3025(04)	0.1676(05)	0.5489(03)	4.8(2)
C(21)	0.0820(05)	–0.3345(05)	0.5022(03)	5.1(2)
C(22)	0.1714(04)	–0.4612(05)	0.4022(03)	4.8(2)
C(23)	0.2776(04)	–0.4697(05)	0.5796(03)	5.4(3)
C(24)	0.3667(04)	–0.3433(05)	0.4653(03)	4.8(2)
H(2)	0.211(03)	–0.009(03)	0.434(02)	1.9(8)

(OEt)=O], **2**, 3% yield, and $Mn_2(CO)_8\{\mu\text{-}O{=}C[C(H){=}C(OEt)]_2\}$, **3**, 2% yield, were obtained when solutions of $Mn_2(CO)_{10}$ and HC≡COEt were irradiated (UV) at 25 °C. The yield of **3** was significantly larger 16% in the thermal reaction of $Mn_2(CO)_9(NCMe)$ with HC≡COEt, but the yield of **2** was about the same 2%, and **1** was not formed at all. Under no circumstances were we able to obtain good yields of any of these compounds.

Compound **1** was characterized by IR, ^1H NMR, and single-crystal X-ray diffraction analyses. An ORTEP diagram of the molecular structure of **1** is shown in Figure 1. Final atomic positional parameters are listed in Table II. Selected bond distances and angles are listed in Table III and IV, respectively. The molecule contains a metallacyclic ring formed by the coupling of the unsubstituted end of one molecule of HC≡COEt to one CO ligand. This CO group was inserted between the metal atoms with the carbon atom bonded to a $Mn(CO)_5$ grouping, Mn(1)–C(1) = 2.066(4) Å, and the oxygen atom coordinated to the other metal atom, Mn(2)–O = 2.039(3) Å. The CO bond is long, C(1)–O = 1.274(5) Å, and a low-frequency absorption at 1587 cm^{-1} observed in the infrared spectrum is assigned to this CO grouping. Formally, no CO was lost from the $Mn_2(CO)_{10}$ in the formation of **1**, and this probably explains why this compound was not formed in the reaction of $Mn_2(CO)_9(NCMe)$ with HC≡COEt. The C(2)–C(3) bond is double, C(2)–C(3) = 1.356(6) Å, and the entire metallacyclic ring is planar. The hydrogen atom exhibits a characteristic deshielded resonance shift in the ^1H NMR spectrum, δ = 6.49 ppm.

Table III. Intramolecular Distances for 1[a]

Mn(1)–C(1)	2.066(4)	Mn(2)–C(23)	1.835(5)
Mn(1)–C(11)	1.865(5)	Mn(2)–C(24)	1.839(5)
Mn(1)–C(12)	1.844(6)	O–C(1)	1.274(5)
Mn(1)–C(13)	1.842(5)	O(1)–C(3)	1.339(5)
Mn(1)–C(14)	1.833(5)	O(1)–C(4)	1.456(5)
Mn(1)–C(15)	1.847(5)	C(1)–C(2)	1.407(6)
Mn(2)–O	2.039(3)	C(2)–C(3)	1.356(6)
Mn(2)–C(3)	1.996(4)	C(4)–C(5)	1.497(7)
Mn(2)–C(21)	1.840(6)	O–C(av)	1.137(5)
Mn(2)–C(22)	1.793(5)	Mn(1)–Mn(2)	4.800(1)

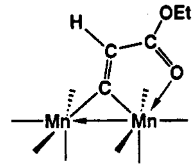
[a] Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Table IV. Intramolecular Bond Angles for 1[a]

C(1)–Mn(1)–C(11)	87.3(2)	C(3)–Mn(2)–C(24)	83.3(2)
C(1)–Mn(1)–C(12)	177.5(2)	Mn(2)–O–C(1)	115.2(2)
C(1)–Mn(1)–C(13)	83.4(2)	C(3)–O(1)–C(4)	119.4(3)
C(1)–Mn(1)–C(14)	83.5(2)	Mn(1)–C(1)–O	116.6(3)
C(1)–Mn(1)–C(15)	91.0(2)	Mn(1)–C(1)–C(2)	126.5(3)
O–Mn(2)–C(3)	78.6(2)	O–C(1)–C(2)	116.8(4)
O–Mn(2)–C(21)	89.9(2)	C(1)–C(2)–C(3)	115.0(4)
O–Mn(2)–C(22)	174.0(2)	Mn(2)–C(3)–O(1)	120.5(3)
O–Mn(2)–C(23)	90.5(2)	Mn(2)–C(3)–C(2)	114.4(3)
O–Mn(2)–C(24)	89.8(2)	O(1)–C(3)–C(2)	125.1(4)
C(3)–Mn(2)–C(21)	86.9(2)	O(1)–C(4)–C(5)	104.9(5)
C(3)–Mn(2)–C(22)	95.4(2)	Mn–C(av)–O	178(1)
C(3)–Mn(2)–C(23)	169.0(2)		

