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Syntheses of Metal Carbonyls, XVI[1]

Metal-Metal Multiple Bonds: Synthesis, Crystal and Molecular Structure of Tri-μ-carbonyl-bis[(η^5-pentamethylcyclopentadienyl)manganese](*Mn*≡*Mn*) – The First Manganese-Manganese Triple Bond

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Photolysis of the manganese half-sandwich complex $(\eta^5\text{-}C_5Me_5)Mn(CO)_3$ (**1**) in tetrahydrofuran (thf) cleanly yields the solvent complex $(\eta^5\text{-}C_5Me_5)Mn(CO)_2(thf)$ (**2**). Compound **2** is stable as a solid at temperatures well below 0 °C but undergoes spontaneous elimination of carbon monoxide at ambient temperature with concomitant formation of the novel dinuclear complex $(\eta^5\text{-}C_5Me_5)_2Mn_2(\mu\text{-}CO)_3$ (**3**). While elemental analysis, infrared and mass spectroscopy as well as the ^1H NMR and ^{13}C NMR spectra unequivocally demonstrate this compound to adopt a highly symmetrical triply carbonyl-bridged structure, a single-crystal X-ray diffraction study supports the presence of the first triple bond between manganese atoms (*d*Mn – Mn 217.0(1) pm). An improved synthesis of tricarbonyl(η^5-pentamethylcyclopentadienyl)manganese (**1**) is also described.

Metallcarbonyl-Synthesen, XVI[1]

Metall-Metall-Mehrfachbindungen: Synthese, Molekül- und Kristallstruktur von Tri-μ-carbonyl-bis[(η^5-pentamethylcyclopentadienyl)mangan](*Mn*≡*Mn*) – die erste Mangan-Mangan-Dreifachbindung

Photolyse des Halbsandwich-Mangan-Komplexes $(\eta^5\text{-}C_5Me_5)Mn(CO)_3$ (**1**) in Tetrahydrofuran (THF) führt ohne Nebenreaktionen zum Solvenskomplex $(\eta^5\text{-}C_5Me_5)Mn(CO)_2(THF)$ (**2**). Dieser ist im festen Zustand im deutlich unter 0 °C liegenden Temperaturbereich haltbar, erleidet aber spontane CO-Eliminierung bei Raumtemperatur; dabei bildet sich der neue Zweikernkomplex $(\eta^5\text{-}C_5Me_5)_2Mn_2(\mu\text{-}CO)_3$ (**3**). Während Elementaranalyse, Infrarot- und Massenspektren sowie die ^1H- und ^{13}C-NMR-Spektren dieser Verbindung eine hochsymmetrische dreifach Carbonyl-verbrückte Struktur zuweisen, stützt eine Einkristall-Röntgenstrukturanalyse das Vorliegen der ersten bisher bekannten Mangan-Mangan-Dreifachbindung (*d*Mn – Mn 217.0(1) pm). Eine verbesserte Darstellung von Tricarbonyl(η^5-pentamethylcyclopentadienyl)mangan (**1**) wird beschrieben.

Effective syntheses of many organometallic compounds frequently depend on the availability of precursors exhibiting metal-metal multiple bonds that allow addition of

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simple molecules with a concomitant drop of bond order and/or elimination of other ligands. One typical example is the addition of alkylidenes to metal-metal multiple bonds – a general synthetic methodology for the nowadays easy-to-make three-membered metallacycles of type $\overline{M-CR_2-M}$[2-4]. Following a preliminary communication[5], this paper describes the synthesis as well as the crystal and molecular structure of the first compound revealing a triple bond between manganese atoms. At the same time, the prediction that this metal-metal bond length ranges in the order of 215 – 220 pm[5] is shown to be correct.

Synthesis

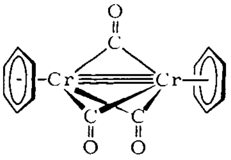
As reported[5] the manganese half-sandwich complex **1** undergoes clean elimination of *one* out of three carbonyl ligands upon photolysis conducted in tetrahydrofuran solutions at ambient temperature. In a simple ligand displacement reaction typical for the parent compound $(\eta^5\text{-}C_5H_5)Mn(CO)_3$[6], the heavier congener $(\eta^5\text{-}C_5H_5)Re(CO)_3$[7], and the related half-sandwich complexes of composition $(\eta^5\text{-}C_5R_5)M(CO)_4$ (R = H, CH_3; M = Nb, Ta)[8,9], the corresponding carmine-red thf complex $(\eta^5\text{-}C_5Me_5)Mn(CO)_2(thf)$ (**2**) is formed according to Eq. (1).

