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Reactions of Mn$_2$(CO)$_9$(NCMe) with Alkynes Containing Electron-Donating Substituents

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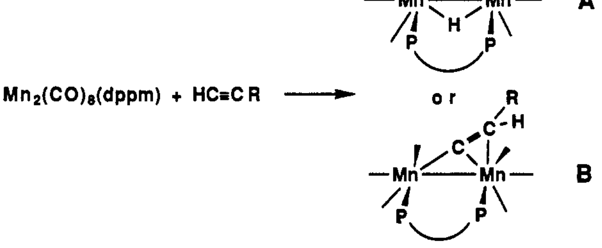
The addition of the electron-rich alkynes, MeC≡CX, X = NMe$_2$ or OEt, to the dimanganese complex Mn$_2$(CO)$_9$(NCMe), **1**, has yielded the vinylidene complexes Mn$_2$(CO)$_8$[μ-η^2-C=C(Me)C=O(X)], **2a**, X = NMe$_2$, and **2b**, X = OEt, respectively, by an addition and a rearrangement of the alkyne that included a CO insertion step. Both products will also add 1 equiv of MeC≡CNMe$_2$ to form the complexes Mn$_2$(CO)$_7$[μ-η^2-CC(Me)C(NMe$_2$)C(Me)C=O(X)], **3a**, X = NMe$_2$, and **3b**, X = OEt, which contain a four-membered carbocyclic ring formed by the addition of the C–C triple bond across the C–C double bond of the vinylidene ligand. The carbocyclic ring in complex **3a** was opened thermally at 80 °C to yield the complex Mn$_2$(CO)$_6$[μ-η^5-(Me$_2$N)CC(Me)CC(Me)C=O(NMe$_2$)], **4**, that contains a carbene center. It was also opened by treatment with acetic acid to yield the mononuclear metal complex Mn(CO)$_3$[η^4-(Me$_2$N)CC(Me)C(H)C(Me)C=O(NMe$_2$)], **5**, by proton addition and the loss of a manganese carbonyl fragment. The fragment was not isolated, but when the acidification was carried out in the presence of PPh$_3$, compound **5** and a coproduct, Mn(CO)$_3$(PPh$_3$)$_2$(O$_2$CMe), **6**, were isolated. Compound **6** is slowly transformed into the known compound Mn(CO)$_2$(PPh$_3$)$_2$(η^2-O$_2$CMe), **7**. Compounds **2a,b**, **3a**, **4**, and **5** were characterized by single-crystal X-ray diffraction analyses. Crystal data for **2a**: space group = $P\bar{1}$, a = 10.422(2) Å, b = 10.628(2) Å, c = 8.934(1) Å, α = 113.74(1)°, β = 97.55(1)°, γ = 93.27(1)°, Z = 2, 1931 reflections, R = 0.027. Crystal data for **2b**: space group = $P\bar{1}$, a = 10.3802(8) Å, b = 11.852(2) Å, c = 7.217(1) Å, α = 91.29(1)°, β = 91.16(1)°, γ = 98.40(1)°, Z = 2, 2482 reflections, R = 0.027. Crystal data for **3a**: space group = $P2_1/c$, a = 11.976(2) Å, b = 10.092(2) Å, c = 18.429(3) Å, β = 107.18(2)°, Z = 4, 2155 reflections, R = 0.027. Crystal data for **4**: space group = $P\bar{1}$, a = 12.496(2) Å, b = 16.481(4) Å, c = 10.398(2) Å, α = 93.97(2)°, β = 103.30(1)°, γ = 95.53(2)°, Z = 4, 4057 reflections, R = 0.043. Crystal data for **5**: space group = $P\bar{1}$, a = 9.540(2) Å, b = 12.166(3) Å, c = 7.888(1) Å, α = 92.06(2)°, β = 104.75(2)°, γ = 111.11(2)°, Z = 2, 2035 reflections, R = 0.029.

Introduction

There have been relatively few studies of reactions of dimanganese carbonyl complexes with alkynes.[1-4] Reactions with terminal alkynes have been shown to yield products containing bridging acetylide ligands **A** and vinylidene ligands **B** (eq 1) by cleavage of the acetylenic CH bond.[2] Some recent studies have shown that terminal alkynes will engage in an unusual mode of coupling to CO to yield dimetalated ketonic ligands, **C**.[5]



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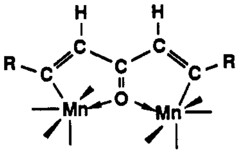

C

The reaction of Mn$_2$(CO)$_{10}$ with the electron-rich ynamine, MeC$_2$NMe$_2$, in the presence of UV irradiation yields the complex Mn$_2$(CO)$_8$(μ-MeCNMe$_2$), **D**, in low yield.[6] The ynamine ligand has been shown to bridge the two metal atoms in an asymmetrical fashion.[6a] This distortion appears to be a result of interactions of the lone pair of electrons on the nitrogen atom with the alkyne carbon atom to which it is bonded.[7]

We observed a novel insertion of the alkyne into a rhenium–rhenium bond in the reaction of the dirhenium complex Re$_2$(CO)$_9$(NCMe),[8] **1**, with alkynes containing electron-withdrawing groups (e.g. HC≡CCO$_2$Me, eq 2) to

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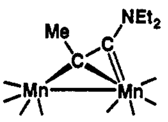
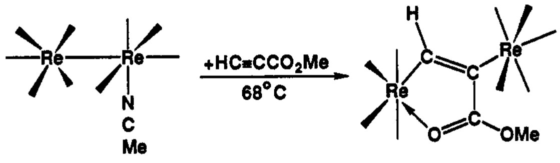


D

yield dimetalated olefin complexes, $Re(CO)_4$[*trans*-μ-$HC{=}C(CO_2Me)$]$Re(CO)_5$, **E**, that have a *trans*-stereochemistry at the C–C double bond.



E

(2)

In this report we describe the reaction of the related manganese complex $Mn_2(CO)_9(NCMe)$ with electron-rich alkynes, alkoxyacetylenes, and ynamines. These reactions are characterized by a bond cleavage at the heteroatomic grouping that is accompanied by an insertion of a CO ligand. A preliminary report of some of these results has been published.[9]

Experimental Section

All reactions were carried out under an atmosphere of nitrogen. Hexane and heptane were freshly distilled over sodium before use. CH_2Cl_2 and benzene were dried and stored over CaH_2. Other reagent-grade solvents were stored over 4-Å molecular sieves. ^{13}CO (containing 99% ^{13}C) was purchased from Cambridge Isotope Laboratories. 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. $Mn_2(CO)_9(MeCN)$,[10] **1**, $MeC{\equiv}CNMe_2$,[11] and $MeC{\equiv}COEt$,[11] were prepared by literature methods.

Reaction of $Mn_2(CO)_9(MeCN)$, 1, with $MeC{\equiv}CNMe_2$. (1) At 40 °C. A 45.0-mg (0.112-mmol) amount of **1** in 50 mL of hexane was allowed to react with a 26.0-μL (0.250-mmol) amount of $MeC{\equiv}CNMe_2$ at 40 °C for 45 min. After cooling, the solvent was removed in vacuo. The residue was dissolved in a minimum of CH_2Cl_2 and separated using a CH_2Cl_2/hexane (1/4) solvent mixture to yield the following compounds in order of elution: 2.5 mg of $Mn_2(CO)_{10}$; 4.6 mg of orange $Mn_2(CO)_8[\mu\text{-}\eta^2\text{-}C{=}C(Me)C{=}O(NMe_2)]$, **2a**, 10% yield; and 5.0 mg of unreacted **1**. The baseline was extracted and separated by using a CH_2Cl_2/hexane (4/1) solvent mixture to give 23.0 mg of red $Mn_2(CO)_7[\mu\text{-}CC(Me)C(NMe_2)C(Me)C(NMe_2){=}O]$, **3a**, 41% yield. IR (ν_{CO} in hexane, cm^{-1}) for **2a**: 2094 (w), 2053 (s), 2013 (vs), 1997 (s), 1975 (m), 1952 (s), 1928 (w), 1554 (w); IR (ν_{CO} in CH_2Cl_2, cm^{-1}) for **3a**: 2036 (m), 1974 (s), 1933 (s, br), 1894 (w), 1583 (w), 1622 (w, C=N). ^1H NMR (δ in acetone-d_6): for **2a** 3.34 (s, br, 3H, N*Me*), 3.07 (s, br, 3H, N*Me*), 2.65 (s, 3H, C*Me*); for **3a** 2.53 (s, 3H, N*Me*), 3.33 (s, 3H, N*Me*), 3.07 (s, 3H, N*Me*), 2.78 (s, 3H, N*Me*), 1.98 (s, 3H, C*Me*), 1.93 (s, 3H, C*Me*). The mass spectrum for **2a**: $m/z = 445 - 28x$, $x = 0$–8 ($M^+ - x$CO). The mass spectrum of **3a** showed a weak parent ion (M^+, $m/z = 500$) with stronger ions $M^+ - x$CO ($x = 1$, 4–7). Anal. Calcd (Found): for **2a** ($Mn_2C_{14}H_9O_9N$) C, 37.78 (37.51); H, 2.04 (1.75); N, 3.15 (3.18); for **3a** ($Mn_2C_{18}H_{18}O_8N_2$) C, 43.22 (43.34); H, 3.63 (3.40); N, 6.00 (5.65).

