

# Synthesis and electrochemistry of polymeric complexes with cationic manganese carbonyl fragments coordinated to polyphosphazenes through nitrile ligands

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## Abstract

The cyclotriphosphazenes  $N_3P_3(O-C_6H_4-R-4)_5(O-C_6H_4-CN-4)$ ,  $R = H$  (**1a**) or  $^tBu$  (**1b**), reacted with *trans*-[MnBr(CO)<sub>2</sub>(dppm){P(OPh)<sub>3</sub>}] and TlPF<sub>6</sub> in dichloromethane to give the monocationic complexes  $\{[N_3P_3(O-C_6H_4-R-4)_5(O-C_6H_4-CN)]Mn(CO)_2(dppm)\{P(OPh)_3\}\}[PF_6]$ ,  $R = H$  (**2a**) or  $^tBu$  (**2b**). Similarly, the hexafunctionalized cyclotriphosphazene  $N_3P_3(O-C_6H_4-CN-4)_6$  (**4**) reacted in CH<sub>2</sub>Cl<sub>2</sub> with *trans*-[MnBr(CO)<sub>2</sub>(dppm){P(OPh)<sub>3</sub>}] in the presence of TlPF<sub>6</sub>, and with *fac*-[Mn(OCIO<sub>3</sub>)(CO)<sub>3</sub>(PP)] (PP = dppm or dppe), to give the hexacationic complexes  $[N_3P_3\{(O-C_6H_4-CN)Mn(CO)_2(dppm)\{P(OPh)_3\}\}_6][PF_6]_6$  (**5a**),  $[N_3P_3\{(O-C_6H_4-CN)Mn(CO)_3(PP)\}_6](ClO_4)_6$  (PP = dppm, **6a**, or dppe, **6b**). In all cases, the changes in the <sup>31</sup>P NMR chemical shifts for the phosphorus of the phosphazene ring, the molar conductivities in acetone solution and the cyclic voltammograms in CH<sub>2</sub>Cl<sub>2</sub> of the complexes containing the *trans*-Mn(CO)<sub>2</sub>(dppm){P(OPh)<sub>3</sub>} moiety showed a good correlation with the number of metal–carbonyl units bonded to the phosphazene in the mono- and hexa-cationic complexes. Similarly, the nitrile-containing phosphazene polymers  $\{NP(O-C_6H_5)_{2-x}(O-C_6H_4-CN-4)_x\}_n$  ( $x = 0.06$ , **7a**;  $x = 0.28$ , **7b**), reacted with the corresponding manganese carbonyls to give the complexes  $\{NP(O-C_6H_5)_{2-x}\{[O-C_6H_4-CN]Mn(CO)_2(dppm)\{P(OPh)_3\}\}_x\}_n$  ( $x = 0.06$ , **8a**;  $x = 0.28$ , **8b**) and  $\{NP(O-C_6H_5)_{1.94}[O-C_6H_4-CN]Mn(CO)_3(dppe)(ClO_4)_{0.06}\}_n$  (**9**). The cyclic voltammogram of the polymers **8a** and **8b** in CH<sub>2</sub>Cl<sub>2</sub> showed a very extended oxidation wave with large  $\Delta E_p$ .

**Keywords:** Manganese; Phosphazene; Complexes; Carbonyls; Polymeric; Cationic

## 1. Introduction

It has been shown that polyphosphazene molecules bearing potential coordinating groups can form complexes with the transition metals [1,2]. However, the carbonyl complexes that have been prepared are scarce and all of them are neutral. Moreover, apart from several arenetricarbonylchromium derivatives [3], most of the known complexes contain phosphines [4]. Here we describe the synthesis and characterization of new mono- and poly-cationic compounds having manganese carbonyl moieties coordinated to polyphosphazenes through nitrile groups.

## 2. Results and discussion

The cyclotriphosphazenes  $N_3P_3(O-C_6H_4-R-4)_5(O-C_6H_4-CN-4)$ ,  $R = H$  (**1a**) or  $^tBu$  (**1b**), bearing one nitrile group reacted with the complex *trans*-[MnBr(CO)<sub>2</sub>(dppm){P(OPh)<sub>3</sub>}] in CH<sub>2</sub>Cl<sub>2</sub> in the presence of Tl[PF<sub>6</sub>] to give the cationic complexes  $\{[N_3P_3(O-C_6H_4-R-4)_5(O-C_6H_4-CN)]Mn(CO)_2(dppm)\{P(OPh)_3\}\}[PF_6]$  (**2a**, **2b**) (Fig. 1), that were isolated as orange microcrystalline solids, and characterized by the analytical and spectroscopic data (Experimental and Table 1). The <sup>31</sup>P NMR spectra (Table 1) showed that the phosphorus atoms of the phosphazene ring are sensitive to the coordination of the manganese fragment to the terminal CN group and there is a decrease of ca. 0.25 ppm in the position of the pseudo-singlet (AB<sub>2</sub> system) on going from **1** to **2**.

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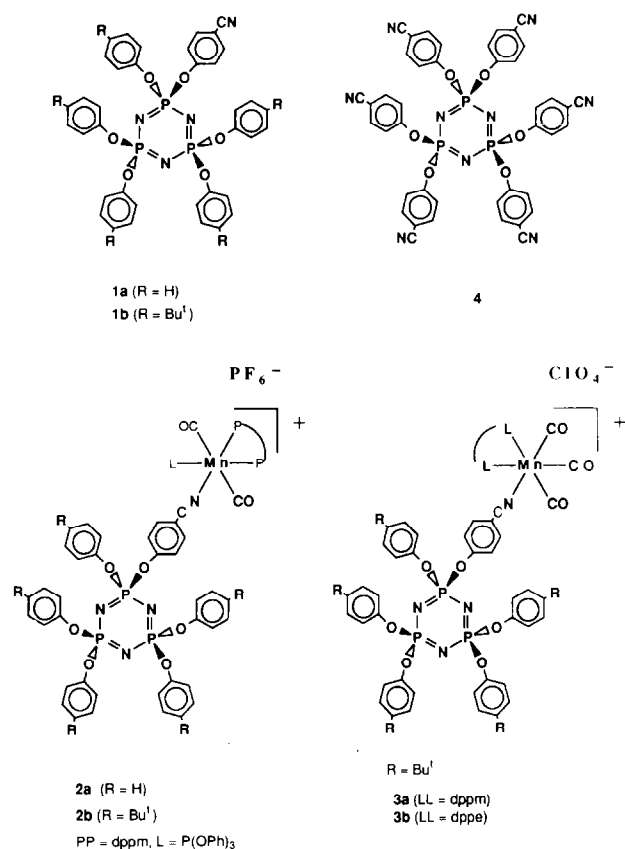


Fig. 1. Structural formulae of compounds **1a**, **1b**, **2a**, **2b**, **3a**, **3b**, and **4**.

