The Coordination and Transformations of a Dicarboxylate Substituted Allene on a Dimanganese Carbonyl Grouping

Richard D. Adams* and Mingsheng Huang

Department of Chemistry and Biochemistry, University of South Carolina,
Columbia, SC 29208, U.S.A.

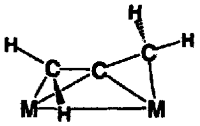
Received August 5, 1996

Key Words: Allenes / Manganese complexes

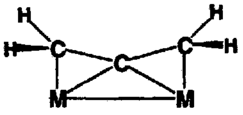
Two products, $Mn_2(CO)_7(PMe_2Ph)[\mu\text{-}\eta^2\text{-}\eta^2\text{-}MeO_2C(H)CCC(H)CO_2Me]$ (**1**) in 9% yield and $Mn_2(CO)_6(PMe_2Ph)[\mu\text{-}\eta^3\text{-}\eta^1\text{-}MeO_2CC(H)CC(H)CO_2Me]$ (**2**) in 34% yield, were obtained from the reaction of $Mn_2(CO)_8(PMe_2Ph)(MeCN)$ with $MeO_2C(H)C{=}C{=}C(H)CO_2Me$. Compound **1** contains a bridging $\eta^2\text{-}\eta^2\text{-}MeO_2C(H)CCC(H)CO_2Me$ allene ligand and compound **2** contains a bridging $\eta^3\text{-}\eta^1\text{-}MeO_2C(H)CCC(H)CO_2Me$ allene ligand in which the oxygen atom of one of the carbonyl groups is also coordinated. Compound **1** slowly converts to **2**, which establishes that it is a precursor to **2**. Compound **2** reacts with $NEtH_2$ to give the mononuclear manganese complex *fac*-$Mn(CO)_3(PMe_2Ph)[MeO_2CCH_2\text{-}C{=}C(H)CO_2Me]$ (**3**) in 96% yield. Compound **3** contains a chelating 1,3-di(methoxycarbonyl)propenyl grouping formed by addition of a hydrogen atom to the allene and the loss of a manganese grouping. Compounds **1**–**3** were characterized by single crystal x-ray diffraction methods.

Introduction

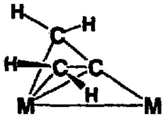
Studies of the coordination chemistry of allenes have shown that they may bridge pairs of metal atoms in four different ways. There are two $\mu\text{-}\eta^2\text{-}\eta^2$ forms: a C_2 form **A**[1] and symmetric C_{2v} form **B**[2], one $\mu\text{-}\eta^1\text{-}\eta^3$ form **C**[3] that has C_s symmetry, and a $\mu\text{-}\eta^1\text{-}\eta^1$ form **D** with C_s symmetry that was found for a mixed-metal complex[4]. Substituted bridging allenes generally assume one of these basic forms although distortions will be introduced by the effects of the substitutents[5].



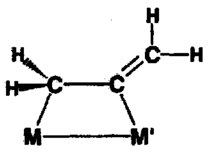
A



B



C



D

Allene has been shown to coordinate to $M_2(CO)_8$ groupings, M = Mn and Re, in the $\mu\text{-}\eta^2\text{-}\eta^2$ form **A**[1c–f]. However, we have recently shown that the substituted allene $MeO_2C(H)C{=}C{=}C(H)CO_2Me$ adopts the $\mu\text{-}\eta^3\text{-}\eta^1$ form **C** when it is coordinated to the $Re_2(CO)_6(PMe_2Ph)$ grouping and the carbonyl group of one of carboxylate substitutents is also coordinated to one of the metal atoms[6].

1,3-Disubstituted allenes are of synthetic interest because of their intrinsic chirality and potential to form stereogenic centers in reaction products[7]. In further studies of our investigations of the coordination of of chiral allenes to dinuclear metal centers, we have investigated the reactions of $MeO_2C(H)C{=}C{=}C(H)CO_2Me$ with $Mn_2(CO)_8(PMe_2Ph)(NCMe)$. Details of this study are reported here.

Results

Our efforts to obtain dimanganese complexes from reactions of $MeO_2C(H)C{=}C{=}C(H)CO_2Me$ with $Mn_2(CO)_9(NCMe)$ were unsuccessful. On the other hand, two products, red $Mn_2(CO)_7(PMe_2Ph)[\mu\text{-}\eta^2\text{-}\eta^2\text{-}MeO_2C(H)CCC(H)CO_2Me]$ (**1**) in 9% yield and orange $Mn_2(CO)_6(PMe_2Ph)[\mu\text{-}\eta^3\text{-}\eta^1\text{-}MeO_2CC(H)CC(H)CO_2Me]$ (**2**) in 34% yield, were obtained from the reaction of the phosphine derivative $Mn_2(CO)_8(PMe_2Ph)(NCMe)$ (prepared in situ) with $MeO_2C(H)C{=}C{=}C(H)CO_2Me$ at 25 °C in hexane solvent over 30 h. Both products were characterized by a combination of IR, ^1H-NMR, elemental and single-crystal x-ray diffraction analyses. ORTEP drawings of the molecular structures of **1** and **2** are shown in Figures 1 and 2, respectively.