(2) At 50 °C. A 50.0-mg (0.124-mmol) amount of **1** and a 40.0-μL (0.385-mmol) amount of $MeC{\equiv}CNMe_2$ were dissolved in 50 mL of hexane. The solution was heated at 50 °C for 80 min. After being cooled to room temperature, the solvent was removed under vacuum. The residue was separated using a CH_2Cl_2/hexane (3/2) solvent mixture to yield the following compounds in order of elution: 3.0 mg of $Mn_2(CO)_{10}$; 1.1 mg of orange $Mn_2(CO)_6[\mu\text{-}\eta^5\text{-}(Me_2N)CC(Me)CC(Me)C{=}O(NMe_2)]$, **4**, 2% yield; and 29.0 mg of **3a** in 47% yield. IR (ν_{CO} in hexane, cm^{-1}) for **4**: 2028 (m), 1986 (s), 1951 (m), 1933 (w, br), 1915 (m), 1903 (w), 1580 (w, in CH_2Cl_2), 1634 (w, in CH_2Cl_2, C=N). ^1H NMR for **4** (δ in acetone-d_6): 3.72 (s, 3H, N*Me*), 3.47 (s, 3H, N*Me*), 3.36 (s, 3H, br, N*Me*), 2.89 (s, 3H, br, N*Me*), 2.42 (s, 3H, C*Me*), 2.18 (s, 3H, C*Me*). Anal. Calcd (Found) for **4** ($Mn_2C_{17}H_{18}O_7N_2$): C, 43.23 (42.92); H, 3.84 (3.84); N, 5.93 (5.93).

Reaction of 2a with $MeC{\equiv}CNMe_2$. To a 15.0-mg (0.034-mmol) amount of **2a** dissolved in 30 mL of hexane was added a 20.0-μL (0.192-mmol) amount of $MeC{\equiv}CNMe_2$. The solution was heated at 35 °C for 20 min. After the solution was cooled to room temperature, the solvent was removed under vacuum. The residue was separated by TLC using a CH_2Cl_2/hexane (2/3) solvent mixture to yield 8.2 mg of **3a**, 48% yield.

Pyrolysis of 3a. A 50.0-mg (0.100-mmol) amount of **3a** was dissolved in 30 mL of benzene. The solution was heated to reflux for 1.5 h. After the solution was cooled to room temperature, the solvent was removed under vacuum, and the residue was separated by TLC using a CH_2Cl_2/hexane (3/2) solvent mixture to give 5.2 mg of **4** in 11% yield.

Reaction of 3a with $MeCO_2H$. (1) To a solution of 10.0 mg (0.020 mmol) of **3a** in 10 mL of CH_2Cl_2 was added a 1.0-mL amount of glacial acetic acid. The solution gradually turned from red to yellow. After 1 h, the solvent was removed under vacuum, and the residue was separated by TLC using a CH_2Cl_2/hexane (1/1) solvent mixture to yield 6.3 mg of pale yellow $Mn(CO)_3[\eta^4\text{-}(Me_2N)CC(Me)C(H)C(Me)C{=}O(NMe_2)]$, **5**, in 95% yield. IR (ν_{CO} in hexane, cm^{-1}) for **5**: 2013 (s), 1941 (s), 1913 (s), 1629 (w), 1601 (w). ^1H NMR (δ in C_6D_6) for **5**: 6.97 (s, 1H, C*H*), 3.00 (s, 6H, N*Me*), 2.74 (s, 3H, N*Me*), 2.04 (s, 3H, N*Me*), 1.31 (s, 3H, C*Me*), 0.80 (s, 3H, C*Me*). Anal. Calcd (Found) for **5** ($MnC_{14}H_{19}O_4N_2$): C, 50.30 (50.16); H, 5.69 (6.01); N, 8.38 (8.28).

(2) In the Presence of PPh_3. When this same reaction was conducted in the presence of a 30.0-mg (0.115-mmol) amount of PPh_3, the following compounds were obtained by TLC separation: 10.7 mg of yellow *trans*-$Mn(CO)_2(PPh_3)_2(O_2CMe)$, **7**, 84% yield; 1.5 mg of yellow *fac*-$Mn(CO)_3(PPh_3)_2(O_2CMe)$, **6**, 11% yield; and 6.2 mg of **5**, 93% yield. An IR spectrum of the reaction solution after 1 h indicated that it was principally **5** and **6** with only a small amount of **7**. It is believed that most of the transformation of **6** to **7** occurred during chromatographic workup. In the end only a small amount of impure **6** (mixed with **7**) was obtained. Attempts to purify the **6** by fractional crystallization were not successful, and most of **6** was converted into **7** during this process. The identity of compound **7** was established by comparison of its IR spectra [1935 (s) and 1855 (s) cm^{-1}] in $CDCl_3$ and crystallographic unit cell: $a = 17.710(16)$ Å, $b = 9.708(4)$ Å, $c = 20.96(1)$ Å, $\alpha = 89.95(4)°$, $\beta = 106.16(6)°$, $\gamma = 89.95(6)°$ with previously reported values.[12] IR (ν_{CO} in hexane, cm^{-1}) for **6**: 2038 (s), 1954 (s), 1855 (s). A *fac*-structure is proposed for **6** on the basis of comparisons with the patterns of IR spectra of related known compounds (e.g. *fac*-$Mn(CO)_3Br[P(OPh)_3]_2$ (2053 (s), 2000 (s), 1949 (s)) and *mer,trans*-$Mn(CO)_3Br[P(OPh)_3]_2$ (2070 (w), 2000 (vs), 1949 (s)).[13]

Reaction of 4 with $MeCO_2H$. (a) A 10.0-mg (0.021-mmol) amount of **4** was dissolved in 20 mL of heptane. To this solution was added a 1.0-mL amount of glacial acetic acid. The mixture was heated to reflux for 1 h. The solvent was removed under vacuum, and the residue was separated by TLC using a CH_2-

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Table I. Crystallographic Data

	2a	**2b**	**3a**	**4**	**5**
formula	$Mn_2O_9NC_{14}H_9$	$Mn_2O_{20}C_{14}H_8$	$Mn_2O_8N_2C_{18}H_{18}$	$Mn_2O_7N_2C_{17}H_{18}$	$MnO_4N_2C_{14}H_{19}$
fw	445.10	446.09	500.22	472.21	334.25
cryst syst	triclinic	triclinic	monoclinic	triclinic	triclinic
lattice params					
a (Å)	10.422(1)	10.3802(8)	11.976(2)	12.496(2)	9.540(2)
b (Å)	10.628(2)	11.852(2)	10.092(2)	16.481(4)	12.166(3)
c (Å)	8.934(1)	7.217(1)	18.429(3)	10.398(2)	7.888(1)
α (deg)	113.74(1)	91.29(1)	90.0	93.97(2)	92.06(2)
β (deg)	97.55(1)	91.16(1)	107.18(2)	103.30(1)	104.75(2)
γ (deg)	93.27(1)	98.40(1)	90.0	95.53(2)	111.11(2)
V (Å^3)	891.4(3)	877.9(2)	2128(1)	2065.2(7)	817.5(7)
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
Z value	2	2	4	4	2
ρ_{calc} (g/cm^3)	1.66	1.69	1.56	1.52	1.36
μ(Mo Kα) (cm^{-1})	14.05	14.29	11.84	12.11	7.89
temp (°C)	23	23	23	23	20
$2\theta_{max}$ (deg)	44.0	48.0	45.0	45.0	46.0
no. of obs rflns ($I > 3\sigma$)	1931	2482	2155	4057	2035
residuals: R; R_w	0.027; 0.033	0.027; 0.038	0.027; 0.029	0.043; 0.048	0.029; 0.040

Cl_2/hexane (1/1) solvent mixture to give 6.2 mg of **5**, 90% yield. This reaction proceeded very slowly in refluxing hexane solvent, and there was no reaction between **4** and $MeCO_2H$ at 25 °C.