Similar variations in the chemical shifts of the phosphorus of the phosphazene ring were observed upon reaction of **1b** with the neutral perchlorato complexes *fac*-[Mn(OCIO<sub>3</sub>)(CO)<sub>3</sub>(PP)] (PP = bis(diphenylphos-

Table 2  
Molar conductivities (*A*) in acetone at 20°C

Compound	<i>A</i> <sup>a</sup>	<i>A</i> <sub>0</sub> <sup>b</sup>	Slope	<i>R</i> <sup>c</sup>
<i>trans</i> -[Mn(NCMe)(CO) <sub>2</sub> (dppm)- {P(OPh) <sub>3</sub> }] [PF <sub>6</sub> ]	143	164	885	0.89
<i>fac</i> -[Mn(NCMe)(CO) <sub>3</sub> (dppe)]ClO <sub>4</sub>	141	160	853	0.99
<b>2a</b>	133	156	1060	0.92
<b>2b</b>	150	174	1042	0.98
<b>5a</b>	397	526	5228	0.98
<b>5b</b> (1:1)	114	148	1486	0.99
<b>5c</b> (1:2)	190	242	2260	0.98
<b>5d</b> (1:4)	303	415	4811	0.99
<b>6a</b>	343	479	5830	0.98
<b>6b</b>	303	407	4407	0.97

<sup>a</sup> At 5 × 10<sup>-4</sup> M.

<sup>b</sup> At infinite dilution.

<sup>c</sup> Linear coefficient.

phino)methane (dppm) or 1,2-bis(diphenylphosphino)ethane (dppe)), in CH<sub>2</sub>Cl<sub>2</sub>, to generate solutions of the cationic complexes [(N<sub>3</sub>P<sub>3</sub>(O-C<sub>6</sub>H<sub>4</sub>-<sup>t</sup>Bu-4)<sub>5</sub>(O-C<sub>6</sub>H<sub>4</sub>-CN))Mn(CO)<sub>3</sub>(PP)]ClO<sub>4</sub> (PP = dppm, **3a**, or dppe, **3b**). The IR ν(CO) in CH<sub>2</sub>Cl<sub>2</sub>, **3a**: 2043 s, 1978 s, 1959 s; **3b**: 2042 s, 1966 s, br and <sup>31</sup>P NMR spectra of the solutions (Table 1) clearly show the formation of the cationic manganese *fac*-tricarbonyls (Fig. 1) with a decrease in the chemical shifts of the ring phosphorus of 0.2–0.3 ppm (see Table 1). This is probably caused by the positive charge induced on the ring phosphorus atoms by the cationic carbonyl moiety. The cyclic triphosphazene N<sub>3</sub>P<sub>3</sub>(O-C<sub>6</sub>H<sub>4</sub>-<sup>t</sup>Bu)<sub>6</sub> carrying no CN groups does not react with *fac*-[Mn(OCIO<sub>3</sub>)(CO)<sub>3</sub>(PP)] in CH<sub>2</sub>Cl<sub>2</sub>. Therefore, it can be assumed that the Mn fragments in **3a** and **3b** are only coordinated to the nitrile groups.

Table 1  
<sup>31</sup>P NMR data<sup>a</sup>

Compound	{NP(OR) <sub>2</sub> } <sub>n</sub>	dppm or dppe	P(OPh) <sub>3</sub>
<b>1a</b>	9.00 <sup>b</sup>		
<b>1b</b>	9.02 <sup>c</sup>		
<b>2a</b>	8.70	21.04 dd (50.1, 34.4);	169.04 dd (58.1, 50.1)
<b>2b</b>	8.79	20.9 dd (49.8, 35.0);	169.00 dd (58.2, 49.8)
<b>3a</b>	8.72	13.7	
<b>3b</b>	8.7	74.6	
<b>4</b>	7.47		
<b>5a</b>	5.69	20.5 dd (50.4, 35.3)	169.9 dd (58.4, 50.4)
<b>6a</b>	5.55	14.1	
<b>6b</b>	5.86	74.7	
<b>7a</b>	-19.34 <sup>d</sup>		
<b>8a</b>	-16.3; -19.3; -21.0	20.9, dd (44.7, 36.2)	169.2, dd (48.8, 44.7)
<b>8b</b>	-19.3; -21.0	20.9 (br)	169.2 (br)
<b>9</b>	-16.5; -19.4; -21.47	74.19	

<sup>a</sup> In CH<sub>2</sub>Cl<sub>2</sub>, δ in ppm, *J* (Hz) in italics.

<sup>b</sup> 9.48 in C<sub>6</sub>D<sub>6</sub>.

<sup>c</sup> 9.68 in C<sub>6</sub>D<sub>6</sub>.

<sup>d</sup> -18.32 in C<sub>6</sub>D<sub>6</sub>.

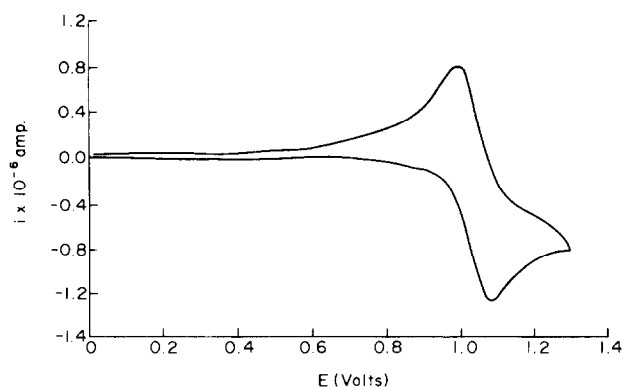


Fig. 2. Cyclic voltammogram of **5a** in  $\text{CH}_2\text{Cl}_2$  at  $100 \text{ mV s}^{-1}$  between 0 and 1.3 V.

The molar conductivities of the complexes **2a** and **2b** at  $20\text{--}22^\circ\text{C}$  in acetone solution at concentrations between  $10^{-3}$  and  $10^{-4} \text{ M}$  varied linearly with the square root of the concentration, and the values obtained for  $\Lambda_0$ , were these expected for 1:1 electrolytes (Table 2) [5]. We found very similar values for the smaller cationic manganese carbonyl complexes *trans*- $[\text{Mn}(\text{NCMe})(\text{CO})_2(\text{dppm})\{\text{P}(\text{OPh})_3\}][\text{PF}_6]$  and *fac*- $[\text{Mn}(\text{NCMe})(\text{CO})_3(\text{PP})]\text{ClO}_4$  (see Table 2).

Cyclic voltammograms (CV) of the two phosphazene-based cationic complexes with the *trans*-dicarbonyl moiety **2a** and **2b** (Table 3) showed (Fig. 2) a diffusion-controlled oxidation wave ( $i_{pa}/v^{1/2} = \text{constant}$ ), not totally chemically reversible ( $i_{pa}/i_{pc} = 0.9$  at  $50 \text{ mV s}^{-1}$ ), with an  $E^0$  very close to that of the related complex *trans*- $[\text{Mn}(\text{NCMe})(\text{CO})_2(\text{dppm})\{\text{P}(\text{OPh})_3\}][\text{PF}_6]$ , 1.05 V [6].

The reactions of the phosphazene mononitrile **1** with the manganese carbonyl precursors were extended to the hexafunctionalized  $\text{N}_3\text{P}_3(\text{O}-\text{C}_6\text{H}_4-\text{CN})_6$  (**4**) (see Fig. 1).

