

# Synthesis and Reactivity of Bromo-*mer*-tricarbonyl-*trans*-bis[tri(1-cyclohepta-2,4,6-trienyl)phosphane]-manganese, $\text{MnBr}(\text{CO})_3[\text{P}(\text{C}_7\text{H}_7)_3]_2$

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The reaction of  $\text{Mn}(\text{X})(\text{CO})_5$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) with 2 equivalents of tri(1-cyclohepta-2,4,6-trienyl)phosphane,  $\text{P}(\text{C}_7\text{H}_7)_3$  (**1**; [P] if coordinated to a metal) led stepwise first to *cis*- $\{\text{Mn}(\text{X})(\text{CO})_4[\text{P}]\}$  ( $\text{X} = \text{Cl}$  (**4a**),  $\text{Br}$  (**4b**),  $\text{I}$  (**4c**)) and then to *mer,trans*- $\{\text{Mn}(\text{X})(\text{CO})_3[\text{P}]_2\}$  ( $\text{X} = \text{Cl}$  (**5a**),  $\text{Br}$  (**5b**),  $\text{I}$  (**5c**)). Nucleophilic displacement of the bromo ligand from (**5b**) by one-, three- or five-electron ligands gave the pseudohalide complexes *mer,trans*- $\{\text{Mn}(\text{X})(\text{CO})_3[\text{P}]_2\}$  ( $\text{X} = \text{NCO}$  (**5d**) and  $\text{NCS}$  (**5e**)), the acetylacetonate derivative  $\text{Mn}(\text{acac})(\text{CO})_2[\text{P}]_2$  (**6**) and the halfsandwich complexes  $\text{CpMn}(\text{CO})_2[\text{P}]$  (**7**) or  $\text{TpMn}(\text{CO})_3$  (**8**). According to the X-ray structure determination of **5e** the thiocyanate ligand is N-coordinated.

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

## Introduction

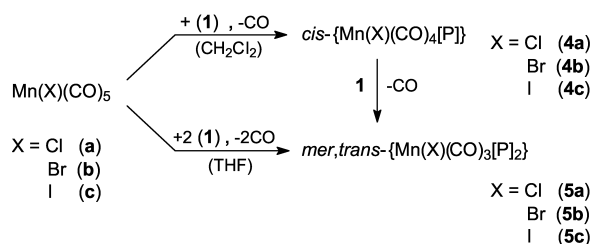
Due to steric constraints, bulky tertiary phosphanes ( $\text{PR}_3$ ) tend to occupy *trans* positions in octahedral carbonylmanganese complexes if more than one  $\text{PR}_3$  ligand is coordinated. We have confirmed this rule for some mononuclear carbonylmanganese compounds with the voluminous ligand tri(1-cyclohepta-2,4,6-trienyl)phosphane,  $\text{P}(\text{C}_7\text{H}_7)_3$  (**1**), which contains flexible olefinic side arms [1]. If only one equivalent of **1** is available per metal atom, one or more olefinic bonds can eventually be used for coordination to make **1** a chelate-type ligand.

## Results and Discussion

### Syntheses and spectroscopy

Under photochemical conditions the dinuclear complex  $\text{Mn}_2(\text{CO})_{10}$  reacts with  $\text{P}(\text{C}_7\text{H}_7)_3$  (**1**; [P] if coordinated to a metal) in toluene solution under stepwise substitution of the two axial carbonyl ligands [1] to give *ax*- $\{\text{Mn}_2(\text{CO})_9[\text{P}]\}$  (**2**) and *ax,ax*- $\{\text{Mn}_2(\text{CO})_8[\text{P}]_2\}$  (**3**). The analogous stepwise reaction of the mononuclear pentacarbonyl manganese halides,  $\text{Mn}(\text{X})(\text{CO})_5$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ), with one or two equivalents of the phosphane **1** takes place (without photolysis) in boiling dichloromethane or tetrahy-

drofuran solution to give at first the yellow *cis*-tetracarbonylmanganese halides **4a-c** [1] and then the yellow *mer*-tricarbonylmanganese halides **5a-c**. The halogeno ligand X occupies a position *cis* to the [P] ligand(s).

