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Reactions of $EtO_2CC{\equiv}CCO_2Et$ with Dimanganese Carbonyls. Alkyne Insertion into the Mn—Mn Bond, Coupling to CO, and a New Route to Carboxylate-Substituted Pyrans

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The reaction of $Mn_2(CO)_{10}$ with $EtO_2CC{\equiv}CCO_2Et$ in the presence of UV irradiation has yielded the compounds $Mn(CO)_4[\mu\text{-}(Z)\text{-}(EtO_2C)C{=}(CO_2Et)]Mn(CO)_5$ (**1**) in 36% yield and $Mn(CO)_4[\mu\text{-}(E)\text{-}(EtO_2C)C{=}C(CO_2Et)]Mn(CO)_4$ (**2**) in 8% yield. Compounds **1** and **2** are *Z*- and *E*-dimetalated olefin complexes that contain one and two coordinated carboxylate groups, respectively. Compound **1** can be converted to **2** by further exposure to UV irradiation. Compound **1** isomerizes thermally to the new compound $Mn_2(CO)_8[\mu\text{-}(EtO_2C)C{=}C(CO_2Et)C{=}O]$, (**3**) in 58% yield. Compound **3** was also obtained in 22% yield from the reaction of $Mn_2(CO)_9(MeCN)$ with $EtO_2CC{\equiv}CCO_2Et$ at 25 °C. Compound **3** contains an enone metallacycle, $EtO_2CC{=}C(CO_2Et)C{=}OMn$, formed by a coupling of the alkyne to a CO ligand and coordination of the CO oxygen atom and one of the alkyne carbon atom to one of the manganese atoms. Compound **3** reacts with the alkynes $HC{\equiv}CCO_2Me$, $EtO_2CC{\equiv}CCO_2Et$, and $HC{\equiv}CH$ in the presence of UV irradiation to form the new compounds $Mn_2(CO)_7[\mu\text{-}\eta^4\text{-}COC(CO_2Me)C(H)C(CO_2Et)C(CO_2Et)]$ (**4a**) and $Mn_2(CO)_7[\mu\text{-}\eta^4\text{-}COC(CO_2Et)C(CO_2Et)C(CO_2Et)C(CO_2Et)]$ (**4b**), and $Mn_2(CO)_7[\mu\text{-}\eta^4\text{-}COCHCHC(CO_2Et)C(CO_2Et)]$ (**4c**) in yields of 28%, 26%, and 29%, respectively. These compounds contain metalated pyran rings formed by a novel 1,4-cycloaddition of the alkyne to the *cis*-cyclomanganated enone grouping in **3**. One of the metal atoms is shifted to a π-bonding coordination involving four of the carbon atoms of the pyran ring. Treatment of compounds **4a–c** with a combination of gaseous HCl and CO resulted in cleavage of the metal groupings from the organic residue and formation of the free α-pyrans $2\text{-}MeO_2C\text{-}4,5\text{-}(EtO_2C)_2C_5OH_3$ (**5a**), $2,3,4,5\text{-}(EtO_2C)_4C_5OH_2$ (**5b**), and $4,5\text{-}(EtO_2C)_2C_5OH_4$ (**5c**) in yields of 40–60%. Treatment of **3** with PMe_2Ph in the presence of H_2O resulted in the cleavage of one metal grouping from the complex and addition of PMe_2Ph and one hydrogen atom to the remaining metal grouping to yield the new metal complex $Mn(CO)_4[OCC(CO_2Et)C(H)(CO_2Et)(PMe_2Ph)]$ (**6**) in 80% yield. The phosphine and a hydrogen atom were added to one of the carboxylate-substituted carbon atoms. Complex **6** is zwitterionic with a positive charge on the phosphonium center and a negative charge delocalized across an acyl grouping. The methynyl hydrogen atom is labile and is readily exchanged by treatment with D_2O at 25 °C. Compounds **1**, **3**, **4a**, and **6** were characterized by single-crystal X-ray diffraction analyses. Crystal data: for **1**, space group $P2_1/c$, $a = 10.160(1)$ Å, $b = 11.593(2)$ Å, $c = 18.569(3)$ Å, $\beta = 100.72(1)°$, $Z = 4$, 1754 reflections, $R = 0.031$; for **3**, space group $P\bar{1}$, $a = 11.395(2)$ Å, $b = 14.252(3)$ Å, $c = 6.7910(9)$ Å, $\alpha = 91.59(1)°$, $\beta = 91.54(1)°$, $\gamma = 84.97(1)°$, $Z = 2$, 1717 reflections, $R = 0.031$; for **4a**, space group $P\bar{1}$, $a = 9.380(2)$ Å, $b = 19.390(4)$ Å, $c = 6.997(2)$ Å, $\alpha = 90.28(2)°$, $\beta = 106.11(2)°$, $\gamma = 99.27(2)°$, $Z = 2$, 1534 reflections, $R = 0.041$; for **6**, space group $P\bar{1}$, $a = 11.830(2)$ Å, $b = 13.589(2)$ Å, $c = 8.456(2)$ Å, $\alpha = 92.49(2)°$, $\beta = 108.60(2)°$, $\gamma = 89.67(2)°$, $Z = 2$, 1976 reflections, $R = 0.047$.

Introduction

Metal-mediated coupling reactions between alkynes and CO have led to the synthesis of a wide variety of new organic ligands[1] and new organic molecules.[2] Recent studies of the reactions of alkynes with dinuclear manganese carbonyl complexes have revealed a strong tendency for coupling of the alkynes to one or more of the CO ligands.[3-6] A characteristic feature of these reactions is

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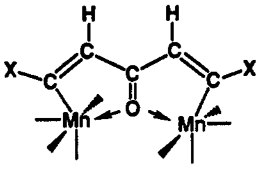
the coordination of the oxygen atom of the CO group to the metal atoms. The reaction of the terminal alkynes $HC{\equiv}CX$ (X = CO_2Me, OEt) with $Mn_2(CO)_{10}$ under UV irradiation or with $Mn_2(CO)_9(NCMe)$ by heating yields the dimetalated ketone complexes $Mn_2(CO)_8\{\mu\text{-}O{=}C\text{-}[C(H){=}CX]_2\}$ (**A**), formed by a novel coupling of two alkynes to the carbon atom of a CO ligand. The oxygen atom of the CO grouping is coordinated to *both* metal atoms.[3,4] In some cases, the CO ligand can even be inserted into the C—X bond of certain activated alkynes $RC{\equiv}CX$ (X = OR, NR_2) to form ester and amido functional groups.[7]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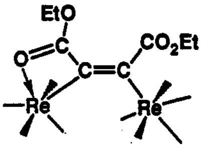
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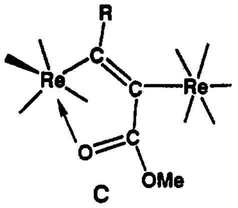
C

In contrast, no coupling was observed between the alkyne and CO in the reactions of $Re_2(CO)_9(NCMe)$ with $EtO_2CC{\equiv}CCO_2Et$[8a] or $HC{\equiv}CCO_2Me$.[8b] Instead, the alkyne was inserted into the metal–metal bond to yield the *cis*- and *trans*-dimetalated olefin complexes $Re(CO)_4[\mu\text{-}(Z)\text{-}(EtO_2C)C{=}C(CO_2Et)]Re(CO)_5$ (**B**) and $Re(CO)_4[trans\text{-}\mu\text{-}(E)\text{-}RC{=}C(CO_2R')]Re(CO)_5$ (**C**: R = H, R′ = Me; R = CO_2Et, R′ = Et), in which the carbonyl oxygen atom of an ester grouping was coordinated to one of the metal atoms.

We have now investigated the reactions of $EtO_2CC{\equiv}CCO_2Et$ with $Mn_2(CO)_{10}$ by UV irradiation and with $Mn_2(CO)_9(NCMe)$ by heating. The first reaction proceeds by decarbonylation and insertion of the alkyne into the metal–metal bond to yield the compound $Mn(CO)_4[\mu\text{-}(Z)\text{-}(EtO_2C)C{=}C(CO_2Et)]Mn(CO)_5$ (**1**), the manganese homologue of **B**. Compound **1** isomerizes to the new compound $Mn_2(CO)_8[\mu\text{-}(EtO_2C)C{=}C(CO_2Et)C{=}O]$ (**3**), which contains a *cis*-cyclomanganated enone grouping by a coupling of one of the CO ligands to the alkyne. The reaction of $Mn_2(CO)_9(NCMe)$ with $EtO_2CC{\equiv}CCO_2Et$ is slow and yields **3** directly. No dimetalated ketone complexes of the type **A** were formed. Compound **3** reacts further with alkynes to form a series of complexes containing metalated pyran rings (e.g. $Mn_2(CO)_7[\mu\text{-}\eta^4\text{-}\overline{COC(CO_2Me)C(H)C(CO_2Et)C}(CO_2Et)]$ (**4a**)) by a novel 1,4-cycloaddition of the alkyne to the *cis*-cyclomanganated enone grouping in **3**. These metalated pyran compounds provide a synthetic route to carboxylated pyran derivatives by treatment with hydrochloric acid under CO. Compound **3** also reacts with PMe_2Ph in the presence of H_2O by the elimination of one manganese grouping and the addition of the phosphine and one hydrogen atom to one of the carboxylate-substituted carbon atoms. The results of this study are reported here. A preliminary report on this work has been published.[9]

Experimental Section

Unless specified otherwise, all reactions were carried out under an atmosphere of nitrogen. Hexane and heptane solvents were freshly distilled from sodium before use. $EtO_2CC{\equiv}CCO_2Et$ (95%), PMe_2Ph (99%), and D_2O (99.8%) were purchased from Aldrich Co. and were used without further purificatation. UV irradiations were performed by using an externally positioned 360-W high-pressure mercury lamp purchased from Gates Raymaster Products (Franklin Square, NY) on solutions in Pyrex glassware. TLC separations were performed in air by using silica gel (60 Å, F_{254}) on plates (Whatman, 0.25 mm). IR spectra were recorded on a Nicolet 5DXB FT-IR spectrophotometer. ^1H NMR spectra were taken at 300 MHz on a Bruker AM-300 spectrometer or at 500 MHz on a Bruker AM-500 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 reported procedure.[10]