Table 3  
CV data<sup>a</sup>

Compound	$E^0$ (at $50 \text{ mV s}^{-1}$ )	$\Delta E_p$ ( $20\text{--}300 \text{ mV s}^{-1}$ )
<b>2a</b>	1.02	65–91
<b>2b</b>	1.03	80–127
<b>5a</b>	0.99	70–80
<b>8a</b>	1.05	550–660

<sup>a</sup> SCE as reference. Under the same experimental conditions ferrocene has  $E^0 = 0.46 \pm 0.01 \text{ V}$ ,  $\Delta E_p = 70 \text{ mV}$ .

This compound reacted in  $\text{CH}_2\text{Cl}_2$  with an excess of *trans*- $[\text{MnBr}(\text{CO})_2(\text{dppm})\{\text{P}(\text{OPh})_3\}]$  in the presence of  $\text{Ti}[\text{PF}_6]$  to give the stable hexacationic complex  $[\text{N}_3\text{P}_3\{(\text{O}-\text{C}_6\text{H}_4-\text{CN})\text{Mn}(\text{CO})_2(\text{dppm})\{\text{P}(\text{OPh})_3\}\}_6][\text{PF}_6]_6$  (**5a**), that was isolated as an orange solid (Fig. 3). The IR spectrum in the carbonyl stretching region of this complex in solution and in the solid state showed slow partial isomerization of the *trans*-dicarbonyl group to *cis*-dicarbonyl. After ca. 18 months in the solid state, ca. 27% of the  $\text{Mn}(\text{CO})_2$  moieties had become *cis*, as determined by  $^{31}\text{P}$  NMR spectroscopy. This spontaneous isomerization also occurs with the analogous mononuclear cationic manganese dicarbonyl *trans*- $[\text{Mn}(\text{NCMe})(\text{CO})_2(\text{dppm})\{\text{P}(\text{OPh})_3\}][\text{PF}_6]$ .

The hexanitride **4** also reacted with the neutral perchlorato complexes *fac*- $[\text{Mn}(\text{OCIO}_3)(\text{CO})_3(\text{PP})]$  (PP = dppm or dppe) in  $\text{CH}_2\text{Cl}_2$  to generate, respectively, the cationic complexes  $[\text{N}_3\text{P}_3\{(\text{O}-\text{C}_6\text{H}_4-\text{CN})\text{Mn}(\text{CO})_3(\text{PP})\}_6][\text{ClO}_4]_6$  (PP = dppm, **6a**; PP = dppe, **6b**) that were isolated as yellow microcrystalline solids. In all cases, the analytical and spectroscopic data were in accord with the formulations shown in Fig. 3.

The  $^{31}\text{P}$  NMR spectra of the hexacationic complex **5a** showed that the singlet corresponding to the three P atoms of the phosphazene ring (Table 1) was 1.78 ppm

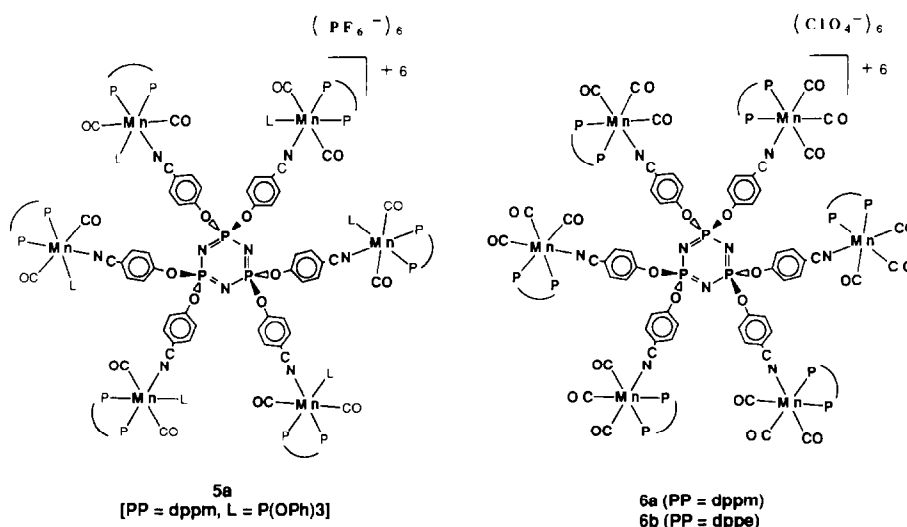


Fig. 3. Structural formulae of complexes **5a**, **6a** and **6b**.

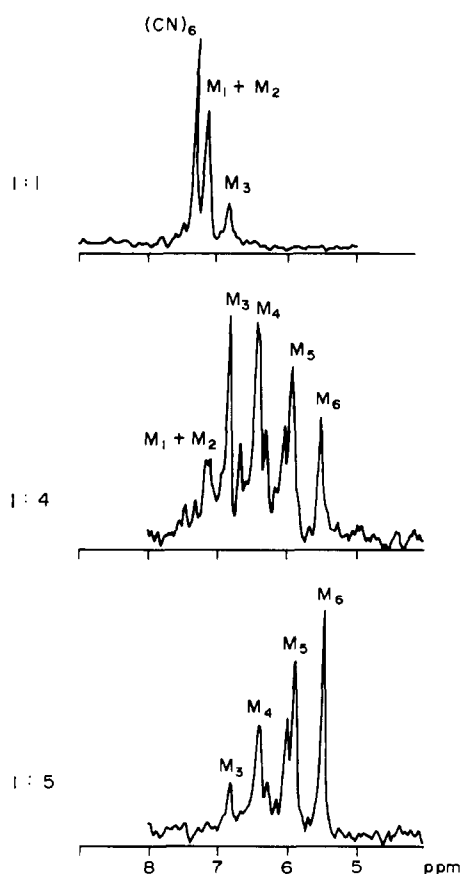


Fig. 4.  $^{31}\text{P}$  NMR spectra corresponding to the final mixture of the reaction of **4** with 1, 4 and 5 equiv. of *fac*- $[\text{Mn}(\text{O}_3\text{ClO})(\text{CO})_3(\text{dppm})]$ .  $(\text{CN})_6$  stands for  $\text{N}_3\text{P}_3(\text{O}-\text{C}_6\text{H}_4-\text{CN}-4)_6$  and  $\text{M}_x$  stands for  $[\text{N}_3\text{P}_3(\text{O}-\text{C}_6\text{H}_4-\text{CN})_{6-x}\{(\text{O}-\text{C}_6\text{H}_4-\text{CN})-\text{Mn}(\text{CO})_3(\text{dppm})\}_x](\text{ClO}_4)_x$ .

lower than in the free hexanitride **4**. This is roughly six times the decrease observed on the formation of the monocationic complex **2a** from the mononitrile phosphazene **1a**. Similar values were measured for **6a** and **6b**.

In contrast, it has been reported [7] that the coordination of various neutral metal–ligand fragments to the hexaphosphine phosphazene  $\text{N}_3\text{P}_3(\text{O}-\text{C}_6\text{H}_4-\text{PPh}_2)_6$  occurs without significant changes in the chemical shifts of the phosphazene ring phosphorus resonances.