(b) In the Presence of PPh_3. To the solution of 10.0 mg (0.021 mmol) of **4** and 30.0 mg (0.115 mmol) of PPh_3 in 20 mL of heptane was added a 1.0-mL amount of glacial acetic acid. The reaction mixture was heated to reflux for 1 h. Separation as described above gave 1.0 mg of **7**, 7% yield, and 6.3 mg of **5** in 90% yield.

Reaction of 1 with $MeC{\equiv}COEt$. A 300.0-mg (0.744-mmol) amount of **1** in 150 mL of hexane was allowed to react with a 0.177-mL (1.86-mmol) amount of $MeC{\equiv}COEt$ at 25 °C for 24 h. The product was isolated by TLC using a CH_2Cl_2/hexane (1/4) solvent mixture for elution to yield 128.2 mg of orange $Mn_2(CO)_8[\mu\text{-}C{=}C(Me)C(OEt){=}O]$, **2b**, 39% yield, and 28.3 mg of unreacted starting material. IR (ν_{CO} in hexane, cm^{-1}) for **2b**: 2098 (w), 2058 (s), 2018 (vs), 2003 (s), 1981 (m), 1961 (s), 1932 (w), 1581 (w). ^1H NMR (δ in $CDCl_3$) for **2b**: 4.27 (q, $^3J_{H-H}$ = 7.1 Hz, 2H, OCH_2CH_3), 2.25 (s, 3H, C*Me*), 1.32 (t, $^3J_{H-H}$ = 7.1 Hz, 3H, CH_2CH_3). Anal. Calcd (Found) for **2b** ($Mn_2C_{14}H_8O_{10}$): C, 37.50 (37.67); H, 1.17 (1.79).

Reaction of 2b with $MeC{\equiv}CNMe_2$. A solution containing a 10.0-mg (0.022-mmol) amount of **2b** and a 15.0-μL (0.144-mmol) amount of $MeC{\equiv}CNMe_2$ in 20 mL of hexane was heated to 40 °C for 40 min. After cooling, the solvent was removed under vacuum, and the residue was separated by TLC using a CH_2Cl_2/hexane (1/1) solvent mixture for elution to yield 1.0 mg of starting material and 2.4 mg of orange $Mn_2(CO)_7[\mu\text{-}CC(Me)C(NMe_2)C(Me)C(OEt){=}O]$, **3b**, in 21% yield. IR (ν_{CO} in CH_2Cl_2, cm^{-1}) for **3b**: 2040 (m), 2094 (w), 1978 (s), 1934 (s, br), 1901 (m, sh), 1646 (w), 1623 (w). ^1H NMR (δ in acetone-d_6) for **3b**: 4.47 (q, $^3J_{H-H}$ = 7.1 Hz, 2H, CH_2Me), 3.36 (s, 3H, N*Me*), 3.10 (s, 3H, N*Me*), 2.27 (s, 3H, C*Me*), 2.01 (s, 3H, C*Me*), 1.40 (t, $^3J_{H-H}$ = 7.1 Hz, 3H, CH_2*Me*). Anal. Calcd (Found) for **3b** ($Mn_2C_{18}H_{17}O_9N$): C, 42.54 (43.11); H, 3.22 (3.39); N, 2.54 (2.79).

Preparation of Compound 2b* with ^{13}C Enrichment in the CO Groups. A 350-mg amount of $Mn_2(CO)_{10}$ was enriched with ^{13}CO by being dissolved in 10 mL of octane and heating to 125 °C in a Parr high-pressure reaction vessel under 1 atm of ^{13}CO for 4 h. After cooling, the reaction solution was filtered over a short silica gel column. A 270-mg amount of $Mn_2(^{12}CO)_n(^{13}CO)_{10-n}$ was obtained after the solvent was removed. A mass spectrum showed it to contain approximately 45% ^{13}CO in the carbonyl ligands. The 45% ^{13}CO-enriched $Mn_2(CO)_{10}$ was converted to $Mn_2(CO)_9(MeCN)$ and then **2b*** by the procedure described above. ^1H NMR (δ in acetone-d_6) for **2b***: 4.41 (qt, $^3J_{H-H}$ = 7.1 Hz, $^3J_{C-H}$ = 2.8 Hz, 2H, CH_2Me), 2.29 (t, $^3J_{H-H}$ = 3.4 Hz, 3H, C*Me*), 1.34 (t, $^3J_{H-H}$ = 7.1 Hz, 3H, CH_2*Me*). ^{13}C NMR (δ in $CDCl_3$) for **2b***: 222.75 (1CO), 221.65 (1CO), 214.67 (1CO), 213.16 (2CO), 210.98 (1CO), 209.14 (2CO), 184.00 (1C). IR ($\nu(CO_2Et)$ in hexane, cm^{-1}): 1581 (w), 1567 (w).

Crystallographic Analysis. Crystals of compounds **2a** and **2b** suitable for X-ray diffraction analysis were grown by slow evaporation of solvent from solutions in hexane/CH_2Cl_2 (3/1) solvent mixtures at −3 °C. Crystals of compounds **3a** and **3b** were grown by slow evaporation of solvent from solutions in hexane/CH_2Cl_2 (1/4) solvent mixtures at −3 °C. Crystals of compound **4** were grown by slow evaporation of solvent from a solution in a CH_2Cl_2/hexane (1/1) solvent mixture by cooling to −3 °C. Crystals of compound **5** were grown by slow evaporation of solvent from a solution in a hexane/CH_2Cl_2 (5/2) solvent mixture by cooling to −3 °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.[14a] Anomalous dispersion corrections were applied to all non-yydrogen atoms.[14b] 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 $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (0.02I_{net})^2]^{1/2}/Lp$. 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 **2a,b**, **4**, and **5** crystallized in the 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. For compounds **2a**, **4**, and **5**, 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. These atoms were included in the structure factor calculations, but were not refined, except in the analysis of **5** where the hydrogen atom H(1) was refined. For **2b**, all non-hydrogen atoms were refined anisotropically, and the positions of all hydrogen atoms were located and refined with isotropic thermal parameters.

Compound **3a** crystallized in a monoclinic crystal system. The space group $P2_1/c$ was identified uniquely from the systematic absences in the data. All non-hydrogen atoms were refined

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[14] (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.

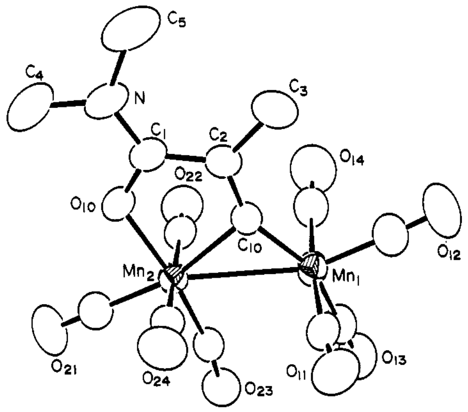

Figure 1. ORTEP diagram of $Mn_2(CO)_8[\mu\text{-}C{=}C(Me)C{=}O(NMe_2)]$, **2a**, showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg) are Mn(1)–Mn(2) = 2.8828(8), Mn(1)–C(10) = 1.880(3), Mn(2)–C(10) = 2.105(3), Mn(2)–O(10) = 2.024(2), C(10)–C(2) = 1.348(4), C(1)–C(2) = 1.457(4), C(1)–O(10) = 1.280(3), C(1)–N = 1.329(4), Mn(1)···C(23) = 2.853(3), Mn(2)–C(10)–C(2) = 114.9(2), and Mn(1)–C(10)–C(2) = 152.2(2).

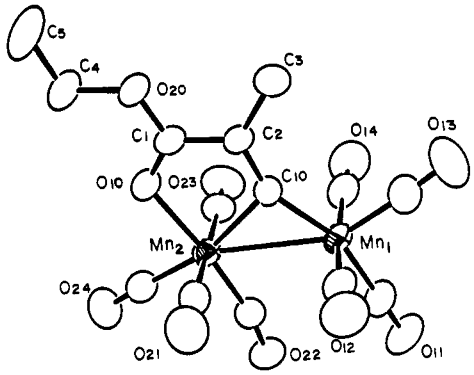

Figure 2. ORTEP diagram of $Mn_2(CO)_8[\mu\text{-}C{=}C(Me)C{=}O(OEt)]$, **2b**, showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) are Mn(1)–Mn(2) = 2.9147(6), Mn(1)–C(10) = 1.874(2), Mn(2)–C(10) = 2.125(2), Mn(2)–O(10) = 2.068(2), C(10)–C(2) = 1.339(3), C(1)–C(2) = 1.440(3), C(1)–O(10) = 1.249(3), C(1)–O(20) = 1.317(3), Mn(1)···C(22) = 2.853(3), Mn(2)–C(10)–C(2) = 113.5(2), and Mn(1)–C(10)–C(2) = 153.1(2).

anisotropically, and the positions of all hydrogen atoms were located and refined with isotropic thermal parameters.