Compound **1** contains two mutually bonded manganese atoms with a bridging $\eta^2\text{-}\eta^2\text{-}MeO_2C(H)CCC(H)CO_2Me$ allene ligand. The Mn–Mn distance is slightly longer than that found for $Mn_2(CO)_8(\mu\text{-}\eta^2\text{-}\eta^2\text{-}H_2CCCH_2)$ (**4**) [Mn–Mn = 2.848(2) Å for **1** vs. 2.799(1) Å[1e] for **4**], but slightly shorter than that of $Mn_2(CO)_{10}$ (**5**) [2.9038(6) Å[8]] and $Mn_2(CO)_9(PMe_2Ph)$ (**6**) [2.904[9]], which do not have bridging ligands. The increase of the Mn–Mn bond length relative to **4** may be due to removal of electron density from the region of the metal–metal bond by the CO_2Me groups. The effect of the phosphine on the metal–metal bond distance is expected to be small since the Mn–Mn distances in **5** and **6** are virtually the same. The Mn–C distances to the terminal carbon atoms of the allene in **1** are slightly longer than those in **4**: Mn(1)–C(3) = 2.212(7) Å and

0009–2940/96/1212–1447 $ 15.00+.25/0

Figure 1. An ORTEP diagram of $Mn_2(CO)_7(PMe_2Ph)[\mu\text{-}\eta^2\text{-}\eta^2\text{-}MeO_2C(H)CCC(H)CO_2Me]$ (**1**) showing 40% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (°) are: Mn(1)−Mn(2) = 2.848(2), Mn(1)−C(1) = 2.021(7), Mn(1)−C(3) = 2.212(7), Mn(2)−C(1) = 1.980(7), Mn(2)−C(2) = 2.214(7), Mn(2)−P = 2.290(2), C(1)−C(2) = 1.397(9), C(1)−C(3) = 1.387(9), C(2)−C(4) = 1.49(1), C(4)−O(1) = 1.209(8), C(5)−O(3) = 1.193(7); C(2)−C(1)−C(3) = 136.4(7), C(1)−Mn(2)−P = 130.5(2), Mn(1)−Mn(2)−P = 166.80(7).

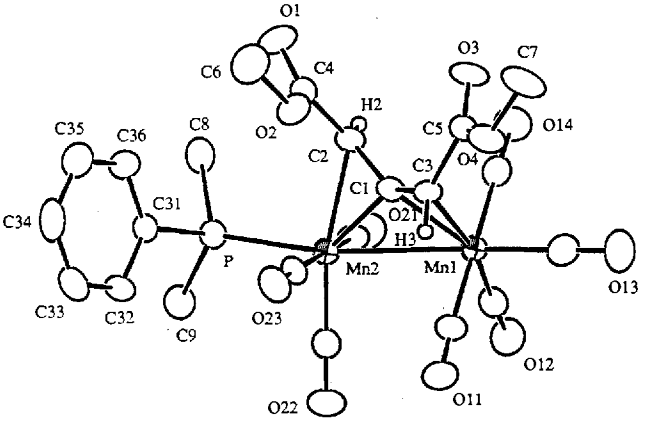
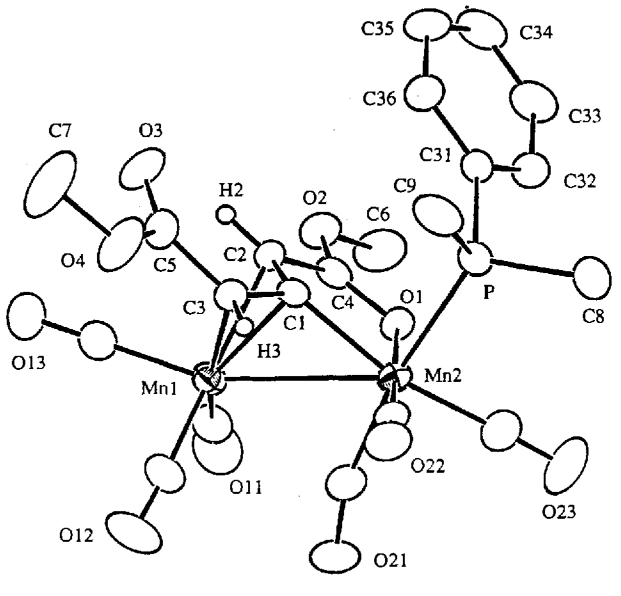