Reaction of $Mn_2(CO)_{10}$ with $EtO_2CC{\equiv}CCO_2Et$ by UV Irradiation. A 30.0-mg amount (0.077 mmol) of $Mn_2(CO)_{10}$ and a 30.0-μL amount (0.177 mmol) of $EtO_2CC{\equiv}CCO_2Et$ were dissolved in 80 mL of hexane. The solution was exposed to UV–vis irradiation at 25 °C for 15 min in the presence of a purge with nitrogen. After the solvent was removed in vacuo at room temperature, the residue was separated by TLC using a hexane/CH_2Cl_2 (1/1) solvent mixture to give the following compounds in order of elution: 4.4 mg of unreacted $Mn_2(CO)_{10}$, 3.0 mg of yellow $Mn(CO)_4[\mu\text{-}(E)\text{-}(EtO_2C)C{=}C(CO_2Et)]Mn(CO)_4$ (**2**; 8% yield), and 14.7 mg of yellow $Mn(CO)_4[\mu\text{-}(Z)\text{-}(EtO_2C)C{=}C(CO_2Et)]Mn(CO)_5$ (**1**; 36% yield). Data for **1**: IR (ν_{co} in hexane, cm^{-1}) 2122 (w), 2085 (m), 2064 (w), 2038 (vs), 2030 (s), 2006 (s), 1997 (s), 1940 (s), 1706 (w, br), 1559 (w, br), 1545 (w, br); ^1H NMR (δ in C_6D_6, ppm) 4.03 (q, $^3J_{H-H}$ = 7.2 Hz, 2H, CH_2), 3.49(q, $^3J_{H-H}$ = 7.0 Hz, 2H, CH_2), 1.05 (t, $^3J_{H-H}$ = 7.2 Hz, 3H, CH_3), 0.65 (t, $^3J_{H-H}$ = 7.0 Hz, 3H, CH_3). Anal. Calcd (found) for **1**: C, 36.46 (36.52); H, 2.62 (1.67). Data for **2**: IR (ν_{co} in hexane, cm^{-1}) 2076 (m), 2004 (vs), 1994 (s), 1956 (s), 1559 (w, br), 1545 (w, br); ^1H NMR (δ in C_6D_6, ppm) 3.67 (q, $^3J_{H-H}$ = 7.1 Hz, 4H, CH_2), 0.83 (t, $^3J_{H-H}$ = 7.1 Hz, 3H, CH_3). The mass spectrum for **2** showed the parent ion at *m*/*e* 504 and ions corresponding to the loss of 3–5 and 7–9 carbonyl groups.

Conversion of 1 to 2. At 25 °C a solution of 10.0 mg (0.019 mmol) of **1** in 75 mL of hexane was exposed to UV–vis irradiation (1000-W mercury lamp obtained from Cooper Lighting, Vicksburg, MS) for 15 min in the presence of a purge with nitrogen. The solvent was then removed in vacuo at room temperature, and the residue was separated using a hexane/CH_2Cl_2 (2/1), solvent mixture to give 5.2 mg of **2** (55% yield) and 1.5 mg of unreacted starting material **1**.

Preparation of $Mn_2(CO)_8[(EtO_2C)C{=}C(CO_2Et)C{=}O]$ 3. A 50-mg amount (0.123 mmol) of $Mn_2(CO)_9(MeCN)$ was dissolved in 40 mL of hexane. A 29.5-μL amount (0.184 mmol) of $EtO_2CC{\equiv}CCO_2Et$ was added, and the solution was stirred at 25 °C for 20 h. The solvent was evaporated, and the residue was transferred to TLC plates by dissolving in a minimum amount of CH_2Cl_2 and was then separated by using a hexane/CH_2Cl_2 (1/1) solvent mixture. This yielded the following compounds in order of elution: 0.6 mg of $Mn_2(CO)_{10}$, 2.9 mg of unreacted $Mn_2(CO)_9(MeCN)$, and 14.2 mg of orange $Mn_2(CO)_8[(EtO_2C)C{=}C(CO_2Et)C{=}O]$, (**3**; 22% yield). Data for **3**: IR (ν_{co} in hexane, cm^{-1}) 2100 (w), 2084 (s), 2019 (s, sh), 2000 (s), 1973 (s), 1964 (s), 1722 (w, br), 1593 (m, br), 1534 (w, br); ^1H NMR (δ in $CDCl_3$, ppm) 4.21 (2H, q, $^3J_{H-H}$ = 7.1 Hz, CH_2), 3.51 (2H, q, $^3J_{H-H}$ = 7.1 Hz, CH_2), 1.09 (3H, t, $^3J_{H-H}$ = 7.1 Hz, CH_3), 0.68 (3H, t, $^3J_{H-H}$ = 7.1 Hz, CH_3). The mass spectrum of **3** showed the parent

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ion at *m/e* 532 and ions corresponding to the loss of each of the nine CO ligands. Anal. Calcd (found) for **3**: C, 38.37 (38.55); H, 1.89 (1.77).

Isomerization of 1 to 3. A solution of 12.2 mg (0.023 mmol) of **1** in 30 mL of CH_2Cl_2 was stirred in the dark at 25 °C for 12 h. The solvent was removed in vacuo at room temperature, and the residue was separated by TLC using a hexane/CH_2Cl_2 (1/1) solvent mixture to give 7.1 mg of **3** (58% yield).

Reaction of 3 with Alkynes. (a) With $HC{\equiv}CCO_2Me$. A 20.0-mg amount (0.038 mmol) of **3** and 20.0 μL (0.23 mmol) of $HC{\equiv}CCO_2Me$ were dissolved in 40 mL of hexane. The solution was exposed to UV radiation at 25 °C for 5 min. After the solvent was evaporated, the residue was separated by TLC using a hexane/CH_2Cl_2 (2/1) solvent mixture to give 7.3 mg of unreacted starting material and 6.1 mg of orange $Mn_2(CO)_7[\mu\text{-}\eta^4\text{-}COC(CO_2Me)C(H)C(CO_2Et)C(CO_2Et)]$ (**4a**; 28% yield). Data for **4a**: IR (ν_{co} in hexane, cm^{-1}) 2104 (w), 2029 (s), 2020 (m), 1987 (sh), 1984 (m), 1955 (m), 1949 (sh), 1944 (sh), 1748 (w, br), 1739 (w, br), 1577 (w, br); ^1H NMR (δ in C_6D_6, ppm) 6.25 (s, 1H, CH), 4.12 (dq, $^2J_{H-H}$ = 10.7 Hz, $^3J_{H-H}$ = 7.1 Hz, 1H, CH_2), 3.93 (dq, $^2J_{H-H}$ = 10.7 Hz, $^3J_{H-H}$ = 7.1 Hz, 1H, CH_2), 3.69 (dq, $^2J_{H-H}$ = 10.6 Hz, $^3J_{H-H}$ = 7.1 Hz, 1H, CH_2), 3.56 (dq, $^2J_{H-H}$ = 10.6 Hz, $^3J_{H-H}$ = 7.1 Hz, 1H, CH_2), 3.48 (s, 3H, OCH_3), 0.94 (s, 3H, CH_3), 0.79 (s, 3H, CH_3). Anal. Calcd (found): C, 40.84 (40.78); H, 2.40 (2.36). When this reaction was carried in refluxing heptane for 6 h, 1.7 mg of unreacted starting material and 2.9 mg (13%) of **4a** were obtained.

(b) With $EtO_2CC{\equiv}CCO_2Et$. A 20.0-mg amount (0.038 mmol) of **3** and 20.0 μL (0.12 mmol) of $EtO_2CC{\equiv}CCO_2Et$ in 40 mL of hexane was irradiated with UV at 25 °C for 5 min. Separation by the procedure described above gave 7.0 mg of unreacted **3** and 6.7 mg of orange $Mn_2(CO)_7[\mu\text{-}\eta^4\text{-}COC(CO_2Et)C(CO_2Et)C(CO_2Et)C(CO_2Et)]$ (**4b**; 26% yield). Data for **4b**: IR (ν_{co} in hexane, cm^{-1}) 2105 (w), 2031 (s), 2023 (m), 1986 (m), 1958 (m), 1952 (m), 1735 (w, br), 1581 (w, br); ^1H NMR (δ in C_6D_6, ppm) 4.26 (m, 2H, CH_2), 4.08 (m, 2H, CH_2), 4.07 (m, 2H, CH_2), 3.56 (m, 2H, CH_2), 1.13 (t, $^3J_{H-H}$ = 7.1 Hz, 3H, CH_3), 1.03 (t, $^3J_{H-H}$ = 7.1 Hz, 3H, CH_3), 0.96 (t, $^3J_{H-H}$ = 7.1 Hz, 3H, CH_3), 0.74 (t, $^3J_{H-H}$ = 7.1 Hz, 3H, CH_3). The mass spectrum for **4b** showed the parent ion at *m/e* 674 and ions corresponding to the loss of each of six carbonyl ligands.

(c) With $HC{\equiv}CH$. A solution of 50.0 mg (0.094 mmol) of **3** in 300 mL of hexane was purged with $HC{\equiv}CH$ for 10 min. Then the solution was exposed to UV at 25 °C with $HC{\equiv}CH$ purging for 5 min. After the solvent was evaporated under vacuum, the residue was separated by TLC using a hexane/CH_2Cl_2 (1/1) solvent mixture to give 14.4 mg of $Mn_2(CO)_7[\mu\text{-}\eta^4\text{-}COCHCHC(CO_2Et)C(CO_2Et)]$ (**4c**; 29% yield) and 4.0 mg of starting material. Data for **4c**: IR (ν_{co} in hexane, cm^{-1}) 2103 (m), 2025 (s), 2015 (m), 1980 (m), 1947 (m), 1931 (m), 1731 (w, br), 1575 (w, br); ^1H NMR (δ in C_6D_6, ppm) 5.71 (d, $^3J_{H-H}$ = 4.3 Hz, 1H, CH), 5.33 (d, $^3J_{H-H}$ = 4.3 Hz, 1H, CH), 4.13 (dq, $^2J_{H-H}$ = 10.7 Hz, $^3J_{H-H}$ = 7.1 Hz, 1H, CHH), 3.96 (dq, $^2J_{H-H}$ = 10.8 Hz, $^3J_{H-H}$ = 7.1 Hz, 1H, CHH), 3.71 (dq, $^2J_{H-H}$ = 10.6 Hz, $^3J_{H-H}$ = 7.2 Hz, 1H, CHH), 3.61 (dq, $^2J_{H-H}$ = 10.6 Hz, $^3J_{H-H}$ = 7.1 Hz, 1H, CHH), 0.97 (t, $^3J_{H-H}$ = 7.1 Hz, 3H, CH_3), 0.83 (t, $^3J_{H-H}$ = 7.1 Hz, 3H, CH_3). The mass spectrum of **4c** showed the parent ion at *m/e* 530 and ions corresponding to the loss of each of 2–8 carbonyl groupings.

