

Dinuclear Derivatives of $\text{Mn}_2(\text{CO})_{10}$ with the Ligand Tri(1-cyclohepta-2,4,6-trienyl)phosphane, $\text{P}(\text{C}_7\text{H}_7)_3$, and their Oxidative Cleavage

Max Herberhold, Wolfgang Milius, and Andreas Pfeifer

Laboratorium für Anorganische Chemie der Universität Bayreuth,
Postfach 10 12 51, D-95440 Bayreuth, Germany

Reprint requests to Prof. Dr. M. Herberhold. Fax: +49 (0) 921 55 2157.
E-mail: Max.Herberhold@uni-bayreuth.de

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The photo-induced reaction of $\text{Mn}_2(\text{CO})_{10}$ with the olefinic phosphane $\text{P}(\text{C}_7\text{H}_7)_3$ (**1**; [P] if coordinated to a metal) leads stepwise to the axially substituted derivatives $ax\text{-}\{\text{Mn}_2(\text{CO})_9[\text{P}]\}$ (**2**) and $ax,ax\text{-}\{\text{Mn}_2(\text{CO})_8[\text{P}]_2\}$ (**3**). Oxidative cleavage of **3** by halogens gives $cis\text{-}\{\text{Mn}(\text{X})(\text{CO})_4[\text{P}]\}$ ($\text{X} = \text{Cl}$ (**4a**), Br (**4b**), I (**4c**)), whereas oxidation of **3** with NOBF_4 provides a route to the salt $\{\text{Mn}(\text{CO})_4[\text{P}]\}\text{BF}_4$ (**5**) which is also accessible by halide abstraction from **4b** by AgBF_4 . The reactivity of the bromo complex **4b** has been studied, and analogues such as $cis\text{-}\{\text{Mn}(\text{R})(\text{CO})_4[\text{P}]\}$ ($\text{R} = \text{Me}$ (**4d**), Fc (**4e**) and $\text{N}(\text{tPr})_2$ (**4f**)) have been prepared. The displacement of a carbonyl ligand from **4b** by iodide leads to $mer\text{-}\{\text{Mn}(\text{I})(\text{CO})_3[\text{P}]\}$ (**6c**) and by **1** to $mer,trans\text{-}\{\text{Mn}(\text{Br})(\text{CO})_3[\text{P}]_2\}$ (**7b**). The complexes $mer\text{-}\{\text{Mn}(\text{X})(\text{CO})_3[\text{P}]\}$ (**6a-c**) are obtained by splitting the dimers, $\text{Mn}_2(\text{CO})_6(\text{CH}_3\text{CN})_2(\mu\text{-X})_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), with $\text{P}(\text{C}_7\text{H}_7)_3$ (**1**). The cation in **5** and the halogeno compounds **6a-c** contain [P] (**1**) as a chelating four-electron ligand which uses one cyclohepta-2,4,6-trienyl substituent for π -complexation. The coordinated double bond in **6c** can be displaced by phosphites $\text{P}(\text{OR})_3$ ($\text{R} = \text{Me}, \text{Et}$) to give $fac\text{-}\{\text{Mn}(\text{I})(\text{CO})_3[\text{P}(\text{C}_7\text{H}_7)_3][\text{P}(\text{OR})_3]\}$ (**8c**).

The structures of the new complexes **2-8** have been assigned on the basis of their carbonyl stretching absorption patterns in the IR spectra and by their NMR spectra (^1H , ^{13}C , ^{31}P). Single-crystal X-ray structure analyses have been carried out for **3** and **6c**.

Key words: Manganese, Olefinic Phosphanes, Carbonyl-manganese Complexes

Introduction

The substitution of carbonyl ligands in $\text{Cr}(\text{CO})_6$ has been used to prepare a series of mononuclear, octahedral complexes, $\text{Cr}(\text{CO})_{6-n}[\text{P}(\text{C}_7\text{H}_7)_3]$ ($n = 1, 2, 3, 4$), in which the olefinic phosphane $\text{P}(\text{C}_7\text{H}_7)_3$ (**1**) is coordinated through the lone pair of electrons at phosphorus, but may also use 0-3 olefinic double bonds of the cycloheptatrienyl substituents for π -complexation [1]. A similar mononuclear series, $\text{Fe}(\text{CO})_{5-n}[\text{P}(\text{C}_7\text{H}_7)_3]$ ($n = 1, 2, 3$), of basically trigonal-bipyramidal coordination geometry has been synthesized starting from $\text{Fe}_3(\text{CO})_{12}$ [2]. We have now included the binuclear $\text{Mn}_2(\text{CO})_{10}$ into these studies.

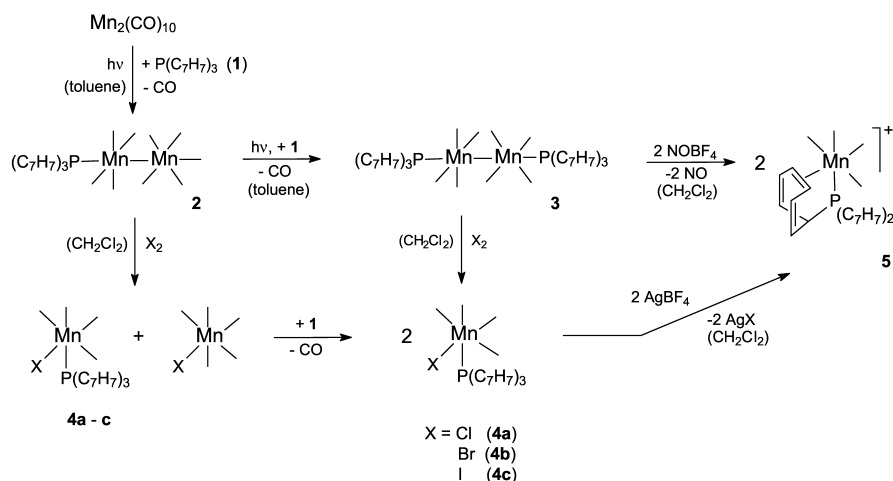
Since the early investigations of Hieber *et al.* [3], the thermal and photochemical reactions of $\text{Mn}_2(\text{CO})_{10}$ with tertiary phosphanes [4] have been studied extensively [5]. In general, the photo-induced substitution of CO ligands leads to diamagnetic, dinuclear derivatives with intact Mn—Mn bond.

Results and Discussion

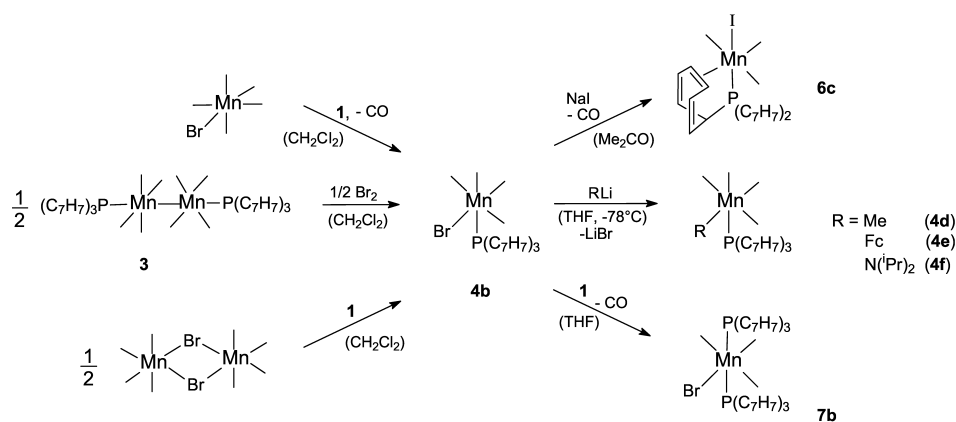
Syntheses

Irradiation of decarbonyl dimanganese, $\text{Mn}_2(\text{CO})_{10}$, in toluene solution in the presence of either 1 or 2 equivalents of $\text{P}(\text{C}_7\text{H}_7)_3$ (**1**; [P] if coordinated to a transition metal) led to the stepwise introduction of **1** into the axial positions (Scheme 1). The products $ax\text{-}\{\text{Mn}_2(\text{CO})_9[\text{P}]\}$ (**2**) and $ax,ax\text{-}\{\text{Mn}_2(\text{CO})_8[\text{P}]_2\}$ (**3**) were isolated as yellow, air-stable powders. The dinuclear structure of **3** has been confirmed by X-ray structure analysis (see below); however, under field desorption conditions (FD-MS) the molecule is homolytically split into the (paramagnetic) mononuclear fragments.