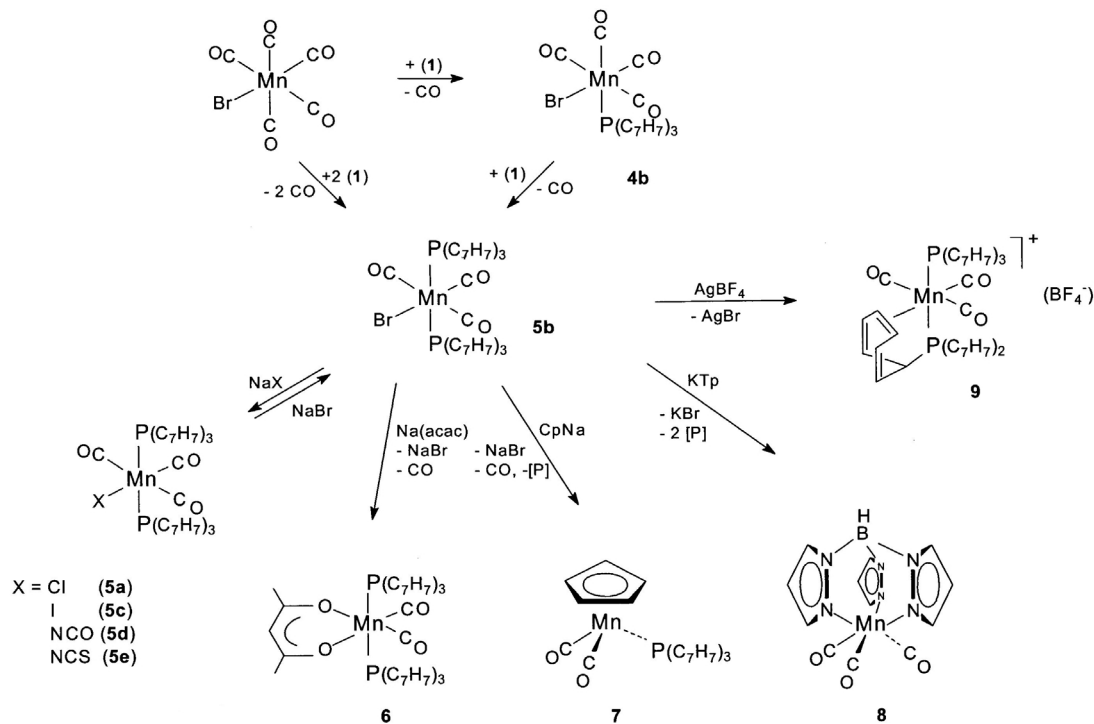


Nucleophilic displacement of bromide in **5b** by other halide or pseudohalide (one-electron) ligands leaves the coordination geometry intact (**5a,c** and **5d,e**). Three-electron ligands such as acetylacetonate eliminate one CO ligand, five-electron ligands such as cyclopentadienyl both one CO and one [P] ligand in addition to bromide (**6** and **7**). However, the five-electron anions hydro-tris(1-pyrazolyl)borate (Tp) and hydro-tris(3,5-dimethyl-1-pyrazolyl)borate (Tp\*) displace both *tert*.phosphane ligands [P] to give the known tricarbonylmanganese halfsandwich compounds  $\text{TpMn}(\text{CO})_3$  [**2**] (**8**) and  $\text{Tp}^*\text{Mn}(\text{CO})_3$  [2,3] which have been thoroughly studied and character-

Table 1. Spectroscopic data.