Reactions of 4a–c with HCl/CO. A 10.0-mg amount (0.017 mmol) of **4a** was dissolved in 30 mL of heptane. CO was saturated with HCl gas by purging it through a 36% HCl aqueous solution. This gaseous mixture was dried by passing through a 5-in. column of P_2O_5 and was then purged through the solution of **4a** for 20 min at 25 °C. The solution was heated to reflux for 6 h while the HCl/CO purge was continued. An IR analysis of the reaction solution showed the formation of $Mn(CO)_5Cl$.[11] After the mixture was cooled, the solvent was evaporated under vacuum. The residue was separated by TLC using a hexane/CH_2Cl_2 (1/1) solvent mixture to give 0.9 mg of unreacted starting material and 2.9 mg of the colorless α-pyran analyzed as $C_{13}O_7H_{16}$ (**5a**; 61% yield). Data for **5a**: IR (ν_{co} in hexane, cm^{-1}) 1756, 1744, 1735 (sh), 1723, 1637; ^1H NMR (δ in $CDCl_3$, ppm) 7.60 (s, 1H, CH), 6.31 (d, $^3J_{H-H}$ = 4.6 Hz, 1H, CH), 4.23 (dq, 1H, CHH, $^2J_{H-H}$ = 10.9 Hz, $^3J_{H-H}$ = 7.2 Hz), 4.18 (d, 1H, CHH, $^2J_{H-H}$ = 10.9 Hz, $^3J_{H-H}$ = 7.2 Hz), 4.18 (q, 2H, CH_2, $^3J_{H-H}$ = 7.2 Hz), 4.17 (d, $^3J_{H-H}$ = 4.6 Hz, 1H, CH), 3.83 (s, 3H, OCH_3), 1.27 (t, 3H, CH_3, $^3J_{H-H}$ = 7.2 Hz), 1.26 (t, 3H, CH_3,$^3J_{H-H}$ = 7.2 Hz). A high-resolution mass spectrum of **5a** showed the parent ion at *m/e* 284.0907 (calcd for $C_{13}H_{16}O_7$ 284.0896). Compounds **4b**,**c** were converted to $C_{17}H_{22}O_9 = C_5OH_2(CO_2Et)_4$ (**5b**; 42% yield) and $C_{11}O_5H_{14} = C_5OH_4(CO_2Et)_2$ (**5c**; 61% yield) by similar procedures. Data for **5b**: IR (ν_{co} in hexane, cm^{-1}) 1762, 1752, 1739, 1733, 1716; ^1H NMR (δ in $CDCl_3$, ppm) 7.87 (s, 1H, CH), 5.91 (s, 1H, CH), 4.38 (dq, $^2J_{H-H}$ = 11.0 Hz, $^3J_{H-H}$ = 7.2 Hz, 1H, CHH), 4.32 (dq, $^2J_{H-H}$ = 11.0 Hz, $^3J_{H-H}$ = 7.2 Hz, 1H, CHH), 4.25 (dq, $^2J_{H-H}$ = 10.9 Hz, $^3J_{H-H}$ = 7.2 Hz, 1H, CHH), 4.24 (q, $^3J_{H-H}$ = 7.2 Hz, 2H, CH_2), 4.19 (q, $^2J_{H-H}$ = 7.1 Hz, 2H, CH_2), 4.17 (dq, $^2J_{H-H}$ = 10.9 Hz, $^3J_{H-H}$ = 7.2 Hz, 1H, CHH), 1.35 (t, $^3J_{H-H}$ = 7.2 Hz, 3H, CH_3), 1.28 (t, $^3J_{H-H}$ = 7.0 Hz, 3H, CH_3), 1.26 (t, $^3J_{H-H}$ = 7.1 Hz, 3H, CH_3), 1.24 (t, $^3J_{H-H}$ = 7.1 Hz, 3H, CH_3); mass spectrum parent ion at *m/e* 370.1274 (calcd 370.1264). Data for **5c**: IR (ν_{co} in hexane, cm^{-1}) 1740, 1728; ^1H NMR (δ in C_6D_6, ppm) 7.38 (s, 1H, CH), 5.52 (t, $^3J_{H-H}$ = 4.1 Hz, 1H, CH), 4.10 (q, $^3J_{H-H}$ = 7.1 Hz, 2H, CH_2), 4.02 (q, $^3J_{H-H}$ = 7.1 Hz, 2H, CH_2), 3.87 (d, $^3J_{H-H}$ = 4.3 Hz, 2H, OCH_2CH), 1.02 (t, $^3J_{H-H}$ = 7.1 Hz, 3H, CH_3), 0.95 (t, $^3J_{H-H}$ = 7.1 Hz, 3H, CH_3); mass spectrum parent ion at *m/e* 226.0837 (calcd 226.0841).

Reaction of 3 with PMe_2Ph in the Presence of H_2O. A 50-mL portion of hexane was treated with H_2O (1 mL) by stirring at 25 °C for 12 h. This hexane was then transferred to a 100-mL three-necked flask, and a 50.0-mg amount (0.094 mmol) of **3** was added to it. With stirring a 13.4-μL amount (0.094 mmol) of PMe_2Ph was next added to this solution via syringe at 25 °C. The solution turned quickly from orange to yellow. After 10 min, the solvent was removed under vacuum at 25 °C, and the residue was extracted with CH_2Cl_2. The extract was evaporated to dryness at room temperature and recrystallized from a mininum amount of a hexane/CH_2Cl_2 (1/1) solvent mixture at −14 °C to give 41.0 mg of $Mn(CO)_4[OCC(CO_2Et)C(H)(CO_2Et)(PMe_2Ph)]$ (**6**) as yellow crystals (80% yield). Attempts to identify the manganese fragment that was eliminated were unsuccessful. Data for **6**: IR (ν_{co} in hexane, cm^{-1}) 2056 (m), 1970 (m), 1950 (s), 1924 (m), 1720 (w, br), 1563 (w, br), 1513 (m, br); ^1H NMR (δ in C_6D_6, ppm) 7.48 (m, 2H, C_6H_5), 6.96 (m, 3H, C_6H_5), 6.02 (d, $^2J_{P-H}$ = 14.7 Hz, 1H, CH), 3.99 (m, 2H, CH_2), 3.87 (m, 2H, CH_2), 3.76 (m, 2H, CH_2), 3.27 (m, 2H, CH_2), 2.09 (d, $^2J_{P-H}$ = 13.9 Hz, 3H, CH_3), 1.77 (d, $^2J_{P-H}$ = 13.4 Hz, 3H, CH_3), 0.95 (t, $^3J_{H-H}$ = 7.1 Hz, 3H CH_3), 0.56 (t, $^3J_{H-H}$ = 7.1 Hz, 3H, CH_3). Anal. Calcd (found) for $\mathbf{6}\cdot{}^1/_2CH_2Cl_2$: C, 47.23 (47.93); H, 4.24 (4.16).

Treatment of 6 with D_2O. To a solution of 5.0 mg of **6** in 0.8 mL of C_6D_6 was added 50.0 μL of D_2O. A ^1H NMR spectrum was taken after 30 min, and the intensity of the resonance of **6** at δ 6.02 ppm was completely absent.

Crystallographic Analysis. Crystals of compounds **1** and **4a** suitable for X-ray diffraction analysis were grown by slow evaporation of solvent from a solution in a hexane/CH_2Cl_2 (1/1) solvent mixture at −3 °C. Crystals of compound **3** were grown by slow evaporation of solvent from a solution in diethyl ether at −14 °C. Crystals of compound **6** suitable for X-ray diffraction analysis were grown by cooling a solution in a hexane/CH_2Cl_2 (1/1) solvent mixture 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. The 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)

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[11] Hileman, J. C.; Huggins, D. K.; Kaesz, H. D. *Inorg. Chem.* **1962**, *1*, 933.

Table 1. Crystallographic Data for Compounds 1, 3, 4a, and 6

	1	3	4a	6
empirical formula	$Mn_2O_{13}C_{17}H_{10}$	$Mn_2O_{13}C_{17}H_{10}$	$Mn_2O_{14}C_{20}H_{14}$	$MnPO_9C_{21}H_{22}\cdot{}^1/_2CH_2Cl_2$
fw	532.13	532.13	588.20	546.78
cryst syst	monoclinic	triclinic	triclinic	triclinic
lattice params				
a (Å)	10.160(1)	11.395(2)	9.380(2)	11.830(2)
b (Å)	11.593(2)	14.252(3)	19.390(4)	13.589(2)
c (Å)	18.569(3)	6.7910(9)	6.997(2)	8.456(2)
α (deg)	90.0	91.59(1)	90.28(2)	92.49(2)
β (deg)	100.72(1)	91.54(1)	106.11(2)	108.60(2)
γ (deg)	90.0	84.97(1)	99.27(2)	89.67(2)
V (Å^3)	2149(1)	1097.9(5)	1205(1)	1287.1(8)
space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
Z	4	2	2	2
D_{calc} (g/cm^3)	1.64	1.61	1.62	1.41
μ(Mo Kα) (cm^{-1})	11.90	11.65	10.72	7.01
temp (°C)	20	20	20	20
$2\theta_{max}$ (deg)	42.0	42.0	40.0	42.0
no. of obs rflns ($I > 3\sigma(I)$)	1754	1717	1534	1976
no. of variables	289	289	225	369
residuals: R, R_w	0.031, 0.032	0.031, 0.031	0.041, 0.040	0.047, 0.047
goodness-of-fit indicator	1.75	1.57	1.92	2.20
max shift in final cycle	0.04	0.00	0.00	0.02
largest peak in final diff map (e/Å^3)	0.26	0.25	0.39	0.60
abs cor	empirical	empirical	none	empirical
transmissn coeff, max/min	1.00/0.72	1.00/0.74		1.00/0.92

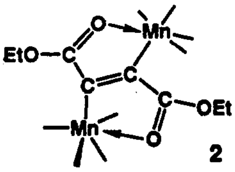
obtained from Molecular Structure Corp., The Woodlands, TX. Neutral atom scattering factors were calculated by the standard procedures.[12a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[12b] Lorentz/polarization (Lp) corrections were applied to the data for each structure. 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 $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (0.02I_{net})^2]^{1/2}/Lp$. All three structures were solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. Crystal data and results of the analyses are listed in Table 1.