Oxidative cleavage of the Mn—Mn bond in **2** and **3** by halogens ($\text{X}_2 = \text{Cl}_2, \text{Br}_2, \text{I}_2$) is a convenient method to prepare the halides $cis\text{-}\{\text{Mn}(\text{X})(\text{CO})_4[\text{P}]\}$ (**4a-c**) which are also obtained by thermal substitution of a



Scheme 1.



Scheme 2.

CO ligand for $\text{P}(\text{C}_7\text{H}_7)_3$ (**1**) in the halides $\text{Mn}(\text{X})(\text{CO})_5$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$). The *cis*-configuration is deduced from the typical *cis*- $\text{Mn}(\text{CO})_4$ pattern in the IR carbonyl stretching region. The oxidative cleavage of **3** by NOBF_4 [cf. 4] gave the salt $\{\text{Mn}(\text{CO})_4[\text{P}(\text{C}_7\text{H}_7)_2(\eta^2\text{-C}_7\text{H}_7)]\}^+\text{BF}_4^-$ (**5**), in which the phosphane **1** uses one of the three cyclohepta-2,4,6-trienyl substituents for olefinic complexation through its central double bond. Complex **5** is also formed by halide abstraction from **4a-c** with AgBF_4 (Scheme 1).

The bromide *cis*- $\{\text{Mn}(\text{Br})(\text{CO})_4[\text{P}]\}$ (**4b**) has been chosen as a model for additional ligand substitutions (Scheme 2). It is prepared by successive incorporation of bromide and the phosphane **1** (or *vice versa*) into carbonylmanganese precursors such as $\text{Mn}_2(\text{CO})_{10}$.

The reactions of **4b** with methyl-, ferrocenyl- and di(isopropyl)amido lithium in THF solution at -78°C gave the structurally analogous derivatives *cis*- $\{\text{Mn}(\text{R})(\text{CO})_4[\text{P}]\}$ ($\text{R} = \text{Me}$ (**4d**), Fc (**4e**) and

$\text{N}(\text{CHMe}_2)_2$ (**4f**)). On the other hand, the replacement of bromide for iodide in the reaction of **4b** with NaI in acetone solution also involved the loss of a CO group and conversion of [P] into a chelating ligand, to give *mer*- $\{\text{Mn}(\text{I})(\text{CO})_3[\text{P}(\text{C}_7\text{H}_7)_2(\eta^2\text{-C}_7\text{H}_7)]\}$ (**6c**), the structure of which was confirmed by X-ray crystallography (see below). A second phosphane ligand can replace a carbonyl group in **4b** to give *mer,trans*- $\{\text{Mn}(\text{Br})(\text{CO})_3[\text{P}]_2\}$ (**7b**). The *trans*-arrangement of the two phosphane ligands [P] in **7b** is supported by the *mer*-pattern of the $[\text{Mn}(\text{CO})_3]$ fragment in the IR spectra [6] and by the equivalence of the P atoms in the ^{31}P NMR spectra.

The mononuclear halides *mer*- $\{\text{Mn}(\text{X})(\text{CO})_3-[\text{P}(\text{C}_7\text{H}_7)_2(\eta^2\text{-C}_7\text{H}_7)]\}$ ($\text{X} = \text{Cl}$ (**6a**), Br (**6b**) and I (**6c**)) are most conveniently prepared by splitting the halogeno-bridged dinuclear precursor $\{\text{Mn}(\text{CO})_3-(\text{CH}_3\text{CN})(\mu-\text{X})\}_2$ [7] using the olefinic phosphane. The other possible routes to **6a-c**, *i.e.* the (thermal)

Table 1. Spectroscopic data.

	$\text{P}(\text{C}_7\text{H}_7)_3$ 1	$\text{Mn}_2(\text{CO})_9[\text{P}]$ 2	$\text{Mn}_2(\text{CO})_8[\text{P}]_2$ 3	$\{\text{Mn}(\text{CO})_4[\text{P}]\}\text{BF}_4$ 5	$\text{Mn}(\text{I})(\text{CO})_3[\text{P}]$ 6c	$\text{Mn}(\text{Br})(\text{CO})_3[\text{P}]_2$ 7b
IR: $\nu(\text{CO})$ [cm^{-1}] (hexane)		2092s, 2008s 1997vs, 1975m 1961m, 1936s	1978sh 1953vs	2102s, 2042w 2026vs, 2002w b,c	2024vs 1958s, 1928s	2087w, 2002s, 1952s
^{13}C NMR (C_6D_6) ^a						
C^1	36.0 [16.3]	39.6 [27.7]	40.1 [24.5]	38.1 [24.4]	38.4 [23.8] 39.7 [18.3]	37.8 [11.9]
C^2, C^7	118.5 [11.8]	112.8	113.5	107.8 109.8	113.8; 114.1 115.0; 120.3	112.5
C^3, C^6	126.7 [7.4]	127.3 [14.6]	127.3 [10.4]	129.0 [8.2] 129.8 [10.2]	^d ^d	127.2(t) [4.5]
C^4, C^5	130.9	130.6	130.6	130.8 131.3	130.4; 131.0 130.2; 131.6	130.2
$\text{C}^{1'}$				37.5 [15.0]	36.7 [11.4]	
$\text{C}^{2'}, \text{C}^{7'}$				116.0		
$\text{C}^{3'}, \text{C}^{6'}$				128.6 [9.4]	^d	
$\text{C}^{4'}, \text{C}^{5'}$				94.5	92.9; 98.3	
^{31}P NMR (C_6D_6) ^a	−12.5	73.6	75.1	121.6	108.2	51.0

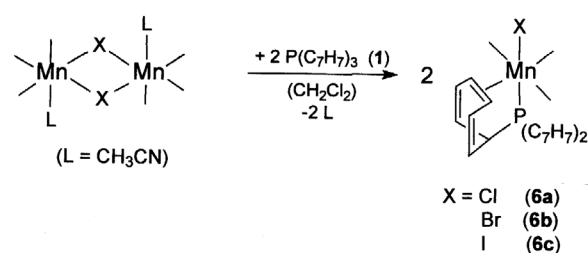
^a The ^{13}C NMR signals are doublets if a coupling constant, [$J(^{31}\text{P}, ^{13}\text{C})$], is quoted. All other ^{13}C NMR and all ^{31}P NMR signals are singlets;

^b IR Spectrum of the salt **5** in CH_2Cl_2 , NMR spectra in CDCl_3 ; ^c data for the isoelectronic $\text{Cr}(\text{CO})_4[\text{P}]$ [**1**]: IR: $\nu(\text{CO})$ (hexane) 2017s, 1935m, 1924vs, 1895m. NMR: δ values (C_6D_6): C^1 38.5 [20.6]; C^2, C^7 , 115.1; C^3, C^6 127.0 [8.5] and 127.2 [10.5]; C^4, C^5 130.5, 131.1; $\text{C}^{1'}$ 37.8 [8.5]; $\text{C}^{2'}, \text{C}^{7'}$ 115.0; $\text{C}^{3'}, \text{C}^{6'}$ 129.6 [9.9]; $\text{C}^{4'}, \text{C}^{5'}$ 83.9. $\delta^{31}\text{P}$ 103.8; ^d the (5) doublet signals of **6c** in the positions 3 and 6 overlap with the signals of the solvent C_6D_6 at 128.0.