$$\begin{tikzcd} 2\,(\eta^5\text{-}C_5Me_5)Mn(CO)_3 \arrow[r, "(thf)", "h\cdot\nu"'] & 2\,(\eta^5\text{-}C_5Me_5)Mn(CO)_2(thf) + 2\,CO \arrow[d, "(thf)"] & (1) \\ \mathbf{1} \quad & \mathbf{2} \quad (\eta^5\text{-}C_5Me_5)_2Mn_2(\mu\text{-}CO)_3 + CO & \\ & \mathbf{3} & \end{tikzcd}$$

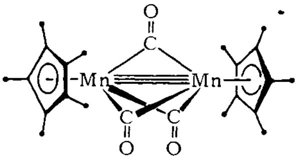
The solvent complex **2** is stable at + 15 °C in thf solution for at least 10 hours. On standing for extended periods of time, however, a slow colour change of such solutions from red to green is observed. Once we had realized that this observation was due to subsequent conversion of **2** into the novel dinuclear organometallic compound **3** in a *dark-reaction,* a more simple and effective route was devised: the thf solution of **2** was vacuum-evaporated to dryness and thereby gave the desired title compound in 38 – 55% yield based upon **1**. The immediate precursor species **2** can be kept as a solid without noticeable decomposition at temperatures well below 0 °C; at – 20 °C, formation of **3** does not occur within hours whereas the same process goes to completion in no more than a few minutes at 30 °C and a pressure of *ca.* 10^{-3} torr.

The new organomanganese compound **3** forms emerald-green crystals that can be handled in air for brief periods of time (no decomposition within *ca.* 30 min). They gradually decompose when heated above 90 °C (sealed capillary). Green solutions in diethyl ether, tetrahydrofuran, and toluene are rapidly decolorized in the presence of air with concomitant precipitation of brown, fluffy manganese dioxide and partial formation of the mononuclear precursor compound **1**.

Both composition and structure were unequivocally assigned on the basis of complete elemental analysis yielding the formula $C_{23}H_{30}Mn_2O_3$, and by spectroscopic means (IR, ^1H and ^{13}C NMR, MS)[5] according to which data the $(\eta^5$-cyclopentadienyl)-manganese compound **3** was predicted to represent the missing isosteric interlink **B** between the structurally well-established (η^6-benzene)chromium and the (η^4-cyclobutadienyl)iron derivatives **A**[10] and **C**[11], respectively. In keeping with the requirements of the EAN rule, all these compounds as well as the rhenium analogue (η^5-$C_5Me_5)_2Re_2$(μ-$CO)_3$ (**D**)[12] contain very short metal-metal *triple bonds**). Using the reported distances Cr≡Cr (**A**) 222 pm (av.)[10], Fe≡Fe (**C**) 217.7 pm[11], and Re≡Re (**D**) 241.1 pm[12], a manganese-manganese triple bond length ranging in the order of 215...220 pm was predicted in the original communication[5]. A value within this range would both perfectly match those of the chromium and iron compounds and be in agreement with the commonly encountered metallic radii difference between manganese and rhenium[13,14]. In order to support our previous structural assignment, we have undertaken a single-crystal X-ray diffraction study described in the following section.



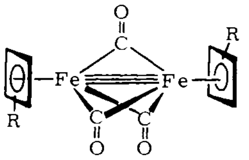
A



3

— = CH_3

B



C

Crystal and Molecular Structure

The molecule consists of two pentamethylcyclopentadienyl rings π-bonded to a core containing two manganese atoms bridged by three carbonyls. The averages of the chemically equivalent bond distances and angles are given in Table 1, based on the atom labeling scheme of Figure 1. By far the most important value in the table is the metal-metal bond distance. At 217.0 pm it is the shortest Mn – Mn bond of all existing di- and polynuclear manganese compounds. This observation correlates nicely with the fact that the EAN rule predicts this to be a *triple bond* – the first ever reported between two manganese atoms. As we pointed out in a previous paper[15], to the best of our knowledge there is only one other multiply-bonded dimanganese compound in the literature, that being $Cp_2Mn_2[\mu$-$NN(SiMe_3)_2]_2$ which has an EAN-predicted bond order of two and a Mn – Mn distance of 239.3(2) pm[16]. There are numerous reports of single bonded molecules, with manganese-to-manganese distances ranging from 250.2 pm[17] to 323.5 pm[18]. Various explanations have been given to account for this wide variation, from *trans* influence to π-acceptor properties of bridging ligands[19], but it still remains impossible to give a definitive value of the Mn – Mn single bond since it's system-dependent. For purposes of comparison, $Cp_2Mn_2(\mu$-$CO)(\mu$-$NO)(CO)(NO)$[20] is probably the closest structure to ours in the literature, and it has a Mn – Mn distance of 257.1 pm. Thus there seems to be about 20 pm contraction in going from a single to a double bond, and an additional 20 pm or so in going to a triple bond. This is quite similar to the relationships noted in chromium and molybdenum compounds[10,21]. Cr