Compound 1 crystallized in the monoclinic space group $P2_1/c$. In the solid state it is isomorphous with its rhenium homologue, which has recently been structurally characterized by us.[8a] Solution of this structure was initiated by using the values of the atomic positional parameters of the rhenium homologue. Refinement was completed using anisotropic thermal parameters for all non-hydrogen atoms. The positions of all hydrogen atoms were calculated by assuming idealized geometries with C–H = 0.95 Å. The scattering contributions of calculated hydrogen atoms were added to the structure factor calculations, but their positions were not refined.

Compounds 3, 4a, and 6 all crystallized in a triclinic crystal system. The space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of each structure. For compound 3 all non-hydrogen atoms were refined with anisotropic thermal parameters. The positions of all hydrogen atoms were calculated by assuming idealized geometries with C–H = 0.95 Å. The scattering contributions of calculated hydrogen atoms were added to the structure factor calculations, but their positions were not refined. Due to the limited amount of data for compound 4a, only the atoms heavier than carbon were refined with anisotropic thermal parameters. For compound 6 all non-hydrogen atoms were refined with anisotropic thermal parameters. The positions of all hydrogen atoms were located and refined on their positional parameters. Hydrogen H(3) was also refined using an isotropic thermal parameter. In the final stages of refinement $^1/_2$ equiv of CH_2Cl_2 from the crystallization solvent was located in the lattice. It was disordered about a center of symmetry but was successfully refined by employing an anisotropic thermal parameter for the chlorine atom and an isotropic thermal parameter for the carbon atom.

Results

The new compound $Mn(CO)_4[\mu$-(Z)-$(EtO_2C)C{=}C(CO_2Et)]Mn(CO)_5$ (1) was obtained in 36% yield from the reaction of $Mn_2(CO)_{10}$ with $EtO_2CC{\equiv}CCO_2Et$ in the presence of UV irradiation. A second minor product that is believed to be $Mn(CO)_4[\mu$-(E)-$(EtO_2C)C{=}C(CO_2Et)]Mn(CO)_4$ (2) was isolated in 8% yield. Compound 2 can be obtained from 1 by irradiation with UV–vis light, and this strongly indicates that 1 is a precursor to 2. Compound 1 was characterized structurally by a single-crystal X-ray diffraction analysis, and an ORTEP drawing of its molecular structure is shown in Figure 1. Final atomic positional parameters are listed in Table 2. The molecule is a Z-dimetalated olefin complex formed by decarbonylation of $Mn_2(CO)_{10}$ and addition and insertion of the alkyne $EtO_2CC{\equiv}CCO_2Et$ into the metal–metal bond. The oxygen atom of the carbonyl group of one of the carboxylate substituents is coordinated to one of the metal atoms to form a four-membered metallacyclic ring. Structurally, this molecule is virtually the same as the rhenium compound $Re(CO)_4[\mu$-(Z)-$(EtO_2C)C{=}C(CO_2Et)]Re(CO)_5$ (**B**), which we recently obtained from the reaction of $Re_2(CO)_9(NCMe)$ with $EtO_2CC{\equiv}CCO_2Et$.[8] The only significant structural difference is that the metal to ligand bond distances are shorter than those in the rhenium compound, and this is due simply to the smaller size of manganese compared to rhenium. On the basis of its IR, ^1H NMR, and mass spectra, we believe that compound 2 is the manganese analogue of the known rhenium compound $Re(CO)_4[\mu$-(E)-$(EtO_2C)C{=}C(CO_2Et)]Re(CO)_4$ (7), which we have obtained from the UV irradiation of compound **B**.



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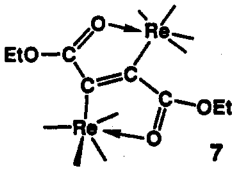

7

When a solution of 1 in methylene chloride solvent was allowed to stand at 25 °C for 12 h, it was converted into

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(12) (a) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1975; Vol. IV, Table 2.2B, pp 99–101. (b) Reference 12a, Table 2.3.1, pp 149–150.

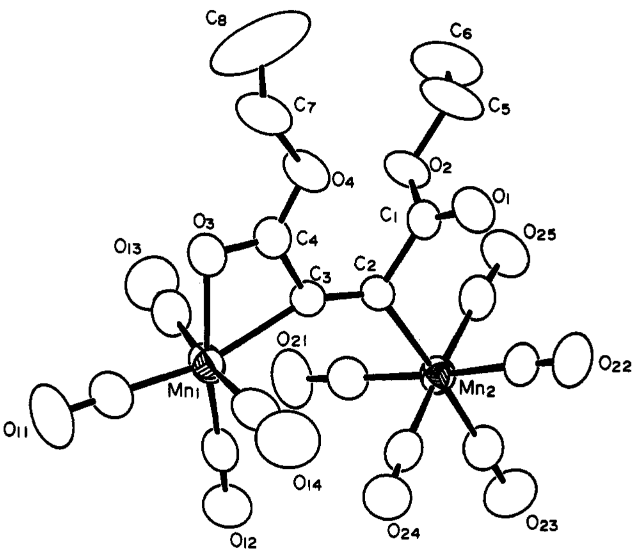


Figure 1. ORTEP diagram of $Mn(CO)_4[\mu\text{-}(Z)\text{-}(EtO_2C)C{=}C(CO_2Et)]Mn(CO)_5$ (1) showing 50% probability thermal ellipsoids. Selected intramolecular bond distances (Å) and angles (deg) are as follows: Mn(1)–C(3) = 2.091(4), Mn(2)–C(2) = 2.109(4), C(1)–C(2) = 1.503(6), C(2)–C(3) = 1.337(5), C(3)–C(4) = 1.461(6), Mn(1)–O(3) = 2.104(3), C(1)–O(1) = 1.196(5), C(4)–O(3) = 1.252(5); Mn(1)–C(3)–C(2) = 148.1(4), Mn(1)–C(3)–C(4) = 87.1(3), Mn(2)–C(2)–C(3) = 129.6(3), Mn(2)–C(2)–C(1) = 110.9(3), C(1)–C(2)–C(3) = 119.5(4), C(2)–C(3)–C(4) = 124.8(4), C(3)–Mn(1)–O(3) = 66.0(1).

Table 2. Positional Parameters and *B*(eq) Values for 1

atom	*x*	*y*	*z*	*B*(eq), Å^2
Mn(1)	0.71853(07)	0.20632(07)	0.00326(04)	3.55(4)
Mn(2)	0.84272(07)	0.14009(06)	0.24452(04)	3.08(3)
O(1)	1.1120(03)	0.3299(03)	0.21981(18)	4.6(2)
O(2)	1.1583(03)	0.1538(03)	0.18262(17)	4.1(2)
O(3)	0.8854(03)	0.2876(03)	–0.02677(17)	4.2(2)
O(4)	1.0769(03)	0.3137(03)	0.05349(17)	5.7(2)
O(11)	0.5406(04)	0.2103(04)	–0.1431(02)	7.9(2)
O(12)	0.5109(04)	0.0880(03)	0.06547(19)	5.4(2)
O(13)	0.8391(04)	–0.0230(04)	–0.0205(02)	6.6(2)
O(14)	0.6215(04)	0.4317(04)	0.0506(02)	7.2(2)
O(21)	0.7701(04)	–0.0544(03)	0.13836(19)	5.4(2)
O(22)	0.9251(04)	0.3504(03)	0.33534(19)	5.6(2)
O(23)	0.7042(04)	0.0319(03)	0.35499(20)	6.0(2)
O(24)	0.6011(04)	0.2805(03)	0.18457(19)	5.2(2)
C(25)	1.0013(06)	0.0649(04)	0.2879(03)	3.6(2)
O(25)	1.0957(04)	0.0219(03)	0.31794(19)	5.2(2)
C(1)	1.0764(05)	0.2412(04)	0.1894(02)	2.9(2)
C(2)	0.9334(04)	0.2081(04)	0.1604(02)	2.6(2)
C(3)	0.8815(04)	0.2255(04)	0.0896(02)	2.8(2)
C(4)	0.9531(05)	0.2778(04)	0.0365(03)	3.5(2)
C(5)	1.2982(05)	0.1726(05)	0.2131(04)	6.5(3)
C(6)	1.3658(06)	0.0629(06)	0.2244(04)	7.9(4)
C(7)	1.1377(06)	0.3622(07)	–0.0049(03)	8.3(4)
C(8)	1.2566(11)	0.3076(06)	–0.0085(06)	13.2(6)
C(11)	0.6102(05)	0.2095(05)	–0.0874(03)	4.9(3)
C(12)	0.5932(05)	0.1345(05)	0.0418(03)	3.8(2)
C(13)	0.7930(06)	0.0637(05)	–0.0130(03)	4.5(3)
C(14)	0.6587(05)	0.3461(05)	0.0315(03)	4.5(3)
C(21)	0.7970(05)	0.0181(04)	0.1796(03)	3.7(2)
C(22)	0.8959(05)	0.2697(05)	0.3008(03)	3.9(3)
C(23)	0.7583(05)	0.0735(05)	0.3132(03)	4.1(3)
C(24)	0.6915(05)	0.2247(04)	0.2050(03)	3.6(2)

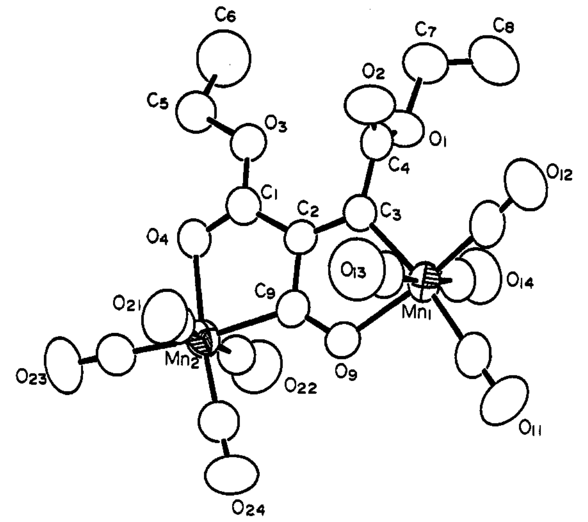


Figure 2. ORTEP diagram of $Mn_2(CO)_8[\mu\text{-}(EtO_2C)C{=}C(CO_2Et)C{=}O]$ (3) showing 50% probablility thermal ellipsoids.