Table 2. Spectroscopic data of *cis*- $\{\text{Mn}(\text{X})(\text{CO})_4[\text{P}(\text{C}_7\text{H}_7)_3]\}$ (**4a-c**) and *cis*- $\{\text{Mn}(\text{R})(\text{CO})_4[\text{P}(\text{C}_7\text{H}_7)_3]\}$ (**4d-f**).

Ligand X or R	Cl (4a)	Br (4b)	I (4c)	Me (4d)	Fc (4e)	$\text{N}(\text{Pr})_2$ (4f)
IR: $\nu(\text{CO})$ [cm^{-1}] (hexane)	2091s 2024s, 2010vs 1956s	2088s 2022s, 2009vs 1957s	2080s 2017s, 2004vs 1959s	2058s 1984s, 1968vs 1939s	2064s 1992s, 1978vs 1949s	2009s 1957w, 1929s 1895s
^{13}C NMR (C_6D_6) ^a						
C^1	36.4 [23.6]	37.0 [24.0]	38.0 [24.5]	37.0 [25.2]	35.9 [22.9]	38.4 [26.4]
C^2, C^7	114.1	114.4	114.1	112.5	107.3	113.1 [3.7]
C^3, C^6	128.2	128.1	128.0	127.8 [19.9]	126.9 [9.1]	127.0 [10.7]
C^4, C^5	130.6	130.7	130.7	130.5	129.7	130.5
CH_3				71.7 [2.0]		22.3
CHMe_2						49.3
Fc (Cp)					69.2	
Fc ($\text{C}^\alpha, \text{C}^\beta$)					69.6; 80.4	
^{31}P NMR (C_6D_6) ^a	48.9	45.4	41.2	54.1	48.2	66.7

^a The ^{13}C NMR signals are doublets if a coupling constant, [$J(^{31}\text{P}, ^{13}\text{C})$], is quoted. All other ^{13}C NMR and all ^{31}P NMR signals are singlets.



decarbonylation of **4a-c**, or the (thermal) reaction of $\text{Mn}(\text{X})(\text{CO})_5$ with **1**, led to product mixtures containing **6a-c** as the main component.

IR and NMR spectroscopy

Tables 1 and 2 contain the IR stretching frequencies of the carbonyl ligands (in hexane solution) and the ^{13}C and ^{31}P NMR data (in C_6D_6 solution, except in the case of the salt **5**). ^1H NMR data are given in the Experimental Part.

Table 3. Spectroscopic data of *fac*- $\{\text{Mn}(\text{I})(\text{CO})_3[\text{P}(\text{C}_7\text{H}_7)_3][\text{P}(\text{OR})_3]\}$ (**8c**).

	R = Me	R = Et
IR: $\nu(\text{CO})$ [cm^{-1}] (hexane)	2026s 1963s, 1928s	2024s 1961s, 1919s
^{13}C NMR (C_6D_6) ^a		
CH_3	53.9 [9.0]	15.8 [5.8]
CH_2		62.9 [8.8]
C^1	36.5 [21.8], [1.9]	36.8 [23.8]
C^2, C^7	104.0 104.6	102.6 103.3
C^3, C^6	126.5 [8.6] 126.7 [8.9]	126.3 [8.5] 126.7 [8.7]
C^4, C^5	129.1 129.4	128.9 129.2
^{31}P NMR (C_6D_6) ^a		
$\text{P}(\text{C}_7\text{H}_7)_3$	31.0 {66.1}	30.2 {72.8}
$\text{P}(\text{OR})_3$	159.4 {66.1}	154.9 {72.8}

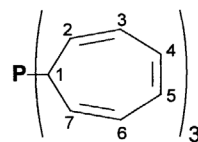
^a All ^{13}C NMR signals are doublets if a coupling constant, $[J(^{31}\text{P}, ^{13}\text{C})]$, is quoted. All ^{31}P NMR signals are doublets; the coupling constant $^2J(^{31}\text{P}, ^{31}\text{P})$, is given in { }.

The $\nu(\text{CO})$ stretching absorptions consistently indicate the presence of only terminal carbonyl ligands, also in the dinuclear compounds **2** and **3**. The simple $\nu(\text{CO})$ pattern of **3** is in good agreement [4] with the *ax,ax*-disubstituted structure of approximate symmetry D_{4d} . The number of $\nu(\text{CO})$ bands observed for the mononuclear complexes (**4a-f**, **5**, **6c** and **7b**) confirms the number of CO ligands. The *cis*- $\{\text{Mn}(\text{X})(\text{CO})_4[\text{P}(\text{C}_7\text{H}_7)_3]\}$ compounds (**4a-f**), in particular, possess very similar band patterns; the strong electron-donating di(isopropyl)amido ligand in **4f** shifts the $\nu(\text{CO})$ pattern to lower wave-numbers (Table 2).

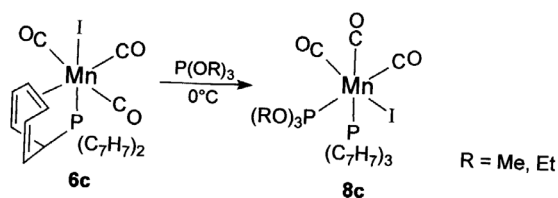
The $\{\text{Mn}(\text{CO})_4[\text{P}(\text{C}_7\text{H}_7)_2(\eta^2\text{-C}_7\text{H}_7)]\}^+$ cation in **5** is isosteric and isoelectronic with the uncharged chromium complex $\text{Cr}(\text{CO})_4[\text{P}(\text{C}_7\text{H}_7)_2(\eta^2\text{-C}_7\text{H}_7)]$ [1]. As expected, the $\nu(\text{CO})$ absorption patterns are similar, but the $\nu(\text{CO})$ stretching bands of the cation are shifted to higher frequencies by *ca.* 100 cm^{-1} , due to reduced $\text{Mn} \rightarrow \text{CO}$ back-bonding (Table 1).

The ^{31}P NMR data can be used to deduce the coordination mode of the olefinic phosphane ligand, $\text{P}(\text{C}_7\text{H}_7)_3$ [8]. If all 3 cyclohepta-2,4,6-trienyl substituents are freely pending side-arms, the chemical shifts are observed in the range $\delta^{31}\text{P}$ 40–75, whereas a chelating $\text{P}(\text{C}_7\text{H}_7)_3$ ligand has the phosphorus signal at lower field, in the area $\delta^{31}\text{P}$ 100–125.

The ^{13}C NMR spectra are simple, as long as the phosphane $\text{P}(\text{C}_7\text{H}_7)_3$ carries 3 uncoordinated cyclohepta-2,4,6-trienyl rings which give rise to 4



signals (as in **2**, **3**, **4a-f** and **7b**). For the cationic chelate complex **5** (and the isoelectronic analogue $\text{Cr}(\text{CO})_4[\text{P}(\text{C}_7\text{H}_7)_2(\eta^2\text{-C}_7\text{H}_7)]$) (Table 1), a total of 11 ^{13}C NMR signals are observed, (*i.e.* 7 originating from the two freely-pending rings and 4 from the η^2 -coordinated cyclohepta-2,4,6-trienyl ring). If a chirality center is created by introduction of a halide ligand for a carbonyl group, as in the *mer*-tricarbonylmanganese complexes **6a-c**, the number of individual signals raises to the maximum of $(7 \times 3) = 21$, because the metal carries – in addition to the *mer*- $\text{Mn}(\text{CO})_3$ arrangement – 3 different ligands (I, P and the olefinic double bond).