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*) *Note added in proof (June 14, 1983):* We have meanwhile also synthesized the heterodinuclear compound (η^5-C_5Me_5)Mn(μ-$CO)_3$Cr(η^6-C_6Me_6) by irradiation of **1** in the presence of (η^6-C_6Me_6)-$Cr(CO)_3$ (yield >85%).

and Mn have about the same single bond covalent radius, and known Cr – Cr triple bonds of 222.1 pm[10)] and 222.0 pm[22)] compare well with our value of 217.0 pm. The relative strength of our Mn – Mn triple bond is, of course, difficult to ascertain since at this time it is the only one in existence.

Table 1. Intramolecular Bond Distances and Angles of **3**[a)]

A. Distances [pm]			
Mn – Mn	217.0(1)	C – O	118.0(5)
Mn – C(CO)	192.9(5)	C – C(C_5Me_5)	141.7(6)
Mn – C(C_5Me_5)	214.7(5)	C – C(Me)	150.9(6)
Mn – Cent[b)]	177.6(5)		
B. Angles [°]			
C(CO) – Mn – C(CO)	91.4(2)	Mn – C – O	145.7(4)
C(CO) – Mn – Cent[b)]	124.2(2)	C(Cp) – C(Cp) – C(Cp)	108.0(5)
Mn – Mn – Cent[b)]	179.6(2)	C(Me) – C(Cp) – C(Cp)	126.0(5)
Mn – C(CO) – Mn	68.5(2)		

[a)] All values are averages of chemically equivalent sites. – [b)] Ring centroid of C_5Me_5 ring (Cp).

Table 2. Data Collection and Processing Parameters of **3**

Space group	$P2_1/c$, monoclinic
Cell constants	a = 972.3(6) pm
	b = 1426.7(2)
	c = 1674.7(2)
	β = 106.1(2)°
	V = 2232 × 10^6 pm^3
Molecular formula	$C_{23}H_{30}Mn_2O_3$
Molecular weight	464.35 g · mol^{-1}
Molecules per cell	$Z = 4$
Density	ρ = 1.38 g · cm^{-3}
Absorption coefficient	μ = 10.8 cm^{-1}
Crystal dimensions	0.2 × 0.2 × 0.4 mm
Radiation (Mo-K_α)	λ = 71.069 pm
Collection range	$4° \leq 2\Theta \leq 45°$
Scan width	$\Delta\Theta = (1.05 + 0.35 \tan\Theta)°$
Maximum scan time	180 s
Scan speed range	0.5 to 4.0° min
Total data collected	3260
Independent data, $I > 3\sigma(I)$	1877
Total variables	284
$R = \Sigma \lvert\lvert F_o \rvert - \lvert F_c \rvert\rvert / \Sigma \lvert F_o \rvert$	0.031
$R_w = [\Sigma w(\lvert F_o \rvert - \lvert F_c \rvert)^2 / \Sigma w \lvert F_o \rvert^2]^{1/2}$	0.029
Weights	$w = (F)^{-2}$

Some inferences can be made, however, by examining analogous systems. $Mo_2(\eta^5\text{-}C_5Me_5)_2(CO)_4$ shows a significantly longer (4 pm) Mo – Mo triple bond than does $Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4$, the non-methylated version[21)]. Similarly, $Cr_2(\eta^5\text{-}C_5Me_5)_2(CO)_4$ has a Cr – Cr triple bond 6.5 pm longer than the non-methylated compound[22,23)]. The

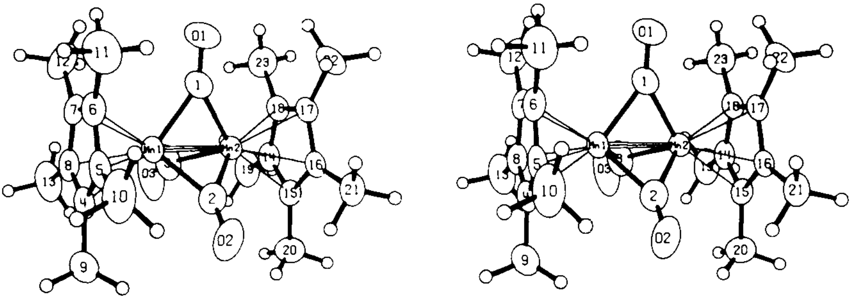

Figure 1. Stereoscopic view of the molecule showing the atom labeling scheme. The thermal ellipsoids are 50% equiprobability envelopes, with hydrogens as spheres of arbitrary diameter. The hydrogen atoms are numbered the same as the carbon to which each is attached