	X = Cl ( <b>5a</b> )	Br ( <b>5b</b> )	I ( <b>5c</b> )	<i>mer, trans</i> - $\{\text{Mn}(\text{X})(\text{CO})_3[\text{P}]_2\}$		$(\eta^3\text{-acac})\text{Mn}(\text{CO})_2[\text{P}]$ ( <b>6</b> )	$\text{CpMn}(\text{CO})_2[\text{P}]$ ( <b>7</b> ), see [5]
				NCO ( <b>5d</b> )	NCS ( <b>5e</b> )		
IR: $\nu(\text{CO})$ [ $\text{cm}^{-1}$ ] (hexane)	2088w 2008s 1957s	2087w 2002s 1952s	2084w 1987s 1934s	2063m 1964vs 1927s	2056m 1956vs 1921s	1923s 1844s acac Me 28.7 CH 100.9 CO 189.9	1934s 1869s Cp 81.5
$^{13}\text{C}$ NMR <sup>a</sup> $\delta$ values ( $\text{C}_6\text{D}_6$ )							
$\text{C}^1$	37.3t [11.2]	37.8t [11.9]	38.8t [12.1]	36.9t [11.9]	36.8t [11.9]	36.2d [17.9]	40.0d [26.0]
$\text{C}^2, \text{C}^7$	112.2	112.5	112.1	110.6	110.1	113.5	115.9
$\text{C}^3, \text{C}^6$	127.3t [4.3]	127.2t [4.5]	127.0t [4.5]	127.3t [6.8]	127.1t [6.7]	126d [4.5]	126.5d [5.3]
$\text{C}^4, \text{C}^5$	130.2	130.2	130.2	130.3	130.5	130.2	130.6
$^{31}\text{P}$ NMR <sup>a</sup>	54.3	51.0	47.3	56.1	56.7	56.6	89.2

<sup>a</sup> The signals of  $\text{C}^1$  and  $\text{C}^3, \text{C}^6$  are either triplets (**5a-e**) or doublets (**6,7**). All  $^{13}\text{C}$  NMR signals without quotation of a  $J(\text{P},\text{C})$  coupling constant (in square brackets) and all  $^{31}\text{P}$  NMR signals are singlets.



ized by X-ray crystallography in connection with their Tc and Re analogues [4]. The halfsandwich complex  $\text{CpMn}(\text{CO})_2[\text{P}(\text{C}_7\text{H}_7)_3]$  (**7**) had been prepared from  $\text{CpMn}(\text{CO})_3$  by photo-induced decarbonylation and structurally characterized [5].

If the bromo ligand is removed from **5b** by the action of  $\text{AgBF}_4$ , the octahedral coordination sphere is stabilized by incorporation of an olefinic double bond

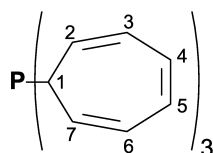
of a cyclohepta-2,4,6-trienyl substituent. The tetrafluoroborate salt **9** is described in the following publication [6] together with other cationic carbonylmanganese complexes.

The spectroscopic characterization of the new complexes **5a-e**, **6** and **7** is given in Table 1.

In the IR spectra, the *mer*- $\text{Mn}(\text{CO})_3$  unit in **5a-e** gives rise to a typical pattern of 3 absorptions [7–9].

The  $\nu(\text{CO})$  frequencies indicate that the electron acceptor capacity of the halogeno- or pseudohalogeno ligand decreases in the order  $\text{X} = \text{Cl} > \text{Br} > \text{I} > \text{NCO} > \text{NCS}$ . The pseudohalides, NCO and NCS, are coordinated exclusively *via* N, as confirmed by an X-ray structure determination of the thiocyanato complex **5e**.

The  $^{31}\text{P}$  NMR singlets of the new complexes in Table 1 show that the  $\text{P}(\text{C}_7\text{H}_7)_3$  ligands are coordinated exclusively through the lone pair of electrons at phosphorus ( $\delta^{31}\text{P} < 100$ ) and that the two  $\text{P}(\text{C}_7\text{H}_7)_3$  ligands in **5a-e** are equivalent, *i.e.* occupying *trans*-positions in the octahedral structure. Under the influence of the two phosphorus nuclei, the  $^{13}\text{C}$  signals observed for the positions  $\text{C}^1$  and  $\text{C}^3$ ,  $\text{C}^6$  of the freely-pending cycloheptatrienyl rings appear as pseudotriplets. Only one type of  $\text{C}_7\text{H}_7$  ring is observed in the  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectra.



#### Crystal structure analysis of *mer,trans*- $\{\text{Mn}(\text{NCS})(\text{CO})_3[\text{P}(\text{C}_7\text{H}_7)_3]_2\}$ (**5e**)

The slightly distorted octahedral coordination sphere of **5e** is shown in Fig. 1; relevant bond distances and angles are collected in Table 2.