Results and Discussion

The addition of the electron-rich alkynes, $MeC{\equiv}CX$, X = NMe_2 and OEt, to $Mn_2(CO)_9(NCMe)$, **1**, yielded the complexes $Mn_2(CO)_8[\mu\text{-}\eta^2\text{-}C{=}C(Me)C{=}O(X)]$, **2a**, X = NMe_2, and **2b**, X = OEt, respectively. A second product which is, in fact, the major product was also isolated in the reaction of $MeC{\equiv}CNMe_2$ with **1**. Its formula was determined to be $Mn_2(CO)_7[\mu\text{-}\eta^2\text{-}CC(Me)C(NMe_2)C(Me)\text{-}C{=}O(NMe_2)]$, **3a**, and it was formed by the addition of a second equivalent of $MeC{\equiv}CNMe_2$ to **2a**. This complex will be described further below.

Table II. Positional Parameters and *B*(eq) Values (Å²) for 2a

atom	*x*	*y*	*z*	*B*(eq)
Mn(1)	0.68804(04)	0.22561(05)	0.76936(05)	3.77(2)
Mn(2)	0.70868(04)	0.30962(05)	1.12213(05)	3.25(2)
O(10)	0.88278(19)	0.3024(02)	1.2470(02)	3.97(8)
O(11)	0.5478(03)	–0.0509(03)	0.6921(03)	6.4(1)
O(12)	0.7830(03)	0.0799(04)	0.4578(04)	9.0(2)
O(13)	0.4459(03)	0.3159(03)	0.6445(03)	7.1(1)
O(14)	0.8599(04)	0.4671(03)	0.7908(04)	8.8(2)
O(21)	0.6270(03)	0.4232(03)	1.4542(03)	7.1(1)
O(22)	0.8148(03)	0.5913(03)	1.1636(03)	6.5(1)
O(23)	0.4389(02)	0.3409(03)	1.0072(03)	6.2(1)
O(24)	0.6462(02)	0.0169(03)	1.0771(03)	5.3(1)
N	1.0841(02)	0.2487(03)	1.2528(03)	4.4(1)
C(1)	0.9720(03)	0.2499(03)	1.1636(04)	3.4(1)
C(2)	0.9392(03)	0.1979(03)	0.9838(04)	3.3(1)
C(3)	1.0243(03)	0.1202(04)	0.8590(04)	4.9(1)
C(4)	1.0938(04)	0.2968(04)	1.4309(05)	6.6(2)
C(5)	1.2031(04)	0.2138(05)	1.1891(06)	8.4(2)
C(10)	0.8181(03)	0.2188(03)	0.9321(03)	3.2(1)
C(11)	0.5996(03)	0.0565(04)	0.7283(04)	4.4(1)
C(12)	0.7433(04)	0.1379(04)	0.5778(05)	5.7(2)
C(13)	0.5389(04)	0.2824(04)	0.6924(04)	5.0(1)
C(14)	0.7907(04)	0.3792(04)	0.7878(04)	5.5(2)
C(21)	0.6588(03)	0.3801(04)	1.3285(04)	4.5(1)
C(22)	0.7728(03)	0.4853(04)	1.1449(04)	4.2(1)
C(23)	0.5457(03)	0.3248(03)	1.0377(04)	4.1(1)
C(24)	0.6655(03)	0.1266(04)	1.0926(04)	3.8(1)

Table III. Positional Parameters and *B*(eq) Values (Å²) for 2b

atom	*x*	*y*	*z*	*B*(eq)
Mn(1)	0.80054(03)	0.16640(03)	–0.02964(05)	3.11(2)
Mn(2)	0.59239(03)	0.29608(03)	0.06651(04)	2.95(2)
O(10)	0.64396(15)	0.44811(14)	0.2140(02)	3.70(7)
O(11)	0.6976(02)	–0.05409(17)	–0.2278(03)	6.2(1)
O(12)	0.8555(02)	0.28200(20)	–0.3877(03)	5.8(1)
O(13)	1.0778(02)	0.1459(02)	–0.0191(04)	7.3(1)
O(14)	0.8022(03)	0.0527(02)	0.3336(03)	7.2(1)
O(20)	0.81080(16)	0.57001(13)	0.3343(02)	3.98(7)
O(21)	0.6353(02)	0.42116(19)	–0.2876(03)	5.9(1)
O(22)	0.47080(18)	0.09223(16)	–0.1495(03)	4.78(8)
O(23)	0.5664(02)	0.1811(02)	0.4329(03)	6.4(1)
O(24)	0.31679(19)	0.33895(19)	0.0872(03)	5.8(1)
C(1)	0.7636(02)	0.47449(19)	0.2444(03)	3.18(9)
C(2)	0.8550(02)	0.40172(18)	0.1836(03)	2.92(8)
C(3)	0.9987(03)	0.4330(03)	0.2251(04)	4.1(1)
C(4)	0.7183(03)	0.6432(03)	0.4012(05)	5.0(1)
C(5)	0.7923(05)	0.7537(03)	0.4603(07)	6.8(2)
C(10)	0.7981(02)	0.30703(18)	0.0932(03)	2.82(8)
C(11)	0.7368(03)	0.0300(02)	–0.1521(04)	4.3(1)
C(12)	0.8291(02)	0.2388(02)	–0.2534(04)	3.9(1)
C(13)	0.9684(03)	0.1520(02)	–0.0263(04)	4.6(1)
C(14)	0.7952(03)	0.0957(02)	0.1983(04)	4.4(1)
C(21)	0.6191(02)	0.3747(02)	–0.1536(04)	3.8(1)
C(22)	0.5292(02)	0.1665(02)	–0.0660(03)	3.5(1)
C(23)	0.5776(02)	0.2223(02)	0.2943(04)	4.1(1)
C(24)	0.4225(03)	0.3252(02)	0.0809(03)	3.9(1)

Compounds **2a** and **2b** were both characterized by IR, ^1H NMR, and single-crystal X-ray diffraction analyses. Compound **2b** was also characterized by ^{13}C NMR spectroscopy. The crystallographic analyses show that **2a** and **2b** are structurally similar, and ORTEP diagrams of their molecular structures are shown in Figures 1 and 2, respectively. Final atomic positional parameters for **2a** and **2b** are listed in Tables II and III, respectively. Both complexes contain two mutually bonded manganese atoms, Mn–Mn = 2.8828(8) Å in **2a** and 2.9147(6) Å in **2b**. This distance is similar to that observed in $Mn_2(CO)_{10}$, Mn–Mn = 2.9038(6) Å, which does not contain a bridging ligand.[15] Each metal atom contains four carbonyl ligands. One CO group is a weak semibridging ligand, Mn(1)···C(23) = 2.853(3) Å in **2a** and Mn(1)···C(22) = 2.823(3) Å in **2b**. The most interesting ligand is the bridging group $C{=}C(Me)C{=}O(X)$, X = NMe_2 in **2a** or OEt in **2b**, which can be described as a vinylidene ligand. The carbon C(10) bridges the metal atoms asymmetrically, Mn(1)–C(10) = 1.880(3) [1.874(2)] Å and Mn(2)–C(10) = 2.105(3) [2.125(2)] Å. All values in brackets refer to **2b**. This could indicate that the Mn(1)–C(10) bond is slightly stronger

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(15) Churchill, M. R.; Amoh, K. N. *Inorg. Chem.* **1981**, *20*, 1609.

than a Mn–C single bond while the Mn(2)–C(10) bond is proportionately less than a Mn–C single bond. The C(10)–C(2) distance of 1.348(4) [1.339(3)] Å is indicative of a C–C double bond characteristic of vinylidene ligands.[16] The oxygen O(10) is part of an amide [or ethyl ester] grouping that is coordinated to Mn(2), Mn(2)–O(10) = 2.024(2) [2.068(2)] Å, ν(CO) = 1554 [1581] cm^{-1}. Similar metrical dimensions were also observed for the compound $Mn_2(CO)_6(dppm)[\mu\text{-}\eta^2\text{-}C{=}C(H)C{=}O(OMe)]$ obtained from the reaction of $Mn_2(CO)_8(dppm)$ with $HC{\equiv}CCO_2Me$ that also contains a carboxylate coordinated bridging vinylidene ligand.[2] The ^1H NMR spectra of these compounds are consistent with the observed structures [for **2a**: δ = 3.34 (s, br, 3H, N*Me*), 3.07 (s, br, 3H, N*Me*), 2.65 (s, 3H, C*Me*); for **2b**: δ = 4.27 (q, J_{H-H} = 7.1Hz, OCH_2), 2.25 (s, C*Me*) and 1.32 (t, J_{H-H} = 7.1 Hz, CH_2CH_3)]. Broadness in the NMe resonances in **2a** is believed to be due to an averaging process involving hindered rotation about the C–N bond.