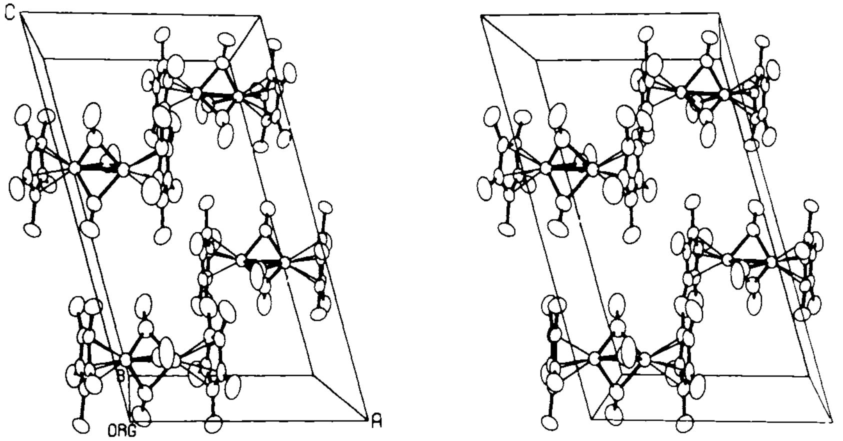

Figure 2. Stereoscopic view of the molecular packing in the unit cell, with hydrogen atoms omitted for clarity

usual explanation for this disparity of bond lengths is that the pentamethyl derivatives have greater electron donating character and therefore higher populations in orbitals with metal-metal anti-bonding components, thus exhibiting longer metal-metal distances despite equal EAN bond orders[23]. It is probably safe to assure that our Mn – Mn distance is near the high end of the possible triple bond range then, with as yet unknown compounds such as $(\eta^5\text{-}C_5H_4CH_3)_2Mn_2(\mu\text{-}CO)_3$ and $(\eta^5\text{-}C_5H_5)_2Mn_2(\mu\text{-}CO)_3$ (see below) expected to show even shorter Mn – Mn bond lengths.

In order to see what effect the ligands have on the Mn – Mn bond, it is necessary to compare the overall geometry of molecule **3** with similar compounds in the literature. Unfortunately not only are there no other triple-bonded Mn_2 species, but there are also no other Mn_2 compounds having well-defined bridging carbonyls. Three structures have been reported with bridging carbonyls, but in one case it is semi-bridging[24], in another it is disordered with nitrosyl[20], and in the third it is severely strained by being opposite a dimethylgermylene bridge[19]. If the Mn – CO distance is essentially constant, we would expect to see a much narrower Mn – C – Mn angle than in single-bonded compounds, but verification of this will have to wait. Much information is available on Mn...Cp contacts, and our Mn – C(Cp) and Mn – Cent values (see Table 1) are only slightly shorter than literature averages[15]. The two C_5Me_5 rings in our compound are eclipsed and the Cent – Mn – Mn angles are both essentially 180°, this apparently producing the lowest energy configuration with respect to the bridging carbonyl groups. Unlike the case in $(\eta^5\text{-}C_5Me_5)_2Cr_2(CO)_4$[23], where all methyl groups are bent at about 4.5° from the plane of this Cp and *exo* to Cr, the least squares planes analyses of our C_5Me_5 rings show that some methyls are bent slightly away from Mn, some slightly towards Mn, and some are essentially in the C_5 plane. Thus it would seem improbable that there is any significant steric strain between the carbonyl groups and the π-bonded ring ligands.

The packing of the molecules in the unit cell is shown in Figure 2. The molecules align themselves with their principal axis approximately along *a*, which made interpretation of the Patterson map somewhat more difficult than usual since the *y* and *z* coordinates of both Mn atoms are almost the same. The packing results in zones along *a*, with C_5Me_5 regions near $a = 0$ and 1/2, and CO regions near $a = 1/4$ and 3/4[*].

Reactivity

Metal-metal multiple bonds are usually considered to be sites of reactivity in organometallic compounds, and numerous addition and metathesis reactions have become familiar for such molecules[4]. One salient prerequisite for pronounced reactivity, however, is the steric accessibility of metal-metal triple bonds. In the present case, this part of the molecule is perfectly shielded by three symmetrically bridging carbonyl groups. Furthermore, we have no evidence for fluxionality of the $Mn_2(CO)_3$-core which process would expose the Mn ≡ Mn bond to other molecules. Otherwise, low or lacking reactivity should result. In fact, the chromium and rhenium compounds **A** and **D** (see above) do not react with diazoalkanes[10,12] which latter species usually attack metal-metal bonds quite readily[2].

Compound **3** is also not very reactive. So far we have only achieved clean cleavage of the dimeric structure by triethyl phosphite: here, the expected mononuclear products of composition **4a** and **4b** are formed in a 1 : 1 ratio. This reaction is useful in light of the fact that the mononuclear precursor species **1** and **2** allow monosubstitution only.

