

Cationic carbonylmanganese complexes of the olefinic ligand tri(1-cyclohepta-2,4,6-trienyl)phosphane, $P(C_7H_7)_3$

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Dedicated to Professor Dr. Dr. h.c. mult. E.O. Fischer on the occasion of his 85th birthday

Abstract

A series of tetrafluoroborate salts of carbonylmanganese cations was obtained which contain the olefinic phosphane, $P(C_7H_7)_3$ (**1**). Whereas **1** is a conventional two-electron phosphane ligand ($[P]$) in $\{Mn(CO)_5[P]\}BF_4$ (**2**)—as in the neutral bromide or trifluoroacetate complexes, *cis*- $\{Mn(X)(CO)_4[P]\}BF_4$ ($X = Br$ (**4b**), CF_3COO (**4d**)) and *mer,trans*- $\{Mn(X)(CO)_3[P]\}BF_4$ ($X = Br$ (**5b**), CF_3COO (**5d**))—it is transformed into a four-electron chelate ligand ($[P']$) if **4b** and **5b** react with $AgBF_4$ to give *cis*- $\{Mn(CO)_4[P']\}BF_4$ (**7**) and *mer,trans*- $\{Mn(CO)_3[P']\}BF_4$ (**8**), respectively, ($[P'] = P(C_7H_7)_2(\eta^2-C_7H_7)$). An analogous halide abstraction by $AgBF_4$ converts *mer*- $\{Mn(I)(CO)_3[P']\}$ (**6c**) into *fac*- $\{Mn(CO)_3[P']\}BF_4$ (**9**) which contains the phosphane as a six-electron ligand ($[P'']$) with an η^4 -norcaradienyl ring ($[P''] = P(C_7H_7)_2(\eta^4-C_7H_7)$). The coordinated η^2 -cyclohepta-2,4,6-trienyl substituent in **7** and **8** is displaced by *tert*-butyl isocyanide (L) to give *cis*- $\{Mn(CO)_4[P](L)\}BF_4$ (**10**) and *mer,trans*- $\{Mn(CO)_3[P]_2(L)\}BF_4$ (**11**), respectively. The structures of the new cations have been assigned on the basis of their carbonyl stretching absorption patterns in the IR spectra and by their 1H -, ^{13}C - and ^{31}P -NMR spectra. Single-crystal X-ray structure analyses were carried out for **7** and **9**.

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1. Introduction

We have recently described [1,2] octahedral carbonylmanganese complexes containing the ligand tri(1-cyclohepta-2,4,6-trienyl)phosphane, $P(C_7H_7)_3$ (**1**; $[P]$ if coordinated to a metal). Although the phosphane **1** is able to use its olefinic substituents for coordinative bonding to the metal, it is primarily and preferentially attached to Mn through the lone pair of electrons at the phosphorus atom, thus acting as a conventional two-electron phosphane ligand. In the series of the (neutral) halogeno-substituted carbonylmanganese complexes, only the compounds of the type *mer*- $\{Mn(X)(CO)_3[P(C_7H_7)_2(\eta^2-C_7H_7)]\}$ ($X = Cl, Br, I$) were found to contain a chelating four-electron phosphane ligand [1].

However, cationic carbonylmanganese complexes were expected to form species with olefinic phosphane chelate ligands more readily. We have therefore studied tetrafluoroborate salts of the cations $\{Mn(CO)_n[P]\}^+$ ($n = 5, 4, 3$) which are isosteric with the neutral carbonylchromium compounds $Cr(CO)_n[P]$ ($n = 5, 4, 3$) [3], and we now present reactions in which Mn forms new bonds to either η^2 -olefin or η^4 -diene functionalities, respectively, of the $P(C_7H_7)_3$ ligand.

Only a limited number of cationic complexes containing $P(C_7H_7)_3$ are known at the present time, among them the halfsandwich species $\{(\eta^7-C_7H_7)Mo[P(C_7H_7)_2(\eta^4-C_7H_7)]\}BF_4$ [3], $\{(\eta^6\text{-mesitylene})Os(Cl)[P(C_7H_7)_2(\eta^2-C_7H_7)]\}PF_6$ [4] and $\{(\eta^5-C_5H_5)M[P(C_7H_7)_2(\eta^2-C_7H_7)]\}BF_4$ ($M = Ni, Pd, Pt$) [5], as well as the cage-shaped cations $\{Rh[P(\eta^2-C_7H_7)_3]\}X$ ($X^- = BF_4^-, CF_3COO^-, CF_3SO_3^-$) [6] and $\{M[P(\eta^2-C_7H_7)_3]\}PF_6$ ($M = Pd, Pt$) [7] in which the

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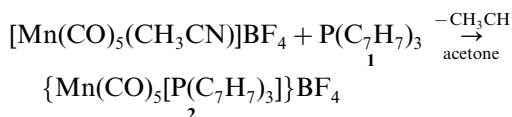
ligand $P(C_7H_7)_3$ behaves as an eight-electron tripod ligand.

2. Results and discussion

2.1. Syntheses and spectroscopy

The established general route to cationic carbonylmanganese complexes involves halide abstraction from $Mn(Br)(CO)_5$ or its derivatives. Heating of $Mn(Br)(CO)_5$ under reflux in acetonitrile leads to *fac*- $[Mn(CO)_3(CH_3CN)_3]^+$ [8], whereas homolytic cleavage of $Mn_2(CO)_{10}$ by $NO^+PF_6^-$ in acetonitrile gives $[Mn(CO)_5(CH_3CN)]^+$ [9].

