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Synthesis and spectroscopic characterization of cyclic and polymeric phosphazenes bearing phosphine complexes

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Abstract

The reactions of the cyclic phosphazenes $[N_3P_3Cl_6]$ and $[N_3P_3(O_2C_{12}H_8)_2Cl_2]$ ($O_2C_{12}H_8 = 2,2'$-dioxybiphenyl) with the diphenylphosphine phenol complex $\{Mn(CO)_2(\eta^5\text{-}C_5H_4Me)[PPh_2(C_6H_4\text{–}OH)]\}$ (**1**) and Cs_2CO_3 in refluxing acetone gave, respectively the phosphazene–phosphine complexes $\{N_3P_3[OC_6H_4PPh_2\text{–}Mn(CO)_2(\eta^5\text{-}C_5H_4Me)]_6\}$ (**2**) and $\{N_3P_3(O_2C_{12}H_8)_2\text{-}[OC_6H_4PPh_2\text{–}Mn(CO)_2(\eta^5\text{-}C_5H_4Me)]_2\}$ (**3**), in good yields. The analogous reaction of the partially substituted clorophosphazene polymer $\{[NP(O_2C_{12}H_8)]_{0.6}[NPCl_2]_{0.4}\}_n$ in THF gave the polymeric complex $[\{NP(O_2C_{12}H_8)\}_{0.6}\{NP[OC_6H_4PPh_2\text{–}Mn(CO)_2(\eta^5\text{-}C_5H_4Me)]_2\}_{0.4}\cdot 0.5[OC_4H_8]_n$ (**4**). Different spectroscopic data are provided for the new compounds that may be useful for the characterization of other more complex polymeric materials.

Keywords: Cyclophosphazenes; Polyphosphazenes; Phenolic phosphine; Macromolecular complexes; Carbonyls; Spectroscopic characterization

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1. Introduction

Transition-metal polymeric complexes deserve a great scientific interest for many reasons, including their potential technological importance [1], relevance to catalysis [2,3] and other applications [4]. One special class of metal-containing polymers are those that consist on a polymeric main chain having pendant complexes Ⓟ-$\sim\sim$-L–ML$_n$ attached to it through a spacer. Although several polymeric complexes of this type are known where the main chain is a linear polyphosphazene, i.e. Ⓟ≡$(NPR_2)_n$ [5], they still remain scarce. Among the best characterized ones, are various transition metal phosphine-complexes (i.e. L = –PPh$_2$) [6–8] and pyridine complexes (L = –C$_5$H$_4$N) [9]. The most common synthetic route to these compounds involves the preparation of a polymer bearing the L group, followed by a substitution reaction with an appropriate transition metal complex having a labile ligand. However, apart from the synthetic difficulties in the preparation of the polymeric ligand itself, this approach implies two main complications, namely: (a) incomplete coordination of MLn fragment to the available L groups, frequently for steric reasons; and (b) crosslinking reactions by a double substitution on the precursor complex by two ligands coming from different polymeric chains [8]. In an earlier paper [8], we reported a new direct route to $W(CO)_5$ complexes supported in phosphazenes based on the reaction of the phenolic complex $(CO)_5W\text{–}Ph_2PC_6H_4\text{–}OH$ with chlorophosphazenes, taking advance of the effective chlorine substitution reaction promoted by the presence of Cs_2CO_3 [10]. Herein we describe an extension of this method that allowed a very convenient preparation in high yield of polyphosphazenes, cyclic and polymeric, with pendant phosphine complexes of the type $OC_6H_4PPh_2\text{–}Mn(CO)_2(\eta^5\text{-}C_5H_4Me)$.

On the other hand, the characterization of complex polymeric substances is far from simple, especially if the solubility is low or in the case of the functionalization of material surfaces. Therefore, all the spectroscopic evidence obtained in well defined systems may be valuable

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to deal with these other cases. Thus, we have tried to provide IR and NMR spectroscopic data leading to general observations that may be useful for the characterization of other phosphazene polymers with organometallic complexes.