The π -coordinated double bond can be displaced from the metal (under mild conditions) by ligands such as phosphites, $\text{P}(\text{OR})_3$ ($\text{R} = \text{Me}, \text{Et}$); the products *fac*- $\{\text{Mn}(\text{I})(\text{CO})_3[\text{P}(\text{C}_7\text{H}_7)_3][\text{P}(\text{OR})_3]\}$ (**8c**) retain their chirality center at the metal, but the number of ^{13}C NMR absorptions for the 3 equivalent 1-cyclohepta-2,4,6-trienyl substituents is now reduced again to 7 (Table 3). The *cis*-arrangement of the two phosphorus ligands is suggested by the $\nu(\text{CO})$ pattern of the carbonyl stretching absorptions in the IR spectra, which is typical of a *fac*- $\text{Mn}(\text{CO})_3$ structure [6,9].

*Molecular structures of ax,ax - $\{\text{Mn}_2(\text{CO})_8[\text{P}(\text{C}_7\text{H}_7)_3]_2\}$ (**3**) and mer - $\{\text{Mn}(\text{I})(\text{CO})_3[\text{P}(\text{C}_7\text{H}_7)_2(\eta^2\text{-C}_7\text{H}_7)]\}$ (**6c**)*

The relevant distances and angles of the inner coordination sphere around the central metal Mn are compiled for **3** in Table 4 and for **6c** in Table 5. The numbering systems are given in the Figures 1 and 2.

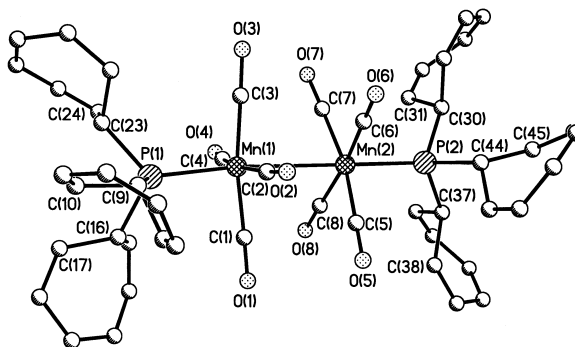
The dinuclear complex **3** contains a $\text{Mn}-\text{Mn}$ single bond ($296.2(3)\text{ pm}$) which is slightly longer than in the parent $\text{Mn}_2(\text{CO})_{10}$ ($290.38(6)\text{ pm}$ [10]) and in the di-axially substituted analogues *ax,ax*- $\{\text{Mn}_2(\text{CO})_8(\text{L})_2\}$

Table 4. Selected bond distances (pm) and angles ($^\circ$) in ax,ax - $\{\text{Mn}_2(\text{CO})_{10}[\text{P}(\text{C}_7\text{H}_7)_3]_2\}$ (**2**).

Mn(1)–Mn(2)	296.2(3)	Mn(2)–P(2)	228.1(4)
Mn(1)–P(1)	227.6(4)	Mn(2)–C(5)	184.1(14)
Mn(1)–C(1)	183.4(16)	Mn(2)–C(6)	182.1(16)
Mn(1)–C(2)	181.7(15)	Mn(2)–C(7)	184.2(15)
Mn(1)–C(3)	180.9(15)	Mn(2)–C(8)	183.6(17)
Mn(1)–C(4)	186.4(17)	P(2)–C(30)	185.8(13)
P(1)–C(9)	186.2(19)	P(2)–C(37)	185.7(13)
P(1)–C(16)	186.8(12)	P(2)–C(44)	184.4(14)
P(1)–C(23)	185.9(13)	C(5)–O(5)	114.5(14)
C(1)–O(1)	113.1(15)	C(6)–O(6)	115.6(15)
C(2)–O(2)	116.5(15)	C(7)–O(7)	114.8(15)
C(3)–O(3)	116.6(16)	C(8)–O(8)	114.9(16)
C(4)–O(4)	114.4(16)		
P(1)–Mn(1)–Mn(2)	174.84(13)	P(2)–Mn(2)–Mn(1)	178.76(13)
P(1)–Mn(1)–C(1)	91.8(4)	P(2)–Mn(2)–C(5)	95.8(4)
P(1)–Mn(1)–C(2)	95.7(4)	P(2)–Mn(2)–C(6)	92.3(4)
P(1)–Mn(1)–C(3)	97.3(4)	P(2)–Mn(2)–C(7)	95.9(4)
P(1)–Mn(1)–C(4)	96.5(4)	P(2)–Mn(2)–C(8)	95.1(4)
Mn(2)–Mn(1)–C(1)	83.1(4)	Mn(1)–Mn(2)–C(5)	85.3(4)
Mn(2)–Mn(1)–C(2)	83.5(4)	Mn(1)–Mn(2)–C(6)	88.4(4)
Mn(2)–Mn(1)–C(3)	87.8(4)	Mn(1)–Mn(2)–C(7)	83.1(4)
Mn(2)–Mn(1)–C(4)	84.5(4)	Mn(1)–Mn(2)–C(8)	84.2(4)
C(1)–Mn(1)–C(2)	90.4(7)	C(5)–Mn(2)–C(6)	90.4(6)
C(1)–Mn(1)–C(3)	170.8(6)	C(5)–Mn(2)–C(7)	168.3(6)
C(1)–Mn(1)–C(4)	90.5(6)	C(5)–Mn(2)–C(8)	88.8(6)
C(2)–Mn(1)–C(3)	87.3(7)	C(6)–Mn(2)–C(7)	88.1(6)
C(2)–Mn(1)–C(4)	167.7(6)	C(6)–Mn(2)–C(8)	172.6(7)
C(3)–Mn(1)–C(4)	89.9(7)	C(7)–Mn(2)–C(8)	91.1(6)
C(9)–P(1)–C(16)	102.6(6)	C(30)–P(2)–C(37)	101.1(6)
C(9)–P(1)–C(23)	101.3(6)	C(30)–P(2)–C(44)	99.0(6)
C(16)–P(1)–C(23)	103.7(6)	C(37)–P(2)–C(44)	101.7(6)
Mn(1)–P(1)–C(9)	113.8(4)	Mn(2)–P(2)–C(30)	117.9(4)
Mn(1)–P(1)–C(16)	114.0(4)	Mn(2)–P(2)–C(37)	118.6(5)
Mn(1)–P(1)–C(23)	119.3(4)	Mn(2)–P(2)–C(44)	115.2(4)
Mn(1)–C(1)–O(1)	178.2(15)	Mn(2)–C(5)–O(5)	178.4(13)
Mn(1)–C(2)–O(2)	175.9(16)	Mn(2)–C(6)–O(6)	176.3(14)
Mn(1)–C(3)–O(3)	178.5(15)	Mn(2)–C(7)–O(7)	177.3(12)
Mn(1)–C(4)–O(4)	176.5(14)	Mn(2)–C(8)–O(8)	179.3(13)

Table 5. Selected bond distances (pm) and angles ($^\circ$) in mer - $\{\text{Mn}(\text{I})(\text{CO})_3[\text{P}(\text{C}_7\text{H}_7)_2(\eta^2\text{-C}_7\text{H}_7)]\}$ (**6c**).