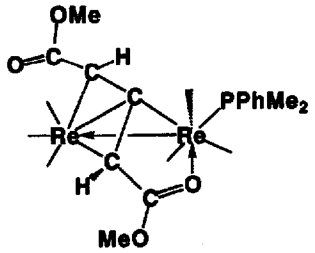
Figure 2. An ORTEP diagram of $Mn_2(CO)_6(PMe_2Ph)[\mu\text{-}\eta^3\text{-}\eta^1\text{-}MeO_2C(H)CCC(H)CO_2Me]$ (**2**) showing 40% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (°) are: Mn(1)−Mn(2) = 2.834(1), Mn(2)−O(1) = 2.060(3), Mn(1)−C(1) = 1.972(5), Mn(1)−C(2) = 2.172(5), Mn(1)−C(3) = 2.215(6), Mn(2)−C(1) = 2.019(5), Mn(2)−P = 2.334(2), C(1)−C(2) = 1.429(6), C(1)−C(3) = 1.403(6), C(2)−C(4) = 1.440(7), C(4)−O(1) = 1.248(6), C(5)−O(3) = 1.194(6), Mn(1)−C(21) = 2.599(6); C(2)−C(1)−C(3) = 120.3(5), C(1)−Mn(2)−P = 81.4(1), Mn(1)−Mn(2)−P = 125.41(7), Mn(2)−C(21)−O(21) = 163.3(5).



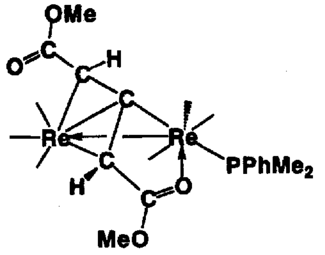
Mn(2)−C(2) = 2.214(7) Å vs. 2.184(3) and 2.193(3) Å. This too is probably due to the electron-withdrawing effects of the CO$_2$Me groups. The Mn−C distances to the central carbon of the allene ligand are similar to those in **4**: Mn(1)−C(1) = 2.021(7) Å and Mn(2)−C(1) = 1.980(7) Å vs. 2.027(3) Å and 2.025(3) Å. Mn(1) contains four linear terminal carbonyl ligands whereas Mn(2) has three terminal carbonyl ligands and the PMe$_2$Ph ligand. The PMe$_2$Ph ligand lies approximately *trans* to the metal−metal bond: Mn(1)−Mn(2)−P = 166.80(7)°.

As expected the ^{1}H-NMR spectrum shows two resonances for the allene protons, δ = 4.58 and 4.49 (1 H), and two for the CO$_2$Me groups, δ = 3.67 and 3.57 (3 H). The complex has no symmetry, thus the methyl groups on the phosphine ligand are inequivalent and two resonances are observed: 1.99 (d, 3 H, $^3J_{P\text{-}H}$ = 9.0 Hz), 1.78 (d, 3 H, $^3J_{P\text{-}H}$ = 9.3 Hz).

Compound **2** contains two mutually bonded manganese atoms with a bridging η^3-η^1-MeO$_2$CC(H)CC(H)CO$_2$Me allene ligand. The Mn−Mn distance is slightly shorter than that found for **1**: Mn−Mn = 2.834(1) Å. The metal−metal bond in **2** is formally a heteropolar (donor−acceptor) bond, see below. The allene ligand is η^3- or π-bonded to Mn(1) and η^1- or σ-bonded to Mn(2). Compound **2** has one less CO ligand than **1**. To compensate for the loss of the CO ligand, the oxygen atom of the carbonyl of one carboxylate groups is coordinated to Mn(2): Mn(2)−O(1) = 2.060(3) Å. The C−O bond length of this carbonyl group is significantly longer than that of the uncoordinated one: C(4)−O(1) = 1.248(6) Å vs. C(5)−O(3) = 1.194(6) Å. This implies that the C−O bond is weakened, and in accord with this a low-energy absorption was observed in the IR spectrum at 1570 cm^{-1}. An absorption at 1710 cm−1 is assigned to the C−O stretching frequency of the uncoordinated CO group. Compound **2** is isostructural and isomorphous to the compound *fac*-$Re_2(CO)_6(PMe_2Ph)[\mu\text{-}\eta^3\text{-}\eta^1\text{-}MeO_2C(H)CCC(H)CO_2Me]$ (**7**) that we recently obtained from the reaction of $Re_2(CO)_8(PMe_2Ph)(NCMe)$ with $MeO_2C(H)C{=}C{=}C(H)CO_2Me$[6]. A second product, *mer*-$Re_2(CO)_6(PMe_2Ph)[\mu\text{-}\eta^3\text{-}\eta^1\text{-}MeO_2C(H)CCC(H)CO_2Me]$ (**8**), was also obtained from that reaction. Compounds **7** and **8** differ in stereochemistry at the phosphine-substituted metal atom, and **7** is slowly transformed into **8** at room temperature. The manganese homolog of **7** was not observed in this reaction.