If the reaction between $[Mn(CO)_5(CH_3CN)]BF_4$ and $P(C_7H_7)_3$ (**1**) in acetone solution is conducted at r.t., a simple displacement of the acetonitrile ligand takes place slowly to give **2**.

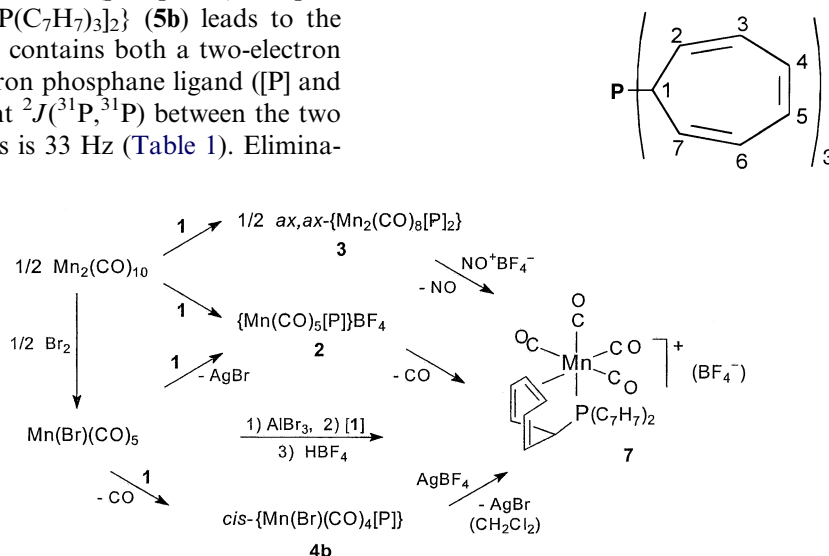


Temperature increase to 50 °C results in liberation of CO and conversion of the two-electron ligand [P] into a chelating four-electron ligand [P'], i.e. **2** is converted to **7**. Several other routes to *cis*- $\{Mn(CO)_4[P(C_7H_7)_2(\eta^2-C_7H_7)]\}BF_4$ (**7**) have been explored, as shown in Scheme 1, among them the cleavage of the di-axially substituted $Mn_2(CO)_{10}$ derivative, *ax,ax*- $\{Mn_2(CO)_8[P(C_7H_7)_3]_2\}$ (**3**) [1] with $NO^+BF_4^-$, and bromide abstraction from *cis*- $\{Mn(Br)(CO)_4[P(C_7H_7)_3]\}$ (**4b**) using $AgBF_4$.

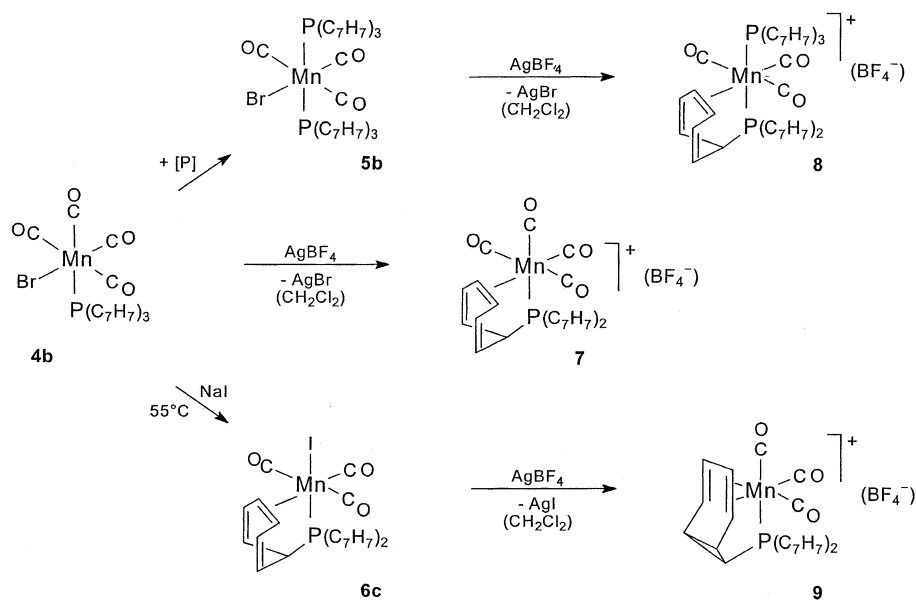
Scheme 2 summarizes the halide abstractions which have been carried out with the help of $AgBF_4$ in CH_2Cl_2 solution. The conversion of **4b** to **7** is straightforward. The analogous reaction of the bis(phosphane) complex *mer,trans*- $\{Mn(Br)(CO)_3[P(C_7H_7)_3]_2\}$ (**5b**) leads to the tetrafluoroborate **8** which contains both a two-electron and a chelating four-electron phosphane ligand ([P] and [P']); the coupling constant $^2J(^{31}P, ^{31}P)$ between the two ligating phosphorus atoms is 33 Hz (Table 1). Elimina-