The bond lengths  $\text{Mn}-\text{P}$  (av. 233.7(17) pm) of the two *trans*-phosphane ligands in **5e** are intermediate between those in *ax,ax*- $\{\text{Mn}_2(\text{CO})_8[\text{P}]_2\}$  (av. 227.9(4) pm [1]) and that in *cis*- $\{\text{Mn}(\text{Cl})(\text{CO})_4[\text{PPh}_3]\}$  (239.8(4) pm [10]) where the strong *trans*-influence of the carbonyl ligand in *trans*-position to  $\text{PPh}_3$  leads to an elongated  $\text{Mn}-\text{P}$  bond. Comparable  $\text{Mn}-\text{P}$  bond distances are 226.4(8) pm (av.) in *mer,trans*- $\{\text{Mn}(\text{Br})(\text{CO})_3[\text{PPh}(\text{OMe})_2]_2\}$  [11] and 226.7(2) pm in *mer,trans*- $\{\text{Mn}(\text{H})(\text{CO})_3[\text{PPh}_3]_2\}$  [12]. The angle  $\text{P}(1)-\text{Mn}-\text{P}(2)$  in **5e** ( $172.31(6)^\circ$ ) indicates a slight inclination of the two axial [P] ligands towards the equatorial thiocyanate (Fig. 1), whereas the two *trans*-carbonyl ligands in the equatorial plane (*cis* to NCS) are bent away ( $\text{C}(43)-\text{Mn}-\text{C}(45)$   $174.6(3)^\circ$ ). Analogous  $\text{P}-\text{Mn}-\text{P}$  angles were reported for *mer,trans*- $\{\text{Mn}(\text{Br})(\text{CO})_3[\text{PPh}(\text{OMe})_2]_2\}$  (av.  $178.9^\circ$  [11]) and *mer,trans*- $\{\text{Mn}(\text{H})(\text{CO})_3[\text{PPh}_3]_2\}$  ( $169.66(8)^\circ$  [12]). The (12) “right angles” around the central atom Mn in the distorted octahedral framework of **5e** are all observed between 85 and  $95^\circ$  (Table 2).

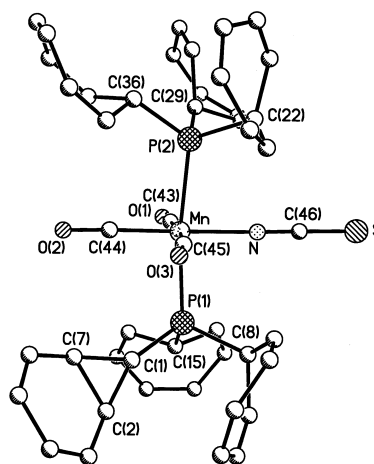


Fig. 1. Molecular Structure of **5e**.

Table 2. Selected bond lengths and angles in thiocyanato-*mer*-tricarbonyl-*trans*-bis[tri(1-cyclohepta-2,4,6-trienyl)phosphane]-manganese (**5e**).