The clear change in the chemical shifts of the phosphorus atoms of the phosphazene ring on coordination of the manganese carbonyl fragments to the nitrile

Table 4  
Resonances of the phosphazene  $^{31}\text{P}$  NMR signals assigned to each partially charged metal complexes formed in the reaction of  $\text{N}_3\text{P}_3(\text{O}-\text{C}_6\text{H}_4-\text{CN}-4)_6$  with several manganese carbonyl compounds

Metal carbonyl fragment, $\text{MnL}_n$	$\text{M}_0^a$	$\text{M}_1$	$\text{M}_2$	$\text{M}_3$	$\text{M}_4$	$\text{M}_5$	$\text{M}_6$
<i>fac</i> - $[\text{Mn}(\text{CO})_3(\text{dppm})]$	7.4	7.1	7.1	6.8	6.4	6.0	5.5
<i>fac</i> - $[\text{Mn}(\text{CO})_3(\text{dppe})]$	7.4	7.2	7.2	6.9	6.4	6.1	5.8
<i>trans</i> - $[\text{Mn}(\text{CO})_2(\text{dppm})\{\text{P}(\text{O}^i\text{Ph})_3\}]$	7.4	7.2	7.1	6.8	6.5	6.1	5.8

<sup>a</sup> In  $\text{CH}_2\text{Cl}_2$ ,  $\delta$  in ppm.  $\text{M}_2$  is for the complex  $[\text{N}_3\text{P}_3(\text{O}-\text{C}_6\text{H}_4-\text{CN})_{6-x}(\text{O}-\text{C}_6\text{H}_4-\text{CN}-\text{MnL}_n)_x]^{2+}$ .

groups of **4** made it possible to follow the reactions leading to the hexacationic complexes **5** and **6** by  $^{31}\text{P}$  NMR spectroscopy (see Fig. 4). The spectra for the reactions of **4** with 6 equiv. of the metal carbonyls and for reactions of **4** with 1, 2 or 4 equiv. of the carbonyls clearly showed that all the intermediate polycations and their corresponding isomers are formed. Table 4 gives the resonance positions corresponding to the signals assigned to the polymetallic complexes. This suggests that the coordination of the  $\text{MnL}_n^+$  moieties occurs almost randomly at all the available CN groups of every phosphazene molecule, without pronounced preference for “uncharged” molecules. Even if only 1 equiv. of the neutral perchlorate complex is used in the reaction with  $\text{N}_3\text{P}_3(\text{O}-\text{C}_6\text{H}_4-\text{CN}-4)_6$ , a mixture of various cationic complexes and their isomers were formed, although the free phosphazene and the 1:1 complex  $[\text{N}_3\text{P}_3(\text{O}-\text{C}_6\text{H}_4-\text{CN})_5\{(\text{O}-\text{C}_6\text{H}_4-\text{CN})-\text{Mn}(\text{CO})_3(\text{dppm})\}]^+$  were the most abundant species.

The observations show that electronic interactions between the different CN groups in each phosphazene molecule are very small, and therefore that they are virtually independent.

The conductivity of the hexametal compounds **5** and **6** were measured in acetone solutions. As observed by IR and  $^{31}\text{P}$  NMR spectroscopy, these complexes did not dissociate substantially in acetone solution during the time required for the data collection. The conductivities (Table 2) varied almost linearly with the square root of the concentration. As expected, the  $\Lambda_0$  values and slopes were much higher than those of the corresponding monocationic derivatives. In the case of the fragment *trans*- $[\text{Mn}(\text{CO})_2(\text{dppm})\{\text{P}(\text{O}^i\text{Ph})_3\}]^+$ , we observed a reasonable linear correlation of  $\Lambda_0$  and slopes with the number of metal ions present in the complex. Thus, the mixture of the cationic complexes with average formulae  $\{\text{N}_3\text{P}_3(\text{O}-\text{C}_6\text{H}_4-\text{CN})_6[\text{Mn}(\text{CO})_2(\text{dppm})\{\text{P}(\text{O}^i\text{Ph})_3\}]_n[\text{PF}_6]_n\}$  with  $n = 1$  (**5b**), 2 (**5c**) and 4 (**5d**) (prepared by reaction of **4** and the appropriate amounts of *trans*- $[\text{MnBr}(\text{CO})_2(\text{dppm})\{\text{P}(\text{O}^i\text{Ph})_3\}]$  in dichloromethane in the presence of  $\text{Ti}[\text{PF}_6]_4$ ) had  $\Lambda_0 = 148$ , 242, and 415, respectively. The data in Table 2 also show that the hexacationic complex with *fac*- $[\text{Mn}(\text{CO})_3(\text{dppe})]^+$  fragments (**6b**) has lower conductivity, probably owing to the lower mobility of the larger cations.

The complex **5a** with the fragment *trans*- $[\text{Mn}(\text{CO})_2(\text{dppm})\{\text{P}(\text{O}^i\text{Ph})_3\}]^+$  was also studied by CV (Table 4), which showed a diffusion-controlled, nearly chemically reversible oxidation wave, very similar to that in Fig. 2, but with  $E^{1/0}$  slightly lower than those for the monometal analogues **2a** and **2b**. The value of the function  $i_{pa} v^{1/2}$  (measured at the same concentration and experimental conditions) was nearly six times the corresponding value of the monocationic complexes. The intensities of the peaks increased exactly in proportion to the concentration of the complex, showing no dependence on the

scan rate. These results, especially the fact that the  $E^{1/2}$  of **5a** is only slightly lower than that of the monometal complex **2a**, indicate that the interaction between the six  $\text{Mn}(\text{CO})_2(\text{dppm})\{\text{P}(\text{OPh})_3\}^+$  fragments present in the hexacation is very small [8]. Other hexametal redox-active complexes containing iron–arene or cyclopentadiene moieties have recently been studied by CV [9].

We tried the chemical oxidation of **5a** in  $\text{CH}_2\text{Cl}_2$  solution using  $\text{NO}[\text{PF}_6]$ , but it was not possible to prepare the desired 12-cation because, as shown by IR spectroscopy, the oxidation of some of the manganese fragments were followed by decomposition and the isomerization of other fragments to the *cis*-isomeric forms. This effect was also observed using small amounts of oxidant, and therefore it can be compared with the isomerization of *trans*- $[\text{MnBr}(\text{CO})_2(\text{dppm})\{\text{P}(\text{OPh})_3\}]$  in the presence of a catalytic amount of the cation *trans*- $[\text{MnBr}(\text{CO})_2(\text{dppm})\{\text{P}(\text{OPh})_3\}]^+$  (or of an oxidant that generates it) [10].

In order to extend these studies to manganese carbonyls bonded to nitrile-containing phosphazene polymers, we used the cyanophenoxyphosphazene polymers  $\{\text{NP}(\text{O}-\text{C}_6\text{H}_5)_{2-x}(\text{O}-\text{C}_6\text{H}_4-\text{CN}-4)_x\}_n$  with  $x = 0.06$  (**7a**) and 0.28 (**7b**) (Fig. 5) that are analogous to the cyclic model **1a**. These polymers [11] have molecular weights of the order of 800 000 and low polydispersities of ca. 2. The degree of functionalization (FG) [12] is 0.258 and 1.18, respectively. In the case of **7a** the chlorine content was ca. 0.6%, and therefore there are a significant number of  $\text{P}(\text{OC}_6\text{H}_5)\text{Cl}$  groups within the polymeric chains, and the formula is ca.  $\{\text{NPCl}_{0.04}(\text{O}-\text{C}_6\text{H}_5)_{1.9}(\text{O}-\text{C}_6\text{H}_4-\text{CN}-4)_{0.06}\}_n$ .