2. Experimental

2.1. General considerations

All the reactions were carried out under dry nitrogen. K_2CO_3 and Cs_2CO_3 were dried at 140 °C prior to use. The C_3H_6O used as solvent was predistilled from $KMnO_4$, and distilled twice from anhydrous $CaSO_4$. The MeOH was distilled from CaH_2. The THF was treated with KOH and distilled twice from Na in the presence of benzophenone. Petroleum ether refers to that fraction with boiling point in the range 60–65 °C. The hexachlorocyclotriphosphazene $[N_3P_3Cl_6]$ (Fluka) was purified from hot petroleum ether and dried in vacuum. The cyclic $[N_3P_3(O_2C_{12}H_8)_2Cl_2]$ [11], and $[N_3P_3(O_2C_{12}H_8)_2(OC_6H_4PPh_2)]$ [8], were prepared as described elsewhere. The polymer $[NPCl_2]_n$ was prepared by heating the $[N_3P_3Cl_6]$ in solution as described by Magill and coworkers [26]. The phosphine $[PPh_2(C_6H_4{-}OH)]$ was prepared as described in the experimental part (a slight modified version of the reported in Ref. [8]).

The IR spectra were recorded with a Perkin–Elmer FT Paragon 1000 spectrometer. NMR spectra were recorded on Bruker AC-200, AC-300 and DPX 300 instruments, using $CDCl_3$ as solvent. ^1H and $^{13}C\{^1H\}$ NMR are given in δ relative to TMS. $^{31}P\{^1H\}$ NMR are given in δ relative to external 85% aqueous H_3PO_4. Coupling constants are in Hz. C, H, N analyses were performed with a Perkin–Elmer 2400 microanalyzer. The chlorine, Mn and P elemental analyses were performed by Galbraith laboratories. GPC were measured with a Perkin–Elmer equipment with a model LC 250 pump, a model LC 290 UV, and a model LC 30 refractive index detector. The samples were eluted with a 0.1% by weight solution of tetra-*n*-butylammonium bromide in THF through Perkin–Elmer PLGel (Guard, 10^5, 10^4 and 10^3 Å) at 30 °C. Approximate molecular weight calibration were obtained using narrow molecular weight distribution polystyrene standards. T_g values were measured with a Mettler DSC 300 differential scanning calorimeter equipped with a TA 1100 computer, at 10 °C min^{-1}. Thermal gravimetric analyses were performed on a Mettler TA 4000 instrument. The polymer samples were heated at a rate of 10 °C min^{-1} from ambient temperature to 800 °C under constant flow of nitrogen.

2.2. Preparation of $PPh_2(C_6H_4{-}OH)$

A mixture of *p*-bromophenol (12.5 g, 72.2 mmol), 2-methoxypropene (13.8 ml, 144.5 mmol) and a drop of $POCl_3$ was stirred in the absence of light for 1 h. Four drops of Et_3N were added and the volatiles were evaporated in vacuo. The resulting pale yellow oil (very light sensitive) was dissolved in petroleum ether (80 ml). To this solution was added dropwise and with stirring a solution of LiBu 2.5 M (31.8 ml, 79.42 mmol) in petroleum ether (30 ml). The stirring was continued for 4 h to give a white precipitate that was filtered and dried in vacuo. The resulting solid was dissolved at −70 °C in THF (70 ml) and to the solution was added dropwise a solution of $PClPPh_2$ (8.4 ml, 47.04 mmol) in THF (30 ml). The mixture was allowed to reach room temperature (r.t.) and stirred overnight. Then, 20% aqueous HCl (36 mL) was added and, after stirring for 3 h, the mixture was extracted with Et_2O (4 × 50 ml). The extracts were stirred with an excess of solid Na_2CO_3, washed with water (3 × 50 ml), dried over Na_2SO_4, and filtered. The solvent was evaporated in vacuo to give an orange oily residue that was dissolved in CH_2Cl_2, filtered through silica-gel, concentrated by evaporation in vacuo, and mixed with petroleum ether to obtain two layers. This mixture was then kept into a freezer until crystallization and then the white microcrystals were dried in vacuo. Yield: 6 g (46%).

Anal. Found: C, 77.3; H, 5.5. Calc.: C, 77.7; H, 5.4%.

^1H NMR ($CDCl_3$): 7.4–6.7 (m.br., 14H, aromatic rings); 5.3 (s.br., 1H, OH). ^{31}P NMR ($CDCl_3$): −6.6. ^{13}C NMR ($CDCl_3$): 157.4 s, 136.5 {d, J ($^{31}P{-}^{13}C$) = 21.6}, 128.5 {d, J ($^{31}P{-}^{13}C$) = 8}, 116.4 {d, J ($^{31}P{-}^{13}C$) = 8.3}, [$P{-}C_6H_4$]; 138.2 {d, J ($^{31}P{-}^{13}C$) = 9.2}, 134.1 {d, J ($^{31}P{-}^{13}C$) = 19.3}, 129.1 {d, J ($^{31}P{-}^{13}C$) = 10.6}, 129.0 [PPh_2].