Distances			
Mn-P(1)	232.72(16)	P(1)-C(1)	181.2(6)
Mn-P(2)	234.70(17)	P(1)-C(8)	186.9(6)
Mn-N	200.1(5)	P(1)-C(15)	184.9(6)
Mn-C(43)	184.9(7)	P(2)-C(22)	187.1(7)
Mn-C(44)	178.1(6)	P(2)-C(29)	184.5(6)
Mn-C(45)	185.2(6)	P(2)-C(36)	184.7(6)
C(43)-O(1)	114.6(8)	C(1)-C(2)	148.5(5)
C(44)-O(2)	115.9(7)	C(1)-C(7)	148.5(9)
C(45)-O(3)	113.4(7)	C(2)-C(7)	153.7(10)
C(46)-N	115.1(8)		
C(46)-S	160.4(7)		
Angles			
P(1)-Mn-P(2)	172.31(6)	Mn-P(1)-C(1)	112.96(19)
P(1)-Mn-N	87.03(15)	Mn-P(1)-C(8)	114.1(2)
P(1)-Mn-C(43)	92.83(19)	Mn-P(1)-C(15)	118.0(2)
P(1)-Mn-C(44)	93.19(19)	Mn-P(2)-C(22)	112.4(2)
P(1)-Mn-C(45)	85.52(18)	Mn-P(2)-C(29)	113.6(2)
P(2)-Mn-N	85.88(15)	Mn-P(2)-C(36)	118.2(2)
P(2)-Mn-C(43)	89.89(19)	Mn-C(43)-O(1)	176.3(6)
P(2)-Mn-C(44)	94.1(2)	Mn-C(44)-O(2)	178.5(5)
P(2)-Mn-C(45)	92.40(19)	Mn-C(45)-O(3)	171.2(5)
C(43)-Mn-C(45)	174.6(3)	Mn-N-C(46)	172.1(6)
C(44)-Mn-N	176.6(2)	N-C(46)-S	179.8(8)
C(1)-C(2)-C(7)	58.9(4)	C(2)-C(1)-C(7)	62.3(5)
C(1)-C(7)-C(2)	58.8(4)		

The mean deviation from the equatorial plane (Mn, C(43), C(44), C(45), N) is only 1.5 pm.

The N-coordinated thiocyanato ligand in **5e** ( $\text{Mn}-\text{N}$  200.1(5) pm) is almost exactly linear ( $\text{Mn}-\text{C}(44)-\text{S}$   $179.8(8)^\circ$ ), but slightly deviates from linearity at the N atom ( $\text{Mn}-\text{N}-\text{C}(44)$   $172.1(6)^\circ$ ). Very similar parameters

were observed for *fac*- $\{\text{Mn}(\text{NCS})(\text{CO})_3(\text{dppm})\}$   $\text{dppm} = \text{bis}(\text{diphenylphosphinyl})\text{methane}$ ; ( $\text{Mn}-\text{N}$  201.6(4) pm,  $\text{N}-\text{C}-\text{S}$  178.9(4)° and  $\text{Mn}-\text{N}-\text{C}$  175.2(4)°) [13]. The  $\text{N}-\text{C}$  and  $\text{C}-\text{S}$  distances are typical for linear terminal thiocyanato ligands [*cf.* 14]. In both thiocyanato-manganese complexes, the bond distance between Mn and the CO ligand *trans* to NCS is significantly shortened as compared with that to the two carbonyl groups *cis* to the NCS ligand (178.1(6) pm (*trans*) versus av. 185.05(7) pm (*cis*) in **5e**; *cf.* 178.9(4) pm (*trans*) versus av. 182.35(5) pm (*cis*) in *fac*- $\{\text{Mn}(\text{NCS})(\text{CO})_3(\text{dppm})\}$  [13]).

The P—C bond lengths to the 1-cyclohepta-2,4,6-trienyl substituents in **5e** are comparable (av. 185.6(7) pm) with one exception: the distance P(1)—C(1) is shorter (181.2(6) pm), and the ring substituent involving C(1) is present as the norcaradienyl isomer with an isosceles triangle C(1),C(2),C(7) attached to the phosphorus atom; the transannular distance C(2)—C(7) (153.7(10) pm) corresponds to a single bond. This isomerisation can be ascribed to the steric situation in the solid state, as the  $^1\text{H}$  and  $^{13}\text{C}$  solution NMR spectra show only one type of seven-membered ring substituents,  $\text{C}_7\text{H}_7$ . The cyclohepta-2,4,6-trienyl substituents of the  $\text{P}(\text{C}_7\text{H}_7)_3$  ligands above and below the equatorial plane deviate by about 5° from the expected eclipsed arrangement.

## Experimental Section

The starting complex  $\text{Mn}(\text{Br})(\text{CO})_5$  was obtained by the action of  $\text{Br}_2$  on commercial  $\text{Mn}_2(\text{CO})_{10}$  in  $\text{CCl}_4$  or  $\text{CS}_2$  solution [15, 16], and *cis*- $\{\text{Mn}(\text{Br})(\text{CO})_4[\text{P}(\text{C}_7\text{H}_7)_3]\}$  (**4b**) was prepared from  $\text{Mn}(\text{Br})(\text{CO})_5$  according to the established procedure [1]. All reactions were carried out in Schlenk tubes under argon, using dry and oxygen-free solvents. The instrumentation is given in Ref. [1].