Mn–I	268.38(18)	P–C(5)	187.2(10)
Mn–P	225.0(3)	P–C(8)	184.7(10)
Mn–C(1)	238.4(14)	P–C(15)	185.5(10)
Mn–C(2)	241.7(13)	C(1)–C(2)	135(2)
P–Mn–I	177.02(10)	C(1)–Mn–C(2)	32.7(5)
P–Mn–C(1)	88.4(4)	I–Mn–C(1)	89.2(4)
P–Mn–C(2)	87.3(4)	I–Mn–C(2)	89.7(4)
P–Mn–C(22)	93.5(3)	I–Mn–C(22)	85.6(3)
P–Mn–C(23)	94.1(4)	I–Mn–C(23)	88.7(4)
P–Mn–C(24)	99.7(6)	I–Mn–C(24)	81.6(6)
C(1)–Mn–C(22)	107.8(5)	C(2)–Mn–C(22)	75.2(5)
C(1)–Mn–C(23)	162.2(5)	C(2)–Mn–C(23)	164.9(5)
C(1)–Mn–C(24)	78.6(6)	C(2)–Mn–C(24)	111.0(6)
C(22)–Mn–C(23)	89.7(5)	Mn–C(1)–C(2)	75.0(8)
C(22)–Mn–C(24)	165.6(7)	Mn–C(1)–C(7)	114.5(9)
C(23)–Mn–C(24)	83.6(6)	Mn–C(2)–C(1)	72.3(8)
		Mn–C(2)–C(3)	116.9(8)
Mn–P–C(5)	112.4(0)	C(5)–P–C(8)	99.6(5)
Mn–P–C(8)	123.4(4)	C(5)–P–C(15)	101.5(5)
Mn–P–C(15)	112.7(3)	C(8)–P–C(15)	104.4(5)



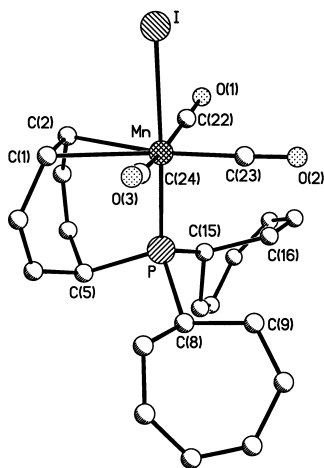


Fig. 2. Molecular structure of *mer*- $\text{Mn}(\text{I})(\text{CO})_3[\text{P}(\text{C}_7\text{H}_7)_2(\eta^2\text{-C}_7\text{H}_7)]$ (**6c**).

av. 101.57°) are marginally enlarged. The 1-cyclohepta-2,4,6-trienyl substituents are bound to phosphorus in equatorial positions.

The mononuclear iodo complex **6c** contains a distorted octahedral coordination sphere in which the phosphorus atom pushes the 3 meridional (equatorial) carbonyl groups towards the apical iodo ligand (P—Mn—CO angles $93.5(3)–99.7(6)^\circ$, I—Mn—CO angles $81.6(6)–88.7(4)^\circ$). However, the quality of the structural data obtained for **6c** is not sufficient for a discussion of bond lengths and angles in the carbonyl groups; in particular, the oxygen atoms of the CO ligands show large thermal vibrational ellipsoids.

The Mn—P bond length ($225.0(3)$ pm) in **6c** is short if compared with various other octahedral halogeno-phosphane tetracarbonylmanganese complexes, *cis*- $\{\text{Mn}(\text{X})(\text{CO})_4[\text{PR}_3]\}$, which, however, all contain an electron-withdrawing CO ligand *trans* to the *tert*.phosphane, as, e.g., in *cis*- $\{\text{Mn}(\text{Cl})(\text{CO})_4[\text{PPh}_3]\}$ (Mn—P $239.8(4)$ pm [14]), *cis*- $\{\text{Mn}(\text{Br})(\text{CO})_4[\text{PPh}_2\text{R}]\}$ (Mn—P $235.3(1)$ pm or $235.8(1)$ pm for $\text{R} = n\text{-propyl}$ and $n\text{-pentyl}$, respectively [15]) and *cis*- $\{\text{Mn}(\text{I})(\text{CO})_4[\text{PPh}_2(\text{SiMe}_3)]\}$ (Mn—P $238.8(1)$ pm [16]). The Mn—I bond length ($268.38(18)$ pm) in **6c**, on the other hand, is not unusual, if compared with that in *cis*- $\{\text{Mn}(\text{I})(\text{CO})_4[\text{PPh}_2(\text{SiMe}_3)]\}$ (Mn—I $268.8(1)$ pm [16]) and *cis*- $\{\text{Mn}(\text{I})(\text{CO})_4[\text{CH}_2\text{PPh}_3]\}$ (Mn—I $271.7(1)$ pm [17]).

The coordinated double bond, $\text{C}(1)=\text{C}(2)$ ($135(2)$ pm), is essentially coplanar with the 3 carbonyl carbon atoms $\text{C}(22)\text{C}(23)\text{C}(24)$; the dihedral

angle between the vector $\text{C}(1)–\text{C}(2)$ and this plane is 1.5° . The central metal Mn is part of the almost perfect plane $\text{C}(1)\text{C}(2)\text{MnC}(23)\text{O}(2)$, whereas the two *cis*-carbonyl groups $\text{C}(22)\text{O}(1)$ and $\text{C}(24)\text{O}(3)$ are bent out (angle $\text{C}(22)–\text{Mn}–\text{C}(24)$ $165.6(7)^\circ$).

The two freely pending C_7H_7 substituents carry the phosphorus atom in an equatorial position of $\text{C}(8)$ and $\text{C}(15)$, whereas the coordinated ring is (necessarily) attached to phosphorus via an axial $\text{C}(5)–\text{P}$ bond.

Experimental Section

An atmosphere of dry argon was routinely used for the preparative work and for the handling of samples; the solvents were dry and saturated with argon.

The parent compound $\text{Mn}_2(\text{CO})_{10}$ and the bromide $\text{Mn}(\text{Br})(\text{CO})_5$ are commercially available (Strem, Fluka). $\text{Mn}_2(\text{CO})_6(\text{CH}_3\text{CN})_2(\mu\text{-X})_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) [7] and the ligand $\text{P}(\text{C}_7\text{H}_7)_3$ [13] were prepared according to established literature procedures. Ferrocenyl lithium (FcLi) was obtained by lithiation of ferrocene [18].

Instrumentation: IR: Perkin Elmer, GX-1 FTIR. ^1H , ^{13}C and ^{31}P NMR: Bruker ARX 250; chemical shifts are given relative to SiMe_4 ($\delta^1\text{H}$ (C_6D_6) 7.15, $\delta^{13}\text{C}$ (C_6D_6) 128.0) and external 85% aqueous H_3PO_4 (with $\delta^{31}\text{P} = 0$ for $\Xi(^{31}\text{P}) = 40.480747$ MHz). EI-MS: Finnigan MAT 8500 (ionisation energy 70 eV); FD-MS: Varian MAT 311A.

a) Synthesis of *ax*- $\{\text{Mn}_2(\text{CO})_9[\text{P}]\}$ (**2**) and *ax,ax*- $\{\text{Mn}_2(\text{CO})_8[\text{P}]_2\}$ (**3**)

A yellow toluene solution (30 ml) containing 250 mg (0.64 mmol) of $\text{Mn}_2(\text{CO})_{10}$ and 195 mg (0.64 mmol) of $\text{P}(\text{C}_7\text{H}_7)_3$ (**1**) was irradiated with a high-pressure mercury arc (Heraeus, Original Hanau, TQ 718) for 2 h. The red solution was concentrated in a high vacuum to *ca.* 10 ml and then filtered over silica. The solvent toluene was evaporated under vacuum and the remaining orange oil dissolved in 2 ml of methanol. Treatment in an ultrasound bath led to separation of **2** as a yellow powder which was washed repeatedly with small amounts of methanol and finally dried under high vacuum. Yield 337 mg (89%), dec. 70°C . ^1H NMR (C_6D_6): $\delta = 2.40$ (dt, 3H, H^1), 5.14 (m, 6H, $\text{H}^{2,7}$), 5.99 (m, 6H, $\text{H}^{3,6}$), 6.31 (m, 6H, $\text{H}^{4,5}$).