2.3. Preparation of $\{Mn(CO)_2(\eta^5\text{-}C_5H_4Me)[PPh_2(C_6H_4{-}OH)]\}$ (*1*)

To a solution of $PPh_2(C_6H_4{-}OH)$ (1.85 g, 6.65 mmol) in THF (40 ml) cooled at −30 °C was added the complex $[Mn(THF)(CO)_2(\eta^5\text{-}C_5H_4Me)]$, obtained by irradiating with UV light a solution of $[Mn(CO)_3(\eta^5\text{-}C_5H_4Me)]$ (1.88 g, 8.62 mmol) in THF (45 ml) at −30 °C until the carbonyl band at 2018 cm^{-1} could not longer be observed (approximately 3.5 h). The mixture was stirred at r.t. overnight and the volatiles were removed in vacuo. The residue was chromatographed in silica–gel eluting first with petroleum ether and then with CH_2Cl_2. The CH_2Cl_2 fraction was evaporated to give $\{Mn(CO)_2(\eta^5\text{-}C_5H_4Me)[PPh_2(C_6H_4{-}OH)]\}$ as a brown solid. Yield: 2.2 g, 71%.

Anal. Found: C, 66.6; H, 4.6. Calc.: C, 66.7; H, 4.7%.

IR (ν-CO-region): (CH_2Cl_2) 1926s, 1859s; (THF) 1930s, 1867s.

IR (KBr): 3509s (ν-OH), 3056w (ν-CH, aryl rings), 2922vw (ν-CH, C_5H_4–Me), 1912vs, 1893m, 1850s, 1828vs (ν-CO), 1600m, 1582m, 1560w, 1498m, 1482w, 1458vw, 1434m, 1420w (OC_6H_4–PPh_2) 1399vw, 1375vw (δ-CH_3, C_5H_4–Me), 1328w, 1273m, 1191w, 1174m, 1094s, 1029w, 829s, 748m, 696s (OC_6H_4–PPh_2), 667m, 634w, 622m (δ-MnCO), 524s.

^{1}H NMR ($CDCl_3$): 7.3–6.8 (m.br., 14H, aromatic rings); 5.3 (s.br., 1H, OH); 4.2, 4.0 (m., 4H, C_5H_4); 1.9 (s, 3H, CH_3). ^{31}P NMR ($CDCl_3$): 91.3. ^{13}C NMR ($CDCl_3$): 234.0 {d, J (^{31}P–^{13}C) = 23, CO}; 157.3, 139.4 {d, J (^{31}P–^{13}C) = 40}, 135.6 {d, J (^{31}P–^{13}C) = 11}, 133.2 {d, J (^{31}P–^{13}C) = 9}, 129.9, 129.3br., 128.7 {d, J (^{31}P–^{13}C) = 7.5}, 115.8 {d, J (^{31}P–^{13}C) = 9} (aromatic carbons); 99.7, 83.9, 82.6 (C_5H_4Me), 14.5 (Me).

2.4. *Preparation of* $\{N_3P_3[OC_6H_4PPh_2{-}Mn(CO)_2(\eta^5\text{-}C_5H_4Me)]_6\}$ (**2**)

A mixture of $[N_3P_3Cl_6]$ (0.1 g, 0.29 mmol) and $[Mn(CO)_2(\eta^5\text{-}C_5H_4Me)[PPh_2(C_6H_4{-}OH)]\}$ (0.84 g, 1.8 mmol) and Cs_2CO_3 (1.13 g, 3.47 mmol) in THF (20 ml) was refluxed for 3 h. The solvent was removed in vacuo and the residue was extracted with CH_2Cl_2 (5 × 20 ml). The solution was filtered and evaporated to dryness. The residue was washed with MeOH (3 × 30 ml) to give **5** as a yellow solid. Yield: 0.72 g, 85%.

Anal. Found: C, 62.9; H, 4.4; N: 1.4. Calc.: C, 63.7; H, 4.3; N, 1.4%.

IR (ν-CO-region): (CH_2Cl_2) 1926s, 1859s; (THF) 1929s, 1866s.