$(\eta^5\text{-}C_5Me_5)Mn(CO)_2[P(OEt)_3]$ **4a**

$(\eta^5\text{-}C_5Me_5)Mn(CO)[P(OEt)_3]_2$ **4b**

Fast metal-metal bond cleavage is observed upon exposure of **3** to carbon monoxide at room temperature (thf solution) and ambient pressure. **1** is the sole product of this reaction. With diazoalkanes, no isolable derivative has been obtained but further investigation into these reactions is in progress.

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[*] Further details of the structure determination are deposited at the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen (West Germany). These data are available with quotation of the registry number CSD 50430, the authors, and the reference to this publication.

Finally, it should be noted that our search for compound **3** had been initiated by *Hoffmann's* prediction of the non-methylated analogue $(\eta^5\text{-}C_5H_5)_2Mn_2(\mu\text{-}CO)_3$[25]. This latter species, however, is certainly not stable under ordinary conditions. In our hands, the thf complex $(\eta^5\text{-}C_5H_5)Mn(CO)_2(thf)$ can be purified by means of column chromatography on silica at −20°C and is thus obtained crystalline (off-white crystals). When an electron-impact mass spectrum of this compound is recorded, the parent-ion peak of $(C_5H_5)_2Mn_2(CO)_3$ as well as the entire fragmentation pattern expected for this species is observed (*m/e* 324, 296, 268, 240) rather than the thf complex. While the non-methylated analogue of **3** is definitely formed in the gas-phase, all attempts of synthesis and isolation on a preparative scale were hitherto unsuccessful.

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Experimental Part

All manipulations were performed under scrupulous exclusion of air and moisture employing standard Schlenk tube techniques[26]. In order to avoid partial formation of N_2-complexes[5], the synthesis of compound **3** should be carried out in argon rather than in nitrogen atmosphere. Decacarbonyldimanganese was a product of Strem Chemicals (Newburyport, Mass./USA) and was purified by vacuum sublimation ($40-50\,^\circ C/10^{-3}$ torr) prior to use. Pentamethylcyclopentadiene was synthesized according to the published procedure of *Marks* et al.[27].

1) *Tricarbonyl(η^5-pentamethylcyclopentadienyl)manganese* (**1**): A yield-improved synthesis of this starting material uses the method of *King* et al.[28] but does not employ a solvent. 7.00 g (17.9 mmol) of sublimed $Mn_2(CO)_{10}$ and 8.4 ml of distilled pentamethylcyclopentadiene are placed in a 100 ml-Schlenk flask equipped with magnetic stir bar, reflux condenser, and a mercury pressure-relief valve on top of this assembly. The solution is heated to 180 ± 5°C in a thermostated oil bath and kept there, under continuous magnetic stirring, for approx. 12 – 15 h. During this period of time, evolution of gas (CO and H_2) is observed, and the desired product **1** precipitates as an off-white yellowish powder from excess pentamethylcyclopentadiene, accompanied by some insoluble brown decomposition products. These decomposition products mainly appear when the suspension is cooled to ordinary temperature. After the resulting suspension has slowly cooled down to room temperature, excess ligand (C_5Me_5H) is removed under reduced pressure (*ca.* 10^{-3} torr). The solid residue is then subjected to column chromatography using silica (Merck 7734; act. II – III; column dimensions 60 × 1.4 cm; cooling jacket at +15°C). Compound **1** is eluted with *n*-hexane as a bright yellow band[*]. Recrystallization is not necessary. Yield: 5.4 – 7.4 g (55 – 75%). – IR (νCO; cm^{-1}): 2015 vs, 1925 vs [*n*-hexane].

2) *Tri-μ-carbonyl-bis[(η^5-pentamethylcyclopentadienyl)manganese](Mn≡Mn)* (**3**): A solution of 1.37 g (5.0 mmol) of **1** in 230 ml of tetrahydrofuran is placed in a water-cooled immersion-well apparatus as described earlier[26]. The solution is irradiated, under vigorous magnetic stirring,

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[*] *Note added in proof (October 12, 1983):* If this synthesis is scaled up to *ca.* 25 g $Mn_2(CO)_{10}$, chromatography is not recommended. In this case, the crude product is rather dissolved in diethylether, with the resulting solution being filtered over silica (air-free conditions not required). **1** is washed from the support with diethylether; typical yield 65% (*R. Hörlein,* unpublished results).