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

Compound **2** was obtained in very small amounts both from the photoreaction of HC≡COEt with $Mn_2(CO)_{10}$ and the thermal reaction with $Mn_2(CO)_9(NCMe)$. Compound **2** is not stable for long periods of time. The proposed structure of **2** shown is based on spectral similarities to the compounds **A** that we obtained in our previous studies of the corresponding reactions of the alkynes MeC≡CX, X = NMe_2 or OEt, with $Mn_2(CO)_9(NCMe)$.[1] The mass spectrum *m*/*e* = 432 confirms the molecular weight. The pattern of IR absorptions is very similar to those of the compounds **A**, and **2** also exhibits the expected low-frequency absorption, 1565 cm^{-1}, of the C=O of the coordinated ester group. The hydrogen atom of the bridging vinylidene ligand exhibits a deshielded shift, δ = 6.99 ppm, typical of bridging vinylidene ligands.[9]



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(9) Doherty, N. M.; Elshenbroich, C.; Kneuper, H.-J.; Knox, S. A. R. *J. Chem. Soc., Chem. Commun.* **1985**, 170.

(10) Derunov, V. V.; Shilova, O. S.; Batsanov, A. S.; Yannovskii, A. I.; Struchkov, Yu. T.; Kolobova, N. E. *Metalloorg. Khim.* **1991**, *4*, 1166.

(11) (a) Olah, G. A. *Friedel-Crafts and Related Reactions*; Interscience Publishers: New York, 1964. (b) Palm, V. A.; Haldna, U. L.; Talvik, A. J. In *The Chemistry of the Carbonyl Group*; Patai, S., Ed.; Interscience: London, 1966.

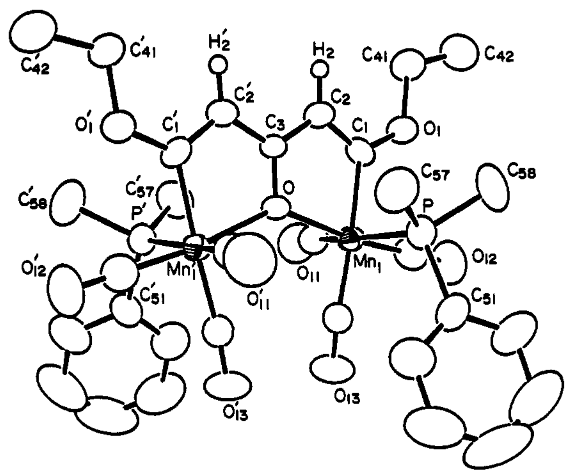

Figure 2. ORTEP diagram of $Mn_2(CO)_6(PMe_2Ph)_2\{\mu\text{-}O{=}C\text{-}[C(H){=}C(OEt)]_2\}$, 4, showing 50% probability thermal ellipsoids.

Table V. Positional Parameters and *B*(eq) Values (Å²) for 4

atom	*x*	*y*	*z*	*B*(eq)
Mn(1)	0.43193(04)	0.15514(10)	0.13051(06)	2.90(4)
P	0.37322(07)	0.1389(02)	0.20856(11)	3.58(8)
O	$^1/_2$	0.0712(06	$^1/_4$	2.8(2)
O(1)	0.37659(17)	–0.1149(04)	0.0356(03)	3.8(2)
O(11)	0.4848(02)	0.1720(07)	–0.0031(03)	6.4(3)
O(12)	0.3329(02)	0.2322(06)	–0.0343(06)	6.8(3)
O(13)	0.4540(02)	0.4722(06)	0.1579(04)	7.0(3)
C(1)	0.4196(02)	–0.0595(07)	0.1095(04)	3.3(3)
C(2)	0.4577(02)	–0.1478(07)	0.1764(04)	3.3(3)
C(3)	$^1/_2$	–0.0724(09)	$^1/_4$	2.6(4)
C(11)	0.4674(03)	0.1595(08)	0.0535(04)	3.9(3)
C(12)	0.3724(03)	0.2016(07)	0.0314(05)	4.4(3)
C(13)	0.4473(02)	0.3477(08)	0.1553(04)	3.8(3)
C(41)	0.3694(03)	–0.2746(07)	0.0287(05)	5.2(3)
C(42)	0.3161(03)	–0.3102(08)	–0.0459(06)	7.1(4)
C(51)	0.3514(03)	0.3164(08)	0.2335(05)	4.1(3)
C(52)	0.2984(03)	0.3698(09)	0.1818(05)	6.2(4)
C(53)	0.2843(05)	0.5099(13)	0.1974(08)	8.9(7)
C(54)	0.3214(07)	0.5966(12)	0.2628(10)	10.1(8)
C(55)	0.3739(05)	0.5473(11)	0.3148(07)	8.4(6)
C(56)	0.3889(03)	0.4064(09)	0.2990(06)	6.2(4)
C(57)	0.3977(03)	0.0423(08)	0.3199(05)	5.4(4)
C(58)	0.3082(03)	0.0425(09)	0.1435(05)	5.9(4)