7

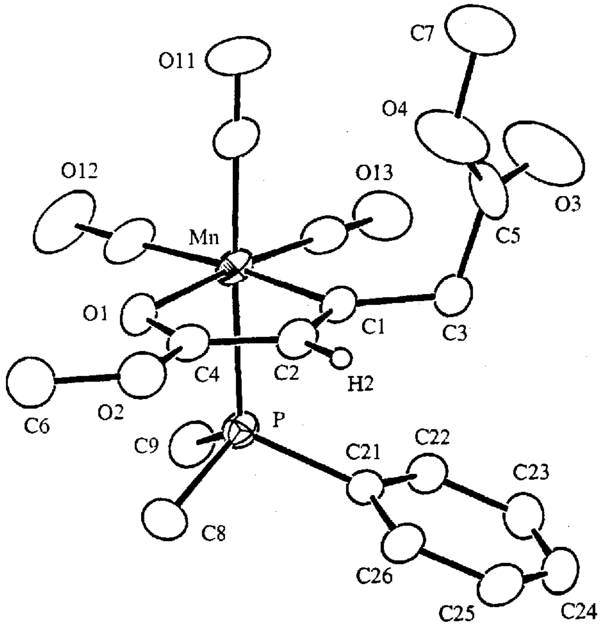


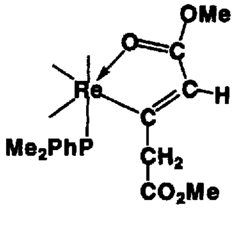
8

Mn(1) contains three linear terminal carbonyl ligands while Mn(2) has three terminal carbonyl ligands, the PMe$_2$Ph ligand and the oxygen atom of the coordinated CO$_2$Me group. The PMe$_2$Ph ligand is no longer *trans* to the metal−metal bond: Mn(1)−Mn(2)−P = 125.41(7)°. Assuming that the allene ligand donates one electron to Mn(2) and three electrons to Mn(1), then Mn(2) has 18 electrons and Mn(1) has 16 electrons in the absence of a metal−metal bond. Accordingly, Mn(2) donates two electrons to Mn(1) to form a donor−acceptor Mn(2)→Mn(1) metal−metal bond. Several years ago Cotton suggested that the formation of such heteropolar metal–metal bonds often results in the formation of semibridging carbonyl ligands[10]. Indeed, a weak semi-bridging carbonyl ligand is found on Mn(2) in **2**. This is C(21)–O(21): Mn(2)–C(21)–O(21) = 163.3(5)° and Mn(1)···C(21) = 2.599(6) Å. As expected the ^{1}H-NMR spectrum of **2** shows two resonances for the allene protons [δ = 4.95 (1 H) and δ = 4.40 (1 H)] and two for the CO$_2$Me groups [δ = 3.66 (s, 3 H, OCH$_3$) and δ = 3.23 (3 H). This complex also has no symmetry: two resonances were observed for the methyl groups on the phosphine ligand [2.06 (d, 3 H, $^3J_{P\text{-}H}$ = 9.4 Hz) and 1.98 (d, 3 H, $^3J_{P\text{-}H}$ = 9.4 Hz)]. Compound **1** is slowly decarbonylated at 50°C to **2**. The yield is essentially 100% after 20 h.

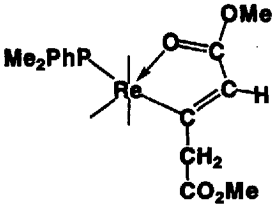
In our previous studies we found that compound **8** reacts with water to yield a mononuclear rhenium compound, *fac*-Re(CO)$_3$(PMe$_2$Ph)[MeO$_2$CCH$_2$CC(H)CO$_2$Me] (**9**), in 46% yield[6]. An isomer of **9**, *mer*-Re(CO)$_3$(PMe$_2$Ph)[MeO$_2$CCH$_2$CC(H)CO$_2$Me] (**10**), was obtained from the reaction of Re$_2$(CO)$_8$(PMe$_2$Ph)(NCMe) with MeO$_2$C(H)C=C=C(H)CO$_2$Me and was characterized structurally. For comparison, we investigated a similar reaction in this study, **2** plus NEtH$_2$, and observed a similar result. The reaction of **2** with NEtH$_2$ in a 1:10 ratio at 25°C for 8 h produced the new compound, *fac*-Mn(CO)$_3$(PMe$_2$Ph)[MeO$_2$CCH$_2$C=C(H)CO$_2$Me] (**3**), in 96% yield. Compound **3** was characterized crystallographically and an ORTEP diagram of its molecular structure is shown in Figure 3. Compound **3** is a six-coordinate complex. Three of the ligands are CO groups and these are arranged in a *fac*-form. There is a bidentate 1,3-di(methoxycarbonyl)propenyl group MeO$_2$CCH$_2$C=C(H)CO$_2$Me that is coordinated through the alkenyl carbon C(1) and the carbonyl oxygen atom O(1), Mn–O(1) = 2.088(3), Mn–C(1) = 2.033(4). The alkenyl bond is double: C(1)–C(2) = 1.345(6) Å. The coordinated carbonyl group exhibits some bond elongation [C(4)–O(1) = 1.253(5) Å] relative to the uncoordinated carbonyl group [C(5)–O(3) = 1.184(7) Å], and the presence of a weakened C=O grouping is revealed by a low-frequency absorption in the IR spectrum: 1592 cm^{-1} for the coordinated carbonyl group and 1742 cm^{-1} for the uncoordinated CO group.