with the light of a 150 Watt high-pressure mercury lamp (*e. g.*, Original Hanau Quarzlampengesellschaft mbH). Under these conditions, CO-elimination of **1** proceeds rapidly, with the solution changing colour from light yellow to carmine within the first minutes of irradiation. No starting material is present any longer after approx. 4 h, and only the solvent complex (η^5-C_5Me_5)-$Mn(CO)_2$(thf) (**2**) is detected by IR spectroscopy (νCO absorptions at 1910 vs and 1836 cm^{-1} vs). The solution is now evaporated to dryness (*ca.* 10^{-3} torr) at −20°C which operation yields a carmine-coloured crystalline residue representing compound **2**. For the purpose of synthesizing the dinuclear species **3**, this residue is left under vacuum while gradually being warmed to room temperature. A rapid colour change to emerald-green occurs, indicating formation of **3**. After *ca.* 30 min at 20−30°C, the crude title compound thus obtained is purified by column chromatography (silica column, 40 × 1.2 cm; degassed SiO_2, Merck 7734, act. II−III; cooling jacket at −5°C). With a toluene/*n*-hexane mixture (50/50 vol. %), some precursor **1** is first eluted as a light yellow band. The intensively coloured dark-green band of compound **3** occurs when toluene alone is employed as an eluent. After evaporation of the eluate *in vacuo* and subsequent recrystallization of the air-sensitive residue from *n*-hexane/diethyl ether mixtures, analytically and spectroscopically pure **3** is obtained as green needles, dec. *ca.* 90°C (sealed capillary), by drying the compound in a high-vacuum. Yield: 440−640 mg (38−55%); the typical yield amounts to *ca.* 40% based upon **1**. − IR (νCO; cm^{-1}): 1770 vs [KBr]; 1785 vs [*n*-hexane]. − ^{1}H NMR (300 MHz; C_6D_6, +27°C): δCH_3 1.66 [s]. − {^{1}H}^{13}C NMR (67.9 MHz; C_6D_6, +25°C): δCH_3 10.00 [s], δC_5Me_5 98.99 [s], δCO 275.31 [s]. A ^{13}CO-enriched sample (*ca.* 30% ^{13}CO) was used in order to obtain a high-intensity resonance for the CO ligands. [^{13}CO]-**3** was synthesized according to the sequence **1** → **2** + CO; **2** + ^{13}CO → [^{13}CO]-**1**; [^{13}CO]-**1** → → [^{13}CO]-**3** (preparation no. 2), see above).

$C_{23}H_{30}Mn_2O_3$ (464.4)	Calcd.	C 59.49	H 6.51	Mn 23.66	N 0.00	O 10.34
	Found	C 59.35	H 6.43	Mn 23.40	N 0.00	O 10.09

(Mikroanalytische Laboratorien, Gummersbach); molecular weight 464 (field desorption mass spectrum; toluene solution).

3) *Reaction of* **3** *with Triethyl Phosphite:* A solution of 300 mg (0.65 mmol) of **3** and 1.5 ml (9.3 mmol) of freshly distilled $P(OC_2H_5)_3$ in 50 ml of thf is refluxed for *ca.* 20 h, after which period of time the colour of the solution has turned yellowish green and its IR spectra show the complete disappearance of bridging carbonyl ligands. The presence of new absorptions at 1850, 1865, and 1930 cm^{-1} rather indicates the formation of products that have only terminal CO ligands (**4a, b**). The solvent is then removed at 20°C *in vacuo* (*ca.* 10^{-3} torr). The solid residue is dissolved in a few ml of *n*-hexane and is transferred to a silica column (SiO_2, act. II−III; Merck 7734; column dimensions 50 × 1.2 cm; +15°C). With *n*-hexane/toluene (2:1), a first yellow-greenish band containing **4a** is obtained. Compound **4b** is eluted as a second yellow band when a 10:1-mixture of toluene and diethyl ether is employed as eluent. Both products are recrystallized from *n*-hexane (+25... −30°C), subsequently washed with little cold *n*-hexane and dried in a high-vacuum for several hours. Yield ca. 45% for each compound.

4a: pale-yellow crystals, (η^5-C_5Me_5)$Mn(CO)_2[P(OEt)_3]$; m. p. 46°C. − IR: ν(CO) 1865 vs, 1930 cm^{-1} vs [KBr]; 1875 vs, 1937 cm^{-1} m [*n*-hexane]. − Mass spectra: *m/e* = 412 (field desorption, toluene). − ^{1}H NMR (270 MHz; $CDCl_3$; 25°C): δCH_2CH_3 1.27 [t, $^3J_{H,H}$ = 6.8 Hz; 9H]; δ$C_5(CH_3)_5$ 1.82 [s, 15H]; δCH_2CH_3 3.89 [m, 6H].