IR (KBr): 3056w (ν-CH, aryl rings), 2961w, 2922w (ν-CH, C_5H_4–Me), 1927vs, 1859vs (ν-CO), 1587m, 1483s, 1434m (aryl rings), 1376w (δ-CH_3, C_5H_4–Me), 1267m (ν-C–OP), 1204s, 1189s, 1163vs (ν-PN), 1091s (ν-P–OC), 953m, 940m (δ-POC), 884m, 833m, 745m, 696s (aryl rings and δ-PNP), 662m, 619m, 596m (δ-MnCO), 524m,br.

^{1}H NMR ($CDCl_3$): 7.3–7.2–7.0 (m.br., 84H, aromatic rings); 4.1, 3.9 (m., 24H, C_5H_4); 1.9 (s, 18H, CH_3). ^{31}P NMR ($CDCl_3$): 92.9 (s, PPh_2); 8.0 (s, P_3N_3). ^{13}C NMR ($CDCl_3$): 233.4 {d, J (^{31}P–^{13}C) = 24, CO}; 151.8, 138.7 {d, J (^{31}P–^{13}C) = 40}, 135.9 {d, J (^{31}P–^{13}C) = 40}, 135.0 {d, J (^{31}P–^{13}C) = 11.5}, 133.3 {d, J (^{31}P–^{13}C) = 10.5}, 130.1, 128.8 {d, J (^{31}P–^{13}C) = 9), 121 {d, J (^{31}P–^{13}C) = 8}, (aromatic carbons); 99.6, 83.7, 82.4 (C_5H_4Me), 14.4 (Me).

2.5. *Preparation of* $\{N_3P_3(O_2C_{12}H_8)_2[OC_6H_4PPh_2{-}Mn(CO)_2(\eta^5\text{-}C_5H_4Me)]_2\}$ (**3**)

2.5.1. *Method a*

To a solution of $[N_3P_3(O_2C_{12}H_8)_2(OC_6H_4PPh_2)_2]$ (**2**) (0.2 g, 0.19 mmol) in THF (30 ml) cooled at −30 °C was added the complex $[Mn(THF)(CO)_2(\eta^5\text{-}C_5H_4Me)]$, obtained by irradiating with UV light a solution of $[Mn(CO)_3(\eta^5\text{-}C_5H_4Me)]$ (0.11 g, 0.50 mmol) in THF (30 ml) at −30 °C until the carbonyl band at 2018 cm^{-1} could no longer be observed (approximately 1.5 h). The mixture was allowed to reach r.t. and stirred for 6 h. The volatiles were removed in vacuo, and the oily residue was chromatographed in silica–gel eluting first with petroleum ether and then with CH_2Cl_2. The CH_2Cl_2 fraction was evaporated to give **6** as a yellow solid. Yield: 0.17 g, 62%.

Anal. Found: C, 63.4; H, 4.0; N, 2.7. Calc.: C, 63.5; H, 4.1; N, 2.9%.

IR (ν-CO-region): (CH_2Cl_2) 1928s, 1861s; (THF) 1929s, 1866s.

IR (KBr): 3058w (ν-CH, aryl rings), 2961w, 2922w (ν-CH, C_5H_4–Me), 1927vs, 1859vs (ν-CO), 1587m, 1478m, 1435m, 1396w (aryl rings), 1376w (δ-CH_3, C_5H_4–Me), 1273m (ν-C–OP), 1229m, 1170vs (ν-PN), 1093s (ν-P–OC), 936s,br. (δ-POC), 885s, 837w, 786m, 752m (aryl rings and δ-PNP), 718w, 695m, 662m, 617sh, 608m, 590sh (aryl-rings and δ-MnCO), 524m.

^{1}H NMR ($CDCl_3$): 7.3–7.1 (m.br., 44H, aromatic rings); 4.2, 4.0 (m., 8H, C_5H_4); 1.9 (s, 6H. CH_3). ^{31}P NMR ($CDCl_3$): 92.9 (s., PPh_2), 25.7 [d, $P(O_2C_{12}H_8)$] 9.7 [dd, $P(OC_6H_4PP_2)_2$]{M_2X spin system, J (P–P) = 93}. ^{13}C NMR ($CDCl_3$): 233.5 {d, J (^{31}P–^{13}C) = 24, CO}; 152.1m, 138.9 {d, J (^{31}P–^{13}C) = 40.5}, 136.5 {d, J (^{31}P–^{13}C) = 40.5}, 135.1 (d, J (^{31}P–^{13}C) = 11.5}, 133.4 (d, J (^{31}P–^{13}C) = 10.5), 130.1, 128.8 (d, J (^{31}P–^{13}C) = 9), 121.4m, ($OC_6H_4PPh_2$); 148.6, 130.4, 130.3, 129.3, 126.8, 122.5 ($OC_{12}H_8$); 99.7, 83.8, 82.5 (C_5H_4Me); 14.5 (Me).