The polymers **7** reacted readily with *trans*- $[\text{BrMn}(\text{CO})_2(\text{dppm})\{\text{P}(\text{OPh})_3\}]$  in  $\text{CH}_2\text{Cl}_2$  in the presence of  $\text{Tl}[\text{PF}_6]$ , to give the complexes  $[\text{NP}(\text{O}-\text{C}_6\text{H}_5)_{2-x}(\text{O}-\text{C}_6\text{H}_4-\text{CN}-\text{Mn}(\text{CO})_2(\text{dppm})\{\text{P}(\text{OPh})_3\})(\text{PF}_6)]_x$  ( $x = 0.06$ , **8a**, and 0.28, **8b**), as pale orange solids. During this process, some of the  $\text{Mn}(\text{CO})_2(\text{dppm})\{\text{P}(\text{OPh})_3\}^+$  fragments generated from the reaction of the  $\text{Tl}[\text{PF}_6]$  with the starting bromo complex which fail to coordinate a nitrile group quickly may decompose, forming other carbonyl species. The isolation required high-speed centrifugation to eliminate all traces of  $\text{Tl}^+$  salts. Several independent preparations were not completely reproducible, and the analytical purity of the products was only moderate (see Experimental). These effects were more pronounced in the case of the very low metal-content species **8a**, for which small impurities represent a large proportion relative to the manganese coordinated to the CN.

As in the oligomeric models, a fraction of the *trans*-dicarbonyl fragments attached to the polymeric chains spontaneously isomerized to *cis*-dicarbonyl.

The reaction of the nitrile polymer **7a** with *fac*- $[(\text{O}_3\text{ClO})\text{Mn}(\text{CO})_3(\text{dppe})]$  in  $\text{CH}_2\text{Cl}_2$  gave the related yellow polymeric complex  $\{\text{NP}(\text{O}-\text{C}_6\text{H}_5)_{1.94}[\text{O}-\text{C}_6\text{H}_4-$

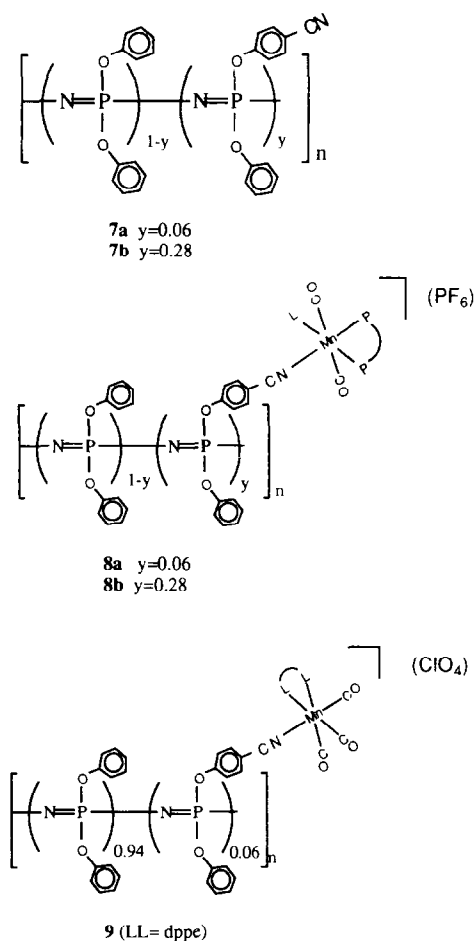


Fig. 5. Structural formulae of the polymers **7a**, **7b**, **8a**, **8b** and **9**.

$\text{CN}-\text{Mn}(\text{CO})_3(\text{dppe})(\text{ClO}_4)_{0.06}\}_n$  (**9**), that was characterized spectroscopically, although again the elemental analysis showed that it is difficult to obtain the compound analytically pure.

However, the coordination of the carbonyl fragment to the polymers were clearly shown by the IR and  $^{31}\text{P}$  NMR spectra (see Experimental and Table 1). The  $^{31}\text{P}$  NMR signal corresponding to the phosphazene phosphorus atoms showed an intense peak at  $-19.3$  ppm, and a broad smaller peak 1.3 ppm to lower frequency, that is assigned to the P atoms that bear the  $\text{O}-\text{C}_6\text{H}_4-\text{CN}-\text{Mn}^+$  groups. This is reasonable because, as shown above, the coordination of a cationic Mn fragment in the cyclic models decreased the chemical shift of the phosphazene phosphorus atoms.

In the case of **8a**, and **9**, however, a signal of low intensity with the appearance of a triplet, centred at  $-16$  ppm were clearly observed. Evidently this belongs to the phosphorus atoms of the type  $\text{NPCl}(\text{O}-\text{C}_6\text{H}_5)$  in the polymeric complexes that, as noted previously were present in the original nitrile-containing polymer **7a**.

The electrochemical oxidation of the polymers **8** was studied by CV (Table 4). Surprisingly, in the case of **8a**

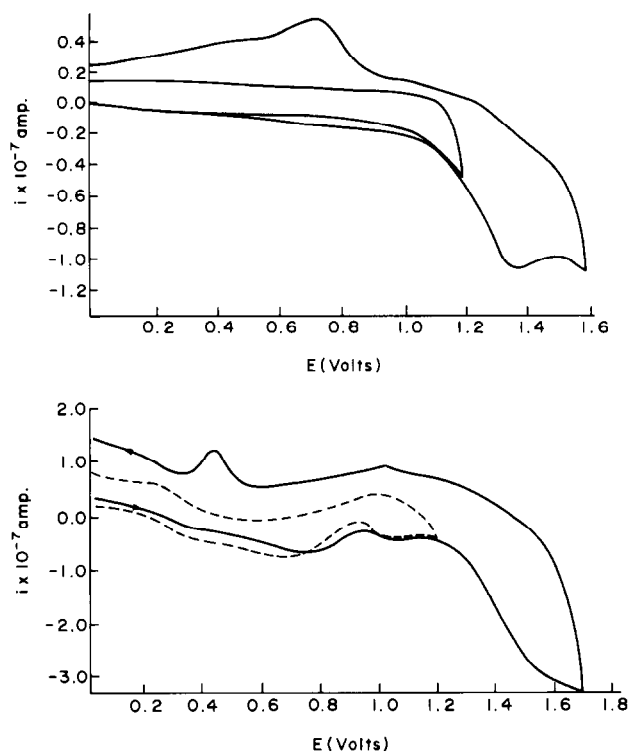


Fig. 6. Cyclic voltammogram of **8a** (upper) and **8b** (lower) in  $\text{CH}_2\text{Cl}_2$  at  $200 \text{ mV s}^{-1}$  between 0 and 1.6 V (upper) or 0 and 1.7 V (lower) and between 0 and 1.2 V.

the voltammograms showed a very extended oxidation wave (Fig. 6a) with broad anodic and cathodic peaks having a  $E^0$  very close to that of the model complex **2b**. Consistent with the assumption that the reduction peak really corresponds to the oxidation process that occurs above 1.3 V, this peak is not observed when the switch potential is not sufficiently high to produce the oxidation. The peak potential separation  $\Delta E_p$  was very large, and  $i_{pa}/v^{1/2}$  that increased linearly with the concentration, was ca. 25–30% of that corresponding to the model complex **2a** under the same concentration at  $\text{Mn}(\text{CO})_2$  moieties. However, a very weak symmetric wave centred at 1.0 V with peak separation near to 0.0 V was also observed in some voltammograms at scan rates higher than  $200 \text{ mV s}^{-1}$ , suggesting the formation of films on the electrode surface.