Table VI. Intramolecular Distances for 4[a]

Mn(1)–P	2.325(2)	O–C(3)	1.312(9)
Mn(1)–O	2.136(2)	O(1)–C(1)	1.345(6)
Mn(1)–C(1)	1.992(6)	O(1)–C(41)	1.469(7)
Mn(1)–C(11)	1.796(7)	C(1)–C(2)	1.376(8)
Mn(1)–C(12)	1.750(7)	C(2)–C(3)	1.413(7)
Mn(1)–C(13)	1.811(7)	C(41)–C(42)	1.45(1)
P–C(51)	1.814(7)	Mn(1)–Mn′(1)	3.988(2)
P–C(57)	1.819(7)	O–C(av)	1.15(1)
P–C(58)	1.822(7)	C(Ph)–C(av)	1.38(1)

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

Table VII. Intramolecular Bond Angles for 4[a]

P–Mn(1)–O	91.00(6)	C(51)–P–C(58)	104.1(3)
P–Mn(1)–C(1)	85.7(2)	C(57)–P–C(58)	100.8(4)
P–Mn(1)–C(11)	170.6(2)	Mn(1)–O–Mn′(1)	138.0(3)
P–Mn(1)–C(12)	86.2(2)	Mn(1)–O–C(3)	111.0(1)
P–Mn(1)–C(13)	95.0(2)	C(1)–O(1)–C(41)	118.4(5)
O–Mn(1)–C(1)	79.3(2)	Mn(1)–C(1)–O(1)	122.4(4)
O–Mn(1)–C(11)	96.6(2)	Mn(1)–C(1)–C(2)	115.6(4)
O–Mn(1)–C(12)	172.7(3)	O(1)–C(1)–C(2)	122.0(5)
O–Mn(1)–C(13)	97.2(2)	C(1)–C(2)–C(3)	115.0(6)
C(1)–Mn(1)–C(11)	90.3(3)	O–C(3)–C(2)	119.2(4)
C(1)–Mn(1)–C(12)	93.8(3)	C(2)–C(3)–C′(2)	121.7(8)
C(1)–Mn(1)–C(13)	176.4(3)	O(1)–C(41)–C(42)	109.6(6)
Mn(1)–P–C(51)	113.0(2)	P–C(51)–C(52)	121.3(6)
Mn(1)–P–C(57)	118.6(2)	P–C(51)–C(56)	120.1(6)
Mn(1)–P–C(58)	114.2(2)	Mn–C(av)–O	173(1)
C(51)–P–C(57)	104.3(3)	C(Ph)–C(av)–C	120(1)

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

Attempts to grow crystals of compound 3 suitable for an X-ray diffraction analysis were unsuccessful. Thus, it was converted to the bis-PMe_2Ph derivative $Mn_2(CO)_6(PMe_2Ph)_2\{\mu\text{-}O{=}C[C(H){=}C(OEt)]_2\}$, 4, by ligand substitution using PMe_2Ph. Crystals of 4 suitable for single-crystal X-ray diffraction analysis were obtained, and the analysis was successfully completed. An ORTEP drawing of the molecular structure of $Mn_2(CO)_6(PMe_2Ph)_2\{\mu\text{-}O{=}C[C(H){=}C(OEt)]_2\}$, 4, 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. Compound 4 contains two metallacyclic rings formed by the coupling of two $HC{\equiv}COEt$ alkynes to one CO ligand. This $(EtOC{=}CH)_2C{=}O$ ligand bridges the two metal atoms with the oxygen atom of the carbonyl group bonded directly to both metal atoms, Mn(1)–O = 2.136(2) Å. There is a crystallographically-imposed C_2 rotation axis that passes through the carbonyl C(3)–O bond. The Mn(1)···Mn(1′) distance of 3.988(2) Å is too long to permit any significant direct metal–metal bonding. This C=O bond is significantly longer, 1.312(9) Å, than that found in 1, and there is delocalized unsaturation throughout the entire planar C(1)–C(2)–C(3)–C(2′)–C(1′) chain, C(1)–C(2) = 1.376(8) Å and C(2)–C(3) = 1.413(7) Å. The $Mn_2O{=}C$ grouping is planar. The $(EtOC{=}CH)_2C{=}O$ ligand was evidently formed by the coupling of two $HC{\equiv}COEt$ molecules at their unsubstituted ends to the carbon atom of a carbonyl ligand.[12] The ligand is also σ-coordinated to the metal atoms through the carbons C(1) and C(1′). The EtO-substituted carbon atoms are bonded directly to the metal atoms, and the Mn(1)–C(1) distance, 1.992(6) Å, is essentially the same as the corresponding distance in 1, 1.996(4) Å. The hydrogen atom on the carbon C(2) shows the expected deshielded shift, δ = 5.77 ppm. The PMe_2Ph ligands occupy coordination sites cis to the oxygen atom O and the carbon atom C(1), and as a result, the methyl groups are inequivalent, δ = 1.63 and 1.45 ppm.