Figure 3. An ORTEP diagram of *fac*-Re(CO)$_3$(PMe$_2$Ph)[C(CH$_2$CO$_2$Me)=C(H)CO$_2$Me] (**3**) showing 40% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (°) are: Mn–O(1) = 2.088(3), Mn–P = 2.325(1), Mn–C(1) = 2.033(4), C(1)–C(2) = 1.345(6), C(2)–C(4) = 1.424(6), C(1)–C(3) = 1.520(6), C(4)–O(1) = 1.253(5), C(5)–O(3) = 1.184(7); P–Mn–C(1) = 88.7(1), Mn(1)–C(1)–C(3) = 127.5(3).





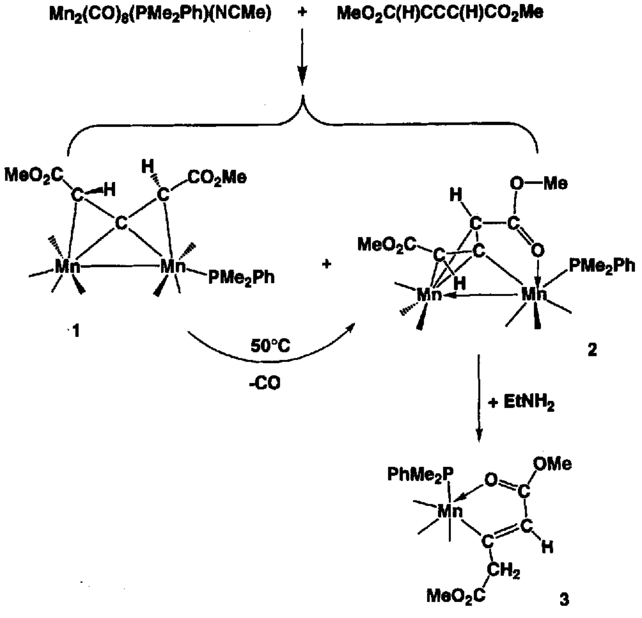
9



10

Discussion

A summary of the reactions reported here is given in Scheme 1. Two complexes **1** and **2** containing a π-bonded MeO$_2$C(H)CCC(H)CO$_2$Me ligand were obtained from the reaction of Mn$_2$(CO)$_8$(PMe$_2$Ph)(MeCN) with MeO$_2$C(H)C=C=C(H)CO$_2$Me. Compound **1** contains a bridging η^2-η^2-MeO$_2$C(H)CCC(H)CO$_2$Me allene ligand and compound **2** contains a bridging η^3-η^1-MeO$_2$C(H)CCC(H)CO$_2$Me allene ligand in which the oxygen atom of one of the carbonyl groups is also coordinated. Compound **1** slowly loses CO at 50°C and is converted into **2**. This appears to be the first example of the transformation of an η^2-η^2-allene ligand into an η^3-η^1-coordinated allene ligand. However, this does not necessarily establish that the η^3-η^1-form is intrinsically more stable than the η^2-η^2-form, because the carbonyl group is also coordinated in compound **2** and that will contribute to the stabilization of complex.



The reaction of **2** with ethylamine yields the mononuclear manganese complex **3** containing a chelating 1,3-di(methoxycarbonyl)propenyl grouping by addition of a hydrogen atom to the allene and the loss of a manganese grouping. The presence of the PMe_2Ph ligand in complex **3** strongly suggests that it was the manganese atom that was η^3-bonded to the allene ligand that was eliminated; however, the fates of the eliminated manganese group and the remainder of the amine molecule have not been established.

This research was supported by the Office of Basic Energy Sciences of the U. S. Dept. of Energy. We thank Professor *Thomas Bryson* for providing us with a sample of $MeO_2C(H)C{=}C{=}C(H)CO_2Me$.