tion of the iodide ligand from *mer*- $\{Mn(I)(CO)_3[P(C_7H_7)_2(\eta^2-C_7H_7)]\}$ (**6c**) does not result in π -coordination of a second cyclohepta-2,4,6-trienyl substituent, but induces isomerisation of a cyclohepta-2,4,6-trienyl ring into a η^4 -coordinated norcaradienyl substituent to give **9**. It is obvious that in octahedral complexes an η^4 -norcaradienyl ring is more attractive for the three-legged piano-stool fragments $[Mn(CO)_3]^+$ and $[Cr(CO)_3]$ [3] than two η^2 -cyclohepta-2,4,6-trienyl rings. In the case of trigonal-bipyramidal complexes a thermal valence isomerisation of $M(CO)_2[P(C_7H_7)(\eta^2-C_7H_7)_2]$ ($M = Fe, Ru$) to $M(CO)_2[P(C_7H_7)_2(\eta^4-C_7H_7)]$ has been observed in solution [10], which points again to the higher stability of the bicyclic η^4 -norcaradienyl ring ligand.

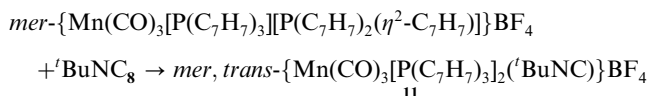
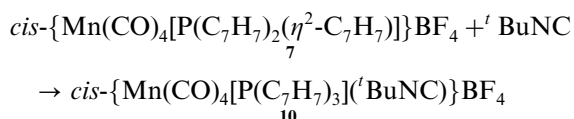
The structures of the cations in **7–9** can be deduced from the pattern of the CO stretching absorptions in the IR spectra (Table 1); the assignments are confirmed in the cases of **7** and **9** by X-ray crystallography (see below). The *mer*- $Mn(CO)_3$ configuration in **8** is expected in analogy to the synthesis of **7** from **4b** (Scheme 2); indeed, the pattern of the $\nu(CO)$ bands in **8** corresponds to that in the neutral halide and pseudo-halide compounds, *mer,trans*- $\{Mn(X)(CO)_3[P]_2\}$ ($X = Cl, Br$ (**5b**), I, NCO, NCS) [2]. In the ^{13}C -NMR spectra of **7–9** the signals of the freely pending and of the one π -coordinated C_7H_7 substituents are distinguishable, the diagnostic upfield shift of the olefinic carbon atoms C^4, C^5 (in **7** and **8**) and of the diene carbons $C^{3''}-C^{6''}$ (in **9**) as a result of π -complexation is particularly remarkable. The ^{31}P -NMR chemical shifts clearly indicate whether a $P(C_7H_7)_3$ ligand contains 3 free cycloheptatrienyl substituents ($\delta(^{31}P) < 60$) or only 2 free in addition to one metal-coordinated C_7H_7 side-arm ($\delta(^{31}P) 110–130$).



Scheme 1. Routes to *cis*- $\{Mn(CO)_4[P(C_7H_7)_2(\eta^2-C_7H_7)]\}BF_4$ (**7**) by introduction of $P(C_7H_7)_3$ (**1**) into carbonylmanganese complexes.

Scheme 2. Synthesis of the tetrafluoroborate salts 7–9 by halide abstraction with AgBF₄.

The chelate ring [P] in 7 and 8 may be opened by suitable two-electron ligands such as isocyanides. Thus, displacement of the π -coordinated double bond by *tert*.butyl isocyanide leads to 10 and 11, respectively.



The ¹³C-NMR spectra of the tri(1-cyclohepta-2,4,6-trienyl)phosphane ligands in 10 and 11 are considerably simplified as compared with 7 and 8, since all C₇H₇ substituents are now freely pending again and equivalent, and the ³¹P-NMR signals are now observed all in the typical range ($\delta(^{31}\text{P}) < 60$) for two-electron [P] ligands. The two ³¹P doublets (${}^2J(\text{P},\text{P}) = 33.0$ Hz) in 8 collapse into a singlet in 11.

As expected, bromide abstraction from 4b and 5b using AgBF₄ (Scheme 1) which leads to the tetrafluoroborate salts 7 and 8, respectively, can be similarly be carried out with AgPF₆. On the contrary, silver

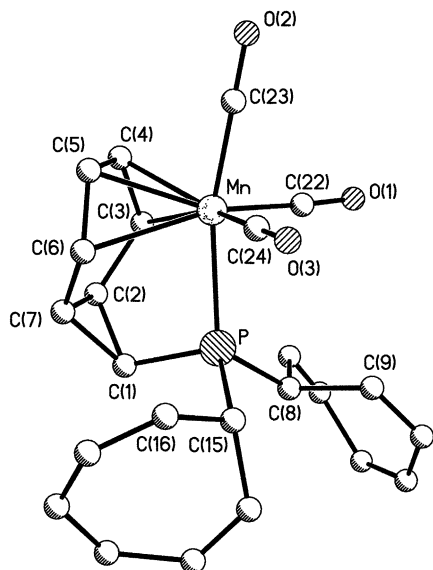
Table 1
Spectroscopic data of the tetrafluoroborate salts 2 and 7–9