The behaviour at the electrode of the polymer with higher manganese content (**8b**) is qualitatively similar to that of the **8a**. In this case the voltammogram (Fig. 6b) showed a very weak and broad oxidation peak that depended markedly on the scan rate, appearing between 1.45 and more than 1.5 V (and overlapping with the background broad signal). The intensity of the peak varied slightly with the sample but was of the order of 23% of that expected from the Mn content. The presence of a weak reduction peak between 0.4 and 0.5 V that disappeared with switch potentials of 1.3 V suggests a very extended asymmetric wave centered near

1.0 V, with a peak separation of 1000 mV. In this case the presence of a film of polymer that tended to coat the electrode was clearly shown by a symmetric wave centred at 1.0 V with peak separation of 30 to 0 mV that was observed better at higher scan rates, and after repeating the voltammograms without polishing the electrode surface.

We confirmed this overall behaviour of the polymeric complexes at the electrode by measuring CVs of samples having ca. 60% of the maximum Mn content to show that the general features of the oxidation wave were reproduced but that the  $\Delta E_p$ s were less (ca. 800 mV at  $50 \text{ mV s}^{-1}$ ), and that the peak intensities were slightly closer to the values for the monometal models (25%).

The shapes of the voltammograms are unexpected, and the  $\Delta E_p$  values are very large for materials of this type. Thus, a polyphosphazene having pendant ferrocene groups in the same proportions (1.94/0.06) as **8a** has well behaved cyclic voltammetric waves [13] with  $\Delta E_p$  of 121 mV at  $20 \text{ mV s}^{-1}$ . The ferrocenyl polymer  $\{\text{CH}_2\text{CH}_2-(\text{RC}_5\text{H}_3)\text{Fe}(\text{C}_5\text{H}_3\text{R})\}_n$  (MW = 810 000) having almost noninteracting ferrocene units in the polymer chain [14] has a  $\Delta E_p$  of 300 mV at scan rates between 500 and  $1000 \text{ mV s}^{-1}$ . Very high  $\Delta E_p$  values have been observed in cyclic voltammograms of other polyphosphazenes-measured using electrodes modified with polymer films [15], where the effect was attributed to a chemical reaction following the oxidation. However, considering that the oxidations of the model complexes **2a**, **2b** and **5d** and also of the hexametallic **5a** are nearly chemically reversible, the electrochemical behaviour of the solutions of the polymer **8a** is unlikely to be due to a chemical reaction following the oxidation.

Another possibility is that the voltammograms imply that the electrode oxidation of the  $\text{Mn}(\text{CO})_2$  fragments attached to the polymers is slow, giving rise to electrochemically irreversible waves. Although the mono- and hexa-metal cyclic models showed that the electron-transfer rate at the electrode surface was fast enough to give thermodynamically controlled oxidation waves, it is not unlikely that the large octahedral manganese fragments of the polymers have some difficulties in reaching the electrode area.

However, the shape of the voltammogram could also be due to adsorption at the electrode surface to form films. The formation of films with soluble polymers is unexpected, but possible [16]. In the case of polymers where the redox active centre is in the polymer chain, the cyclic voltammograms of the electrode coated with films have characteristic shapes with peak separations of 30 to 0 mV (See ref. [4], cited in Ref. [17]). It is possible that with a polymeric complex with low charge and pendant redox active centres, a film coating the electrode might hinder the oxidation process, broaden-

ing the CV waves and reducing substantially their peak intensities.

The chemical oxidation of the manganese-containing polymers with  $\text{NO}[\text{PF}_6]$  in  $\text{CH}_2\text{Cl}_2$  showed that the dicationic sites generated were unstable and decomposed before the oxidized polymers could be isolated. The final products contained some  $\text{Mn}(\text{CO})_2(\text{dppm})\{\text{P}(\text{OPh})_3\}^+$  fragments attached to the polymer bound CN, with *cis*-dicarbonyls instead of the starting *trans*. This behaviour parallels that observed for the cyclic oligomeric models described above.

### 3. Experimental

All reactions were carried out under dry dinitrogen using standard Schlenk techniques. IR of spectra were recorded with a Perkin-Elmer FT 1720-X spectrometer. NMR spectra were recorded on a Bruker AC-200 or AC-300 instrument. Elemental analyses were performed with a Perkin-Elmer 240 microanalyser. The Mn content was determined by Galbraith Laboratories. Glass transition temperatures ( $T_g$ ) were measured with a Mettler DSC 300 differential scanning calorimeter equipped with a TA 1100 computer. Thermogravimetric analysis was performed on a Mettler TA 4000 instrument. The polymer samples were heated at a rate of  $10^\circ\text{C min}^{-1}$  from ambient temperature to  $800^\circ\text{C}$  under a constant flow of dinitrogen. The cyclic voltammograms were measured with a PAR M273 instrument. The auxiliary electrode was a platinum wire and the working electrode a platinum disc. The reference electrode was SCE separated from the solution by a fine-porosity frit and an agar agar bridge saturated with KCl. Solutions were  $0.5 \times 10^{-4}$  M in the complexes and 0.1 M in  $[\text{N}^n\text{Bu}_4][\text{PF}_6]$  as supporting electrolyte. Under the same experimental conditions,  $E^0$  for the ferrocene–ferrocenium couple was  $0.46 \pm 0.01$  V with a peak separation of 70 mV. In the case of the manganese-containing polymers 0.095 and  $2 \times 0.095$  g (**8a**) or 0.037 and  $2 \times 0.037$  g (**8b**) were used. This gave concentrations of the  $\text{Mn}(\text{CO})_2(\text{dppm})\{\text{P}(\text{OPh})_3\}$  centres of  $1 \times 10^{-3}$  and  $2 \times 10^{-3}$  M, respectively.

The cyclic phosphazenes  $\text{N}_3\text{P}_3\text{Cl}(\text{OC}_6\text{H}_5)_5$ ,  $\text{N}_3\text{P}_3(\text{OC}_6\text{H}_4\text{-R-4})_5(\text{O-C}_6\text{H}_4\text{-CN-4})$  (R = H [17], **1a**, or <sup>t</sup>Bu, **1b**),  $\text{N}_3\text{P}_3(\text{O-C}_6\text{H}_4\text{-CN-4})_6$  (**4**) and the polymers  $\{[\text{NP}(\text{O-C}_6\text{H}_5)]_{1-y}(\text{O-C}_6\text{H}_4\text{-CN-4})_y\}_n$  were obtained as described elsewhere [11]. Owing to the method of preparation, the cyclophosphazenes **1a** and **1b** used to obtain the cationic complexes **2a** and **2b** contained 7–11% of the the corresponding hexasubstituted  $\text{N}_3\text{P}_3(\text{OC}_6\text{H}_4\text{-R-4})_6$  (R = H or <sup>t</sup>Bu) [11], but the latter are easily separated from the complexes because of their high solubility in diethyl ether. The complexes *trans*- $[\text{MnBr}(\text{CO})_2(\text{dppm})\{\text{P}(\text{OPh})_3\}]$  [18] and *fac*- $[\text{Mn}(\text{O}_3\text{-ClO})(\text{CO})_3(\text{chel})](\text{chel} = \text{diphenylphosphinomethane}$

(dppm) [19], 1,2-bis(diphenylphosphino)ethane (dppe) [19] or 2,2-bipyridine (bipy) [20]) were prepared by the published procedures.