Experimental

General: Unless specified otherwise, all reactions were carried out under an atmosphere of nitrogen. All solvents were appropriately dried and degassed prior to use. Dimethylphenylphosphine and $NEtH_2$ (70 wt.%) were purchased from Aldrich. – 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 5DXBO FT-IR spectrophotometer. – ^1H-NMR spectra were taken at 400 MHz on a Bruker AM-400 spectrometer. – Elemental analyses were performed by Desert Analytics, Tucson, AZ. $Mn_2(CO)_9(PMe_2Ph)$[11] and $MeO_2C(H)C{=}C{=}C(H)CO_2Me$[12] were prepared by literature methods.

Reaction of $Mn_2(CO)_9(PMe_2Ph)(NCMe)$ with $MeO_2C(H)$-$C{=}C{=}C(H)CO_2Me$: $Mn_2(CO)_8(PMe_2Ph)(MeCN)$ was prepared in situ by the reaction of $Mn_2(CO)_9(PMe_2Ph)$ with Me_3NO in the presence of NCMe[13]. Me_3NO (36 mg, 0.48 mmol) was added to a solution of $Mn_2(CO)_9(PMe_2Ph)$ (200 mg, 0.40 mmol) in 75 ml of NCMe in a 200-ml three-neck flask. The solution was stirred at room temperature for 1 h. The solvent was removed under vacuum, and 100 ml of hexane was added to the flask. $MeO_2CC(H)CC(H)$-CO_2Me (180.0 µl, 1.14 mmol) was then added via a syringe. This mixture was then stirred at 25 °C for 30 h. After the solvent was removed in vacuo, the residue was separated on a silica-gel column. This yielded, in order of elution: 24.7 mg of unreacted $Mn_2(CO)_9(PMe_2Ph)$ (eluted with a 5:1 hexane/CH_2Cl_2 solvent mixture); 77.6 mg of orange $Mn_2(CO)_6(PMe_2Ph)[\mu$-η^3-η^1-$MeO_2C(H)CCC(H)CO_2Me]$ (**2**) in 34% yield (eluted with 1:2 hexane/CH_2Cl_2 solvent mixture); and 22.3 mg of red $Mn_2(CO)_7$-$(PMe_2Ph)[\mu$-η^2-η^2-$MeO_2C(H)CCC(H)CO_2Me]$ (**1**) in 9% yield (eluted with THF solvent). – Spectral data for **1**: IR (hexane, cm^{-1}): $\tilde{\nu}_{co}$ = 2076 (s), 2016 (m), 2005 (s), 1998 (s), 1976 (s), 1953 (m), 1949 (m), 1725 (w, br.), 1704 (w, br.). – ^1H NMR ($CDCl_3$): δ = 7.47 (m, 5 H, C_6H_5), 4.58 (s, 1 H, CH), 4.49 (s, 1 H, CH), 3.67 (s, 3 H, OCH_3), 3.57 (s, 3 H, OCH_3), 1.99 (d, $^3J_{P\text{-}H}$ = 9.0 Hz, 3 H, PCH_3), 1.78 (d, $^3J_{P\text{-}H}$ = 9.0 Hz, 3 H, PCH_3). – Anal. calcd. (found): C, 44.02 (44.58); H, 2.92 (3.19). – Spectral data for **2**: IR (hexane, cm^{-1}): $\tilde{\nu}_{co}$ = 2040 (s), 2012 (m), 2004 (s), 1958 (s), 1953 (s), 1936 (m), 1914 (m), 1710 (w, br.), 1570 (w, br.). – ^1H NMR ($CDCl_3$): δ = 7.42 (m, 5 H, C_6H_5), 4.95 (s, 1 H, CH), 4.40 (s, 1 H, CH), 3.66 (s, 3 H, OCH_3), 3.23 (s, 3 H, OCH_3), 2.06 (d, $^3J_{P\text{-}H}$ = 9.4 Hz, 3 H, PCH_3), 1.98 (d, $^3J_{P\text{-}H}$ = 9.4 Hz, 3 H, PCH_3). – Anal. calcd. (found): C, 44.08 (44.35); H, 3.37 (3.34).

*Transformation of **1** to **2**:* Compound **1** (5.0 mg) and 0.6 ml of $CDCl_3$ were placed in a 5-mm NMR tube. The tube was placed in a 50 °C oil bath. The transformation was monitored by ^1H-NMR spectroscopy. Compound **1** was slowly transformed to **2**. The transformation was complete in 20 h.