Cation ^a (BF ₄ ⁻ salt)	{Mn(CO) ₅ [P]} ⁺ (2)	{Mn(CO) ₄ [P]} ⁺ (7) [2]	{Mn(CO) ₃ [P][P]} ⁺ (8)	{Mn(CO) ₃ [P'']} ⁺ (9)
IR: $\nu(\text{CO})$ (cm ⁻¹) (CH ₂ Cl ₂)	2142w 2078s, 2051s	2102s, 2042w 2026vs, 2004w (<i>cis</i>)	2049w 1974s, 1953br (<i>mer</i>)	2068s 2026s, 1999s (<i>fac</i>)
¹³ C-NMR: δ values (CDCl ₃)				
Phosphane ^{a,b}	[P]	[P]	[P]; [P]	[P'']
C ¹	36.6 [27.2]	38.1 [24.4]	34.4 [25.1]; 37.6 [25.7]	[27.5]
C ² , C ⁷	106.1	107.8, 109.8	100.1; 105.1, 106.1	111.2, 112.0
C ³ , C ⁶	129.4 [10.2]	129.0 [8.2], 129.8 [10.2]	129.0 [9.1]; 128.3 [9.1], 128.8 [9.7]	129.7 [8.9], 130.0 [9.4]
C ⁴ , C ⁵	130.9	130.8, 131.3	130.4, 130.6	131.1
(π -coordinated ring) ^{a,b}		($\eta^2\text{-C}_7\text{H}_7$):	($\eta^2\text{-C}_7\text{H}_7$):	($\eta^4\text{-C}_7\text{H}_7$):
C ^{1'}		37.5 [15.0]	36.9 [15.3]	C ^{1''} 39.0 [40.4]
C ^{2'} , C ^{7'}		136.0	134.9	C ^{2''} , C ^{7''} 14.2 [3.4]
C ^{3'} , C ^{6'}		128.6 [9.4]	128.3	C ^{3''} , C ^{6''} 88.0
C ^{4'} , C ^{5'}		94.5	94.4	C ^{4''} , C ^{5''} 91.8
³¹ P-NMR: δ -values (CDCl ₃)	36.1s	121.6s	42.0d {33.0} ^c 116.5d {33.0} ^c	127.8s

^a Abbreviations: [P] = P(C₇H₇)₃, [P'] = P(C₇H₇)₂($\eta^2\text{-C}_7\text{H}_7$), [P''] = P(C₇H₇)₂($\eta^4\text{-C}_7\text{H}_7$). The ¹³C atoms of the $\eta^2\text{-C}_7\text{H}_7$ cycloheptatrienyl ring are primed, those of the $\eta^4\text{-C}_7\text{H}_7$ norcaradienyl substituent are doubly-primed.

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

^c Coupling constant, [${}^2J(^{31}\text{P}, ^{31}\text{P})$].

Fig. 2. Structure of the cation in **9**.

to phosphorus) assume an almost eclipsed arrangement with respect to the two CO ligands of the equatorial plane. As in the chromium complex, the distance between phosphorus and the η^4 -norcaradienyl ring (P–C(1) 177.7(6) pm in **9**, cf. 178.6(2) pm in the chromium compound [3]) is remarkably short; comparable P–C bond lengths are observed in phosphonium

Table 3
Selected bond lengths (pm) and bond angles ($^\circ$) in the cation of *cis*-{Mn(CO)₄[P(C₇H₇)₂(η^2 -C₇H₇)]}BF₄ (**7**)

Bond lengths			
Mn–P	232.7(3)	C(22)–O(1)	113.1(15)
Mn–C(22)	184.9(15)	C(23)–O(2)	112.0(13)
Mn–C(23)	186.7(13)	C(24)–O(3)	112.3(13)
Mn–C(24)	181.9(13)	C(25)–O(4)	111.2(13)
Mn–C(25)	188.5(13)	C(1)–C(2)	148.8(17)
Mn–C(4)	213.5(12)	C(1)–C(7)	152.5(19)
Mn–C(5)	242.3(12)	C(2)–C(3)	133.6(17)
P–C(1)	186.6(12)	C(3)–C(4)	145.6(18)
P–C(8)	184.1(12)	C(5)–C(6)	143.0(17)
P–C(15)	190.9(13)	C(6)–C(7)	131.0(17)
C(4)–C(5)	138.2(16)		
Bond angles			
P–Mn–C(22)	177.0(5)	Mn–C(22)–O(1)	178.3(13)
P–Mn–C(23)	90.7(4)	Mn–C(23)–O(2)	175.0(12)
P–Mn–C(24)	92.7(4)	Mn–C(24)–O(3)	175.7(11)
P–Mn–C(25)	88.3(4)	Mn–C(25)–O(4)	176.0(11)
P–Mn–C(4)	87.5(3)	Mn–C(4)–C(5)	73.0(7)
P–Mn–C(5)	88.6(3)	Mn–C(5)–C(4)	74.0(7)
P–C(1)–C(2)	107.6(8)	Mn–P–C(1)	111.1(4)
P–C(1)–C(7)	111.9(9)	Mn–P–C(8)	112.6(4)
P–C(8)–C(9)	117.7(9)	Mn–P–C(15)	113.3(4)
P–C(8)–C(14)	114.3(9)	C(22)–Mn–C(23)	89.6(6)
P–C(15)–C(16)	112.3(8)	C(22)–Mn–C(24)	90.3(6)
P–C(15)–C(21)	118.0(10)	C(22)–Mn–C(25)	91.6(6)
C(4)–Mn–C(5)	33.1(4)	C(23)–Mn–C(24)	86.6(5)
C(23)–Mn–C(25)	175.8(5)	C(24)–Mn–C(25)	89.4(5)