### Syntheses

a) Halogeno-*mer*-tricarbonyl-*trans*-bis[tri(1-cyclohepta-2,4,6-trienyl)phosphane]-manganese, *mer,trans*- $\{\text{Mn}(\text{X})(\text{CO})_3[\text{P}]_2\}$  ( $\text{X} = \text{Cl}$  (**5a**),  $\text{Br}$  (**5b**),  $\text{I}$  (**5c**))

Method A: The THF solution (20 ml) containing 0.47 mmol  $\text{Mn}(\text{X})(\text{CO})_5$  and 285 mg (0.94 mmol)  $\text{P}(\text{C}_7\text{H}_7)_3$  (**1**) was heated under reflux for 3 h. The solvent was then removed under high-vacuum, the remaining oil taken up in toluene, and the toluene solution filtered over  $\text{Na}_2\text{SO}_4$  in order to remove insoluble components. The toluene extracts were concentrated, and 10 ml of hexane was added. Upon stirring, the products **5a-c** separated as yellow solids. The slightly yellow hexane phase was discarded and **5a-c** dried

in a high vacuum at room temperature; the yields are in the range of  $80 \pm 10\%$ .

$\text{X} = \text{Cl}$  (**5a**), yield 313 mg (85%), dec. 146 °C.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = 3.08$  (dt, 3H,  $\text{H}^1$ ), 5.57 (m, 12H,  $\text{H}^{2,7}$ ), 6.09 (m, 12H,  $\text{H}^{3,6}$ ), 6.29 (m, 12H,  $\text{H}^{4,5}$ ).

$\text{X} = \text{Br}$  (**5b**), yield 346 mg (89%), dec. 155 °C.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = 3.07$  (dt, 6H,  $\text{H}^1$ ), 5.46 (m, 12H,  $\text{H}^{2,7}$ ), 6.08 (m, 12H,  $\text{H}^{3,6}$ ), 6.28 (m, 12H,  $\text{H}^{4,5}$ ).

$\text{X} = \text{I}$  (**5c**), yield 304 mg (74%), dec. 161 °C.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = 3.11$  (dt, 6H,  $\text{H}^1$ ), 5.54 (m, 12H,  $\text{H}^{2,7}$ ), 6.09 (m, 12H,  $\text{H}^{3,6}$ ), 6.29 (m, 12H,  $\text{H}^{4,5}$ ).

Method B: Equimolar amounts (0.24 mmol) of the complex *cis*- $\{\text{Mn}(\text{X})(\text{CO})_4[\text{P}(\text{C}_7\text{H}_7)_3]\}$  (**4a**, **4b**, **4c**) and of  $\text{P}(\text{C}_7\text{H}_7)_3$  (**1**) (0.24 mmol) were dissolved in 20 ml of THF, and the solution was kept under reflux for 3 h. Work-up as in method A) gave pure complexes in yields of 154 mg (82%) (**5a**), 183 mg (92%) (**5b**) and 157 mg (75%) (**5c**).

Method C: A yellow solution containing 108 mg (0.13 mmol) of the bromide **5b** in 15 ml of acetone was kept under reflux (55°) for 24 h in the presence of a 20-fold (2.6 mmol) excess of either NaCl (152 mg) or NaI (390 mg). Acetone was evaporated, toluene (10 ml) was added and the suspension filtered over  $\text{Na}_2\text{SO}_4$  in order to remove the salts  $\text{NaX}$ . The solvent toluene was then evaporated in a high vacuum, the remaining yellow oil taken up in hexane (5–10 ml) and treated in the ultrasonic bath, until the complexes **5a** or **5c**, respectively, separated as yellow solids. The supernatant hexane phase was discarded and the product dried in a high vacuum. Yields: 76 mg (74%) **5a** and 75 mg (66%) **5c**.