*Reaction **2** with $NEtH_2$:* Compound **2** (40.0 mg, 0.070 mmol) was dissolved in 40 ml of hexane. To this solution was added 56.4 µl (0.70 mmol) of $NEtH_2$. The mixture was stirred at room temperature for 8 h. After the solvent was removed via rotary evaporation, the residue was separated by TLC using a 2:1 hexane/CH_2Cl_2 solvent mixture. This yielded 29.0 mg of pale yellow *fac*-$Mn(CO)_3$-$(PMe_2Ph)[MeO_2CCH_2CC(H)CO_2Me]$ (**3**) in 96% yield. Spectral data for **3**: IR (hexane, cm^{-1}): $\tilde{\nu}_{co}$ = 2017 (s), 1942 (s), 1897 (s), 1742 (w, br.), 1592 (w, br.). – ^1H NMR ($CDCl_3$): δ = 7.34–7.29 (m, 5 H, C_6H_5), 6.16 (s, 1 H, CH), 3.83 (dd, $^2J_{H\text{-}H}$ = 15.3 Hz, 2 H, CH_2), 3.70 (s, 3 H, OCH_3), 3.31 (s, 3 H, OCH_3), 1.66 (d, $^3J_{P\text{-}H}$ = 7.8 Hz, 3 H, PCH_3), 1.60 (d, $^3J_{P\text{-}H}$ = 7.8 Hz, 3 H, PCH_3). – Anal. calcd. (found): C, 49.79 (49.84); H, 4.64 (4.49).

Crystallographic Analyses: Crystals of **1** suitable for x-ray diffraction analysis were obtained by slow evaporation of a solution in a hexane/Et_2O 2:1 solvent mixture at −20 °C. Crystals of **2** suitable for x-ray diffraction analysis were obtained from slow evaporation of solvent from a solution in a hexane/Et_2O 1:1 solvent mixture at −14 °C. Crystals of **3** suitable for x-ray diffraction analysis were obtained by slow evaporation of a solution in a hexane/Et_2O 1:2 solvent mixture at −14 °C. The crystals used in intensity measurements were mounted in thin-walled glass capillaries. Diffraction measurements were made on a Rigaku AFC6S fully automated four-circle diffractometer using graphite-monochromated Mo-K_α radiation. The unit cells were determined and refined from 15 randomly selected reflections obtained by using the AFC6S automatic search, center, index, and least-squares routines. Crystal data, data collection parameters, and results of these analyses are listed in Table 1. All data processing was performed on a Silicon Graphics Indigo2 computer by using the TEXSAN structure-solving program library obtained from the 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-hydrogen atoms[14b]. Lorentz-polarization (Lp) and absorption corrections were applied in each analysis. Full matrix least-squares refinements minimized the function: $\Sigma_{hkl}w(|F_o|-|F_c|)^2$, where $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_o^2)/2F_o$, and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (0.02 \cdot I_{net})^2]^{1/2}/Lp$. The scattering contributions of all calculated hydrogen atom positions were added to the structure factor calculations, but their positions were not refined.

Compound **1** crystallized in the monoclinic crystal system. The patterns of systematic absences observed during the collection of intensity data identified the space group uniquely as $P2_1/n$. The structure was solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms H(2) and H(3) on the allene ligand were located and refined with isotropic thermal parameters. The positions of all other hydrogen atoms were calculated by assuming idealized geometries with all C−H distances at 0.95 Å.

Compound **2** crystallized in the orthorhombic crystal system. The patterns of systematic absences in the data were consistent uniquely with the space group Pbca. The structure was solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms H(2) and H(3) on the allene ligand were located and refined with isotropic thermal parameters. The positions of all other hydrogen atoms were calculated by assuming idealized geometries with all C−H distances at 0.95 Å.

Compound **3** 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. The structure was solved by a

Table 1. Crystal data for compounds **1**–**3**

Compound	**1**	**2**	**3**
Formula	$Mn_2PO_{11}C_{22}H_{19}$	$Mn_2PO_{10}C_{21}H_{19}$	$MnPO_7C_{18}H_{20}$
Formula wt.	600.24	572.22	434.26
Crystal system	monoclinic	orthorhombic	triclinic
Lattice parameters:			
a (Å)	8.262(1)	17.333(3)	9.244(2)
b (Å)	34.423(8)	27.898(3)	15.363(3)
c (Å)	9.492(1)	10.418(2)	8.036(2)
α (°)	90.00	90.00	102.10(2)
ß (°)	105.82(1)	90.00	110.97(2)
γ (°)	90.00	90.00	95.53(2)
V (Å³)	2597.3(8)	5037.8(11)	1023.5(5)
Space group	$P2_1/n$ (#14)	*Pbca* (#61)	$P\bar{1}$ (#2)
Z value	4	8	2
ρ_{calc} (g/cm³)	1.54	1.51	1.41
μ(Mo-K_α) (cm^{-1})	10.89	11.16	7.57
Temperature (°C)	20	20	20
$2\Theta_{max}$ (°)	43	43	45
No. Obs. ($I > 3\sigma$)	1747	1852	2349
No. Variables	333	316	296
Goodness of fit GOF[a]	1.48	1.61	3.97
Max shift/error	0.01	0.01	0.02
Residuals: *R*[a]; R_w	0.039; 0.034	0.034; 0.032	0.046; 0.057
Abs. corr.	difabs	difabs	empirical
Trans. coeff, max/min	1.00/0.71	1.00/0.65	1.00/0.77
Largest pk in final diff. map (e^-/Å³)	0.22	0.21	0.89