2.5.2. *Method b*

A mixture of $[N_3P_3(O_2C_{12}H_8)_2Cl_2]$ (0.2 g, 0.35 mmol) and $[Mn(CO)_2(\eta^5\text{-}C_5H_4Me)[PPh_2(C_6H_4{-}OH)]\}$ (0.35 g, 0.75 mmol) and Cs_2CO_3 (0.46 g, 1.4 mmol) in THF (25 ml) was refluxed for 2 h. The solvent was removed in vacuo and the residue was extracted with CH_2Cl_2 (5 × 20 ml). The solution was filtered and evaporated to dryness to give **6** as a yellow solid that was washed with methanol (2 × 40 ml) and dried in vacuo. Yield: 0.45 g, 90%.

Anal. Found: C, 62.9; H, 4.2; N, 2.7. Calc.: C, 63.5; H,4.1; N, 2.9%.

2.6. *Preparation of* $[\{NP(O_2C_{12}H_8)\}_{0.6}\{NP[OC_6H_4PPh_2{-}Mn(CO)_2(\eta^5\text{-}C_5H_4Me]_2\}_{0.4}\cdot 0.5(OC_4H_8)]_n$ (**4**)

A mixture of $[NPCl_2]_n$ (1.0 g, 8.63 mmol), 2,2′-HO–C_6H_4–C_6H_4–OH (0.965 g, 5.18 mmol) and K_2CO_3 (2.86 g, 20.69 mmol) in THF (130 ml) was refluxed with mechanical stirring for 10 h. Then, the complex $\{[Mn(CO)_2(\eta^5\text{-}C_5H_4Me)][PPh_2(C_6H_4{-}OH)]\}$ (4.85 g, 10.35 mmol) and Cs_2CO_3 (3.37 g, 10.34 mmol) were added, and the reaction was continued for another 131

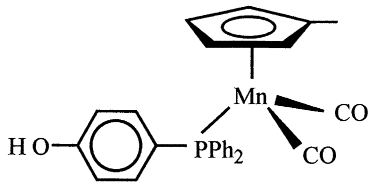

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Chart 1.

h. The resulting mixture was poured into water (1.5 l) to give a precipitate that was washed twice with water (1 l) and dissolved in THF (200 ml). The solution was filtered and concentrated until a viscous liquid was formed that was precipitated slowly into water (1.5 l). The reprecipitation procedure was repeated in the same way from THF/isopropyl alcohol, and THF/petroleum ether to give a yellow solid that was dried in vacuo at r.t. for a week. Yield: 3.3 g, 68%.

Anal. Found: C, 62.9; H, 4.7; N, 2.6; P, 10.8; Mn, 7.5. Calc.: C, 63.7; H, 4.6; N, 2.5; P, 9.9; Mn, 7.8. Chlorine content: 0.03%.

IR (ν-CO-region): (CH_2Cl_2) 1927s, 1860s; (THF) 1929s, 1866s.

IR (KBr): 3058w (ν-CH, aryl rings), 2927w, 2857w (ν-CH, PTHF), 1928vs, 1861vs(ν-CO), 1588w, 1480m,br., 1435m, (aryl rings), 1376w (δ-CH_3, C_5H_4–Me), 1263m (ν-C–OP), 1246m, 1198vs (ν-PN), 1170m, 1095m (ν-P–OC), 940s,br. (δ-POC), 832w, 786m, 752m (aryl rings and δ-PNP), 696m, 663m, 617m, 598m (aryl-rings and δ-MnCO), 526m.

^1H NMR ($CDCl_3$): 7.1–6.7 (m.br., 16H, aromatic rings); 3.9, 3.7(m., 3.2H, C_5H_4); 3.4m, 1.6m (4H, OC_4H_8); 1.8 (s, 2.4H, CH_3). ^{31}P NMR ($CDCl_3$): 92.1 (s., PPh_2); −6.4 [m., $P(O_2C_{12}H_8]$; −23.6 [m., $P(OC_6H_4PPh_2)_2]$. ^{13}C NMR ($CDCl_3$): 234 {d, J (^{31}P–^{13}C) = 23, CO}; 153, 139, 134, 133, 130, 129, 121, [(all broad, OC_6H_4–$P(C_6H_5)_2$], 150, 126, 121 (all broad, $O_2C_{12}H_8$); 100.0, 83.7, 82.4 (C_5H_4Me); 71.3, 27.2, (OC_4H_8); 14.1 (Me).