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

atom	*x*	*y*	*z*	*B*(eq), Å^2
Mn(1)	0.41125(06)	0.27821(05)	0.74789(10)	4.17(4)
Mn(2)	0.23062(06)	0.00652(05)	0.47964(10)	4.10(4)
O(1)	0.2201(03)	0.4184(02)	0.3994(06)	6.4(2)
O(2)	0.1196(03)	0.4217(03)	0.6820(06)	7.1(2)
O(3)	0.0469(03)	0.2605(02)	0.3533(05)	5.0(2)
O(4)	0.1014(03)	0.1055(02)	0.3653(04)	4.3(2)
O(9)	0.3915(03)	0.13846(20)	0.6689(04)	3.9(2)
O(11)	0.6458(03)	0.2265(03)	0.9393(06)	8.2(3)
O(12)	0.4040(04)	0.4800(03)	0.8535(07)	9.0(3)
O(13)	0.2749(04)	0.2401(03)	1.0998(06)	9.0(3)
O(14)	0.5112(04)	0.3242(03)	0.3635(06)	7.6(3)
O(21)	0.1171(03)	0.0070(03)	0.8692(06)	7.1(3)
O(22)	0.3720(03)	0.0143(03)	0.1147(06)	7.4(3)
O(23)	0.1066(04)	–0.1551(03)	0.3088(06)	7.7(3)
O(24)	0.4248(03)	–0.1101(03)	0.6651(06)	7.3(3)
C(1)	0.1173(04)	0.1882(04)	0.4130(07)	3.9(3)
C(2)	0.2188(04)	0.2089(03)	0.5358(06)	3.5(2)
C(3)	0.2554(04)	0.2916(03)	0.6036(06)	3.6(2)
C(4)	0.1875(05)	0.3843(04)	0.5677(09)	4.7(3)
C(5)	–0.0465(05)	0.2433(04)	0.2108(09)	6.7(3)
C(6)	–0.0712(07)	0.3255(05)	0.0961(11)	11.3(5)
C(7)	0.1683(06)	0.5115(05)	0.3444(12)	9.6(5)
C(8)	0.2492(07)	0.5778(05)	0.3674(13)	12.2(6)
C(9)	0.2968(04)	0.1247(03)	0.5789(06)	3.6(3)
C(11)	0.5556(05)	0.2458(04)	0.8652(08)	5.5(3)
C(12)	0.4098(05)	0.4004(04)	0.8151(08)	5.9(3)
C(13)	0.3296(05)	0.2559(04)	0.9699(08)	5.4(3)
C(14)	0.4754(04)	0.3043(04)	0.5100(08)	5.0(3)
C(21)	0.1564(04)	0.0071(03)	0.7181(08)	4.7(3)
C(22)	0.3178(05)	0.0125(03)	0.2518(08)	4.9(3)
C(23)	0.1525(05)	–0.0932(04)	0.3743(08)	5.2(3)
C(24)	0.3478(05)	–0.0663(04)	0.5878(08)	5.1(3)

the new compound $Mn_2(CO)_8[\mu\text{-}(EtO_2C)C{=}C(CO_2Et)C{=}O]$ (3) in 58% yield. This same product was obtained from the reaction of $Mn_2(CO)_9(MeCN)$ with $EtO_2CC{\equiv}CCO_2Et$ in hexane solvent at 25 °C, although the yield was lower (22%). Compound 3 was characterized structurally by a single-crystal X-ray diffraction analysis, and an ORTEP diagram of its molecular structure is shown in Figure 2. Final atomic positional parameters are listed in Table 3. Selected bond distances and angles are listed in Tables 4 and 5, respectively. The molecule contains a $EtO_2CC{=}C(CO_2Et)C{=}O$ ligand that was formed by a coupling of the alkyne to the carbon atom of a CO ligand. The oxygen atom of the CO group is coordinated to one metal atom Mn(1), resulting in the formation of a five-membered metallacyclic ring Mn(1)–O(9) = 2.078(3) Å. Similar five-membered rings were found in the complexes $Mn_2(CO)_8[\mu\text{-}(EtO)C{=}C(H)C{=}O]$ (8), $Mn_2(CO)_8\{\mu\text{-}O{=}C[C(H){=}C(CO_2Me)]_2\}$ (9) (A, X = CO_2Me), and $Mn_2(CO)_6(PMe_2Ph)_2[\mu\text{-}O{=}C[C(H){=}C(OEt)]_2\}$ (10).[3] The C—O bond length (C(9)–O(9) = 1.254(5) Å) is similar to that found in 8 (1.274(5) Å) but significantly shorter than that found in 9 (1.312(9) Å), where the oxygen is

Table 4. Intramolecular Distances for 3[a]

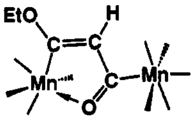
Mn(1)–O(9)	2.078(3)	O(9)–C(9)	1.254(5)
Mn(1)–C(3)	2.002(4)	C(1)–C(2)	1.454(6)
Mn(2)–O(4)	2.096(3)	C(2)–C(3)	1.349(6)
Mn(2)–C(9)	1.998(4)	C(2)–C(9)	1.462(6)
O(1)–C(4)	1.329(6)	C(3)–C(4)	1.495(6)
O(1)–C(7)	1.458(6)	C(5)–C(6)	1.428(8)
O(2)–C(4)	1.192(6)	C(7)–C(8)	1.380(8)
O(3)–C(1)	1.315(5)	Mn–C (av)	1.833(6)
O(3)–C(5)	1.451(6)	O–C (av)	1.141(5)
O(4)–C(1)	1.242(5)		

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

Table 5. Intramolecular Bond Angles for 3[a]

O(9)–Mn(1)–C(3)	79.4(2)	Mn(1)–C(3)–C(2)	113.6(3)
O(4)–Mn(2)–C(9)	80.8(2)	Mn(1)–C(3)–C(4)	123.5(3)
C(4)–O(1)–C(7)	117.8(5)	C(2)–C(3)–C(4)	122.9(4)
C(1)–O(3)–C(5)	118.4(4)	O(1)–C(4)–O(2)	127.1(5)
Mn(2)–O(4)–C(1)	113.7(3)	O(1)–C(4)–C(3)	109.6(5)
Mn(1)–O(9)–C(9)	114.9(3)	O(2)–C(4)–C(3)	123.1(5)
O(3)–C(1)–O(4)	122.8(4)	O(3)–C(5)–C(6)	108.6(5)
O(3)–C(1)–C(2)	117.0(5)	O(1)–C(7)–C(8)	111.1(5)
O(4)–C(1)–C(2)	120.2(5)	Mn(2)–C(9)–O(9)	131.7(4)
C(1)–C(2)–C(3)	131.1(4)	Mn(2)–C(9)–C(2)	112.5(3)
C(1)–C(2)–C(9)	112.6(4)	O(9)–C(9)–C(2)	115.9(4)
C(3)–C(2)–C(9)	116.2(4)	Mn–C–O (av)	177.4(5)

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



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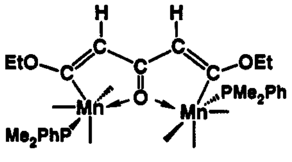


9

coordinated to two metal atoms. The carbon atom of the alkyne-coupled CO group and the oxygen atom O(4) of one of the carboxylate groups are coordinated to the metal Mn(2) to form a second five-membered metallacyclic ring (Mn(2)–O(4) = 2.096(3) Å). The two five-membered rings have the C(2)–C(9) bond in common. Both are planar and nearly coplanar. No atom deviates from the least-squares plane through all eight atoms by more than 0.10 Å. The infrared spectrum contains two low frequency absorptions (1593 and 1534 cm^{-1}). These are almost certainly due to the C=O groupings of the alkyne-coupled CO and the coordinate carboxylate group, but a specific assignment cannot be unambiguously made at this time. The C(2)–C(3) bond is a double bond at 1.349(6) Å. The metal–carbon distances Mn(1)–C(3) and Mn(2)–C(9) are nearly identical in length (2.002(4) Å and 1.998(4) Å, respectively).

The reaction of 3 with $HC{\equiv}CCO_2Me$ in the presence of UV–vis irradiation at 25 °C for 5 min yielded the new compound $Mn_2(CO)_7[\mu\text{-}\eta^4\text{-}COC(CO_2Me)C(H)C(CO_2Et)C(CO_2Et)]$ (**4a**) in 28% yield. This same product can be obtained in a thermal reaction in refluxing heptane, but the yield is lower, 13%. The corresponding products $Mn_2(CO)_7[\mu\text{-}\eta^4\text{-}COC(CO_2Et)C(CO_2Et)C(CO_2Et)C(CO_2Et)]$ (**4b**) and $Mn_2(CO)_7[\mu\text{-}\eta^4\text{-}COCHCHC(CO_2Et)C(CO_2Et)]$ (**4c**) were obtained in 26% and 29% yields, respectively, from the reactions of 3 with $EtO_2CC{\equiv}CCO_2Et$ and $HC{\equiv}CH$ in the presence of UV–vis irradiation at 25 °C for 5 min. The structures of these products were established by a single-crystal X-ray diffraction analysis of **4a**. An ORTEP diagram of the molecular structure of **4a** is shown in Figure 3. Final atomic positional parameters are listed in Table 6. Selected bond distances and angles are listed in Tables 7 and 8, respectively. This molecule contains a 2-manganio-2,3-bis(ethoxycarbonyl)-6-(methoxycarbonyl)pyran ring that is π-coordinated to a manganese tricarbonyl group. Carbons C(3), C(2), C(31), and

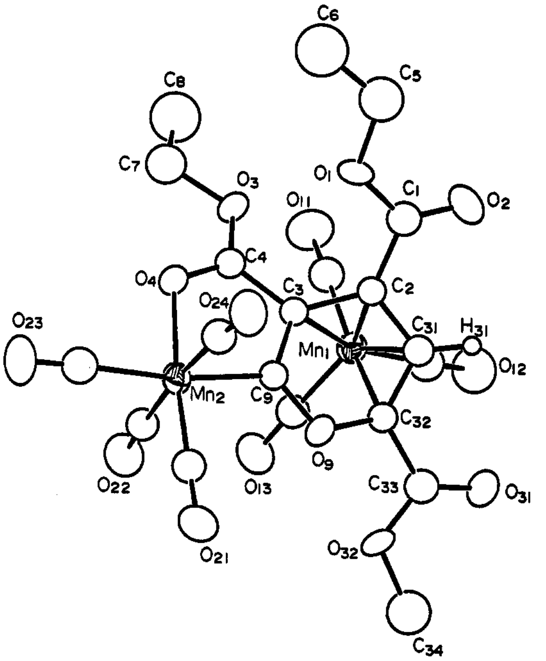


Figure 3. ORTEP diagram of $Mn_2(CO)_7[\mu\text{-}\eta^4\text{-}COC(CO_2Me)C(H)C(CO_2Et)C(CO_2Et)]$ (**4a**) showing 50% probablility thermal ellipsoids.