In an analogous manner, a toluene solution (40 ml) of 187 mg (0.48 mmol) of $\text{Mn}_2(\text{CO})_{10}$ and 290 mg (0.95 mmol) of $\text{P}(\text{C}_7\text{H}_7)_3$ (**1**) was stirred in a 100 ml Schlenk tube in front of the ultraviolet light source (TQ 718) for 2.5 h. The orange reaction mixture was concentrated to *ca.* 20 ml and then filtered over Na_2SO_4 . The solvent toluene was removed in a high vacuum and the remaining red oil taken up in 5 ml of hexane. Upon exposure to ultrasound, a yellow precipitate of

Table 6. ^1H and ^{31}P NMR spectra of $\text{mer-}\{\text{Mn}(\text{X})(\text{CO})_3 [\text{P}(\text{C}_7\text{H}_7)_2(\eta^2\text{-C}_7\text{H}_7)]\}$ and $\text{Cr}(\text{CO})_4[\text{P}(\text{C}_7\text{H}_7)_2(\eta^2\text{-C}_7\text{H}_7)]$.

	X = Cl (6a)	$\text{mer-}\{\text{Mn}(\text{X})(\text{CO})_3[\text{P}]\}$ X = Br (6b)	X = I (6c)	$\text{Cr}(\text{CO})_4[\text{P}]\$ [1]
^1H NMR (C_6D_6) ^a				
Free C_7H_7 rings (A and B)				
Substituent A:				
H^1	2.01 (dt, 1)	1.94 (dt, 1)	1.84 (dt, 1)	1.83 (dt, 2)
H^2, H^7	5.25(1) or 5.49(1)	5.24(1); 5.47(1)	5.12(1); 5.43(1)	5.14(2) and 5.43(2)
H^3, H^6	6.15(2)	6.14(2)	6.13(2)	5.96(2) and 6.15(2)
H^4, H^5	6.43(2)	6.40(2)	6.35(2)	6.36(4)
Substituent B:				
H^1	3.25 (dt, 1)	3.21 (dt, 1)	3.15 (dt, 1)	
H^2, H^7	5.26(1) or 5.98(1)	5.24(1); 5.87(1)	5.18(1); 5.83(1)	
H^3, H^6	6.10(1) or 6.17(1)	6.08(1); 6.14(1)	5.93(1); 6.13(1)	
H^4, H^5	6.42(2)	6.40(2)	6.35(2)	
η^2 -Coordinated ring:				
$\text{H}^{1'}$	4.10(1)	3.99(1)	3.86 (dt, 1)	3.46 (dt, 1)
$\text{H}^{2'}, \text{H}^{7'}$	5.29(2)	5.24(2)	5.10(2)	5.10(2)
$\text{H}^{3'}, \text{H}^{6'}$	6.15(2)	6.08(2)	5.79(2)	5.79(2)
$\text{H}^{4'}, \text{H}^{5'}$	5.21(2)	5.17(2)	4.94(2)	4.94(2)
^{31}P NMR (C_6D_6)	112.7	110.3	108.2	103.8

^a δ Values, intensities in parentheses. The signals for H^1 (A and B) and $\text{H}^{1'}$ are triplets of doublets (dt) due to the spin-spin couplings $^3J(\text{H},\text{H})$ (with the protons H^2, H^7 or $\text{H}^{2'}, \text{H}^{7'}$) and $^2J(\text{P},\text{H})$. All other signals appear as multiplets. The assignments are based on two-dimensional ^1H , ^1H and ^{13}C , ^1H shift correlations.

3 was formed which was recrystallized from CH_2Cl_2 / pentane mixtures. Yield 303 mg (67%), dec. 79 °C. ^1H NMR (C_6D_6): δ = 2.51 (dt, 3H, H^1), 5.34 (m, 6H, $\text{H}^{2,7}$), 6.00 (m, 6H, $\text{H}^{3,6}$), 6.32 (m, 6H, $\text{H}^{4,5}$). FD-MS: m/e (%) = 942(1) $[\text{M}]^+$, 471(100) $[\text{M}^+ / 2]$, 443(8) $[\text{M}^+ / 2 - \text{CO}]$.

*b) Synthesis of $\text{cis-}\{\text{Mn}(\text{X})(\text{CO})_4[\text{P}]\}$ (X = Cl (**4a**), Br (**4b**), I (**4c**))*

*Method A: Reaction of $\text{ax,ax-}\{\text{Mn}_2(\text{CO})_8[\text{P}]_2\}$ (**3**) with halogen*

A yellow solution of 114 mg (0.12 mmol) of **3** in 20 ml of CH_2Cl_2 was cooled to -78 °C and exposed to Cl_2 under rigorous stirring for 20 min. The yellow-brown reaction mixture was then concentrated under vacuum, and the remaining oil dissolved in 5 ml of toluene. After filtration over Na_2SO_4 the toluene was removed under vacuum, and 10 ml of hexane was added. Upon exposure to an ultrasound source a light yellow precipitate of **4a** was formed. The supernatant solution was decanted and **4a** dried in a high vacuum. Yield 40 mg (33%), dec. 85 °C.

In a similar manner, the yellow solution of 94 mg (0.1 mmol) of **3** in 20 ml of CH_2Cl_2 was cooled to -40 °C, and a solution of 5 ml (0.1 mmol) of Br_2 in 5 ml of CH_2Cl_2 was then dropwise added. The orange solution was brought to room temperature within 1 h and the solvent CH_2Cl_2 evaporated. The yellow-brown oily residue was taken up in 3 ml

of toluene, and **4b** isolated as described for **4a** above. Yellow powder, yield 52 mg (47%), dec. 91 °C.

For the homolytic cleavage of **3** (58 mg, 0.06 mmol) by a stoichiometric amount of I_2 (16 mg, 0.06 mmol) in CH_2Cl_2 (20 ml), the solution was stirred for 3.5 h at room temperature. The solvent CH_2Cl_2 was then evaporated under vacuum and the orange residue dissolved in 2 ml of toluene. Upon chromatography over silica, some I_2 was first removed as a hexane solution, while **4c** was eluted as a yellow-orange band using hexane / CH_2Cl_2 (5 : 1). The solvents were removed in vacuo and **4c** isolated as a yellow powder, yield 54 mg (75%), dec. 98 °C.

*Method B: Reaction of $\text{Mn}(\text{X})(\text{CO})_5$ (X = Cl, Br, I) with $\text{P}(\text{C}_7\text{H}_7)_3$ (**1**)*

A yellow solution of $\text{Mn}(\text{X})(\text{CO})_5$ (0.47 mmol) and $\text{P}(\text{C}_7\text{H}_7)_3$ (143 mg, 0.47 mmol) in 20 ml of CH_2Cl_2 was heated under reflux (39 °C) overnight (14 h). The solvent CH_2Cl_2 was then removed under vacuum, and 20 ml of hexane was added to the sticky residue. Exposure to ultrasound resulted in separation of the products **4a-c** as yellow powders in yields of 200 mg (94%) **4a**, 205 mg (79%) **4b** and 190 mg (67%) **4c**.