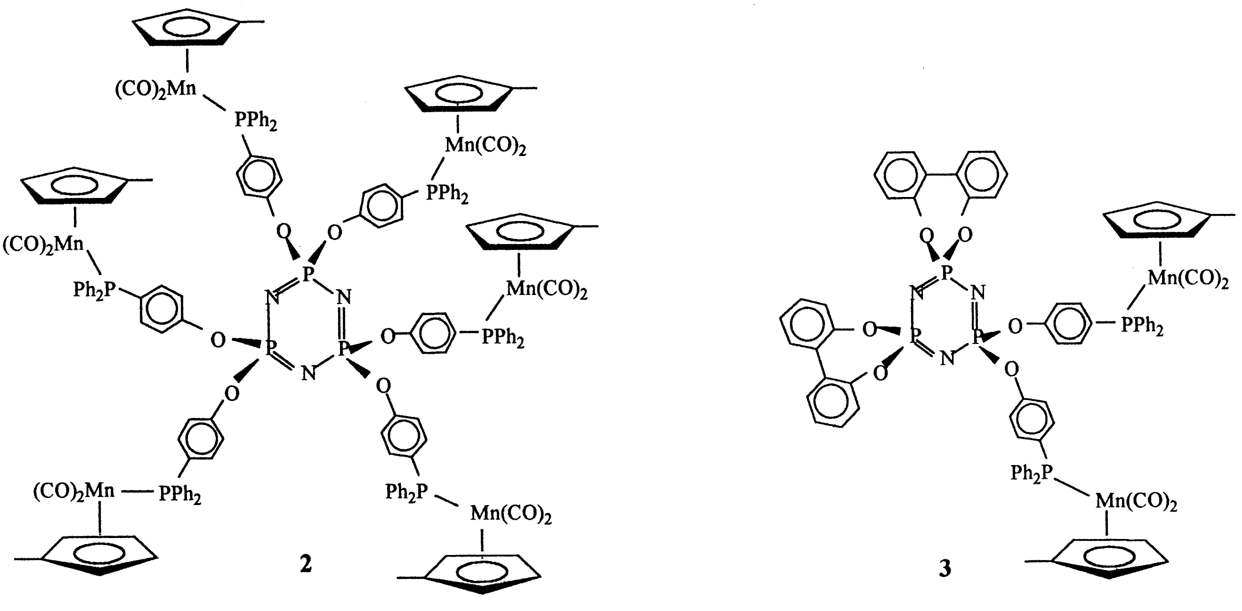
M_w (GPC): 1,100,000 ($M_w/M_n = 4$). T_g (DSC): 128 °C ($\Delta C_p = 0.16$ J g^{-1} K^{-1}. TGA: −22% (350 °C), −36% (425 °C). Residue at 800 °C: 41%.

3. Results and discussion

Following a method previously described by us for other phosphazene phosphine complexes [8], the hexachlorocyclotriphosphazene $[N_3P_3Cl_6]$ was reacted with 6 equiv. of the phenolic phosphine complex $\{Mn(CO)_2(\eta^5\text{-}C_5H_4Me)[PPh_2(C_6H_4\text{–}OH)]\}$ (**1**) (Chart 1) in acetone in the presence of Cs_2CO_3 to give the hexametallic phosphazene complex $\{N_3P_3[OC_6H_4PPh_2\text{–}Mn(CO)_2(\eta^5\text{-}C_5H_4Me)]_6\}$ (**2**) in good yield and analytically pure (Chart 2).

This result is interesting, because it has been reported [12] that the direct substitution reaction of the cyclophosphazene–hexaphosphine $\{N_3P_3[OC_6H_4PPh_2]_6\}$ with the precursor $[Mn(THF)(CO)_2(\eta^5\text{-}C_5H_5)]$ in THF gives a mixture of complexes with $OC_6H_4PPh_2\text{–}Mn(CO)_2(\eta^5\text{-}C_5H_5)$ units, and the saturation of all the PPh_2 sites required the presence of an important excess of the organometallic manganese precursor. Thus, the synthesis of the pure totally substituted complex analogous to (**2**) was not reported.