salts such as [P(C₇H₇)₄]⁺ (181.5–183.6 pm [14]) and [PPh₄]⁺ (178–180 pm [14,15]). The norcaradienyl substituent in **9** is present in the chair conformation, with dihedral angles C(1)–C(2)–C(7)/C(2)–C(3)–C(6)–C(7) of 113.9 $^\circ$ and C(2)–C(3)–C(6)–C(7)/C(3)–C(4)–C(5)–C(6) of 145.1 $^\circ$. The manganese atom forms a nearly perfect plane with the carbonyl carbon atoms C(22), C(24) and the center of the diene system C(3)–C(4)–C(5)–C(6). The inner carbon atoms C(4) and C(5) of the diene unit in the cation of **9** are closer to the metal (Mn–C(4) 212.9(8) and Mn–C(5) 213.5(7) pm) than the corresponding carbon atoms in the neutral chromium analogue (Cr–C 216.0(2) and 216.9(2) [3]), and the manganese–carbonyl distances (Mn–C(22) 183.6(9) and Mn–C(24) 182.8(9) pm) are also slightly shorter than the analogous Cr–CO distances (185.7(2) and 186.0(2) pm [3]), indicating slightly stronger manganese–carbon bonds as a result of the reduced charge density in the cation and therefore slightly reduced back-bonding to the π -ligands.

Table 4
Selected bond lengths (pm) and bond angles ($^\circ$) in the cation of *fac*-{Mn(CO)₃[P(C₇H₇)₂(η^4 -C₇H₇)]}BF₄ (**9**)

Bond lengths			
Mn–P	232.50(18)	C(22)–O(1)	113.7(11)
Mn–C(22)	183.6(9)	C(23)–O(2)	112.3(9)
Mn–C(23)	184.4(8)	C(24)–O(3)	113.5(10)
Mn–C(24)	182.8(9)	C(1)–C(2)	152.7(11)
Mn–C(3)	225.6(8)	C(1)–C(7)	151.7(10)
Mn–C(4)	212.9(8)	C(2)–C(3)	149.0(11)
Mn–C(5)	213.5(7)	C(2)–C(7)	150.5(13)
Mn–C(6)	228.8(7)	C(3)–C(4)	141.0(10)
P–C(1)	177.7(6)	C(4)–C(5)	141.2(15)
P–C(8)	183.5(7)	C(5)–C(6)	138.9(11)
P–C(15)	187.1(7)	C(6)–C(7)	146.0(11)
Bond angles			
P–Mn–C(22)	87.8(2)	C(2)–C(3)–C(4)	118.5(8)
P–Mn–C(23)	165.7(3)	Mn–C(22)–O(1)	176.5(8)
P–Mn–C(24)	85.6(2)	Mn–C(23)–O(2)	179.7(8)
P–Mn–C(3)	80.6(2)	Mn–C(24)–O(3)	179.5(8)
P–Mn–C(4)	113.3(2)	Mn–P–C(1)	101.6(2)
P–Mn–C(5)	110.6(2)	Mn–P–C(8)	121.1(2)
P–Mn–C(6)	76.92(19)	Mn–P–C(15)	118.2(2)
P–C(1)–C(2)	111.3(5)	C(22)–Mn–C(23)	83.8(4)
P–C(1)–C(7)	107.9(5)	C(22)–Mn–C(24)	100.3(4)
P–C(8)–C(9)	111.7(6)	C(23)–Mn–C(24)	84.6(4)
P–C(8)–C(14)	118.0(6)	C(1)–P–C(8)	107.0(4)
P–C(15)–C(16)	114.6(5)	C(1)–P–C(15)	108.9(3)
P–C(15)–C(21)	114.4(5)	C(8)–P–C(15)	99.5(3)
C(1)–C(2)–C(3)	121.0(6)	C(2)–C(7)–C(6)	114.4(7)
C(1)–C(2)–C(7)	60.0(5)	C(3)–C(2)–C(7)	113.0(7)
C(1)–C(7)–C(2)	60.7(5)	C(3)–C(4)–C(5)	116.6(8)
C(1)–C(7)–C(6)	121.8(6)	C(4)–C(5)–C(6)	117.8(7)
C(2)–C(1)–C(7)	59.3(5)	C(5)–C(6)–C(7)	119.4(8)

3. Conclusion

We have shown that mononuclear carbonylmanganese complexes may contain tri(cyclohepta-2,4,6-trienyl)phosphane (**1**) either as a regular two-electron phosphane ligand ([P]), or as a chelate ligand in which one of the 3 seven-membered C₇H₇ substituents acts as a η²-monoolefin ([P']) or η⁴-diene ([P'']) functionality in addition to the lone pair of electrons at the phosphorus atom. At least 2 cyclohepta-2,4,6-trienyl substituents remain freely pending. The function of P(C₇H₇)₃ as two-, four- or six-electron ligand ([P], [P'] or [P'']), respectively) is clearly indicated by characteristic chemical shifts in the ¹H-, ¹³C- and ³¹P-NMR spectra.