Table 6. Positional Parameters and *B*(eq) Values for 4a

atom	*x*	*y*	*z*	*B*(eq), Å^2
Mn(1)	–0.00105(13)	0.23932(06)	0.40910(17)	3.04(5)
Mn(2)	0.42663(13)	0.34082(06)	0.90310(18)	3.08(5)
O(1)	0.1439(06)	0.0895(02)	0.7814(08)	4.1(2)
O(2)	–0.1059(06)	0.0769(03)	0.6709(09)	6.2(3)
O(3)	0.3220(05)	0.1574(02)	0.5662(07)	3.6(2)
O(4)	0.4463(05)	0.2505(02)	0.7667(07)	3.3(2)
O(9)	0.1016(05)	0.3341(02)	0.7683(07)	3.3(2)
O(11)	0.0769(07)	0.1388(03)	0.1543(08)	6.0(3)
O(12)	–0.3071(07)	0.2090(03)	0.1362(09)	7.2(3)
O(13)	0.1026(06)	0.3643(03)	0.2162(08)	5.3(3)
O(21)	0.3591(06)	0.4661(03)	1.0721(09)	5.5(3)
O(22)	0.4224(06)	0.4193(03)	0.5357(08)	5.4(3)
O(23)	0.7637(06)	0.3824(03)	1.0589(09)	6.8(3)
O(24)	0.3905(06)	0.2676(03)	1.2650(09)	5.5(3)
O(31)	–0.2884(06)	0.3235(03)	0.5282(09)	5.6(3)
O(32)	–0.0910(05)	0.4109(03)	0.6115(09)	4.7(3)
C(1)	0.0154(10)	0.1129(04)	0.7070(12)	3.8(2)
C(2)	0.0400(08)	0.1888(04)	0.6732(10)	2.7(2)
C(3)	0.1825(07)	0.2344(03)	0.6776(10)	2.6(2)
C(4)	0.3256(09)	0.2126(04)	0.6737(11)	3.0(2)
C(5)	0.1329(11)	0.0156(05)	0.8171(14)	6.4(2)
C(6)	0.2769(13)	–0.0059(06)	0.8642(17)	9.1(3)
C(7)	0.4700(10)	0.1410(05)	0.5640(13)	5.3(2)
C(8)	0.4394(12)	0.0897(06)	0.3985(16)	8.5(3)
C(9)	0.2158(08)	0.3014(04)	0.7762(10)	2.6(2)
C(11)	0.0475(09)	0.1773(04)	0.2585(13)	4.1(2)
C(12)	–0.1881(10)	0.2226(04)	0.2428(13)	4.3(2)
C(13)	0.0622(09)	0.3145(04)	0.2885(12)	3.7(2)
C(21)	0.3879(09)	0.4168(04)	1.0083(12)	3.6(2)
C(22)	0.4274(08)	0.3885(04)	0.6748(12)	3.4(2)
C(23)	0.6371(10)	0.3654(04)	1.0020(12)	4.2(2)
C(24)	0.4083(09)	0.2948(04)	1.1285(13)	3.7(2)
C(31)	–0.0773(08)	0.2257(04)	0.6606(10)	3.1(2)
C(32)	–0.0420(08)	0.2971(04)	0.6343(10)	2.8(2)
C(33)	–0.1564(10)	0.3444(04)	0.5876(12)	3.8(2)
C(34)	–0.1901(11)	0.4623(05)	0.5653(14)	6.3(2)

Table 7. Intramolecular Distances for 4a[a]

Mn(1)–C(2)	2.066(7)	O(31)–C(33)	1.193(9)
Mn(1)–C(3)	2.182(7)	O(32)–C(33)	1.324(9)
Mn(1)–C(31)	2.079(7)	O(32)–C(34)	1.45(1)
Mn(1)–C(32)	2.084(7)	C(1)–C(2)	1.48(1)
Mn(2)–O(4)	2.049(5)	C(2)–C(3)	1.472(9)
Mn(2)–C(9)	1.954(7)	C(2)–C(31)	1.390(9)
O(1)–C(1)	1.327(9)	C(3)–C(4)	1.48(1)
O(1)–C(5)	1.45(1)	C(3)–C(9)	1.414(9)
O(2)–C(1)	1.196(9)	C(5)–C(6)	1.43(1)
O(3)–C(4)	1.297(8)	C(7)–C(8)	1.46(1)
O(3)–C(7)	1.48(1)	C(31)–C(32)	1.396(9)
O(4)–C(4)	1.250(8)	C(32)–C(33)	1.49(1)
O(9)–C(9)	1.318(8)	Mn–C (av)	1.818(9)
O(9)–C(32)	1.480(8)	O–C (av)	1.145(9)

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

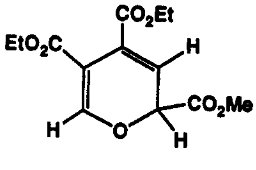
Table 8. Intramolecular Bond Angles for 4a[a]

C(2)–Mn(1)–C(3)	40.4(2)	C(2)–C(3)–C(4)	127.3(6)
C(2)–Mn(1)–C(31)	39.2(3)	C(2)–C(3)–C(9)	118.7(6)
C(2)–Mn(1)–C(32)	68.7(3)	C(4)–C(3)–C(9)	108.5(6)
C(3)–Mn(1)–C(31)	68.0(3)	O(3)–C(4)–O(4)	122.3(7)
C(3)–Mn(1)–C(32)	73.2(3)	O(3)–C(4)–C(3)	119.2(7)
C(31)–Mn(1)–C(32)	39.2(2)	O(4)–C(4)–C(3)	118.4(7)
O(4)–Mn(2)–C(9)	78.5(2)	O(1)–C(5)–C(6)	111.7(8)
C(1)–O(1)–C(5)	116.7(7)	O(3)–C(7)–C(8)	105.8(7)
C(4)–O(3)–C(7)	115.7(6)	Mn(2)–C(9)–O(9)	124.5(5)
Mn(2)–O(4)–C(4)	116.1(5)	Mn(2)–C(9)–C(3)	118.2(5)
C(9)–O(9)–C(32)	112.8(5)	O(9)–C(9)–C(3)	117.2(6)
C(33)–O(32)–C(34)	116.5(6)	Mn(1)–C(31)–C(2)	69.9(4)
O(1)–C(1)–O(2)	123.8(8)	Mn(1)–C(31)–C(32)	70.6(4)
O(1)–C(1)–C(2)	112.1(7)	C(2)–C(31)–C(32)	114.4(6)
O(2)–C(1)–C(2)	124.0(8)	Mn(1)–C(32)–O(9)	110.2(4)
Mn(1)–C(2)–C(1)	129.6(5)	Mn(1)–C(32)–C(31)	70.2(4)
Mn(1)–C(2)–C(3)	74.1(4)	Mn(1)–C(32)–C(33)	121.1(5)
Mn(1)–C(2)–C(31)	70.9(4)	O(9)–C(32)–C(31)	116.0(6)
C(1)–C(2)–C(3)	127.9(7)	O(9)–C(32)–C(33)	110.4(6)
C(1)–C(2)–C(31)	118.6(7)	C(31)–C(32)–C(33)	123.3(7)
C(3)–C(2)–C(31)	112.9(6)	O(31)–C(33)–O(32)	125.8(8)
Mn(1)–C(3)–C(2)	65.5(4)	O(31)–C(33)–C(32)	123.1(8)
Mn(1)–C(3)–C(4)	123.0(5)	O(32)–C(33)–C(32)	111.0(7)
Mn(1)–C(3)–C(9)	106.0(5)	Mn–C–O (av)	177.3(8)

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

C(32) are strongly bonded to Mn(1) (2.066(7), 2.182(7), 2.079(7), and 2.084(7) Å, respectively). The two adjacent distances C(2)–C(31) = 1.390(9) Å and C(31)–C(32) = 1.396(9) Å are short while the third distance C(2)–C(3) = 1.472(9) Å is substantially longer. If the metal is ignored, carbon C(9) has only the two substituents C(3) and O(9) (C(9)–C(3) = 1.414(9) Å, C(9)–O(9) = 1.318(8) Å) and is formally a carbene center that is coordinated to Mn(2) (Mn(2)–C(9) = 1.954(7) Å). These bond distances are typical of alkoxycarbenes.[13] The oxygen atom O(4) of one of the carboxylate groups is also coordinated to Mn(2) (Mn(2)–O(4) = 2.049(5) Å). Formal electron-counting procedures indicate that these complexes should be zwitterionic in character. The manganese atom with three carbonyl ligands should be negatively charged, and the maganese atom with four carbonyl ligands should be positively charged. Compounds **4b,c** are believed to be structurally similar.