The composition of the vinylidene ligands shows that one of the CO ligands of **1** was combined with a rearranged alkyne. The positions of the atoms belonging to the CO ligand were established through a ^{13}C tracer study by using **1** isotopically enriched with ^{13}CO. An analysis of **2b*** by ^{13}C NMR spectroscopy showed one strong resonance located at 184.00 ppm, but on the basis of shift alone could be assigned either to the metal-bonded vinylidene carbon C(10)[16] or to the ester carbon C(1). Its assignment to the ester site C(1) was unambiguously established by the observation of three-bond C–H coupling both to the methylene group C(4), $^3J_{C-H}$ = 2.75 Hz and the methyl group C(3), $^3J_{C-H}$ = 3.36 Hz, in its ^1H NMR spectrum. This was also supported by the observation of a new, mass-reduced absorption for the ester grouping at 1567 cm^{-1} in the IR spectrum which is 14 cm^{-1} lower than that observed for the unlabeled **2b**. In the absence of isolable intermediates, it is not possible to establish the details of the mechanism of the formation of the vinylidene ligand in **2b**, but the process must involve the cleavage of the C–O bond to the OEt group in the alkyne, a CO insertion, possibly forming a metallocarboxylate species, and a transfer of the carboxylate grouping to the methyl-substituted carbon of the alkyne fragment. The formation of **2a** probably occurs by a similar process.

Compounds **2a** and **2b** also add 1 equiv of $MeC{\equiv}CNMe_2$ to form the complexes $Mn_2(CO)_7[\mu\text{-}\eta^2\text{-}CC(Me)C(NMe_2)C(Me)C{=}O(X)]$, **3a**, X = NMe_2, and **3b**, X = OEt, in yields of 48% and 21%, respectively. Compound **3a** was characterized by a single crystal X-ray diffraction analysis. An ORTEP drawing showing the molecular structure of **3a** is shown in Figure 3. Final atomic positional parameters are listed in Table IV. Selected bond distances and angles are listed in Tables V and VI, respectively. This complex also contains two mutually bonded manganese atoms, Mn–Mn = 2.8104(8) Å. Mn(1) has three carbonyl ligands while Mn(2) has four. The most interesting ligand is the group $CC(Me)C(NMe_2)CMeC{=}O(NMe_2)$ which contains a four-membered carbocyclic ring consisting of the atoms C, C(7), C(1), and C(2). There is a dimethylamino substituent on C(1) and an amido group on C(7) that has its oxygen atom coordinated to the metal Mn(1), Mn(1)–O = 2.064(2) Å, and ν(CO) = 1583 cm^{-1}. The carbon atom labeled C could be viewed as a carbene center that bridges the two metal atoms, Mn(1)–C = 2.094(3), Mn(2)–C = 1.941 (3) Å. Two of the C–C distances in the ring are short, C–C(2) = 1.450(4) and C(1)–C(2) = 1.414(4) Å, and two are long C–C(7) = 1.590(4) and C(1)–C(7) = 1.535(4) Å. Carbon

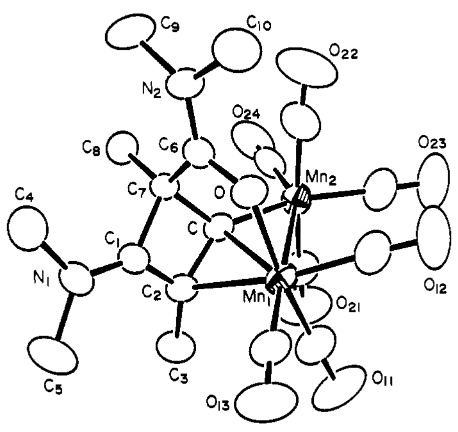

Figure 3. ORTEP diagram of $Mn_2(CO)_7[\mu\text{-}\eta^2\text{-}CC(Me)C(NMe_2)C(Me)C{=}O(NMe_2)]$, **3a**, showing 50% probability thermal ellipsoids.

Table IV. Positional Parameters and *B*(eq) Values (Å^2) for 3a

atom	*x*	*y*	*z*	*B*(eq)
Mn(1)	0.64604(04)	0.20648(05)	0.36239(03)	2.69(2)
Mn(2)	0.88027(04)	0.28493(05)	0.39119(03)	3.11(2)
O	0.64825(18)	0.0889(02)	0.27121(11)	2.9(1)
O(11)	0.6172(02)	0.3983(03)	0.47482(16)	6.6(2)
O(12)	0.5942(03)	0.4301(03)	0.25486(20)	7.5(2)
O(13)	0.4008(02)	0.1453(03)	0.35189(15)	5.6(1)
O(21)	0.8888(03)	0.4002(04)	0.54156(19)	7.8(2)
O(22)	0.8924(03)	0.2098(04)	0.23774(18)	8.0(2)
O(23)	0.8713(03)	0.5578(03)	0.3299(02)	7.8(2)
O(24)	1.1334(02)	0.2471(03)	0.45219(16)	6.6(2)
N(1)	0.6575(02)	–0.1630(03)	0.40942(15)	3.0(1)
N(2)	0.7440(02)	–0.0529(03)	0.21880(14)	3.1(1)
C	0.8102(02)	0.1182(03)	0.40719(16)	2.4(1)
C(1)	0.7179(03)	–0.0554(03)	0.41072(17)	2.5(1)
C(2)	0.7429(03)	0.0629(03)	0.45363(17)	2.7(1)
C(3)	0.7416(04)	0.0904(05)	0.5337(02)	4.0(2)
C(4)	0.6489(04)	–0.2699(05)	0.3551(03)	4.4(2)
C(5)	0.5887(05)	–0.1813(07)	0.4624(03)	5.3(3)
C(6)	0.7277(03)	0.0038(03)	0.27971(17)	2.5(1)
C(7)	0.7974(03)	–0.0180(03)	0.36213(16)	2.3(1)
C(8)	0.9134(03)	–0.0926(04)	0.3861(02)	3.2(2)
C(9)	0.8313(05)	–0.1524(05)	0.2166(03)	4.9(2)
C(10)	0.6743(05)	–0.0049(06)	0.1439(03)	4.9(2)
C(11)	0.6347(03)	0.3216(04)	0.4330(02)	4.0(2)
C(12)	0.6169(03)	0.3428(04)	0.2965(02)	4.3(2)
C(13)	0.4959(03)	0.1633(03)	0.35296(10)	3.4(2)
C(21)	0.8800(03)	0.3518(04)	0.4841(02)	4.6(2)
C(22)	0.8840(03)	0.2334(04)	0.2966(02)	4.6(2)
C(23)	0.8749(03)	0.4524(04)	0.3551(02)	4.8(2)
C(24)	1.0335(03)	0.2632(04)	0.42770(20)	4.0(2)

Table V. Intramolecular Distances[a] for 3a

Mn(1)–Mn(2)	2.8104(8)	N(1)–C(4)	1.454(5)
Mn(1)–O	2.064(2)	N(1)–C(5)	1.463(5)
Mn(1)–C	2.094(3)	N(2)–C(6)	1.325(4)
Mn(1)–C(2)	2.263(3)	N(2)–C(9)	1.459(5)
Mn(1)–C(11)	1.779(4)	N(2)–C(10)	1.467(5)
Mn(1)–C(12)	1.799(4)	C–C(2)	1.450(4)
Mn(1)–C(13)	1.808(4)	C–C(7)	1.590(4)
Mn(2)–C	1.941(3)	C(1)–C(2)	1.414(4)
Mn(2)–C(21)	1.842(4)	C(1)–C(7)	1.535(4)
Mn(2)–C(22)	1.832(4)	C(2)–C(3)	1.505(5)
Mn(2)–C(23)	1.811(4)	C(6)–C(7)	1.518(4)
Mn(2)–C(24)	1.772(4)	C(7)–C(8)	1.527(4)
O–C(6)	1.257(4)	O–C(av)	1.148(4)
N(1)–C(1)	1.301(4)		

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

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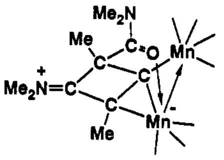
[16] (a) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197. (b) Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, *22*, 59.