Compound 3 is believed to have a structure similar to 4 with CO ligands in the positions of the PMe_2Ph groups. The structure of the related compound $Mn_2(CO)_8\{\mu\text{-}O{=}C[C(H){=}CCO_2Me]_2\}$, 7, obtained from the photoreaction of $Mn_2(CO)_{10}$ with $HC{\equiv}CCO_2Me$ was recently reported.[10] The IR absorption of the bridging carbonyl group in 3 was observed at 1498 cm^{-1}. This is nearly 100 cm^{-1} lower in frequency than that observed in 1, where the oxygen atom is coordinated to only one metal atom. The identity of the CO absorption was confirmed by the preparation of ^{13}CO-labeled compound 3*, which showed the IR absorption of the ketonic double bond shifted to 1483 cm^{-1}. We feel that greater reduction of the frequency of the absorption of the CO group in 3 is direct evidence for a higher degree of C=O bond reduction for the bridging CO group in 3 than in 1. This is also supported by the longer C-O bond length observed in 4; *vide supra*. Interestingly, it was possible to obtain 3 from 1 in 29% yield by reaction with $HC{\equiv}COEt$ in hexane solvent at 40 °C for 24 h.

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(12) Dalton, D. M.; Fernandez, J. M.; Emerson, K.; Larsen, R. D.; Arif, A. M.; Gladysz, J. *J. Am. Chem. Soc.* **1990**, *112*, 9198.

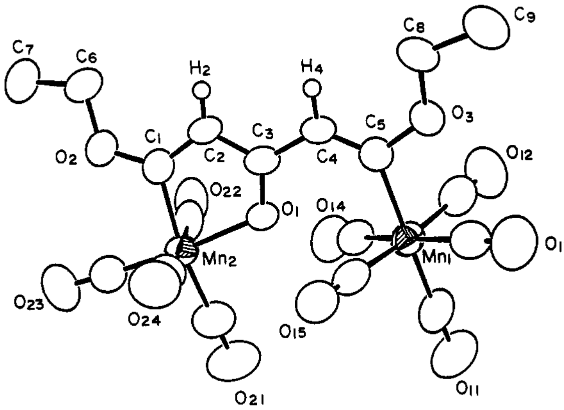

Figure 3. ORTEP diagram of $Mn_2(CO)_9\{\mu\text{-}O{=}C[C(H){=}C(OEt)]_2\}$, **5**, showing 50% probability thermal ellipsoids.