In a similar manner, the cyclic chorophosphazene $[N_3P_3(O_2C_{12}H_8)_2Cl_2]$ where ($O_2C_{12}H_8$ = 2,2′-dioxybiphenyl) was reacted with (**1**) to give the bimetallic cyclic



2

3

Chart 2.

phosphazene complex $\{N_3P_3(O_2C_{12}H_8)_2[OC_6H_4PPh_2-Mn(CO)_2(\eta^5\text{-}C_5H_4Me)]_2\}$ (**3**), also in good yield. We observed that, in this case, the same complex **3** could be also prepared by ligand replacement reaction from the diphosphine $\{N_3P_3(O_2C_{12}H_8)_2[OC_6H_4PPh_2]_2\}$ [8] and $[Mn(THF)(CO)_2(\eta^5\text{-}C_5H_4Me)]$ in THF.

The reactions of the phenolic complex **1** with the cyclic models could be successfully extended to the partially substituted phosphazene copolymer $\{[NP(O_2C_{12}H_8)]_{0.6}[NPCl_2]_{0.4}\}_n$, which is a polymeric counterpart of the cyclic bis-spirophosphazene $[N_3P_3(O_2C_{12}H_8)_2Cl_2]$. Thus, the reaction of this latter with **1** in THF in the presence of Cs_2CO_3 gave the high molecular weight polymeric complex $[\{NP(O_2C_{12}H_8)\}_{0.6}\{NP[OC_6H_4PPh_2-Mn(CO)_2(\eta^5\text{-}C_5H_4Me)]_2\}_{0.4}\cdot 0.5(OC_4H_8)]_n$ (**4**) (Scheme 1). The yield (68%) was good and much higher than for the analogous polymer with $W(CO)_5$ fragments [8], and the effectiveness of the substitution reaction was very high, as shown by the very low residual chorine content in the isolated polymer (0.03% in weight). This shows that the method in Scheme 1 may be of wide application provided that the necessary phenolic complex $OH-C_6H_4-L-MLn$ is stable under refluxing THF for several hours.

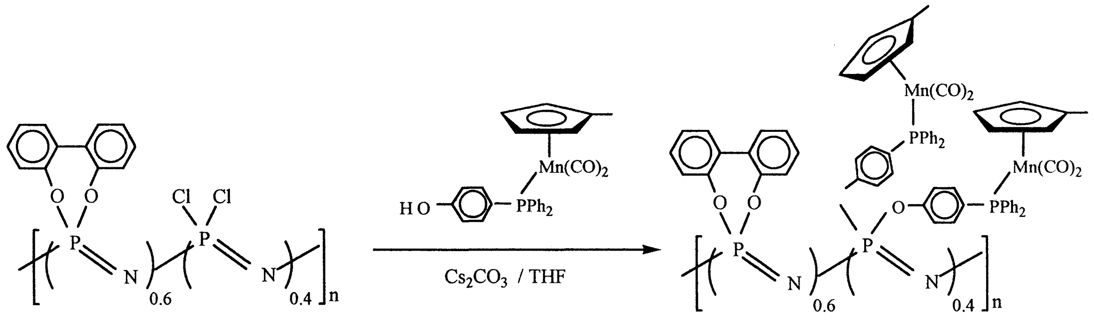
The polymer **4** was very stable and could be stored in the solid state for years unaltered. The M_w (by GPC) was 1,100,000 (polydispersity index = 4). Taking into account that the weight of the chain units is 529.4, the weight-averaged degree of polymerization is approximately 2000 units per chain, a value which is only slightly low for that type of phosphazene random copolymer [11]. The presence of some polytetrahydrofuran (PTHF) in this copolymer, that is expected when using THF as solvent in the substitution reaction from $[NPCl_2]_n$ [11,13], was detected and measured as described below. The PTHF, that can be minimized if necessary [13], represents approximately 6% in weight of the isolated material and does not alter the efficacy of the synthesis of **4**.