4. Experimental

All reactions were carried out in Schlenk vessels under an atmosphere of dry argon; the solvents were routinely dried under reflux (hexane, cyclohexane, diethyl ether and tetrahydrofuran over Na/K alloy, CH₂Cl₂ over P₄O₁₀) and then distilled in a stream of argon. Acetone was dried over molecular sieve and distilled under argon.

The ligand P(C₇H₇)₃ (**1**) was prepared from P(SiMe₃)₃ and tropylium bromide (1:3) according to the established procedure [14]. The parent carbonylmanganese complex, Mn₂(CO)₁₀, is commercially available and can easily be converted into Mn(Br)(CO)₅ by a stoichiometric reaction with Br₂ in either CCl₄ or CS₂ solution [16,17]. The synthesis of the neutral phosphane complexes *ax,ax*-{Mn₂(CO)₈[P(C₇H₇)₃]₂} (**3**) [1], *cis*-{Mn(Br)(CO)₄[P(C₇H₇)₃]} (**4b**) [1], *mer,trans*-{Mn(Br)(CO)₃[P(C₇H₇)₃]₂} (**5b**) [1,2] and *mer,trans*-{Mn(I)(CO)₃[P(C₇H₇)₂(η²-C₇H₇)]} (**6c**) [1] has been described before.

4.1. Preparation of the trifluoroacetate complexes **4d** and **5d**

4.1.1. *cis*-{Mn(OOC-CF₃)(CO)₄[P(C₇H₇)₃]} (**4d**)

Silver trifluoroacetate (33 mg, 0.15 mmol) was added to a yellow solution of the bromide **4b** in 10 ml of CH₂Cl₂, and the solution was stirred for 15 min. at r.t. The reaction mixture was filtered over Na₂SO₄ to remove the precipitate of AgBr. The clear yellow solution was concentrated to a volume of ca. 2 ml and chromatographed over silica (in hexane). Elution with hexane-CH₂Cl₂ (1:2) produced a yellow zone which contained 75 mg (86%) of the trifluoroacetate **4d**, dec. 88 °C.

¹H-NMR (C₆D₆, 25 °C): δ = 2.66 (dt, 3H, H¹), 5.08 (m, 6H, H²,H⁷), 5.96 (m, 6H, H³,H⁶) and 6.25 (m, 6H, H⁴,H⁵).

4.1.2. *mer,trans*-{Mn(OOC-CF₃)(CO)₃[P(C₇H₇)₃]} (**5d**)

In analogy to the synthesis of **4d**, silver trifluoroacetate (29 mg, 0.13 mmol) was added to the solution of the bromide **5b** (110 mg, 0.13 mmol) in 10 ml of CH₂Cl₂, and the solution was stirred for 20 min at r.t. The precipitate of AgBr was removed by filtration over Na₂SO₄, and the solvent CH₂Cl₂ was evaporated under vacuum. The yellow, oily residue was taken up in 5 ml of hexane and the mixture exposed to ultrasound until a yellow solid had been formed. The hexane solution was discarded, and the ultrasound treatment repeated. The product **5d** was finally dried in a high vacuum. Yellow powder, dec. 115 °C. Yield 78 mg (70%).

¹H-NMR (C₆D₆, 25 °C): δ = 2.65 (dt, 3H, H¹), 5.35 (m, 6H, H²,H⁷), 6.09 (m, 6H, H³,H⁶) and 6.28 (m, 6H, H⁴,H⁵).

4.2. Preparation of the tetrafluoroborate salts **2** and **7–11**

4.2.1. {Mn(CO)₅[P(C₇H₇)₃]}BF₄ (**2**)

A solution of 113 mg (0.37 mmol) P(C₇H₇)₃ (**1**) in 2 ml of acetone was added to the yellow solution of 120 mg (0.37 mmol) {Mn(CO)₅(CH₃CN)}BF₄ in 10 ml of acetone, and the combined solution was stirred for 24 h at r.t. The solvent was evaporated under vacuum, the residue rinsed repeatedly with small portions (0.5 ml) of Et₂O in order to remove traces of oily impurities, and the yellow product finally dried in a high vacuum. Yield 208 mg (96%), dec. 87 °C.

¹H-NMR (CDCl₃, 25 °C): δ = 2.55 (dt, 3H, H¹), 4.98 (m, 6H, H²,H⁷), 6.38 (m, 6H, H³,H⁶) and 6.59 (m, 6H, H⁴,H⁵).