When solutions of **4a–c** were treated with a mixture of gaseous HCl and CO, the formation of $Mn(CO)_5Cl$ was observed by IR spectroscopy. From the solutions the metal-free compounds formulated as $C_5OH_3(CO_2Et)_2(CO_2Me)$ (**5a**), $C_5OH_2(CO_2Et)_4$ (**5b**), and $C_5OH_4(CO_2Et)_2$ (**5c**) were obtained in 40–60% yields. Their compositions were established by a combination of ^1H NMR spectroscopy and high-resolution mass spectrometry. These compounds are believed to be pyrans, but it is not possible to distinguish between the α- and γ-pyran structures for **5a** and **5b** on the basis of their ^1H NMR spectra. However, the α structure 4,5-$(EtO_2C)_2C_5OH_4$ was unambiguously established for **5c** by its ^1H NMR spectrum (δ 7.38 (s, 1H, C*H*), 5.52 (t, $^3J_{H-H}$ = 4.1 Hz, 1H, C*H*), 4.10 (q, $^3J_{H-H}$ = 7.1 Hz, 2H, CH_2), 4.02 (q, $^3J_{H-H}$ = 7.1 Hz, 2H, CH_2), 3.87 (d, $^3J_{H-H}$ = 4.3 Hz, 2H, OCH_2CH), 1.02 (t, $^3J_{H-H}$ = 7.1 Hz, 3H, CH_3), 0.95 ppm (t, $^3J_{H-H}$ = 7.1 Hz, 3H, CH_3)), which shows a doublet of intensity 2 at 3.87 ppm for the equivalent methylene protons. Thus, it is believed that **5a,b** also have the α-pyran structures 2-MeO_2C-4,5-$(EtO_2C)_2C_5OH_3$ and 2,3,4,5-$(EtO_2C)_4C_5OH_2$, respectively.



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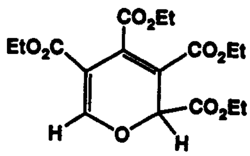

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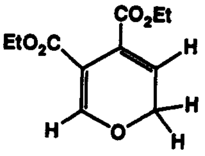

5 c

Pyran ring systems are found in a wide variety of natural products.[14] A major advantage of this reaction is that the new pyrans are obtained from simple organic substrates.

When **3** was treated with PMe_2Ph in the presence of H_2O, the new compound $Mn(CO)_4[OCC(CO_2Et)C(H)(CO_2Et)(PMe_2Ph)]$ (**6**) was obtained in 80% yield. The molecular structure of **6** was established by a single-crystal X-ray diffraction analysis, and an ORTEP diagram of its molecular structure is shown in Figure 4. Final atomic positional parameters are listed in Table 9. Selected bond distances and angles are listed in Tables 10 and 11, respectively. Compound **6** contains only one manganese atom with four linear terminal carbonyl ligands. The remaining ligand was derived from the alkyne-coupled CO group in **3** by the removal of the manganese atom and the addition of the phosphine and one hydrogen atom to the carbon C(3). The phosphorus atom is formally positively charged with P–C(3) = 1.828(6) Å. The opposing negative charge is probably delocalized across the C(1)–C(2)–C(9)–O(9) grouping. C(2) has only three substituents. The C(2)–C(3) distance is fairly long (1.499(8) Å), while the C(1)–C(2), C(2)–C(9), and C(9)–O(9) distances are short (1.390(7), 1.429(8), and 1.235(6) Å, respectively) and are indicative of significant multiple-bonding interactions. There are two low-frequency absorptions in its infrared spectrum (1563 and 1513 cm^{-1}) that can be attributed to the carbonyl of the coordinated carboxylate group and the C(9)–O(9) group. A deshielded resonance

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(14) (a) Boger, D. L.; Weinreb, S. M. *Hetero Diels-Alder Methodology in Organic Synthesis*; Academic Press: New York, 1987; Chapter 7. (b) Desimoni, G.; Tacconi, G. *Chem. Rev.* **1975**, *75*, 651. (c) Hepworth, J. D. In *Comprehensive Heterocyclic Chemistry*; Boulton, A. J., McKillop, A., Eds.; Katritzky, A. R., Rees, C. W., Exec. Eds.; Pergamon Press: Oxford, England, 1984; Vol. 3, Part 2b, p 737. (d) Kametani, T.; Hibino, S. In *Advances in Heterocyclic Chemistry*; Katritzky, A. R., Ed.; Academic Press: Orlando, FL, 1987; Vol. 42, pp 245–333.

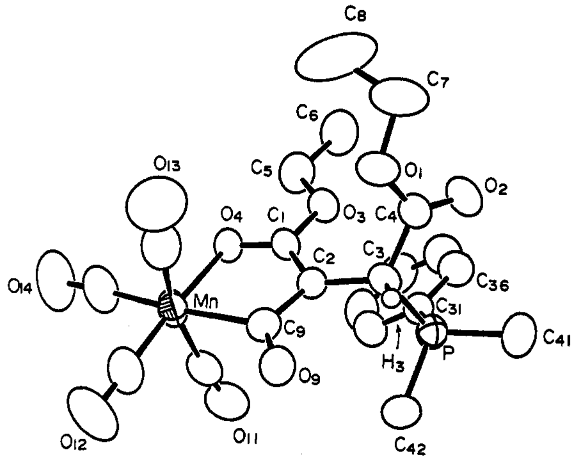


Figure 4. ORTEP diagram of $Mn(CO)_4[OCC(CO_2Et)C(H)(CO_2Et)(PMe_2Ph)]$ (6) showing 50% probablility thermal ellipsoids.

Table 9. Positional Parameters and *B*(eq) Values for 6

atom	*x*	*y*	*z*	*B*(eq), Å^2
Mn(1)	0.89335(08)	0.23021(07)	0.08634(12)	4.05(5)
P	1.26776(14)	0.06653(12)	0.5333(02)	3.73(8)
O(1)	1.1076(04)	0.2771(03)	0.7177(05)	5.0(2)
O(2)	1.2960(04)	0.2236(03)	0.7924(05)	5.5(2)
O(3)	1.2066(03)	0.3237(03)	0.4308(05)	3.9(2)
O(4)	1.0442(03)	0.3128(03)	0.2017(05)	3.6(2)
O(9)	0.9228(03)	0.0702(03)	0.3271(05)	4.2(2)
O(11)	1.0479(05)	0.1018(04)	−0.0514(07)	6.8(3)
O(12)	0.6847(05)	0.1007(04)	−0.0531(06)	7.6(3)
O(13)	0.7827(05)	0.3224(05)	0.3241(09)	8.6(4)
O(14)	0.7998(05)	0.3607(05)	−0.1985(08)	9.6(3)
C(1)	1.1069(05)	0.2754(04)	0.3362(08)	3.2(3)
C(2)	1.0776(05)	0.1877(04)	0.3931(07)	2.9(3)
C(3)	1.1487(05)	0.1464(05)	0.5563(07)	3.3(3)
C(4)	1.1948(07)	0.2193(05)	0.7027(08)	3.7(3)
C(5)	1.2373(07)	0.4129(06)	0.3669(11)	5.8(4)
C(6)	1.3368(09)	0.4603(07)	0.4941(14)	7.8(5)
C(7)	1.1390(09)	0.3554(08)	0.8458(12)	7.2(5)
C(8)	1.0799(12)	0.4442(09)	0.770(02)	12.1(8)
C(9)	0.9666(05)	0.1451(05)	0.2917(07)	3.5(3)
C(11)	0.9856(06)	0.1517(05)	−0.0059(08)	4.5(3)
C(12)	0.7671(06)	0.1518(05)	0.0008(08)	5.1(3)
C(13)	0.8238(06)	0.2896(06)	0.2285(10)	5.5(4)
C(14)	0.8391(06)	0.3129(06)	−0.0862(09)	6.0(4)
C(31)	1.3663(05)	0.1319(04)	0.4530(08)	3.7(3)
C(32)	1.3399(06)	0.1413(05)	0.2835(09)	4.6(4)
C(33)	1.4128(08)	0.1958(06)	0.2206(10)	5.9(4)
C(34)	1.5136(08)	0.2409(07)	0.3286(14)	6.6(5)
C(35)	1.5409(07)	0.2310(06)	0.4958(13)	6.2(4)
C(36)	1.4692(06)	0.1784(05)	0.5615(10)	5.0(3)
C(41)	1.3488(07)	0.0087(07)	0.7213(10)	5.3(4)
C(42)	1.1946(07)	−0.0297(05)	0.3859(10)	4.7(4)
C(50)	0.514(03)	0.565(02)	0.991(03)	11.3(7)
Cl	0.5672(06)	0.4394(08)	0.9452(08)	31.2(7)

at 6.02 ppm of intensity 1 in the ^1H NMR spectrum that is coupled to the phosphorus atom ($^2J_{P-H}$ = 14.7 Hz) is attributed to the hydrogen on carbon C(3). This proton is readily exchanged. When D_2O was added to a sample of 6 in C_6D_6 in an NMR tube and the spectrum was taken 30 min later, the resonance at 6.02 ppm was completely absent.

Discussion

A summary of the results of this study are shown in Scheme 1. The reaction of $Mn_2(CO)_{10}$ with $EtO_2CC{\equiv}CCO_2Et$ in the presence of UV irradiation proceeds by decarbonylation and the addition and insertion of the alkyne into the metal–metal bond to yield the *Z*-dimetalated olefin complex 1. This product is similar to the rhenium compound $Re(CO)_4[\mu\text{-}(Z)\text{-}(EtO_2C)C{=}C(CO_2Et)]Re(CO)_5$ (**B**), which has been obtained from the reaction of $Re_2(CO)_9(NCMe)$ with $EtO_2CC{\equiv}CCO_2Et$.[8a] Irradiation of 1 leads to a further decarbonylation and formation of the new *E*-dimetalated compound 2. This transformation includes a *cis–trans* isomerization at the C=C double bond. The corresponding rhenium compound was also obtained by UV irradiation of **B**. In contrast to the dirhenium compounds, compound 1 thermally isomerizes to the new compound 3 by a coupling of one of the CO ligands to the alkyne ligand. A possible mechanism for this transformation is shown in eq 1. The

Table 10. Intramolecular Distances for 6[a]