Table VIII. Positional Parameters and *B*(eq) Values (Å^2) for 5

atom	*x*	*y*	*z*	*B*(eq)
Mn(1)	0.83640(12)	0.10700(04)	0.82645(06)	4.31(5)
Mn(2)	0.61774(13)	−0.10055(04)	0.74430(06)	4.80(5)
O(1)	0.7208(04)	−0.01951(15)	0.7239(03)	4.2(2)
O(2)	0.6114(05)	−0.14911(16)	0.5369(03)	4.7(2)
O(3)	0.8771(05)	0.15172(15)	0.6256(03)	4.5(2)
O(11)	0.8187(07)	0.1251(02)	1.0511(04)	9.1(3)
O(12)	1.1988(07)	0.1585(02)	0.8189(04)	8.1(3)
O(13)	0.6825(07)	0.2266(02)	0.8013(04)	7.8(3)
O(14)	1.0201(06)	−0.0074(02)	0.8687(03)	7.6(3)
O(15)	0.4686(06)	0.0591(02)	0.8092(04)	6.8(3)
O(21)	0.6149(09)	−0.0851(03)	0.9704(04)	12.6(4)
O(22)	0.9768(07)	−0.1541(02)	0.7501(04)	7.5(3)
O(23)	0.4501(07)	−0.2167(02)	0.7445(04)	8.3(3)
O(24)	0.2599(07)	−0.0519(02)	0.6897(04)	8.0(3)
C(1)	0.6498(07)	−0.1011(03)	0.5927(04)	4.0(3)
C(2)	0.7160(08)	−0.0500(03)	0.5549(04)	4.0(3)
C(3)	0.7485(07)	−0.0063(02)	0.6302(04)	3.8(3)
C(4)	0.8063(08)	0.0520(03)	0.6034(04)	4.0(3)
C(5)	0.8385(07)	0.0978(03)	0.6676(04)	3.9(3)
C(6)	0.6428(09)	−0.1511(03)	0.4285(05)	4.9(4)
C(7)	0.6138(14)	−0.2132(04)	0.3963(08)	7.7(6)
C(8)	0.8617(10)	0.1608(03)	0.5158(05)	4.7(4)
C(9)	0.8864(13)	0.2248(04)	0.4970(07)	6.5(5)
C(11)	0.8253(09)	0.1174(03)	0.9648(05)	6.1(4)
C(12)	1.0620(10)	0.1393(03)	0.8205(05)	5.4(4)
C(13)	0.7391(09)	0.1810(03)	0.8079(05)	5.5(4)
C(14)	0.9450(09)	0.0343(03)	0.8477(04)	5.3(4)
C(15)	0.6110(10)	0.0750(03)	0.8164(04)	4.9(4)
C(21)	0.6129(10)	−0.0907(03)	0.8830(05)	7.8(5)
C(22)	0.8402(10)	−0.1331(03)	0.7513(05)	5.6(4)
C(23)	0.5171(09)	−0.1715(03)	0.7463(05)	5.9(4)
C(24)	0.3961(10)	−0.0694(03)	0.7137(05)	5.8(4)

Table IX. Intramolecular Distances for 5[a]

Mn(1)–C(5)	2.079(5)	Mn(2)–C(24)	1.847(8)
Mn(1)–C(11)	1.823(7)	O(1)–C(3)	1.282(6)
Mn(1)–C(12)	1.864(8)	O(2)–C(1)	1.338(6)
Mn(1)–C(13)	1.852(7)	O(3)–C(5)	1.381(6)
Mn(1)–C(14)	1.865(7)	C(1)–C(2)	1.368(7)
Mn(1)–C(15)	1.854(7)	C(2)–C(3)	1.410(7)
Mn(2)–O(1)	2.027(3)	C(3)–C(4)	1.446(7)
Mn(2)–C(1)	1.999(5)	C(4)–C(5)	1.353(7)
Mn(2)–C(21)	1.821(7)	O–C(av)	1.140(7)
Mn(2)–C(22)	1.838(8)	Mn(1)–O(1)	3.278(3)

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

Table X. Intramolecular Bond Angles for 5[a]

O(1)–Mn(2)–C(1)	79.1(2)	C(2)–C(3)–C(4)	121.7(5)
Mn(2)–O(1)–C(3)	114.8(3)	C(3)–C(4)–C(5)	127.4(5)
Mn(2)–C(1)–O(2)	120.5(4)	Mn(1)–C(5)–O(3)	108.4(4)
Mn(2)–C(1)–C(2)	114.4(4)	Mn(1)–C(5)–C(4)	133.0(4)
O(2)–C(1)–C(2)	125.1(5)	O(3)–C(5)–C(4)	118.5(5)
C(1)–C(2)–C(3)	113.9(5)	O(2)–C(6)–C(7)	106.1(6)
O(1)–C(3)–C(2)	117.6(5)	Mn–C(av)–O	177(1)
O(1)–C(3)–C(4)	120.6(5)		

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

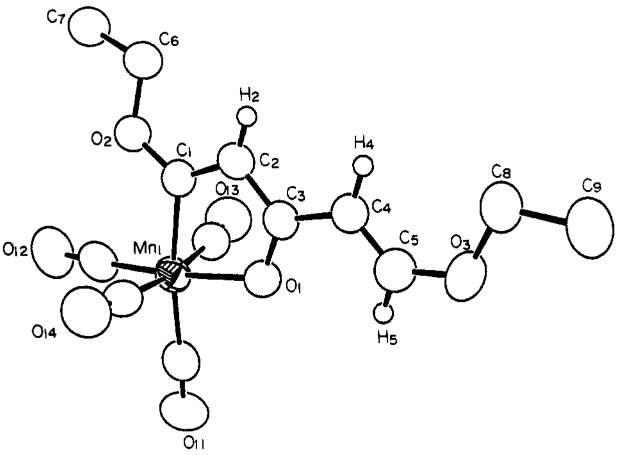

Figure 4. ORTEP diagram of $Mn(CO)_4[C(OEt){=}C(H)C(O)C(H){=}CH(OEt)]$, **6**, showing 50% probability thermal ellipsoids.