4.2.2. *cis*-{Mn(CO)₄[P(C₇H₇)₂(η²-C₇H₇)]}BF₄ (**7**)

a) Thermal decarbonylation of {Mn(CO)₅[P(C₇H₇)₃]}BF₄ (**2**): a yellow solution containing 95 mg (0.16 mmol) **2** in 10 ml of acetone was stirred for 2 h at 50 °C. The solvent was then evaporated and the residue dissolved in CH₂Cl₂. The CH₂Cl₂ solution was filtered over Na₂SO₄, concentrated and kept at -30 °C over night for crystallization. Yield 42 mg (47%).

b) Reaction of *ax,ax*-{Mn₂(CO)₈[P(C₇H₇)₃]₂} (**3**) with NOBF₄: the yellow solution of 132 mg (0.14 mmol) **3** in 10 ml of CH₂Cl₂ was treated with 33 mg (0.28 mmol) NOBF₄. Gas evolution (NO) was observed and the colour became light-yellow. The cloudy reaction mixture was stirred for 1 h, then filtered over Na₂SO₄ and brought to dryness. The oily product was washed twice with Et₂O (1 ml), dried under high vacuum and redissolved in 2–3 ml of CH₂Cl₂. Crystallization over night at -30 °C gave 83 mg (53%) **7**.

c) Stepwise synthesis starting from $\text{Mn}(\text{Br})(\text{CO})_5$: An orange solution of 137 mg (0.50 mmol) $\text{Mn}(\text{Br})(\text{CO})_5$ in 20 ml of cyclohexane was treated with a tenfold excess of AlBr_3 (1.33 g, 5 mmol) and the mixture heated under reflux for 1 h. Then $\text{P}(\text{C}_7\text{H}_7)_3$ (**1**) (152 mg, 0.5 mmol, dissolved in 5 ml of cyclohexane) was added and the reaction mixture stirred at r.t. for another hour. Finally, an equimolar amount (0.5 mmol) HBF_4 , dissolved in 10 ml of water, was added in small portions, which caused the precipitation of **7**. The whole reaction mixture was filtered over Na_2SO_4 , the filtrate brought to dryness and the yellow residue **7** washed with small amounts (0.5 ml) of water. Yield 95 mg (35%), dec. 134 °C.

d) Halide abstraction from *cis*- $\{\text{Mn}(\text{Br})(\text{CO})_4[\text{P}(\text{C}_7\text{H}_7)_3]\}$ (**4b**): silver tetrafluoroborate, AgBF_4 (56 mg, 0.29 mmol), was added to a yellow solution of 160 mg (0.29 mmol) **4b** in 10 ml of CH_2Cl_2 which was then stirred for 30 min. at ambient temperature. The precipitate of AgBr was removed by filtration over Na_2SO_4 , and the clear yellow solution either concentrated for crystallization (at –30 °C over night) or brought to dryness. The yellow powder was washed with small portions (0.5 ml) of Et_2O and dried in a high vacuum. Yield 155 mg (96%).

$^1\text{H-NMR}$ (CDCl_3 , 25 °C): $\delta = 2.14$ (dt, 2H, H^1), 5.05 and 5.26 (m,m, $2 \times 2\text{H}$, H^2 and/or H^7), 5.28 (m, 1H, $\text{H}^{1'}$), 6.15 (m, 4H, H^2, H^7 and H^4, H^5), 6.36 (m, 4H, H^3, H^6), 6.55 (m, 4H, H^4, H^5), 6.60 (m, 2H, $\text{H}^{3'}, \text{H}^{6'}$).

4.2.3. *mer,trans*-

$\{\text{Mn}(\text{CO})_3[\text{P}(\text{C}_7\text{H}_7)_3][\text{P}(\text{C}_7\text{H}_7)_2(\eta^2\text{-C}_7\text{H}_7)]\}\text{BF}_4$ (**8**)

A yellow solution containing 225 mg (0.27 mmol) **5b** in 15 ml of CH_2Cl_2 was stirred in the presence of 53 mg (0.27 mmol) AgBF_4 for 30 min. The reaction mixture was concentrated and the precipitate of AgBr removed by filtration over silica. CH_2Cl_2 was used to wash out traces of unreacted **5b**, before **8** was eluted from the silica column with $\text{CH}_2\text{Cl}_2/\text{THF}$ (1:1). The product **8** is an orange solid, dec. 140 °C. Yield 210 mg (93%).

$^1\text{H-NMR}$ (CDCl_3): $\text{P}(\text{C}_7\text{H}_7)_3$ ligand: $\delta = 2.11$ (dt, 3H, H^1), 4.87 (m, 6H, H^2, H^7), 6.39 (m, 6H, H^3, H^6), 6.60 (m, 6H, H^4, H^5). $\text{P}(\text{C}_7\text{H}_7)_2(\eta^2\text{-C}_7\text{H}_7)$ ligand: $\delta = 2.02$ (m, 2H, H^1), 5.05 (m, 1H, $\text{H}^{1'}$), 5.09 and 5.23 (m,m, $2 \times 2\text{H}$, H^2 and/or H^7), 5.77 (m, 2H, H^4, H^5), 6.18 (m, 2H, H^2, H^7), 6.39 (m, 4H, H^3, H^6), 6.60 (m, 4H, H^4, H^5), 6.62 (m, 2H, $\text{H}^{3'}, \text{H}^{6'}$).

4.2.4. *fac*- $\{\text{Mn}(\text{CO})_3[\text{P}(\text{C}_7\text{H}_7)_2(\eta^4\text{-C}_7\text{H}_7)]\}\text{BF}_4$ (**9**)

A red solution of 142 mg (0.25 mmol) **6c** in 10 ml of CH_2Cl_2 reacted instantaneously with AgBF_4 (48 mg, 0.25 mmol), as indicated by the precipitation of AgI . After 30 min the reaction mixture was concentrated and

added on top of a chromatography column filled with silica (in hexane). Elution with CH_2Cl_2 gave traces of unreacted **6c**, and finally **9** was eluted with acetone. Orange solid, dec. 128 °C. Yield 118 mg (89%). Crystallization from CH_2Cl_2 led to single-crystals which were suitable for X-ray structure analysis.