4b: pale-yellow crystals, (η^5-C_5Me_5)$Mn(CO)[P(OEt)_3]_2$, m. p. 80°C. − IR: ν(CO) 1850 cm^{-1} vs [KBr]; 1859 cm^{-1} vs [*n*-hexane]. − Mass spectra: *m/e* = 550 (field desorption, toluene). − ^{1}H NMR (270 MHz; $CDCl_3$; 25°C): δCH_2CH_3 1.23 [t, $^3J_{H,H}$ = 6.2 Hz; 18H]; δ$C_5(CH_3)_5$ 1.75 [s, 15H]; δCH_2CH_3 3.91 [m, 12H].

4) *X-Ray Diffraction Study:* An Enraf-Nonius CAD-4 automatic diffractometer was used, with Mo-K_α radiation monochromatized by a graphite crystal. Final cell constants, as well as other information pertinent to data collection and refinement, are listed in Table 2. The Laue symmetry was determined to be $2/m$, and from the systematic absences noted the space group was shown unambiguously to be $P2_1/c$. Intensities were measured using the $\Theta-2\Theta$ scan technique, with the scan rate depending on the net count obtained in rapid pre-scans of each reflection. When exposed to the atmosphere, the crystals decay slowly, losing about 50% of their scattering power in three days. Since the entire data collection took six days, it was necessary to use two separate crystals and merge the separate data sets by applying a scale factor based on the intensities of three common standard reflections that were measured periodically. A linear decay correction was also applied based on X-ray exposure time. In reducing the data, Lorentz and polarization

Table 3. Atomic Coordinates and Thermal Parameters of **3** ($\times 10^3$, Mn $\times 10^4$)

ATOM	X/A	Y/B	Z/C	U11	U22	U33	U12	U13	U23
MN1	.25757(9)	.24272(6)	.12567(5)	306(5)	415(6)	410(5)	-20(5)	105(4)	-20(5)
MN2	.04196(9)	.21024(6)	.13051(5)	295(5)	391(5)	357(5)	4(5)	89(4)	7(5)
O1	.0399(5)	.3000(4)	-.0302(3)	59(3)	215(6)	59(3)	-23(4)	0(3)	67(4)
O2	.2288(4)	.0409(3)	.1646(3)	46(3)	41(3)	172(5)	7(2)	39(3)	14(3)
O3	.1822(5)	.3492(4)	.2603(3)	71(4)	148(5)	137(5)	-40(3)	54(3)	-102(4)
C1	.0869(6)	.2668(5)	.0363(3)	40(4)	103(6)	48(4)	-9(4)	7(3)	20(4)
C2	.1945(6)	.1200(4)	.1475(4)	46(4)	42(4)	70(5)	3(3)	17(4)	0(4)
C3	.1667(6)	.2377(4)	.2038(4)	50(4)	57(4)	68(5)	-4(4)	18(4)	-28(4)
C4	.4820(5)	.2224(4)	.1835(4)	26(3)	47(4)	57(4)	-6(3)	11(3)	-7(3)
C5	.4484(6)	.1901(5)	.1008(4)	21(4)	67(5)	71(5)	-4(3)	22(3)	-9(4)
C6	.3948(6)	.2659(5)	.0472(4)	37(4)	83(6)	48(4)	-14(4)	21(3)	0(4)
C7	.3949(6)	.3474(4)	.0978(4)	30(4)	53(5)	71(5)	-4(3)	24(4)	12(4)
C8	.4510(6)	.3196(4)	.1817(4)	35(4)	45(4)	61(5)	-12(3)	16(3)	-8(3)
C9	.5442(6)	.1631(5)	.2593(4)	45(4)	66(5)	89(5)	-1(4)	3(4)	17(4)
C10	.4749(7)	.0919(4)	.0742(4)	57(5)	63(5)	118(6)	-5(4)	45(4)	-37(5)
C11	.3548(7)	.2646(6)	-.0465(3)	68(5)	180(8)	58(5)	-14(6)	33(4)	0(6)
C12	.3492(8)	.4444(4)	.0671(5)	74(6)	66(5)	133(7)	-5(4)	38(5)	39(5)
C13	.4833(7)	.3931(5)	.2560(4)	59(5)	72(5)	96(6)	-19(4)	12(4)	-35(4)
C14	-.1227(5)	.2367(4)	.1911(3)	28(3)	56(5)	54(4)	-4(3)	22(3)	-7(3)
C15	-.0868(5)	.1397(4)	.1974(3)	33(4)	47(4)	42(4)	-4(3)	18(3)	0(3)
C16	-.1196(5)	.1029(4)	.1149(3)	23(3)	47(4)	42(4)	-5(3)	9(3)	0(3)
C17	-.1718(5)	.1770(4)	.0594(3)	23(3)	55(4)	41(4)	-3(3)	9(3)	3(3)
C18	-.1730(5)	.2593(4)	.1064(3)	19(3)	57(5)	54(4)	4(3)	13(3)	6(4)
C19	-.1184(7)	.3017(4)	.2632(4)	58(4)	75(5)	83(5)	-10(4)	38(4)	-27(4)
C20	-.0305(7)	.0847(4)	.2760(3)	66(5)	77(5)	42(4)	-3(4)	17(4)	18(4)
C21	-.1103(6)	.0013(4)	.0916(4)	50(4)	45(4)	65(4)	-10(3)	9(4)	-8(4)
C22	-.2278(6)	.1675(5)	-.0343(3)	45(4)	102(6)	36(4)	-13(4)	-3(3)	4(4)
C23	-.2246(6)	.3557(4)	.0720(4)	43(4)	62(5)	99(6)	16(4)	19(4)	18(4)
H9A	.5348(6)	.2035(5)	.3120(4)	137(5)					
H9B	.6560(6)	.1517(5)	.2640(4)	137(5)					
H9C	.4914(6)	.0964(5)	.2584(4)	137(5)					
H10A	.4264(7)	.0910(4)	.0079(4)	137(5)					
H10B	.4297(7)	.0365(4)	.1029(4)	137(5)					
H10C	.5890(7)	.0815(4)	.0870(4)	137(5)					
H11A	.3105(7)	.3323(6)	-.0686(3)	137(5)					
H11B	.2803(7)	.2103(6)	-.0755(3)	137(5)					
H11C	.4545(7)	.2547(6)	-.0620(3)	137(5)					
H12A	.2926(8)	.4328(4)	.0026(5)	137(5)					
H12B	.4420(8)	.4878(4)	.0710(5)	137(5)					
H12C	.2794(8)	.4792(4)	.0978(5)	137(5)					
H13A	.4143(7)	.4422(5)	.2331(4)	137(5)					
H13B	.5931(7)	.4065(5)	.2766(4)	137(5)					
H13C	.4537(7)	.3514(5)	.3074(4)	137(5)					
H19A	-.0299(7)	.2870(4)	.3171(4)	137(5)					
H19B	-.2171(7)	.3013(4)	.2809(4)	137(5)					
H19C	-.1035(7)	.3697(4)	.2385(4)	137(5)					
H20A	-.0053(7)	.1372(4)	.3244(3)	137(5)					
H20B	.0642(7)	.0441(4)	.2781(3)	137(5)					
H20C	-.1132(7)	.0390(4)	.2854(3)	137(5)					
H21A	-.0172(6)	-.0219(4)	.1394(4)	137(5)					
H21B	-.0923(6)	-.0083(4)	.0314(4)	137(5)					
H21C	-.2024(6)	-.0391(4)	.0951(4)	137(5)					
H22A	-.2327(6)	.2373(5)	-.0600(3)	137(5)					
H22B	-.3325(6)	.1355(5)	-.0541(3)	137(5)					
H22C	-.1526(6)	.1258(5)	-.0559(3)	137(5)					
H23A	-.2157(6)	.3601(4)	.0093(4)	137(5)					
H23B	-.1662(6)	.4127(4)	.1084(4)	137(5)					
H23C	-.3359(6)	.3600(4)	.0711(4)	137(5)					