When compound **3** was treated with CO (1 atm) and $AlCl_3$ in a CH_2Cl_2 solution at 25 °C for 3 h, the CO addition product $Mn_2(CO)_9\{\mu\text{-}O{=}C[C(H){=}C(OEt)]_2\}$, **5**, was obtained in 90% yield. Compound **5** was characterized by a combination of IR, ^1H NMR, and single-crystal X-ray diffraction analyses. An ORTEP drawing of the molecular structure of **5** is shown in Figure 3. Final atomic positional parameters are listed in Table VIII. Selected bond distances and angles are listed in Table IX and X, respectively. Compound **5** contains a bridging $(EtOC{=}CH)_2C{=}O$ ligand similar to that found in **4**, but the ketonic oxygen atom O(1) is coordinated to only one manganese atom, Mn(2)–O(1) = 2.027(3) Å, a carbonyl ligand was added to one manganese atom, Mn(1), and the Mn(1)···O(1) distance was lengthened to a nonbonding value, 3.278(3) Å. The ketonic C(3)–O(1) distance has shortened to 1.282(6) Å, and the C=O absorption frequency increased to 1553 cm^{-1}. The addition of CO to **3** is fully reversible, and when solutions of **5** were purged with nitrogen for 24 h at 25 °C, compound **3** was regenerated in essentially a quantitative yield.

When **3** was treated with HCl or $NaBH_4$, one of the manganese atoms was removed and the new compound $Mn(CO)_4[C(OEt){=}C(H)C(O)C(H){=}CH(OEt)]$, **6**, was formed in 90% and 75% yields, respectively. The eliminated manganese grouping was recovered as $Mn(CO)_5Cl$ in the reaction with HCl, but was not found in the reaction with $NaBH_4$. Compound **6** was also characterized by a single-crystal X-ray diffraction analysis. An ORTEP drawing of the molecular structure of **6** is shown in Figure 4. Final atomic positional parameters are listed in Table XI. Selected bond distances and angles are listed in Table XII and XIII, respectively. Compound **6** contains a $EtOC{=}CHC{=}OCH{=}CHOEt$ ligand with a metallacycle formed by the atoms Mn(1), C(1), C(2), C(3), and O(1). The metallacycle is similar to that found in **1** and **5**, but differs from **5** by the replacement of the $Mn(CO)_5$ grouping with the hydrogen atom H(5). The carbonyl oxygen atom O(1) is coordinated to the manganese atom, and the Mn(1)–O(1) distance is slightly longer than that in **1** or **5**, 2.043(3) Å. The CO bond distance C(3)–O(1) = 1.275(3) Å is essentially the same as that in **1** and **5**. The IR spectrum of **6** shows an absorption at 1512 cm^{-1} that we