b) Pseudohalogeno-*mer*-tricarbonyl-*trans*-bis[tri(1-cyclohepta-2,4,6-trienyl)phosphane]-manganese, *mer,trans*- $\{\text{Mn}(\text{X})(\text{CO})_3[\text{P}]_2\}$  ( $\text{X} = \text{NCO}$  (**5d**),  $\text{NCS}$  (**5e**))

The yellow solution of 150 mg (0.18 mmol) **5b** in 20 ml of acetone was heated to reflux (55 °C) for 24 h, after a 30-fold (5.4 mmol) excess of either  $\text{NaNCO}$  (350 mg) or  $\text{NaNCS}$  (438 mg) had been added. The reaction mixture was brought to dryness and the residue extracted repeatedly with toluene. The combined toluene extracts were filtered over  $\text{Na}_2\text{SO}_4$ . Evaporation of toluene gave yellow solids of **5d** and **5e**, respectively.

$\text{X} = \text{NCO}$  (**5d**), yield 97 mg (68%), dec. 142 °C.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = 2.79$  (dt, 6H,  $\text{H}^1$ ), 5.38 (m, 12H,  $\text{H}^{2,7}$ ), 6.08 (m, 12H,  $\text{H}^{3,6}$ ), 6.39 (m, 12H,  $\text{H}^{4,5}$ ).

$\text{X} = \text{NCS}$  (**5e**), yield 104 mg (72%), dec. 147 °C.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = 2.85$  (dt, 6H,  $\text{H}^1$ ), 5.33 (m, 12H,  $\text{H}^{2,7}$ ), 6.11 (m, 12H,  $\text{H}^{3,6}$ ), 6.40 (m, 12H,  $\text{H}^{4,5}$ ).

c) Acetylacetonato-*cis*-dicarbonyl-*trans*-bis[tri(cyclohepta-2,4,6-trienyl)phosphane]-manganese,  $\text{Mn}(\text{acac})(\text{CO})_2[\text{P}(\text{C}_7\text{H}_7)_3]_2$  (**6**)

A twenty-fold excess of sodium acetylacetonate,  $\text{Na}(\text{acac})$  (244 mg, 2.00 mmol), was added to a solution of 83 mg

(0.1 mmol) of **5b** in 15 ml of acetone. The yellow reaction mixture was stirred overnight (14 h) at 50 °C and then brought to dryness in a high vacuum. The residue was extracted repeatedly with toluene, the combined toluene extracts concentrated to a volume of 2 ml and chromatographed over silica. A yellow zone was eluted with pentane /  $\text{CH}_2\text{Cl}_2$  (3:1) which contained 47 mg (57%) of **6**, dec. 144 °C.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  = 1.56 (s, 6H, Me), 2.52 (dt, 6H,  $\text{H}^1$ ), 5.07 (s, 1H, CH-acac), 5.63 (m, 12H,  $\text{H}^{2,7}$ ), 6.13 (m, 12H,  $\text{H}^{3,6}$ ), 6.36 (m, 12H,  $\text{H}^{4,5}$ ).

d) Crystal structure of *mer,trans*- $\{\text{Mn}(\text{NCS})(\text{CO})_3[\text{P}(\text{C}_7\text{H}_7)_3]_2\}$  (**5e**)

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

Complex **5e** (orange prism of dimensions  $0.25 \times 0.18 \times 0.12$  mm) crystallizes in the monoclinic space group  $P2_1/n$   $a$  = 1061.43(15),  $b$  = 1888.96(16),  $c$  = 2262.98(18) pm,

$\beta$  = 96.525(7)°,  $Z$  = 4,  $\mu$  = 0.567  $\text{mm}^{-1}$ ; 9810 reflections collected in the range 2°–25° in  $\vartheta$ , 7857 reflections independent, 5821 reflections assigned to be observed ( $I > 2\sigma(I)$ ); full matrix least squares refinement with 488 parameters,  $R1/wR2$ -values 0.0997/0.3092, absorption correction ( $\psi$ -scans), min./max. transmission factors 0.4214/0.4421; max./min. residual electron density 3.22/-0.528  $\text{e} \cdot 10^{-6} \text{pm}^{-3}$ .

Crystallographic data (excluding structure factors) for the structure of **5e** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-196162. 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@chemcrys.cam.ac.uk).

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