Table VI. Intramolecular Bond Angles[a] for 3a

Mn(2)–Mn(1)–O	93.6(1)	Mn(1)–C–C(2)	77.0(2)
O–Mn(1)–C	80.8(1)	Mn(1)–C–C(7)	103.1(2)
O–Mn(1)–C(2)	96.3(1)	Mn(2)–C–C(2)	139.8(2)
O–Mn(1)–C(11)	173.3(1)	Mn(2)–C–C(7)	130.5(2)
O–Mn(1)–C(12)	86.4(1)	C(2)–C–C(7)	89.5(2)
O–Mn(1)–C(13)	92.0(1)	N(1)–C(1)–C(2)	137.7(3)
C–Mn(1)–C(2)	38.6(1)	N(1)–C(1)–C(7)	129.2(3)
C–Mn(1)–C(11)	104.8(1)	C(2)–C(1)–C(7)	93.0(3)
C–Mn(1)–C(12)	124.3(1)	Mn(1)–C(2)–C	64.4(2)
C–Mn(1)–C(13)	136.6(1)	Mn(1)–C(2)–C(1)	98.5(2)
C(2)–Mn(1)–C(11)	90.4(1)	Mn(1)–C(2)–C(3)	117.3(3)
C(2)–Mn(1)–C(12)	161.0(1)	C–C(2)–C(1)	93.3(2)
C(2)–Mn(1)–C(13)	101.2(1)	C–C(2)–C(3)	132.5(3)
C–Mn(2)–C(21)	93.3(1)	C(1)–C(2)–C(3)	129.9(3)
C–Mn(2)–C(22)	91.8(1)	O–C(6)–N(2)	119.0(3)
C–Mn(2)–C(23)	153.5(1)	O–C(6)–C(7)	113.3(3)
C–Mn(2)–C(24)	106.3(1)	N(2)–C(6)–C(7)	127.6(3)
Mn(1)–O–C(6)	118.9(2)	C–C(7)–C(1)	83.6(2)
C(1)–N(1)–C(4)	123.9(3)	C–C(7)–C(6)	109.7(2)
C(1)–N(1)–C(5)	120.8(4)	C–C(7)–C(8)	109.6(3)
C(4)–N(1)–C(5)	115.2(4)	C(1)–C(7)–C(6)	115.2(2)
C(6)–N(2)–C(9)	127.3(3)	C(1)–C(7)–C(8)	112.2(3)
C(6)–N(2)–C(10)	118.0(3)	C(6)–C(7)–C(8)	123.1(3)
C(9)–N(2)–C(10)	114.5(4)	Mn–C(av)–O	175.0(3)
Mn(1)–C–Mn(2)	88.2(1)		

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

C(2) is also coordinated to one of the metal atoms, Mn(1)–C(2) = 2.263(3) Å. The four-carbon ring could be described as a cyclobutenylidene ligand with the C–C double bond between the atoms C(1) and C(2), but there is a strong interaction of atom C(2) with Mn(1) in order to satisfy the electron requirements of the metal atoms. This results in the formation of a formal negative charge on Mn(1), a positive charge on N(1), partial multiple bonding between C(1) and N(1), and formation of a formal donor–acceptor bond between the metal atoms, as represented in the line structure



3a

The observation of four resonances for the *N*-methyl groups shows that there is hindered rotation about the C–N bonds of both NMe_2 groups. Compound **3b** is spectroscopically similar to that of **3a** and is presumed to be structurally analogous.

When heated to 80 °C, complex **3a** was decarbonylated and the four-membered ring was opened to yield the complex $Mn_2(CO)_6[\mu\text{-}\eta^5\text{-}(Me_2N)CC(Me)CC(Me)C{=}O(NMe_2)]$, **4**. Compound **4** was also characterized crystallographically. The compound crystallizes with two independent molecules in the asymmetric crystal unit. Both molecules are structurally similar and an ORTEP diagram of the molecular structure of one of these, molecule A, is shown in Figure 4. Final atomic positional parameters are listed in Table VII. Selected bond distances and angles are listed in Tables VIII and IX, respectively. This complex also contains two mutually bonded manganese atoms, Mn–Mn = 2.886(1) [2.869(1)] Å. The quantity in parentheses corresponds to the second molecule. Both metal atoms have three terminal carbonyl ligands. The $C(NMe_2)CMeCCMeC{=}O(NMe_2)$ ligand is a chain extending from C(1) to C(6), and the carbon atoms C(1), C(2), C, and C(7) are coordinated to the metal atoms. Carbon C is a bridge as in **3a**, Mn(1)–C = 2.033(5) [2.038(5)] Å, Mn(2)–C = 2.014(5) [2.028(5)] Å. Both carbon–carbon bonds to carbon C are relatively short, C–C(7) = 1.388(7) [1.410(7)] Å, C–C(2) = 1.403(7) [1.384(7)] Å. The ligand could be described reasonably as a tetrasubstituted bridging allene.[17] The terminal carbon C(1) could be viewed as a NMe_2-substituted carbene center, Mn(2)–C(1) = 1.925(5) [1.919(5)] Å. The C(1)–N distance is short C(1)–N = 1.295(6) [1.299(6)] Å, as characteristically found for heteroatom-substituted carbenes.[18] The presence of four slightly broadened singlets attributed to the *N*-methyl groups indicates that there is hindered rotation about the C–N bonds to both NMe_2 groups. The formation of **4** evidently occurred by a cleavage of one of the long C–C bonds, C(1)–C(7), in **3a**. By including the electron donation from the coordinated amido oxygen atom O(1), the $C(NMe_2)CMeCCMeC{=}O(NMe_2)$ ligand serves as an eight-electron donor and both metal atoms achieve the desired 18 electron configuration upon the formation of a manganese–manganese single bond.

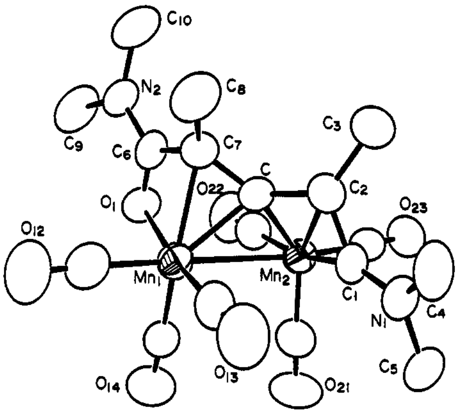


Figure 4. ORTEP diagram of $Mn_2(CO)_6[\mu\text{-}\eta^5\text{-}(Me_2N)CC(Me)CC(Me)C{=}O(NMe_2)]$, **4**, showing 50% probability thermal ellipsoids.

The reaction of **3a** with acetic acid induced the four-membered ring to open at 25 °C with formation of the mononuclear manganese complex $Mn(CO)_3[\eta^4\text{-}(Me_2N)CC(Me)C(H)C(Me)C{=}O(NMe_2)]$, **5**. Compound **5** was characterized crystallographically, and an ORTEP drawing of its molecular structure is shown in Figure 5. Final atomic positional parameters are listed in Table X. Selected bond distances and angles are listed in Tables XI and XII. This complex contains the same $(Me_2N)CC(Me)C(H)C(Me)C{=}O(NMe_2)$ ligand as found in **4** with one exception, the presence of a hydrogen atom bonded to the carbon C(3). The ^1H NMR resonance of this hydrogen atom was observed at $\delta = 6.67$ ppm. In this complex only four of the carbon atoms of the chain are coordinated, C(1), C(2), C(3), and C(4); Mn(1)–C(1) = 1.901(3) Å, Mn(1)–C(2) = 2.146(3) Å, Mn(1)–C(3) = 2.128(3) Å, Mn(1)–C(4) = 2.224(3) Å. The ligand would be viewed as an η^4-diene if it were not for the fact that C(1) has only one substituent. In fact, C(1) is probably better described as a carbene center. The metal–C(1) distance is substantially shorter

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[17] (a) Cayton, R. H.; Chisholm, M. H.; Hampden-Smith, M. J. *J. Am. Chem. Soc.* **1988**, *110*, 4438. (b) Chisholm, M. H.; Rankell, L. A.; Bailey, W. I., Jr.; Cotton, F. A.; Murillo, C. A. *J. Am. Chem. Soc.* **1977**, *99*, 1261; **1978**, *100*, 802.

[18] Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissel, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: West Germany, 1983.

