Coupling of Alkynes to Carbon Monoxide at a Dimanganese Center. A New Route to Carboxylate-Functionalized Pyrans

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Metal-mediated coupling reactions between alkynes and CO have led to 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 tendency for coupling of the alkynes to one or more of the CO ligands.[3-7] A special feature of these reactions is the coordination of the oxygen atom of the CO group of the metal atoms.[3,4]

We have now found that the reaction of $\mathrm{EtO_2CC{\equiv}CCO_2Et}$ with $\mathrm{Mn_2(CO)_9(NCMe)}$ at 25 °C for 20 h produces the new compound $\mathrm{Mn_2(CO)_8[(EtO_2C)C{=}C(CO_2Et)C{=}O]}$, **1**, in a 22% yield.[8,9] Compound **1** was characterized by a single-crystal X-ray diffraction analysis, and an ORTEP diagram of its molecular structure is shown in Figure 1.[10,11] The molecule contains a $\mathrm{EtO_2CC{=}C(CO_2Et)C{=}O}$ ligand formed by the coupling of the alkyne to the carbon atom of a CO ligand. Most importantly, the $\mathrm{EtO_2CC{=}C(CO_2Et)C{=}O}$ ligand has been inserted into the manganese–manganese bond. The oxygen atom of the CO group and one carbon atom of the $\mathrm{EtO_2CC{=}CCO_2Et}$ grouping are coordinated to the metal atom Mn(1), resulting in the formation of a five-membered metallacyclic ring, Mn(1)–C(3)–C(2)–C(9)–O(9), Mn(1)–O(9) = 2.078(3) Å and Mn(1)–C(3) = 2.002(4) Å. The carbon atom of the CO group and the carbonyl oxygen O(4) of one of the carboxylate groups are coordinated to Mn(2) to form a second five-membered metallacyclic ring, Mn(2)–C(9)–C(2)–C(1)–O(4), Mn(2)–O(4) = 2.096(3) Å and Mn(2)–C(9) = 1.998(4) Å. Notably, the C(2)–C(3) and C(9)–O(9) bonds are double at 1.349(6) and 1.254(5) Å, respectively, and have a fixed s-cis configuration at the C(2)–C(9) bond.

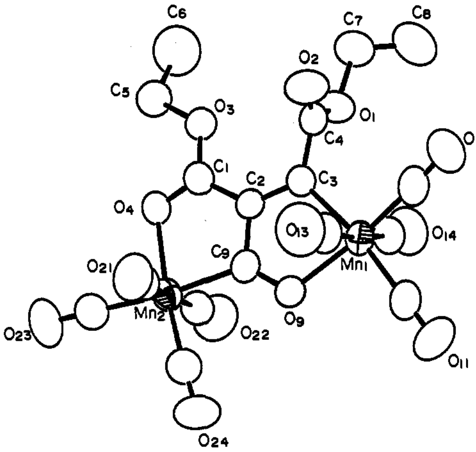

Figure 1. An ORTEP diagram of $\mathrm{Mn_2(CO)_8[\mu\text{-}(EtO_2C)C{=}C(CO_2Et)C{=}O]}$, **1**, showing 50% probability thermal ellipsoids.

Compound **1** was found to react with $\mathrm{HC{\equiv}CCO_2Me}$ in the presence of UV–vis irradiation at 25 °C/5 min to yield the new compound $\mathrm{Mn_2(CO)_7[\mu\text{-}\eta^4\text{-}OCC(CO_2Et)C(CO_2Et)C(H)C(CO_2Me)]}$, **2a**, in 28% yield.[12] It can also be obtained in a thermal reaction at 98 °C, but the yield is lower, 13%. The molecular structure of **2a** was also established by a single-crystal X-ray diffraction analysis; see Figure 2,[11,13] This molecule contains a 2-manganio-3,4-bis(ethoxycarbonyl)-6-(methoxycarbonyl)pyran ring that is π-coordinated to a manganese tricarbonyl grouping through the carbon atoms C(2), C(3), C(31), and C(32), Mn(2)–C = 2.066(7), 2.182(7), 2.079(7), and 2.084(7) Å, respectively. Carbon C(9) has only one substituent, Mn(2), and is formally a carbene center, Mn(2)–C(9) = 1.954(7) Å. The oxygen atom of the carboxylate group O(4) is also coordinated to Mn(2), Mn(2)–O(4) = 2.049(5) Å. Electron-counting procedures indicate that the complex should be zwitterionic with Mn(1) being formally negatively charged and Mn(2) being formally positively charged.