[a] $R = \Sigma_{hkl}(||F_{obs}| - |F_{calc}||)/\Sigma_{hkl}(|F_{obs}|)$; $R_w = [\Sigma_{hkl}w(|F_{obs}| - |F_{calc}|)^2/\Sigma_{hkl}wF_{obs}{}^2]^{1/2}$, $w = 1/\sigma^2(F_{obs})$; $GOF = [\Sigma_{hkl}(w(|F_{obs}| - |F_{calc}|)]^2)/(n_{data} - n_{vari})]^{1/2}$.

combination of direct methods (MITHRIL) and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atom H(2) was located and refined with an isotropic thermal parameter. The positions of all other hydrogen atoms were calculated by assuming idealized geometries with all C–H distances at 0.95 Å[15].

[1] [1a] M. H. Chisholm, L. A. Rankel, W. I. Bailey, Jr., F. A. Cotton and C. A. Murillo, *J. Am. Chem. Soc.*, **1977**, *99*, 1261.– [1b] L. N. Lewis, J. C. Huffman, K. G. Caulton, *Inorg. Chem.*, **1980**, *19*, 1246. – [1c] E. L. Hoel, G. B. Ansell, S. Leta, *Organometallics* **1986**, *3*, 585. – [1d] I. Y. Wu, T. W. Tseng, C. T. Chen, M. C. Cheng, Y. C. Lin, Y. Wang, *Inorg. Chem.*, **1993**, *32*, 1539–40. – [1e] C. G. Kreiter, M. Leyendecker, W. S. Sheldrick, *J. Organomet. Chem.* **1986**, *302*, 35. – [1f] C. G. Kreiter, W. Michels, G. Heeb, G. Z., *Naturforsch.* **1995**, *50b*, 649.

[2] R. H. Cayton, M. H. Chacon, M. H. Chisholm, M. J. Hamden-Smith, J. C. Huffman, K. Folting, P. D. Ellis, B. A. Huggins, *Angew. Chem.* **1989**, *28*, 1523.

[3] [3a] R. E. Davis, *Chem. Commun.* **1968**, 248. – [3b] B. F. G. Johnson, J. Lewis, P. R. Raithby, S. W. Sankey, *J. Organomet. Chem.* **1982**, *231*, C65. – [3c] A. J. Deeming, A. J. Arce, Y. DeSanctis, P. A. Bates, M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.* **1987**, 2935. – [3d] A. Kühn, C. Burschka, H. Werner, *Organometallics* **1982**, *1*, 496.

[4] X. L. R. Fontaine, G. B. Jacobsen, B. L. Shaw, M. Thorton-Pett, *J. Chem. Soc., Dalton Trans.* **1988**, 1185.

[5] R. D. Adams, G. Chen, Y. Chi, *Organometallics* **1992**, *11*, 1473.

[6] R. D. Adams, M. Huang, *Organometallics*, in press.

[7] [7a] H. F. Schuster, *Allenes in Organic Synthesis*, Wiley, **1984**. – [7b] M. Aso, I. Ikeda, T. Kawabe, M. Shiro, K. Kanematsu, *Tetrahedron Lett.* **1992**, *33*, 5787. – [7c] E. J. Corey, N. W. Boaz, *Tetrahedron Lett.* **1984**, *25*, 3059.

[8] [8a] M. R. Churchill, K. N. Amoh, H. I. Wasserman, *J. Inorg. Chem.* **1981**, *20*, 1609. – [8b] L. F. Dahl, R. E. Rundle, *Acta Crystallogr.* **1963**, *16*, 419.

[9] M. Laing, E. Singleton, R. Riemann, *J. Organomet. Chem.* **1973**, *56*, C21.

[10] F. A. Cotton, *Prog. Inorg. Chem.* **1976**, *21*, 1.

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

[12] T. A. Bryson, T. M. Dolak, *Org. Synth.*, **1977**, *57*, 62.

[13] W. L. Ingram, N. J. Coville, *J. Organomet. Chem.* **1992**, *423*, 51.

[14] [14a] *International Tables for X-ray Crystallography;* Vol. IV, Kynoch Press, Birmingham, England, 1975; Table 2.2B, pp. 99–101. – [14b] *Ibid.*, Table 2.3.1, pp. 149–150.

[15] Further details of the crystal structure investigations are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD-59338.

[96164]