In the reactions using  $\text{Ti}[\text{PF}_6]$  much care should be taken in handling this material, which is highly toxic. On the other hand, in all the preparations described below, the reaction times, purity of the products and yields were dependent on the scale. Therefore, it is always advisable to check the completeness of the processes by IR or NMR spectroscopy before initiating the isolation steps.

#### 3.1. Preparation of $\{[\text{N}_3\text{P}_3(\text{O-C}_6\text{H}_4\text{-R-4})_5(\text{O-C}_6\text{H}_4\text{-CN})]\text{Mn}(\text{CO})_2(\text{dppm})\{\text{P}(\text{OPh})_3\}\}[\text{PF}_6]$ (R = H, **2a**; R = <sup>t</sup>Bu, **2b**)

A solution of  $\text{N}_3\text{P}_3(\text{OC}_6\text{H}_5)(\text{OC}_6\text{H}_4\text{CN})$  (0.085 g, 0.12 mmol), and *trans*- $[\text{MnBr}(\text{CO})_2(\text{dppm})\{\text{P}(\text{OPh})_3\}]$  (0.106 g, 0.12 mmol) in dichloromethane (15 ml) was stirred with solid  $\text{Ti}[\text{PF}_6]$  (0.075 g, 0.21 mmol) during 3 d at room temperature and in the absence of light. The mixture was filtered and concentrated to ca. 5 ml. Addition of diethyl ether (15 ml) gave an orange oil that was stirred with light petroleum (10 ml) until a solid was formed. The product, that can contain some of the starting manganese bromodicarbonyl, was recrystallized from dichloromethane–light petroleum. Yield 0.1 g (50%).

Anal.: Found (Calc. for  $\text{C}_{82}\text{H}_{66}\text{F}_6\text{MnN}_4\text{O}_{11}\text{P}_7$ ): C, 59.6 (59.0); H, 4.0 (4.0); N, 3.1 (3.3)%. IR ( $\text{cm}^{-1}$ ):  $\nu(\text{CO})$  in  $\text{CH}_2\text{Cl}_2$ : 2028w, 1944s;  $\nu(\text{CN})$  in Nujol: 2240w.

Compound **2b** was similarly prepared from  $\text{N}_3\text{P}_3(\text{OC}_6\text{H}_4\text{<sup>t</sup>Bu})(\text{OC}_6\text{H}_4\text{CN})$ .

Analysis: Found (Calc. for  $\text{C}_{102}\text{H}_{106}\text{F}_6\text{MnN}_4\text{O}_{11}\text{P}_7$ ): C, 61.8 (62.8); H, 5.1 (5.4); N, 2.2 (2.9)%. IR ( $\text{cm}^{-1}$ ):  $\nu(\text{CO})$  in  $\text{CH}_2\text{Cl}_2$ : 2028w, 1944s;  $\nu(\text{CN})$  in Nujol: 2236w.

#### 3.2. Preparation of $[\text{N}_3\text{P}_3\{(O-C_6H_4-CN)\text{Mn}(\text{CO})_2(\text{dppm})\{\text{P}(\text{OPh})_3\}\}_6][\text{PF}_6]_6$ (**5a**)

A mixture of  $\text{N}_3\text{P}_3(\text{OC}_6\text{H}_4\text{CN})_6$  (0.046 g, 0.055 mmol) and *trans*- $[\text{MnBr}(\text{CO})_2(\text{dppm})\{\text{P}(\text{OPh})_3\}]$  (0.39 g, 0.44 mmol) in dichloromethane (15 ml) was stirred with solid  $\text{TiPF}_6$  (0.2 g, 0.57 mmol) for 36 h at room temperature in the absence of light. More  $\text{TiPF}_6$  (0.15 g, 0.43 mmol) was added and stirring was continued for another 5 h. The mixture was filtered and concentrated to ca. 5 ml. Addition of diethyl ether (15 ml) gave an orange oil that was washed and stirred with diethyl ether (10 ml) until a solid was formed. The resulting product was recrystallized from  $\text{CH}_2\text{Cl}_2$ –diethyl ether as a microcrystalline orange solid. Yield 0.27 g (75%).

Anal.: Found (Calc. for  $\text{C}_{312}\text{H}_{246}\text{F}_{36}\text{Mn}_6\text{N}_9\text{O}_{36}\text{P}_{27}$ ): C, 56.1 (57.2); H, 3.8 (3.8); N, 1.9 (1.9)%. IR ( $\text{cm}^{-1}$ ):

$\nu(\text{CO})$  in  $\text{CH}_2\text{Cl}_2$ : 2029w, 1945s;  $\nu(\text{CN})$  in Nujol: 2233w.

The partially charged complexes  $\{\text{N}_3\text{P}_3(\text{O}-\text{C}_6\text{H}_4-\text{CN})_6[\text{Mn}(\text{CO})_2(\text{dppm})\{\text{P}(\text{OPh})_3\}]_n\}(\text{PF}_6)_n$  ( $n = 1$  (**5b**), 2 (**5c**) and 4 (**5d**)) were similarly prepared in ca. 80% yield using the appropriate amount of *trans*- $\{\text{MnBr}(\text{CO})_2(\text{dppm})[\text{P}(\text{OPh})_3]\}$ . The IR and the NMR data were very similar to those of the hexametal derivative **5a**. The number of manganese carbonyl moieties per phosphazene hexanitride in the isolated products was determined by integrating the  $^{31}\text{P}$  NMR signals in dichloromethane solution. The experimental values were  $n = 1.03$  for **5b**, 2.01 for **5c** and 3.9 for **5d**.

### 3.3. Preparation of $[\text{N}_3\text{P}_3\{(\text{O}-\text{C}_6\text{H}_4-\text{CN})-\text{Mn}(\text{CO})_3(\text{PP})\}_6](\text{ClO}_4)_6$ , ( $\text{PP} = \text{dppm}$ , **6a**; $\text{PP} = \text{dppe}$ , **6b**)

A mixture of  $\text{N}_3\text{P}_3(\text{OC}_6\text{H}_4\text{CN})_6$  (0.062 g, 0.073 mmol) and *fac*- $[\text{Mn}(\text{OCIO}_3)(\text{CO})_3(\text{dppe})]$  (0.31 g, 0.49 mmol) in dichloromethane (10 ml) was stirred for 6 d at room temperature in the absence of light. More  $\text{Ti}[\text{PF}_6]$  (0.15 g, 0.43 mmol) was added, and stirring was continued for another 5 h. The mixture was filtered and concentrated to ca. 5 ml. Addition of diethyl ether (15 ml) gave a yellow solid that was washed with diethyl ether (10 ml). The resulting product was recrystallized from  $\text{CH}_2\text{Cl}_2$ -diethyl ether as a microcrystalline yellow solid (**6b**). Yield 0.31 g (91%).