Table VII. Positional Parameters and *B*(eq) Values (Å^2) for 4

atom	*x*	*y*	*z*	*B*(eq)
Mn(1A)	0.67579(07)	0.33665(05)	0.45524(08)	3.77(4)
Mn(1B)	0.15576(07)	0.17318(05)	0.94035(08)	3.84(4)
Mn(2A)	0.80170(07)	0.19884(05)	0.49590(08)	3.59(4)
Mn(2B)	0.33037(07)	0.30635(05)	0.99933(08)	3.67(4)
O(1A)	0.6616(03)	0.3330(02)	0.6478(03)	3.9(2)
O(1B)	0.1550(03)	0.1846(02)	1.1376(03)	4.3(2)
O(12A)	0.4696(04)	0.2260(03)	0.3415(03)	7.0(2)
O(12B)	−0.0254(05)	0.0376(04)	0.8698(05)	9.2(3)
O(13A)	0.7265(04)	0.3537(03)	0.1965(04)	7.6(3)
O(13B)	0.1868(04)	0.1420(03)	0.6720(04)	8.0(3)
O(14A)	0.5712(06)	0.4877(04)	0.4116(06)	11.1(4)
O(14B)	−0.0027(04)	0.2935(03)	0.8640(05)	7.2(3)
O(12A)	0.9430(04)	0.0675(03)	0.5409(06)	8.6(3)
O(21B)	0.1949(04)	0.4200(03)	0.8484(05)	6.6(2)
O(22A)	0.6165(04)	0.0825(03)	0.3382(06)	9.3(3)
O(22B)	0.2716(04)	0.3498(03)	1.2546(05)	7.2(2)
O(23A)	0.7542(04)	0.1792(03)	0.7599(05)	6.9(2)
O(23B)	0.5187(04)	0.4338(03)	1.0910(05)	5.9(2)
N(1A)	0.8983(04)	0.2306(03)	0.2497(05)	4.6(2)
N(1B)	0.4103(04)	0.2603(03)	0.7439(05)	4.3(2)
N(2A)	0.7650(04)	0.4232(03)	0.8127(04)	4.2(2)
N(2B)	0.2285(04)	0.0952(03)	1.2772(04)	4.2(2)
C(A)	0.8367(04)	0.3213(03)	0.5320(05)	3.2(2)
C(B)	0.3234(04)	0.1835(03)	1.0091(05)	3.4(2)
C(1A)	0.8733(04)	0.2390(03)	0.3637(05)	3.6(2)
C(1B)	0.3848(04)	0.2573(03)	0.8579(05)	3.7(2)
C(2A)	0.9216(04)	0.2977(03)	0.4747(05)	3.5(2)
C(2B)	0.4136(05)	0.2019(03)	0.9559(06)	3.9(2)
C(3A)	1.0434(05)	0.3186(04)	0.5357(06)	4.8(3)
C(3B)	0.5288(05)	0.1784(04)	1.0097(06)	5.5(3)
C(4A)	0.9690(06)	0.2927(05)	0.2052(06)	6.1(3)
C(4B)	0.4586(05)	0.1949(04)	0.6834(06)	5.5(3)
C(5A)	0.8475(06)	0.1623(05)	0.1548(07)	7.1(4)
C(5B)	0.3819(05)	0.3253(04)	0.6617(06)	5.8(3)
C(6A)	0.7491(05)	0.3825(03)	0.6934(06)	3.8(2)
C(6B)	0.2222(05)	0.1318(03)	1.1665(05)	3.7(2)
C(7A)	0.8229(05)	0.3920(03)	0.6042(05)	3.9(2)
C(7B)	0.2866(04)	0.1149(03)	1.0678(05)	3.9(2)
C(8A)	0.8888(06)	0.4740(04)	0.5980(07)	6.5(3)
C(8B)	0.3227(06)	0.0323(04)	1.0384(06)	5.8(3)
C(9A)	0.6758(06)	0.4156(04)	0.8832(06)	5.9(3)
C(9B)	0.1523(06)	0.1137(04)	1.3584(06)	6.7(3)
C(10A)	0.8703(05)	0.4642(04)	0.8862(06)	5.9(3)
C(10B)	0.3138(06)	0.0457(04)	1.3309(06)	6.3(3)
C(12A)	0.5518(06)	0.2687(04)	0.3851(06)	4.8(3)
C(12B)	0.0457(06)	0.0901(04)	0.9014(06)	5.5(3)
C(13A)	0.7062(05)	0.3461(04)	0.2974(06)	5.1(3)
C(13B)	0.1739(05)	0.1552(04)	0.7771(06)	5.1(3)
C(14A)	0.6092(06)	0.4281(05)	0.4322(07)	6.2(3)
C(14B)	0.0611(05)	0.2477(04)	0.8937(06)	4.8(3)
C(21A)	0.8865(05)	0.1184(04)	0.5224(07)	5.1(3)
C(21B)	0.2463(05)	0.3751(04)	0.9101(06)	4.7(3)
C(22A)	0.6873(06)	0.1299(04)	0.4023(07)	5.6(3)
C(22B)	0.2916(05)	0.3295(04)	1.1553(07)	4.8(3)
C(23A)	0.7703(05)	0.1887(03)	0.6567(07)	4.6(3)
C(23B)	0.4455(05)	0.3843(04)	1.0524(06)	4.3(3)

Table VIII. Intramolecular Distances[a] for 4

Mn(1A)–O(1A)	2.055(3)	N(1B)–C(1B)	1.299(6)
Mn(1A)–C(A)	2.033(5)	N(2A)–C(6A)	1.332(7)
Mn(1A)–C(7A)	2.187(6)	N(2B)–C(6B)	1.326(7)
Mn(1B)–O(1B)	2.049(3)	C(A)–C(2A)	1.403(7)
Mn(1B)–C(B)	2.038(5)	C(A)–C(7A)	1.388(7)
Mn(1B)–C(7B)	2.199(5)	C(B)–C(2B)	1.384(7)
Mn(2A)–C(A)	2.014(5)	C(B)–C(7B)	1.410(7)
Mn(2A)–C(1A)	1.925(5)	C(1A)–C(2A)	1.430(7)
Mn(2A)–C(2A)	2.164(5)	C(1B)–C(2B)	1.423(7)
Mn(2B)–C(B)	2.028(5)	C(6A)–C(7A)	1.457(7)
Mn(2B)–C(1B)	1.919(5)	C(6B)–C(7B)	1.472(7)
Mn(2B)–C(2B)	2.169(5)	Mn(1A)–Mn(2A)	2.886(1)
O(1A)–C(6A)	1.273(6)	Mn(1B)–Mn(2B)	2.869(1)
O(1B)–C(6B)	1.269(6)	Mn–C(av)	1.790(7)
N(1A)–C(1A)	1.295(6)	O–C(av)	1.15(1)

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

Table IX. Intramolecular Bond Angles[a] for 4

Mn(1A)–O(1A)–C(6A)	92.9(3)	Mn(2A)–C(1A)–N(1A)	151.5(5)
Mn(1B)–O(1B)–C(6B)	93.4(3)	N(1A)–C(1A)–C(2A)	128.9(5)
Mn(1A)–C(A)–Mn(2A)	91.0(2)	Mn(2B)–C(1B)–N(1B)	150.8(5)
Mn(1A)–C(A)–C(2A)	133.1(4)	N(1B)–C(1B)–C(2B)	129.1(5)
Mn(1A)–C(A)–C(7A)	76.9(3)	C((A))–C(2A)–C(1A)	108.2(5)
Mn(2A)–C(A)–C(2A)	76.2(3)	C((B))–C(2B)–C(1B)	108.4(5)
Mn(2A)–C(A)–C(7A)	147.1(4)	O(1A)–C(6A)–N(2A)	119.7(5)
C(2A)–C(A)–C(7A)	133.7(5)	O(1A)–C(6A)–C(7A)	115.1(5)
Mn(1B)–C(B)–Mn(2B)	89.8(2)	O(1B)–C(6B)–N(2B)	120.2(5)
Mn(1B)–C(B)–C(2B)	135.5(4)	O(1B)–C(6B)–C(7B)	114.9(5)
Mn(1B)–C(B)–C(7B)	76.9(3)	C((A))–C(7A)–C(6A)	116.5(5)
Mn(2B)–C(B)–C(2B)	76.4(3)	C((B))–C(7B)–C(6B)	115.6(5)
Mn(2B)–C(B)–C(7B)	147.4(4)	Mn–C(av)–O	178(1)
C(2B)–C(B)–C(7B)	133.2(5)		

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

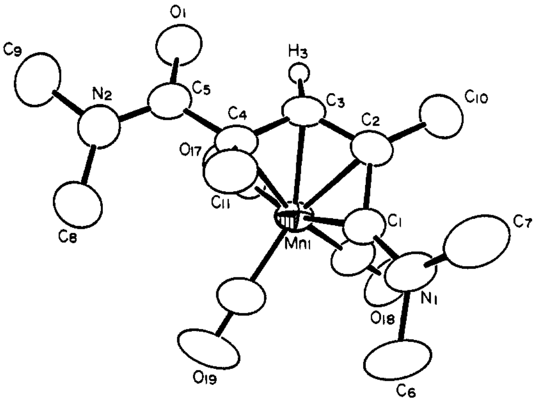


Figure 5. ORTEP diagram of $Mn(CO)_3[\eta^4\text{-}(Me_2N)CC(Me)C(H)C(Me)C{=}O(NMe_2)]$, 5, showing 50% probability thermal ellipsoids.

than all of the other metal–carbon bonds to this ligand. The planar NMe_2 substituent and the short C(1)–N(1) distance, 1.302(3) Å, also support this formulation. However, unlike compounds **2a**,**b**, **3a**,**b**, and **4** the observation of a singlet at 3.00 ppm (6H) indicates that rotation about the C(1)–N(1) bond is rapid on the NMR time scale at room temperature. The formation of **5** included the loss of a manganese carbonyl fragment. The fate of this fragment could not be determined under the original conditions, but when the acidification was carried out in the presence of PPh_3, both **5** and a somewhat unstable coproduct that we have formulated as $Mn(CO)_3(PPh_3)_2(O_2CMe)$, **6**, were formed. This coproduct slowly decarbonylates over a period of hours to yield the known compound $Mn(CO)_2(PPh_3)_2(\eta^2\text{-}O_2CMe)$, **7**. The presence of three strong CO absorptions in the IR spectrum of **6** indicates that it has a *fac*-structure of the CO ligands. In order to have an 18 electron configuration at the manganese atom, the O_2CMe ligand would have only an η^1-coordination.