The complexes **4a-c** show very similar ^1H NMR spectra, indicative of equivalent C_7H_7 substituents pending at the coordinated phosphorus atom, *i.e.* (C_6D_6 solution, 25 °C): δ = 3.01 ± 0.01 (dt, 3H, H^1), 5.29 ± 0.01 (m, 6H, $\text{H}^{2,7}$), 5.98 (m, 6H, $\text{H}^{3,6}$) and 6.21 ± 0.01 (m, 6H, $\text{H}^{4,5}$).

c) Reaction of $\text{cis-}\{\text{Mn}(\text{Br})(\text{CO})_4[\text{P}]\}$ (**4b**) with organolithium compounds

Synthesis of $\text{cis-}\{\text{Mn}(\text{R})(\text{CO})_4[\text{P}]\}$ ($\text{R} = \text{Me}$ (**4d**), Fc (**4e**) and $\text{N}(\text{iC}_3\text{H}_7)_2$ (**4f**))

$\text{cis-}\{\text{Mn}(\text{Me})(\text{CO})_4[\text{P}]\}$ (**4d**): A solution of 90 mg (0.16 mmol) of **4b** in 20 ml of THF was cooled to -78°C , and a solution of 0.16 mmol of MeLi in 5 ml of THF was dropwise added. The yellow reaction mixture was slowly brought to room temperature (within 3 h), then the solvent THF was evaporated. The remaining yellow oil was taken up in toluene (2 ml), and the mixture filtered over Na_2SO_4 in order to remove LiBr. The toluene solution contained **4d** which was isolated as a yellow solid, dec. 77°C . Yield 40 mg. ^1H NMR (C_6D_6 , 25°C): $\delta = 0.01$ (d, 3H, Me), 2.38 (dt, 3H, H^1) 5.15 (m, 6H, $\text{H}^{2,7}$), 6.00 (m, 6H, $\text{H}^{3,6}$), 6.30 (m, 6H, $\text{H}^{4,5}$).

$\text{cis-}\{\text{Mn}(\text{Fc})(\text{CO})_4[\text{P}]\}$ (**4e**): The reaction of 117 mg (0.21 mmol) of **4b** with 41 mg (0.21 mmol) of ferrocenyl lithium, FcLi [18], in THF solution at -78°C gave, after work-up as described for **4d**, orange crystals of **4e**, dec. 84°C , in a yield of 76 mg (55%). ^1H NMR (C_6D_6 , 25°C): $\delta = 2.27$ (dt, 3H, H^1), 4.18 (s, 2H, C_5H_4) and 4.22 (s, 2H, C_5H_4), 4.25 (s, 5H, Cp), 4.87 (m, 6H, $\text{H}^{2,7}$), 5.97 (m, 6H, $\text{H}^{2,6}$), 6.40 (m, 6H, $\text{H}^{4,5}$).

$\text{cis-}\{\text{Mn}(\text{N}^i\text{Pr}_2)(\text{CO})_4[\text{P}]\}$ (**4f**): Starting from 98 mg (0.18 mmol) of **4b**, the reaction with 90 μl (0.18 mmol) of lithium di(isopropyl)amide of a THF solution at -78°C gave – after the usual work-up including removal of LiBr by filtration of a toluene solution over silica – a yellow powder of **4f**, dec. 79°C ; yield 67 mg (65%). ^1H NMR (C_6D_6 , 25°C): $\delta = 1.32$ (d, 6H, CH_3), 2.51 (dt, 3H, H^1), 3.25 (q, 1H, CH), 5.49 (m, 6H, $\text{H}^{2,7}$), 6.10 (m, 6H, $\text{H}^{3,6}$), 6.35 (m, 6H, $\text{H}^{4,5}$).

Synthesis of $\text{cis-}\{\text{Mn}(\text{Fc})(\text{CO})_4[\text{P}]\}$ (**4e**) via $\text{Mn}(\text{Fc})(\text{CO})_5$

The ferrocenyl complex **4e** has also been obtained by heating a hexane solution (20 ml) containing both $\text{Mn}(\text{Fc})(\text{CO})_5$ [19] (160 mg, 0.42 mmol) and $\text{P}(\text{C}_7\text{H}_7)_3$ (**1**) (128 mg, 0.42 mmol) to 60°C for 6 h. The reaction mixture was then concentrated to 2 ml and separated by column chromatography over silica. Small amounts of the two educts were washed out with hexane, followed by a broad orange zone of **4e** when hexane / CH_2Cl_2 (1 : 1) was used for elution. Orange powder, dec. 85°C , yield 187 mg (68%).

d) Synthesis of $\{\text{Mn}(\text{CO})_4[\text{P}]\}\text{BF}_4$ (**5**)

Method A: Reaction of $\text{ax,ax-}\{\text{Mn}_2(\text{CO})_8[\text{P}]_2\}$ (**3**) with NOBF_4

A solution of 94 mg (0.1 mmol) of **3** in 20 ml of CH_2Cl_2 was reacted portionwise with 23 mg (0.2 mmol) of NOBF_4 .

The mixture was stirred for 1 h, then filtered over Na_2SO_4 , and the solvent CH_2Cl_2 removed under vacuo. The yellow oily product was washed twice with diethyl ether, then dried and redissolved in 2–3 ml of CH_2Cl_2 . The salt **5** crystallized over night at -50°C . Yield 55 mg (ca 50%).

Method B: Reaction of $\text{cis-}\{\text{Mn}(\text{Br})(\text{CO})_4[\text{P}]\}$ (**4b**) with AgBF_4

Solid AgBF_4 (56 mg, 0.29 mmol) was added to a yellow solution of 160 mg (0.29 mmol) of **4b** in 10 ml of CH_2Cl_2 . The reaction mixture was stirred for 30 min at r.t. and then filtered over Na_2SO_4 (to remove AgBr). Evaporation of the solvent gave a yellow solid of **5** which was washed repeatedly with Et_2O and finally dried under vacuum. Yield 158 mg (97.6%). ^1H NMR (CDCl_3 , 25°C): $\delta = 2.14$ (dt, 2H, H^1), 5.05 and 5.26 (m, 2x2H, H^2 and H^7), 6.36 (m, 4H, $\text{H}^{3,6}$), 6.55 (m, 4H, $\text{H}^{4,5}$); 5.28 (m, 1H, $\text{H}^{1'}$), 6.15 (m, 4H, $\text{H}^{2',7'}$ and $\text{H}^{4',5'}$), 6.60 (m, 4H, $\text{H}^{3',6'}$).

e) Synthesis of $\text{mer-}\{\text{Mn}(\text{X})(\text{CO})_3[\text{P}]\}$ ($\text{X} = \text{Cl}$ (**6a**), Br (**6b**), I (**6c**))

Method A: Reaction of $\text{Mn}_2(\text{CO})_6(\text{CH}_3\text{CN})_2(\mu - \text{X})_2$ with $\text{P}(\text{C}_7\text{H}_7)_3$ (**1**): Preparation of **6a** and **6b**

A yellow solution of 0.30 mmol of $\text{Mn}_2(\text{CO})_6(\text{CH}_3\text{CN})_2(\mu - \text{X})_2$ and 183 mg (0.60 mmol) of $\text{P}(\text{C}_7\text{H}_7)_3$ (**1**) in 10 ml of dichloromethane was stirred 1 h at r.t. The solution was concentrated under high vacuum and the remaining orange oil chromatographed on silica. Elution using CH_2Cl_2 / THF (10 : 1) produced, in the case of $\text{X} = \text{Cl}$, a yellow zone from which a yellow product **6a** (224 mg (78%), dec. 138°C) could be isolated. In the case of $\text{X} = \text{Br}$, a yellow-orange band was eluted which contained the yellow product **6b** (254 mg (81%), dec. 144°C). The ^1H and ^{31}P NMR spectra of the three analogous complexes **6a–c** are given in Table 6; a comparison of the chemical shifts, $\delta(^1\text{H})$ and $\delta(^{31}\text{P})$, clearly indicates the heavy-atom effect.