Anal.: Found (Calc. for  $\text{C}_{216}\text{H}_{168}\text{Cl}_6\text{Mn}_6\text{N}_9\text{O}_{48}\text{P}_{15}$ ): C, 56.5 (55.6); H, 3.8 (3.6); N, 2.4 (2.7)%. IR ( $\text{cm}^{-1}$ ):  $\nu(\text{CO})$  in  $\text{CH}_2\text{Cl}_2$ : 2040s, 1972s, 1956s;  $\nu(\text{CN})$  in Nujol: 2255w.

The dppm analogue (**6a**) was similarly prepared from *fac*- $[\text{Mn}(\text{OCIO}_3)(\text{CO})_3(\text{dppm})]$  in a 1:10 ratio. The excess of the manganese precursor was separated from the crude reaction product by repeated washings with diethyl ether. The reaction time was 7 d and the yield was 61%.

Anal.: Found (Calc. for  $\text{C}_{210}\text{H}_{156}\text{Cl}_6\text{Mn}_6\text{N}_9\text{O}_{48}\text{P}_{15}$ ): C, 55.1 (55.1); H, 3.3 (3.4); N, 2.5 (2.7)%. IR ( $\text{cm}^{-1}$ ):  $\nu(\text{CO})$  in  $\text{CH}_2\text{Cl}_2$ : 2046s, 1976s, 1958s;  $\nu(\text{CN})$  in Nujol: 2257w.

### 3.4. Preparation of $\{[\text{NP}(\text{O}-\text{C}_6\text{H}_5)_{2-x}[\text{O}-\text{C}_6\text{H}_4-\text{CN}-\text{Mn}(\text{CO})_2(\text{dppm})\{\text{P}(\text{OPh})_3\}(\text{PF}_6)]_x\}_n$ ( $x = 0.06$ , **8a**; $x = 0.28$ , **8b**)

A mixture of the polymer with idealized formula  $\{[\text{NP}(\text{O}-\text{C}_6\text{H}_5)_{1.94}(\text{O}-\text{C}_6\text{H}_4-\text{CN}-4)_{0.06}]_n$  (1 g, 0.258 mmol of CN groups) and *trans*- $[\text{MnBr}(\text{CO})_2(\text{dppm})\{\text{P}(\text{OPh})_3\}]$  (0.40 g, 0.45 mmol) in dichloromethane (150 ml) was stirred with  $\text{Ti}[\text{PF}_6]$  (0.19 g, 0.54 mmol) at room temperature in the absence of light for 3 d. The mixture was centrifuged for 3 h at 4000 cps and decanted. The liquid was concentrated to ca. 15 ml and diethyl ether (40 ml) was added to give an orange

precipitate that was dissolved in  $\text{CH}_2\text{Cl}_2$  (20 ml) to give a clear solution. This solution was poured into ethanol (100 ml) to give a precipitate that was washed with diethyl ether ( $2 \times 20$  ml) and dissolved  $\text{CH}_2\text{Cl}_2$ . Addition of enough diethyl ether gave the polymer **8a** as a pale orange solid. The yield was 0.53 g, (43%).

Anal.: Found (Calc. for  $\text{C}_{14.76}\text{H}_{12.16}\text{F}_{0.36}\text{Mn}_{0.06}\text{N}_{1.06}\text{O}_{2.3}\text{P}_{1.24}$ ): C, 58.9 (61.1); H, 4.0 (4.2); N, 5.3 (5.1); Mn, 1.3 (1.1)%. IR ( $\text{cm}^{-1}$ ):  $\nu(\text{CO})$  in  $\text{CH}_2\text{Cl}_2$ : 2027w, 1943s;  $\nu(\text{CN})$  in Nujol: 2228w,  $T_g = -5.2^\circ\text{C}$ . Thermogravimetric analysis shows weight losses at  $240^\circ\text{C}$  (9%),  $340^\circ\text{C}$  (8%) and  $480^\circ\text{C}$  (51%).

Three independent preparations gave the same type of material with the same Mn content. Other, more soluble, polymeric materials containing manganese dicarbonyl moieties were detected by IR and NMR spectroscopy in the mother liquors.

The polymeric complex **8b** was similarly prepared as a pale orange solid. The yield was 0.7 g (33%).

Analysis: found (calc. for  $\text{C}_{24.88}\text{H}_{20.08}\text{F}_{1.68}\text{Mn}_{0.28}\text{N}_{1.28}\text{O}_{3.4}\text{P}_{2.12}$ ): C, 55.7 (59.2); H, 3.9 (4.0); N, 4.1 (3.6); Mn, 2.8 (3.0)%. IR ( $\text{cm}^{-1}$ ):  $\nu(\text{CO})$  in  $\text{CH}_2\text{Cl}_2$ : 2027w, 1942s;  $\nu(\text{CN})$  in Nujol: 2229w. A glass transition temperature was not detected. Thermogravimetric analysis shows weight losses at  $230^\circ\text{C}$  (12%),  $275^\circ\text{C}$  (6.5%),  $315^\circ\text{C}$  (22%) and  $440^\circ\text{C}$  (32.5%).

### 3.5 Preparation of $\{[\text{NP}(\text{O}-\text{C}_6\text{H}_5)_{1.94}[\text{O}-\text{C}_6\text{H}_4-\text{CN}-\text{Mn}(\text{CO})_3(\text{dppe})(\text{ClO}_4)]_{0.06}\}_n$ (**9**)

A mixture of the polymer  $\{[\text{NP}(\text{O}-\text{C}_6\text{H}_5)_{1.94}(\text{O}-\text{C}_6\text{H}_4-\text{CN}-4)_{0.06}]_n$  (0.20 g, 0.05 mmol of CN groups) and *fac*- $[\text{Mn}(\text{OCIO}_3)(\text{CO})_3(\text{dppe})]$  (0.033 g, 0.053 mmol) in dichloromethane (30 ml) was stirred for 3 d at room temperature in the absence of light. The mixture was filtered and the liquid was concentrated to ca. 2 ml. Diethyl ether was added to give a yellow precipitate that was washed with more diethyl ether ( $2 \times 40$  ml) and dissolved in  $\text{CH}_2\text{Cl}_2$  (50 ml) to give a clear solution. This solution was concentrated to 1 ml and poured dropwise over diethyl ether (120 ml) to give the polymer **9** as a yellow precipitate that was washed with diethyl ether ( $2 \times 15$  ml) and dried in vacuo. The yield was 0.142 g (61%).

Anal.: Found (Calc. for  $\text{C}_{13.8}\text{H}_{11.38}\text{Cl}_{0.06}\text{Mn}_{0.06}\text{N}_{1.06}\text{O}_{2.42}\text{P}_{1.12}$ ): C, 58.6 (61.2); H, 4.2 (4.2); N, 5.2 (5.5). IR ( $\text{cm}^{-1}$ ):  $\nu(\text{CO})$  in  $\text{CH}_2\text{Cl}_2$ : 2040s, 1960s;  $\nu(\text{CN})$  in Nujol: 2229w.

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