Scheme I

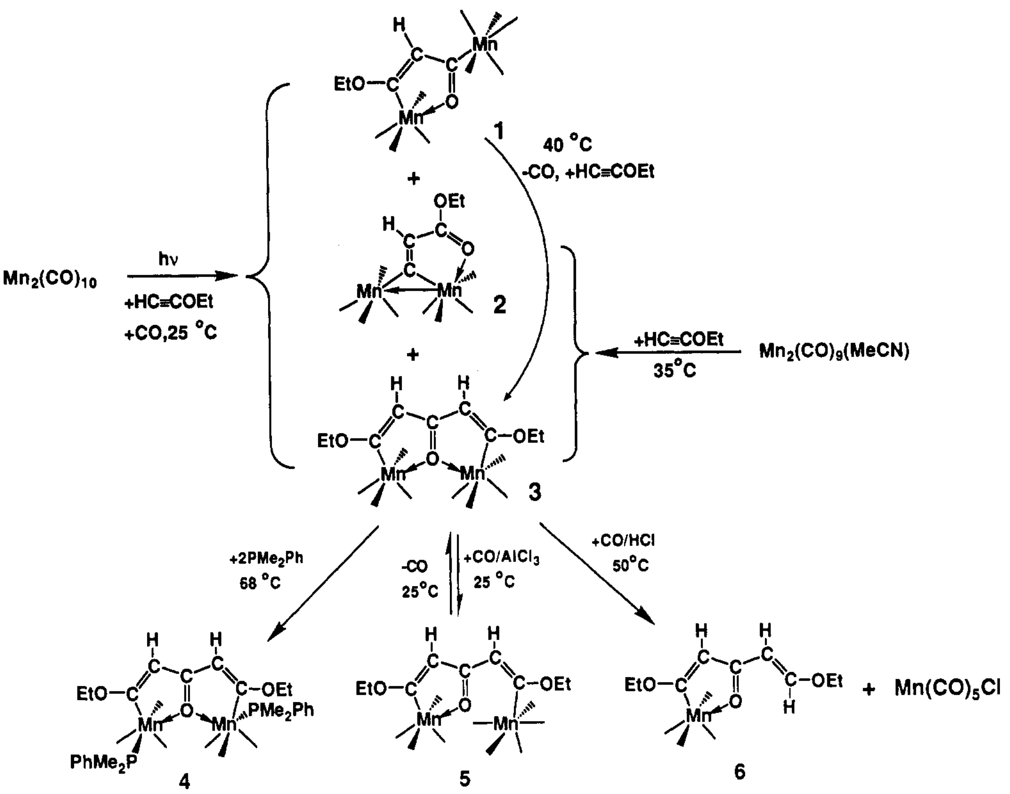

Table XI. Positional Parameters and B(eq) Values (Å^2) for 6

atom	x	y	z	B(eq)
Mn(1)	0.80380(05)	0.40150(04)	0.58808(05)	3.96(3)
O(1)	0.9993(02)	0.28009(20)	0.4534(02)	4.2(1)
O(2)	0.8326(02)	0.26236(20)	0.8378(02)	4.2(1)
O(3)	1.3911(03)	0.0140(02)	0.1932(02)	5.8(1)
O(11)	0.7070(03)	0.6059(02)	0.3929(03)	6.7(2)
O(12)	0.5318(03)	0.5436(03)	0.8014(03)	7.6(2)
O(13)	0.9641(03)	0.5655(03)	0.8245(03)	7.3(2)
O(14)	0.6353(03)	0.2133(03)	0.4079(03)	6.1(2)
C(1)	0.8982(03)	0.2555(03)	0.7041(03)	3.7(1)
C(2)	1.0343(03)	0.1564(03)	0.6401(03)	3.8(2)
C(3)	1.0817(03)	0.1750(03)	0.5019(03)	3.7(1)
C(4)	1.2214(03)	0.0761(03)	0.4145(03)	4.0(2)
C(5)	1.2685(04)	0.0949(04)	0.2881(04)	4.9(2)
C(6)	0.9146(04)	0.1676(04)	0.9299(04)	4.5(2)
C(7)	0.8203(05)	0.2074(05)	1.0758(04)	5.5(2)
C(8)	1.4900(04)	−0.1127(04)	0.2298(04)	5.4(2)
C(9)	1.6168(05)	−0.1828(05)	0.1082(05)	7.0(3)
C(11)	0.7462(04)	0.5272(03)	0.4647(04)	4.8(2)
C(12)	0.6375(04)	0.4902(03)	0.7172(04)	5.0(2)
C(13)	0.9082(04)	0.5041(03)	0.7288(04)	5.0(2)
C(14)	0.7006(03)	0.2850(03)	0.4723(03)	4.2(2)

Table XII. Intramolecular Distances for 6[a]

Mn(1)–O(1)	2.043(2)	C(2)–C(3)	1.412(4)
Mn(1)–C(1)	2.001(3)	C(3)–C(4)	1.453(4)
O(1)–C(3)	1.275(3)	C(4)–C(5)	1.316(4)
O(2)–C(1)	1.342(3)	C(6)–C(7)	1.487(5)
O(2)–C(6)	1.445(3)	C(8)–C(9)	1.488(5)
O(3)–C(5)	1.335(4)	Mn(1)–C(av)	1.836(4)
O(3)–C(8)	1.439(4)	O–C(av)	1.134(4)
C(1)–C(2)	1.362(4)		

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

Table XIII. Intramolecular Bond Angles for 6[a]

O(1)–Mn(1)–C(1)	79.2(1)	O(1)–C(3)–C(2)	119.0(3)
Mn(1)–O(1)–C(3)	113.7(2)	O(1)–C(3)–C(4)	119.8(2)
C(1)–O(2)–C(6)	119.5(2)	C(2)–C(3)–C(4)	121.1(3)
C(5)–O(3)–C(8)	117.9(2)	C(3)–C(4)–C(5)	121.5(3)
Mn(1)–C(1)–O(2)	121.0(2)	O(3)–C(5)–C(4)	129.2(3)
Mn(1)–C(1)–C(2)	114.7(2)	O(2)–C(6)–C(7)	107.3(3)
O(2)–C(1)–C(2)	124.3(3)	O(3)–C(8)–C(9)	107.4(3)
C(1)–C(2)–C(3)	113.5(3)	Mn(1)–C(av)–O	177.7(3)

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

attribute to the carbonyl group. Two other absorptions were observed at 1647 and 1627 cm^{-1}. These may be due to the C–C double bond between carbons C(4) and C(5). The observation of two absorptions suggests that the complex may exist in solution as a mixture of two isomers formed by different rotational conformations at C(3)–C(4) bond; see Figure 4. All three olefinic hydrogen atoms exhibit deshielded NMR resonance shifts: H_4 and H_5 at 7.42 and 5.60 ppm and H_3 at 5.82 ppm. H(4) and H(5) are strongly coupled with $^3J_{H-H}$ = 12.4 Hz, as expected.