The mechanism of the formation of **2a** is not yet established, but bonds are clearly formed between the carboxylate-substituted carbon of the incoming alkyne and the oxygen atom of the alkyne-

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(8) A 50-mg amount (0.123 mmol) of $\mathrm{Mn_2(CO)_9(NCMe)}$[9] and a 29.5-$\mu$L amount (0.184 mmol) of $\mathrm{EtO_2CC{\equiv}CCO_2Et}$ in 40 mL of hexane was stirred at 25 °C for 20 h. The product, orange $\mathrm{Mn_2(CO)_8[(EtO_2C)C{=}C(CO_2Et)C{=}O]}$, **1**, was separated by TLC using a 1/1 hexane/$\mathrm{CH_2Cl_2}$ solvent mixture, yield 22%. IR (ν_{CO} in hexane, cm^{-1}) for **1**: 2100 (w), 2084 (s), 2019 (s, sh), 2000 (s), 1973 (s), 1964 (s), 1722 (w, br), 1593 (m, br), 1534 (w, br). ^{1}H NMR (δ in $\mathrm{CDCl_3}$, 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 **1** showed the parent ion at m/e = 532 and ions corresponding to the loss of each of the nine CO ligands. Anal. Calcd (found) for **1**: C, 38.37 (38.55); H, 1.89 (1.77).

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(10) Crystals of compound **1** were grown by slow evaporation of solvent from a solution in diethyl ether at –14 °C. Crystal data: space group = $P\bar{1}$, a = 11.395(2) Å, b = 14.252(3) Å, c = 6.7910(9) Å, α = 91.59(1)°, β = 91.54(1)°, γ = 84.97(1)°, Z = 2, 1717 reflections, R = 0.031.

(11) Diffraction measurements at 20 °C were made on a Rigaku AFC6S four-circle diffractometer using Mo Kα radiation. The structure solution and refinement was made by using the TEXSAN structure-solving program library (v5.0) of the Molecular Structure Corp., The Woodlands, TX. An absorption correction was applied to the data.

(12) **1** (20.0 mg, 0.038 mmol) and 20.0 μL (0.23 mmol) of $\mathrm{HC{\equiv}CO_2Me}$ were dissolved in 40 mL of hexane and exposed to UV–vis irradiation for 5 min at 25 °C. The product, orange $\mathrm{Mn_2(CO)_7[\mu\text{-}\eta^4\text{-}OCC(CO_2Et)C(CO_2Et)C(H)C(CO_2Me)]}$, **2a**, was isolated in 28% yield by TLC using a 2/1 hexane/$\mathrm{CH_2Cl_2}$ solvent mixture. IR (ν_{CO} in hexane, cm^{-1}) for **2a**: 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). ^{1}H NMR (δ in $\mathrm{C_6D_6}$): 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, 3 H, CH_3). Anal. Calcd (found) for **2a**: C, 40.84 (40.78); H, 2.40 (2.36). Compound **2a** was also obtained by a thermal reaction at 98 °C, but the yield was lower, 13%. The compounds $\mathrm{Mn_2(CO)_7[\mu\text{-}\eta^4\text{-}OCC(CO_2Et)C(CO_2Et)C(CO_2Et)C(CO_2Et)]}$, **2b**, and $\mathrm{Mn_2(CO)_7[\mu\text{-}\eta^4\text{-}OCC(CO_2Et)C(CO_2Et)CHCH]}$, **2c**, were obtained in 26% and 29% yields, respectively, by the irradiation procedure. See supplementary materials for details.

(13) Crystals of compound **2a** were grown by slow evaporation of solvent from a solution in 1/1 hexane/$\mathrm{CH_2Cl_2}$ at –3 °C. Crystal data: space group = $P\bar{1}$, a = 9.380(2) Å, b = 19.390(4) Å, c = 6.997(2) Å, α = 90.28(2)°, β = 106.11(2)°, γ = 99.27(2)°, Z = 2, 1534 reflections, R = 0.041.

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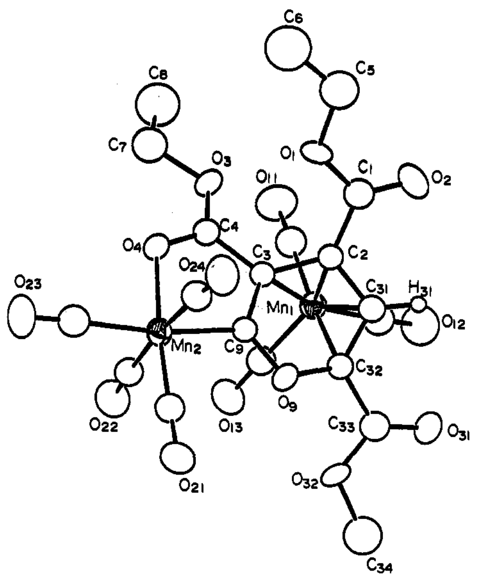
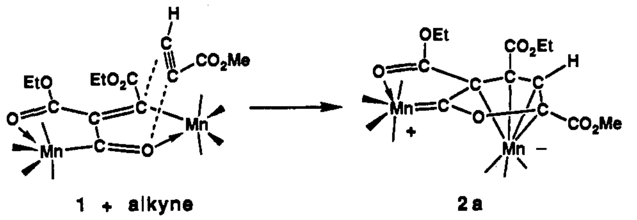