Compound **4** can also be transformed to **5** by reaction with acetic acid, but the reaction conditions are considerably more forcing (i.e. 98 °C). We have not investigated the thermal transformations of **3b** or its reaction with acetic acid. We expect that it will be transformed similarly to that of **3a**.

A summary of the results of this study are shown in Scheme I. The addition of the heteroatom-substituted alkynes MeC≡CX, X = NMe_2 or OEt to compound **1** yielded the disubstituted vinylidene complexes **2a** and **2b** by a rearrangement of the alkyne that also included a CO insertion step. The transformation of heteroatom-substituted alkynes into vinylidene ligands has been observed

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

atom	*x*	*y*	*z*	*B*(eq)
Mn(1)	1.00898(04)	0.25192(03)	0.20398(05)	3.35(2)
O(1)	1.3493(02)	0.17851(18)	0.4829(03)	5.36(8)
O(17)	1.3023(02)	0.31374(18)	0.0956(03)	5.34(8)
O(18)	0.8132(03)	0.2379(03)	−0.1578(03)	7.7(1)
O(19)	1.0470(03)	0.4971(02)	0.3112(04)	8.0(1)
N(1)	0.6841(03)	0.1540(02)	0.2742(03)	4.70(9)
N(2)	1.3796(03)	0.3447(02)	0.6452(03)	5.3(1)
C(1)	0.8216(03)	0.1641(02)	0.2615(03)	3.69(9)
C(2)	0.8803(03)	0.0732(02)	0.2392(03)	3.90(9)
C(3)	1.0384(03)	0.1080(02)	0.3338(03)	3.7(1)
C(4)	1.1140(03)	0.2095(02)	0.4665(03)	3.49(8)
C(5)	1.2894(03)	0.2440(02)	0.5293(04)	4.1(1)
C(6)	0.6410(04)	0.2581(03)	0.2634(05)	6.8(2)
C(7)	0.5759(04)	0.0479(03)	0.3170(06)	7.8(2)
C(8)	0.3339(04)	0.4434(03)	0.6774(05)	6.5(1)
C(9)	1.5431(04)	0.3651(03)	0.7267(05)	7.2(2)
C(10)	0.7910(04)	−0.0383(03)	0.1073(05)	5.7(1)
C(11)	1.0347(03)	0.2238(03)	0.6067(04)	4.6(1)
C(17)	1.1899(03)	0.2882(02)	0.1394(03)	3.8(1)
C(18)	0.8947(03)	0.2462(03)	−0.0173(04)	4.8(1)
C(19)	1.0361(03)	0.4028(03)	0.2689(04)	4.9(1)

Table XI. Intramolecular Distances[a] for 5

Mn(1)–C(1)	1.901(3)	N(2)–C(9)	1.451(4)
Mn(1)–C(2)	2.146(3)	C(1)–C(2)	1.432(3)
Mn(1)–C(3)	2.128(3)	C(2)–C(3)	1.398(4)
Mn(1)–C(4)	2.224(3)	C(2)–C(10)	1.505(4)
O(1)–C(5)	1.225(3)	C(3)–C(4)	1.422(4)
N(1)–C(1)	1.302(3)	C(4)–C(5)	1.510(4)
N(1)–C(6)	1.465(4)	C(4)–C(11)	1.527(3)
N(1)–C(7)	1.447(4)	Mn–C(av)	1.808(3)
N(2)–C(5)	1.355(3)	O–C(av)	1.150(4)
N(2)–C(8)	1.451(4)		

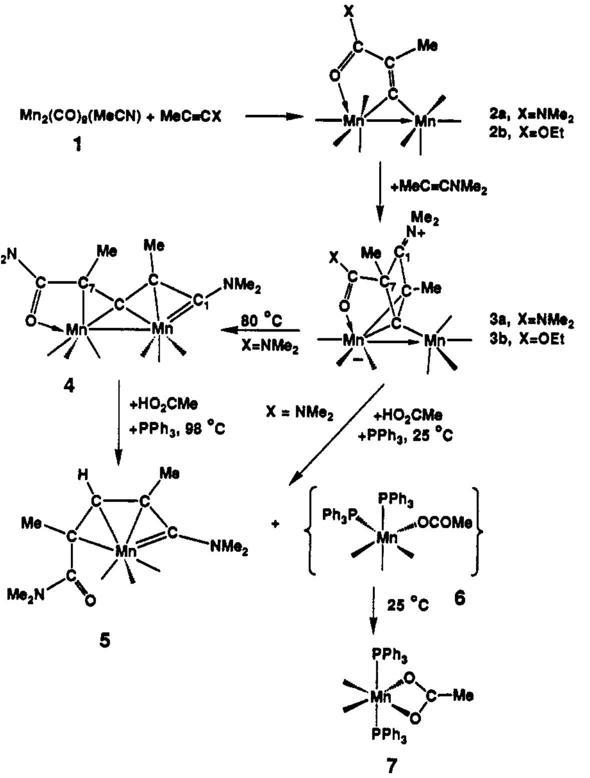
[a] Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Table XII. Intramolecular Bond Angles[a] for 5

C(1)-Mn(1)-C(2)	40.9(1)	Mn(1)-C(2)-C(10)	130.8(2)
C(1)-Mn(1)-C(3)	71.0(1)	C(1)-C(2)-C(3)	112.1(2)
C(1)-Mn(1)-C(4)	80.9(1)	C(1)-C(2)-C(10)	123.9(2)
C(2)-Mn(1)-C(3)	38.2(1)	C(3)-C(2)-C(10)	123.3(2)
C(2)-Mn(1)-C(4)	68.3(1)	Mn(1)-C(3)-C(2)	71.6(1)
C(3)-Mn(1)-C(4)	38.1(1)	Mn(1)-C(3)-C(4)	74.6(1)
C(1)-N(1)-C(6)	119.2(2)	C(2)-C(3)-C(4)	121.0(2)
C(1)-N(1)-C(7)	123.4(2)	Mn(1)-C(4)-C(3)	67.3(1)
C(6)-N(1)-C(7)	117.1(2)	Mn(1)-C(4)-C(5)	118.7(2)
C(5)-N(2)-C(8)	125.5(2)	Mn(1)-C(4)-C(11)	113.7(2)
C(5)-N(2)-C(9)	118.1(3)	C(3)-C(4)-C(5)	112.3(2)
C(8)-N(2)-C(9)	115.7(3)	C(3)-C(4)-C(11)	119.2(2)
Mn(1)-C(1)-N(1)	149.8(2)	C(5)-C(4)-C(11)	116.6(2)
Mn(1)-C(1)-C(2)	78.8(2)	O(1)-C(5)-N(2)	120.0(2)
N(1)-C(1)-C(2)	129.4(2)	O(1)-C(5)-C(4)	120.5(2)
Mn(1)-C(2)-C(1)	60.4(1)	N(2)-C(5)-C(4)	119.4(2)
Mn(1)-C(2)-C(3)	70.2(1)	Mn(1)-C(av)-O	176.8(3)

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

Scheme I



previously, but we are unaware of any examples where this rearrangement is accompanied by a CO insertion.[19] Complexes **2a** and **2b** both add ynamine to yield the complexes **3a** and **3b** containing a four-membered carbocyclic ring by the addition of the ynamine C–C triple bond across the vinylidene double bond. Similar cycloaddition reactions of ynamines to electrophilic olefins have been reported.[20] We have found that the four-membered carbocycle can be opened thermally to yield the complex **4** or by reaction with acetic acid to yield the mononuclear metal complex **5**. In the presence PPh_3 the displaced manganese fragment can be trapped in the form of compound **6** that is subsequently transformed into the more stable product **7**.

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Supplementary Material Available: Tables of atomic positional parameters, hydrogen atom positional parameters, and anisotropic thermal parameters (24 pages). Ordering information is given on any current masthead page.

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