A summary of the results of this study is shown in Scheme I. Unlike the internal alkynes MeC≡CX, X = NMe_2 or OEt, HC≡COEt shows very little tendency to form the rearranged substituted vinylidene complexes **A** although a very small amount of the vinylidene complex **2** was observed. Instead, this alkyne was coupled to a CO ligand at the unsubstituted end with the oxygen atom of the carbonyl group coordinated one of the metal atoms, **1**. The addition of two alkynes yielded the dimetalated ketone complex **3**. Interestingly, we found that it was possible to obtain **3** from **1** by reaction with additional HC≡COEt. A species like **1** may be an intermediate in the formation of **3** with both reactions of $Mn_2(CO)_{10}$ and $Mn_2(CO)_9(NCMe)$ with HC≡COEt.

The electrophilic activation of carbonyl groups by Lewis acids is a well-established method for enhancing their reactivity.[11] Coordination of ketones to chiral metal centers has been found to promote nucleophilic additions with a significant asymmetric induction.[12] There are numerous examples of the coordination of ketones to metal atoms,[13-15] but the bridging mode in which the oxygen atom donates both of its lone pairs of electrons as found in **3** is rare.[10,15] We have shown that this coordination results in a lowering of the C–O bond order both by a lengthening of the C–O bond distance and by a reduction in the C–O stretching frequency. We attempted to cleave the Mn–O bonds in **3**, by the addition of CO. This did not succeed, but when $AlCl_3$ was added in combination with the CO, one Mn–O bond was cleaved and the compound **5** was formed. When **5** was isolated and the $AlCl_3$ removed, **5** slowly lost CO and reverted back to **3**. We suspect that the $AlCl_3$ may have promoted the CO addition to **3** by creating an electron deficiency at one of the metal atoms by interacting with the oxygen atoms of the terminal CO ligands. Thus, CO addition to the metal became more favorable. Reaction of **3** with PMe_2Ph in the absence of CO yielded only the disubstitution product **4**.

We have examined the reactivity of **3** toward HCl and $NaBH_4$ to see if any transformations at the bridging carbonyl grouping would occur. None was found, but both reagents did produce removal of one of the manganese carbonyl groupings and addition of a hydrogen atom to the OEt substituted carbon atom to yield compound **6**. Studies of the reaction of other terminal alkynes with $Mn_2(CO)_{10}$ and $Mn_2(CO)_9(NCMe)$ are in progress.

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Supplementary Material Available: Tables of hydrogen atom positional parameters and anisotropic thermal parameters for all of the structural analyses (12 pages). Ordering information is given on any current masthead page.

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(13) (a) Huang, Y.-H.; Gladysz, J. *J. Chem. Educ.* **1988**, *65*, 298. (b) Klein, D. P.; Dalton, D. M.; Mendez, N. Q.; Arif, A. M.; Gladysz, J. *J. Organomet. Chem.* **1991**, *412*, C7. (c) Harman, W. D.; Fairlie, D. P.; Taube, H. *J. Am. Chem. Soc.* **1986**, *108*, 8223.

(14) (a) Beauchamp, A. L.; Olivier, M. J.; Wuest, J. D.; Zacharie, B. *Organometallics* **1987**, *6*, 153. (b) Palm, J. H.; MacGillavry, C. H. *Acta Crystallogr.* **1963**, *16*, 963. (c) Erker, G.; Dorf, U.; Czisch, P.; Petersen, J. L. *Organometallics* **1986**, *5*, 668. (d) Waymouth, R. W.; Potter, K. S.; Schaefer, W. P.; Grubbs, R. H. *Organometallics* **1990**, *9*, 2843. (e) Adams, H.; Bailey, N. A.; Gauntlett, J. T.; Winter, M. J. *J. Chem. Soc., Chem. Commun.* **1984**, 1360.

(15) (a) Sharma, V.; Simard, M.; Wuest, J. D. *J. Am. Chem. Soc.* **1992**, *114*, 7031. (b) Viet, M. T. P.; Sharma, V.; Wuest, J. D. *Inorg. Chem.* **1991**, *30*, 3026. (c) Bachand, B.; Wuest, J. D. *Organometallics* **1991**, *10*, 2015.