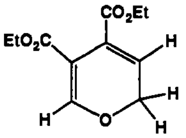
Figure 2. An ORTEP diagram of $Mn_2(CO)_7[\mu\text{-}\eta^4\text{-}OCC(CO_2Et)C(CO_2Et)C(H)C(CO_2Me)]$, **2a**, showing 50% probability thermal ellipsoids.

Scheme 1



coupled CO grouping in **1**, and the unsubstituted carbon of the alkyne and the metal-coordinated carbon of the alkyne portion of alkyne-coupled CO ligand in **1**; see Scheme 1. This reaction is strikingly similar to the well-known hetero Diels–Alder reaction between 1-oxabutadienes and alkenes or alkynes that has been used to synthesize a wide variety of pyran ring systems.[14] The photoenhancement of this reaction may be explained by a requirement of the decarbonylation step at the proximate metal center. This may also clear a pathway for addition of the alkyne to the $EtO_2CC{=}C(CO_2Et)C{=}O$ ligand. Alternatively, it is possible that the alkyne might coordinate to such a decarbonylated metal atom prior to coupling to the $EtO_2CC{=}C(CO_2Et)C{=}O$ ligand. The related compounds $Mn_2(CO)_7[\mu\text{-}\eta^4\text{-}OCC(CO_2Et)C(CO_2Et)C(CO_2Et)C(CO_2Et)]$, **2b**, and $Mn_2(CO)_7[\mu\text{-}\eta^4\text{-}OCC(CO_2Et)C(CO_2Et)CHCH]$, **2c**, were prepared and isolated by similar procedures in 26% and 29% yields from the reactions of **1** with $EtO_2CC{\equiv}CO_2Et$ and $HC{\equiv}CH$, respectively.

Treatment of compounds **2a–c** with a mixture of CO and HCl yielded $Mn(CO)_5Cl$ and the free pyrans $C_5OH_3(CO_2Et)_2(CO_2Me)$, **3a**, $C_5OH_2(CO_2Et)_4$, **3b**, and $C_5OH_4(CO_2Et)_2$, **3c**, in 40–60% yields.[15] It is not possible to distinguish between the α- and γ-pyran structures for **3a** and **3b** on the basis of their ^1H NMR spectra, but the α-structure was unambiguously established for **3c** by its ^1H NMR spectrum: 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_2-CH), 1.02 (t, $^3J_{H-H}$ = 7.1 Hz, 3H, CH_3), 0.95 (t, $^3J_{H-H}$ = 7.1 Hz, 3H, CH_3). Thus, it is believed that **3a** and **3b** also have α-pyran structures.



3c

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. Efforts to extend this reaction to other alkynes are in progress.

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Supplementary Material Available: Synthetic details and spectra for compounds **2a–c** and **3a–c** and tables of crystal data, final atomic positional parameters, bond distances and angles, and anisotropic thermal parameters for the structural analyses of **1** and **2a** (16 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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[15] **2c** (29.0 mg, 0.055 mmol) in 30 mL of heptane was heated to reflux with slow purge of dry mixture gaseous HCl/CO for 1 h. $ClMn(CO)_5$ and $[ClMn(CO)_4]_2$ were detected by IR spectroscopy in the reaction mixture. A colorless compound analyzed as $C_{11}O_5H_{14}$ = $C_5OH_4(CO_2Et)_2$, **3c**, was isolated in 61% yield by TLC on silica gel. For **3c**: IR (ν_{CO} in hexane, cm^{-1}) 1740, 1728; ^1H NMR (δ in C_6D_6, ppm) 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 (t, $^3J_{H-H}$ = 7.1 Hz, 3H, CH_3). The mass spectrum showed the parent ion at *m/e* = 226.0837 (calcd 226.0841). Compounds **2a** and **2b** were converted to $C_{13}H_{16}O_7$ = $C_5OH_2(CO_2Et)_4$, **3a**, and $C_{17}H_{22}O_9$ = $C_5OH_2(CO_2Et)_4$, **3b**, in 61% and 42% yields, respectively, by similar procedures.