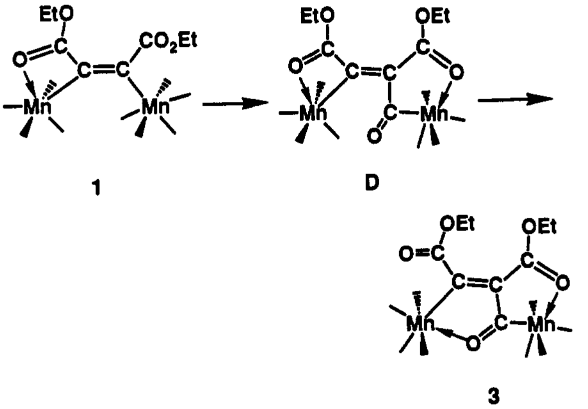
Mn(1)–O(4)	2.053(4)	C(2)–C(3)	1.499(8)
Mn(1)–C(9)	2.076(6)	C(2)–C(9)	1.429(8)
P–C(3)	1.828(6)	C(3)–C(4)	1.510(8)
P–C(31)	1.782(6)	C(5)–C(6)	1.45(1)
P–C(41)	1.787(8)	C(7)–C(8)	1.46(2)
P–C(42)	1.788(7)	C(31)–C(32)	1.378(9)
O(1)–C(4)	1.328(7)	C(31)–C(36)	1.403(8)
O(1)–C(7)	1.45(1)	C(32)–C(33)	1.38(1)
O(2)–C(4)	1.195(7)	C(33)–C(34)	1.38(1)
O(3)–C(1)	1.350(6)	C(34)–C(35)	1.36(1)
O(3)–C(5)	1.443(8)	C(35)–C(36)	1.37(1)
O(4)–C(1)	1.269(6)	Mn–C (av)	1.816(9)
O(9)–C(9)	1.235(6)	O–C (av)	1.146(8)
C(1)–C(2)	1.390(7)		

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

Table 11. Intramolecular Bond Angles for 6[a]

O(4)–Mn(1)–C(9)	81.3(2)	P–C(3)–C(2)	111.5(4)
C(3)–P–C(31)	110.9(3)	P–C(3)–C(4)	111.2(4)
C(3)–P–C(41)	113.4(3)	C(2)–C(3)–C(4)	116.6(5)
C(3)–P–C(42)	105.5(3)	O(1)–C(4)–O(2)	125.2(6)
C(4)–O(1)–C(7)	117.4(6)	O(1)–C(4)–C(3)	110.6(6)
C(1)–O(3)–C(5)	117.0(5)	O(2)–C(4)–C(3)	124.3(6)
Mn(1)–O(4)–C(1)	111.4(3)	O(3)–C(5)–C(6)	108.8(7)
O(3)–C(1)–O(4)	118.6(5)	O(1)–C(7)–C(8)	107(1)
O(3)–C(1)–C(2)	117.9(5)	Mn(1)–C(9)–O(9)	127.0(4)
O(4)–C(1)–C(2)	123.5(5)	Mn(1)–C(9)–C(2)	109.4(4)
C(1)–C(2)–C(3)	123.3(5)	O(9)–C(9)–C(2)	123.6(5)
C(1)–C(2)–C(9)	114.3(5)	Mn–C–O (av)	176.5(8)
C(3)–C(2)–C(9)	122.1(5)		

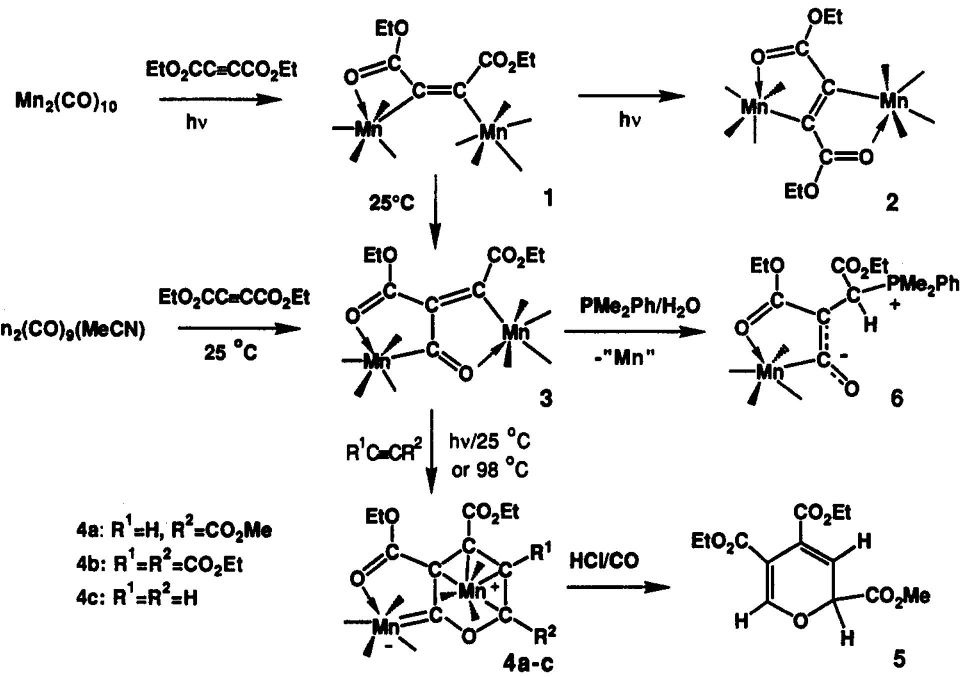
[a] Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.



(1)

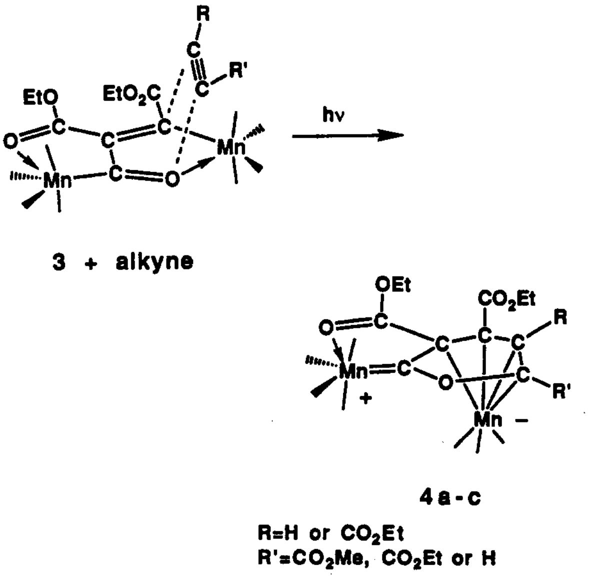
coupling occurs by an insertion reaction at the $Mn(CO)_5$ grouping that could be promoted by attack of the uncoordinated carboxylate group, which then becomes coordinated in the course of the transformation 1 → **D**. In a final step, **D** → 3, the oxygen atom of the inserted CO group becomes coordinated to the neighboring metal atom

Scheme 1



and the carboxylate group that was originally coordinated in 1 is displaced.

Perhaps the most surprising result of this study is the photoinduced coupling of a second alkyne to the *cis*-cyclomanganated enone grouping in 3 to yield the compounds 4a–c, which contain a metalated pyran ring system. There are numerous examples of the metal-induced coupling of CO to alkynes, but these generally proceed to yield cyclopentadienones or quinones.[2] The formation of a pyran ring system appears to be a novel result. The mechanism of the formation of the compounds 4a–c is not yet established, but we think that this may be related to the coordination of the oxygen atom of the carbonyl group to one of the metal atoms. The reaction could be viewed as a 1,4-cycloaddition of the alkyne to the cyclomanganated enone grouping in the complex, and this may be facilitated by the *s*-cis orientation at the C(2)–C(9) bond in 3 (see Figure 2). This orientation is, of course, established and maintained by the coordination of the carbonyl oxygen atom to the metal atom (see eq 2). This reaction may be analogous to the well-known hetero-Diels–Alder reaction between 1-oxabutadienes and alkenes or alkynes that has been used by organic chemists to synthesize a wide variety of pyran ring systems.[14] A recent report described the addition of an alkyne to the oxygen atom of a bridging carbonyl ligand.[15]



(2)

The photoenhancement of reaction 2 could be explained by a decarbonylation step occurring at the proximate metal center. This may help to clear a pathway for addition of the alkyne to the EtO$_2$CC=C(CO$_2$Et)C=O ligand. Alternatively, it is possible that the alkyne might coordinate to such a decarbonylated metal atom prior to coupling to the EtO$_2$CC=C(CO$_2$Et)C=O ligand and the formation of the C—C and C—O bonds then occurs through a series of two reductive-elimination steps, with the metal atom shifting its coordination to the two π bonds of the pyran ring.

In order to obtain the free pyrans, the complexes 4a–c were treated with a mixture of gaseous HCl and CO. It was anticipated that the formation of the stable compound Mn(CO)$_5$Cl would lead to removal of the metal atoms and release of the pyrans. This was accomplished essentially as expected, with one hydrogen atom being added to each of the oxygen-bonded carbon atoms and both manganese groupings being lost.

When treated with PMe$_2$Ph in the presence of traces of H$_2$O, compound 3 was converted to 6. A manganese-containing group was lost, and it was not recovered or identified. In the product 6 that was isolated, a phosphine was found attached to one of the carboxylate-substituted carbon atoms as a phosphonium center. Since the molecule has no overall charge, the remaining portion of the molecule must contain a formal negative charge. We feel that this charge is probably delocalized across the acyl grouping. Low-frequency absorptions in the infrared spectrum are consistent with this formulation. Phosphine additions usually occur at metal centers, but there are other examples of phosphine additions to hydrocarbon ligands in metal

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[15] Shih, K.-Y.; Fanwick, P. E.; Walton, R. A. *J. Am. Chem. Soc.* 1993, *115*, 9319.

cluster complexes.[16] A hydrogen atom, presumably from the H_2O, was added to the same carboxylate-substituted carbon atom as the phosphine. This hydrogen was readily exchanged, probably by removal as H^+, when the complex was treated with D_2O. This facile exchange was probably promoted by the presence of positive charge on the neighboring phosphorus atom.

The results of this study show that the addition of alkynedicarboxylates to dimanganese carbonyls proceeds with insertion into the metal–metal bond to yield dimetalated olefin complexes. This is analogous to the reactions of carboxylate-substituted alkynes with dirhenium carbonyls.[8] An important difference is the facile coupling of the alkyne to a carbonyl ligand. This probably occurs by an insertion reaction. It is well-known that CO insertion reactions are more facile in complexes of the first-row transition metals than those of the third-row metals.[17] Another unusual feature is the tendency of the manganese complexes to engage in coordination to the oxygen atoms of carbonyl ligands.[3–6] We feel this has increased the tendency of these oxygen atoms to undergo further reaction, and in the case of compound **3** this facilitates the addition of a molecule of alkyne to yield the pyran ring systems. Attempts to develop the organic chemistry of **3** further are in progress.

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Supplementary Material Available: Tables of bond distances and angles for **1** and of hydrogen atom positional parameters and anisotropic thermal parameters for **1**, **3**, **4a**, and **6** (13 pages). Ordering information is given on any current masthead page.

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