Method B: Halide substitution: Preparation of **6c**

An excess of NaI (800 mg, 5.34 mmol) was added to a solution of 150 mg (0.27 mmol) of **4b** in 20 ml of acetone. The solution was heated under reflux (56°C) for 2 h, then brought to dryness and the residue taken up in 5 ml of toluene for chromatography. Elution with pentane / CH_2Cl_2 (4 : 1) produced a yellow zone containing $\text{mer,trans-}\{\text{Mn}(\text{I})(\text{CO})_3[\text{P}]_2\}$ (**7c**), and with pentane / CH_2Cl_2 (1 : 1) a red zone of **6c** which was isolated as an orange oil, dec. 139°C , yield 47 mg (31%). EI-MS: $m/e = 570(1) [\text{M}^+]$, 486(8) $[\text{M}^+ - 3\text{CO}]$, 479(2) $[\text{M}^+ - \text{C}_7\text{H}_7]$, 443(2) $[\text{M}^+ - \text{I}]$, 396(2) $[\text{Mn}(\text{I})\text{P}(\text{C}_7\text{H}_7)_2]^+$, 359(3) $[\text{MnP}(\text{C}_7\text{H}_7)_3]^+$, 273(1) $[\text{Mn}(\text{I})\text{C}_7\text{H}_7]^+$, 268(3) $[\text{MnP}(\text{C}_7\text{H}_7)_2]^+$, 146(8) $[\text{MnC}_7\text{H}_7]^+$, 91(100) $[\text{C}_7\text{H}_7]^+$, 55(5) $[\text{Mn}^+]$.

f) Synthesis of *mer,trans*- $\{\text{Mn}(\text{Br})(\text{CO})_3[\text{P}]_2\}$ (**7b**)

A THF solution (20 ml) containing 132 mg (0.24 mmol) of **4b** and 73 mg (0.24 mmol) of **1** was heated 3 h under reflux. The solvent was then removed in a high vacuum. Toluene (2–3 ml) was added to the oily residue and the mixture filtered over Na_2SO_4 in order to remove insoluble particles. The toluene extracts were concentrated, and hexane (10 ml) was added. The yellow precipitate of **7b** was rinsed with hexane and dried under high vacuum to give 183 mg (92%) **7b**, dec. 155 °C. ^1H NMR (C_6D_6): δ = 3.07 (dt, 6H, H^1), 5.46 (m, 12H, $\text{H}^{2,7}$), 6.08 (m, 12H, $\text{H}^{3,6}$), 6.28 (m, 12H, $\text{H}^{4,5}$).

g) Synthesis of *fac*- $\{\text{Mn}(\text{I})(\text{CO})_3[\text{P}(\text{C}_7\text{H}_7)_3][\text{P}(\text{OR})_3]\}$ (**8c**)

The red solution of 97 mg (0.17 mmol) of **6c** in 10 ml of CH_2Cl_2 was cooled to 0 °C. Then 0.17 mmol of $\text{P}(\text{OR})_3$ (R = Me or Et) was added and the solution stirred for 5 h at ambient temperature. The colour of the solution changed from red to yellow. The solvent was removed, and the product purified by column chromatography over silica. Elution with pentane / CH_2Cl_2 (5 : 1) gave yellow zones containing the phosphite complexes **8c**.

R = Me: yield 110 mg (93%), dec. 126 °C. ^1H NMR (C_6D_6): δ = 2.68 (dt, 3H, H^1), 3.33 (d, 9H, $^3\text{J}(\text{P,H})$ 10.50 Hz, Me), 5.05 (m, 3H) and 5.25 (m, 3H) (H^2 and/or H^7), 6.09 (m, 6H, $\text{H}^{3,6}$), 6.28 (m, 6H, $\text{H}^{4,5}$). R = Et: yield 126 mg (90%), dec. 128 °C. ^1H NMR (C_6D_6): δ = 1.02 (t, 9H, CH_3), 2.68 (dt, 3H, H^1), 3.94 (m, 6H, CH_2), 5.02 (m, 3H) and 5.27 (m, 3H) (H^2 and/or H^7), 6.09 (m, 6H, $\text{H}^{3,6}$), 6.27 (m, 6H, $\text{H}^{4,5}$).

h) Crystal structures of **3** and **6c**

The reflection intensities were collected on a Siemens P4 diffractometer (Mo- $\text{K}\alpha$ -radiation, λ = 71.073 pm, graphite monochromated). Structure solution and refinement were carried out with the program package SHELXTL-PLUS V.5.1. Measuring temperature for all structure determinations was 296 K.

All non-hydrogen atoms were refined with anisotropic temperature factors. The hydrogen atoms are in calculated positions. All hydrogen atoms were refined applying the riding model with fixed isotropic temperature factors.

Crystal structure of *ax,ax*- $\{\text{Mn}_2(\text{CO})_8[\text{P}(\text{C}_7\text{H}_7)_3]_2\}$ (**3**)

$\text{C}_{50}\text{H}_{42}\text{Mn}_2\text{O}_8\text{P}_2$, orange plate with dimensions $0.22 \times 0.18 \times 0.08$ mm, crystallizes in the monoclinic space group $\text{C}2/c$ with the lattice parameters a = 2650.8(7), b = 1817.4(4), c = 2343.6(10) pm, β = 119.41(3)°, V = 9836(6) 10^6 pm³, Z = 8, μ = 0.628 mm⁻¹; 9347 reflections collected in the range $2^\circ \leq 2\theta \leq 50^\circ$; 8246 reflections independent, 3145 assigned to be observed [$I > 2\sigma(I)$], full-matrix least squares refinement on F^2 with 560 parameters converged at $R1/wR2$ -values of 0.111/0.260; empirical absorption correction (Ψ -scans) resulted in min./max. transmission factors of 0.9097/0.9985, the max./min. residual electron density was 1.68/−0.67 10^{-6} e pm⁻³.

Crystal structure of *mer*- $\{\text{Mn}(\text{I})(\text{CO})_3[\text{P}(\text{C}_7\text{H}_7)_2(\eta^2\text{-C}_7\text{H}_7)]\}$ (**6c**)

$\text{C}_{24}\text{H}_{21}\text{IMnO}_3\text{P}$, dark red plate with dimensions $0.18 \times 0.5 \times 0.10$ mm, crystallizes in the orthorhombic space group $\text{Pna}2_1$ with the lattice parameters a = 1421.09(12), b = 1156.56(10), c = 1439.12(13) pm, V = 2365.3(4) 10^6 pm³, Z = 4, μ = 1.953 mm⁻¹; 3535 reflections collected in the range $2^\circ \leq 2\theta \leq 55^\circ$; 3003 reflections independent, 2390 assigned to be observed [$I > 2\sigma(I)$], full-matrix least squares refinement on F^2 with 272 parameters converged at $R1/wR2$ -values of 0.067/0.185, Flack parameter 0.01(5), empirical absorption correction (Ψ -scans) resulted in min./max. transmission factors of 0.2198 / 0.2687, the max./min. residual electron density was 0.935/−1.263 10^{-6} e pm⁻³.

Crystallographic Data (excluding structure factors) for the structures of **3** and **6c** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-196160 (**3**) and CCDC-196161 (**6c**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: int. Code+(1223) 336-033; e-mail: deposit@chemcrs.cam.ac.uk).

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