$^1\text{H-NMR}$ (CDCl_3): $\delta = 1.49$ (m, 1H, $\text{H}^{1''}$), 1.53 (m, 2H, $\text{H}^{2''}, \text{H}^{7''}$), 3.45 (dt, 2H, H^1), 4.99 (m, 2H, $\text{H}^{3''}, \text{H}^{6''}$), 5.15 and 5.24 (m,m, $2 \times 2\text{H}$, H^2 and/or H^7), 6.17 (m, 2H, $\text{H}^{4''}, \text{H}^{5''}$), 6.39 (m, 4H, H^3, H^6), 6.55 (m, 4H, H^4, H^5). (The doubly-primed hydrogen atoms refer to the η^4 -norcaradienyl substituent).

4.2.5. *cis*- $\{\text{Mn}(\text{CO})_4[\text{P}(\text{C}_7\text{H}_7)_3](^t\text{BuNC})\}\text{BF}_4$ (**10**)

A yellow solution containing 80 mg (0.14 mmol) **7** and 16 μl (0.14 mmol) *tert*-butyl isocyanide in 5 ml of acetone was stirred at 45 °C over night (14h). The solution was brought to dryness in a high vacuum, the residue washed twice with 2 ml of Et_2O and dried under high vacuum. Yellow solid, dec. 116 °C, yield 85 mg (95%).

$^1\text{H-NMR}$ (CDCl_3 , 25 °C): $\delta = 1.33$ (s, 9H, CH_3), 2.43 (dt, 3H, H^1), 5.02 (m, 6H, H^2, H^7), 6.37 (m, 6H, H^3, H^6), 6.61 (m, 6H, H^4, H^5).

4.2.6. *mer,trans*- $\{\text{Mn}(\text{CO})_3[\text{P}(\text{C}_7\text{H}_7)_3]_2(^t\text{BuNC})\}\text{BF}_4$ (**11**)

A yellow solution of 58 mg (0.07 mmol) **8** and 8 μl (0.07 mmol) *tert*-butyl isocyanide in 5 ml of CH_2Cl_2 was stirred at r.t. for 4 h. Work-up (as described for **10**) gave 58 mg (90%) of a yellow solid, dec. 139 °C.

$^1\text{H-NMR}$ (CDCl_3 , 25 °C): $\delta = 1.27$ (s, 9H, CH_3), 2.38 (dt, 3H, H^1), 4.91 (m, 6H, H^2, H^7), 6.36 (m, 6H, H^3, H^6), 6.61 (m, 6H, H^4, H^5).

4.3. Crystal structures of **7** and **9**

The intensity data were collected on a Siemens P4 diffractometer with $\text{Mo-K}\alpha$ -radiation ($\lambda = 71.073$ pm, graphite monochromator) at r.t. The hydrogen atoms are in calculated positions. All non-hydrogen atoms were refined with anisotropic temperature factors. The hydrogen atoms were refined applying the riding model with fixed isotropic temperature factors.

cis- $\{\text{Mn}(\text{CO})_4[\text{P}(\text{C}_7\text{H}_7)_2(\eta^2\text{-C}_7\text{H}_7)]\}\text{BF}_4$ (**7**), $\text{C}_{25}\text{H}_{21}\text{BF}_4\text{O}_4\text{PMn}$, irregular block of dimensions $0.18 \times 0.14 \times 0.12$ mm, monoclinic, space group $P2_1/c$; $a = 1692.5(2)$, $b = 1768.7(2)$, $c = 1669.6(2)$ pm, $\beta = 95.494(8)^\circ$, $Z = 8$, $\mu = 0.655$ mm^{-1} ; 10 207 reflections collected in the range $2\text{--}25^\circ$ in ϑ , 8623 reflections independent, 3823 reflections assigned to be observed ($I > 2\sigma(I)$). Full-matrix least-squares refinement with 617 parameters, R_1/wR_2 -values 0.110/0.281, absorption correction (ψ -scans), min./max. transmission factors 0.3179/0.3687; max./min. residual electron density $1.481/ -0.671$ $\text{e} \cdot 10^{-6}$ pm^{-3} .

trans-{Mn(CO)₃[P(C₇H₇)₂(η⁴-C₇H₇)]}BF₄ (**9**), C₂₄H₂₁BF₄O₃PMn, yellow prism of dimensions 0.20 × 0.16 × 0.12 mm, orthorhombic, space group *P*2₁2₁2₁; *a* = 904.3(2), *b* = 1157.6(2), *c* = 2240.3(4) pm, *Z* = 4, $\mu = 0.687 \text{ mm}^{-1}$; 3033 reflections collected in the range 2–25° in ϑ , 2848 reflections independent, 2473 reflections assigned to be observed ($I > 2\sigma(I)$). Full-matrix least-squares refinement with 309 parameters, *R*₁/*wR*₂-values 0.064/0.174, absorption correction (ψ -scans), min./max. transmission factors 0.0621/0.2451; max./min. residual electron density 0.798/−0.465 e 10^{−6} pm^{−3}.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 205067 and 205066 for structures **7** and **9**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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