factors were applied. No correction for absorption was made since the absorption coefficient was fairly small. The structure was solved by the Patterson method, which gave the positions of both Mn atoms. The usual sequence of isotropic and anisotropic refinement was followed, after which all hydrogens were easily located in a difference Fourier synthesis. In order to minimize the number of variables in the least squares refinement, each of the methyl groups was treated as a rigid body, with a single isotropic thermal parameter for all hydrogens. After all shift/esd ratios were less than 1.0, the refinement converged to the agreement factors listed in Table 2. There were no unusually high correlations between any of the variables in the final cycle of least squares. The atomic scattering factors for the non-hydrogen atoms were computed from numerical Hartree-Fock wave functions[29]; for hydrogen those of *Stewart, Davidson,* and *Simpson* were used[30]. The anomalous dispersion coefficients of *Cromer* and *Liberman*[31] were used for Mn. Final positional and thermal parameters are shown in Table 3.

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[3] The scope of this reaction has recently been expanded and includes now also multiple bonds between ligand-free main group elements and transition metals (*e. g.* Mn = Te and Mn = Ge), *c.f.* [3a] *W. A. Herrmann, J. Weichmann, R. Serrano, K. Blechschmitt, H. Pfisterer,* and *M. L. Ziegler,* Angew. Chem. **95**, 331 (1983); Angew. Chem., Int. Ed. Engl. **22**, 314 (1983). Angew. Chem. Suppl. **1983**, 363. – [3b] *W. A. Herrmann, J. Weichmann, U. Küsthardt, A. Schäfer, R. Hörlein, Ch. Hecht,* and *E. Voss,* Angew. Chem., in press (December 1983).

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