The successful preparation of polymer **4** from $\{[NP(O_2C_{12}H_8)]_{0.6}[NPCl_2]_{0.4}\}_n$ is valuable considering that it could not be prepared by the ligand substitution reaction from the precursor $[Mn(THF)(CO)_2(\eta^5\text{-}C_5H_4Me)]$, using the known phosphine containing polymer $[\{NP(O_2C_{12}H_8)\}_{0.6}\{NP[OC_6H_4PPh_2]_2\}_{0.4}]_n$ [8,14]. Thus, even using a large excess of the organometallic precursor the product isolated by this method had only 50% of the available PPh_2 ligands coordinated to $Mn(CO)_2(\eta^5\text{-}C_5H_4Me)$ fragments (as measured by ^{31}P NMR), and the elemental analysis showed a Mn content of 9.6%, much larger than the expected (4.4%), indicating the presence of uncharacterized contaminating Mn species. Considering the stability of **4**, this shows that the difficulty in completing the coordination of the PPh_2 groups in the $[\{NP(O_2C_{12}H_8)\}_{0.6}\{NP[OC_6H_4PPh_2]_2\}_{0.4}]_n$ by the THF substitution of $[Mn(THF)(CO)_2(\eta^5\text{-}C_5H_4Me)]$ is mainly due to the large steric effects imposed to the entering $Mn(CO)_2(\eta^5\text{-}C_5H_4Me)$ fragments by those already present in the polymeric chain.

All the spectroscopic data (see Section 2) were in accord with the structure proposed for the new compounds and provided further useful experimental evidences to characterize polymeric complexes of the transition metals.

The IR spectra (cm^{-1}) in CH_2Cl_2 or THF solutions of **1** to **4** (Section 2) showed the expected two strong stretching carbonyl absorptions of the $Mn(CO)_2(C_5H_4CH_3)$ groups at 1927, 1860. The solid state spectra (KBr pellets) showed several helpful features. In Section 2 are quoted all the signals observed with appreciable intensity. However, the assignments given (see the discussion below) correspond only to those more relevant absorptions, and in the region 800–600, where various significant frequencies appear among other from the vibrations of the aromatic rings, they have been quoted under a general assignment.

The IR of the cyclic phosphazene models **2** and **3**, showed the presence of the organometallic fragment by the two carbonyl absortions and also by two of the expected bands of the $Mn-C_5H_4CH_3$ ring [15], that were clearly distinguished at 2922w (ν-CH, CH_3) and 1376vw



4

Scheme 1.

(δ-CH_3), and by three conspicuous bands at 662m, 618m and 596m, that are related to δ-MnCO modes [15]. All those bands were absent in the spectra of the uncoordinated phosphazene phosphines $\{N_3P_3[OC_6H_4$-$PPh_2]_6\}$ and $\{N_3P_3(O_2C_{12}H_8)_2[OC_6H_4PPh_2]_2\}$. However, in the region from 1600 to 680, that could be potentially useful to study P-aryl compounds [16], the IR spectra of **2** and **3** (Section 2) appear almost identical to those of the corresponding free ligands. Thus, except for the commented weak band at 1376, the only significant difference was observed in a pair of very closed but well resolved peaks at 950–940, because, in the case of the metal complexes, the later, that is assignable to δ-POC modes [17], is much stronger than the former. As this feature is also observed for the analogous $W(CO)_5$ complexes, it suggests a decrease intensity of the band at 950 after the complexation of a MLn fragment to the PPh_2 group that could be useful to denote it. However, although all the differences commented between the spectra of the cyclic phosphazene phosphines and its complexes were also found in the spectra of the polymeric complex **4** and its corresponding free ligand $[\{NP(O_2C_{12}H_8)\}_{0.6}\{NP[OC_6H_4$-$PPh_2]_2\}_{0.4}]_n$, in this case, the 950–940 band was too broad to unambiguously show the coordination of a metallic fragment.

A couple of bands at 2927w, 2857w in the IR of the polymer **4**, evidenced the presence of the PTHF, that was expected in this synthesis [13].

Finally, the broad band near 525 cm^{-1}, that is observed in the spectra of **2**, **3** and **4**, may be attributed to the aryloxyphosphazene scheleton (δ-NPO modes) [17], but similar bands are also present in the spectra of the phosphine **1**, therefore is was not assigned in Section 2.

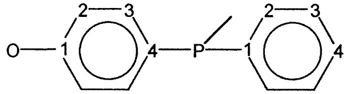
The ^{31}P NMR spectra was specially significant showing the very large deshielding of the phosphorus of the PPh_2 coordinated to the manganese dicarbonyl fragment as compared with those of the free phosphines. Thus, in the free phenolic phosphine $HOC_6H_4PPh_2$, in the cyclic phosphazene hexaphosphine $\{N_3P_3[OC_6H_4$-$PPh_2]_6\}$, and in the spyro-phosphazene bis-phosphine $\{N_3P_3(O_2C_{12}H_8)_2[OC_6H_4PPh_2]_2\}$, the chemical shift is circa -6 ppm, while in their $Mn(CO)_2(C_5H_4-CH_3)$ complexes **1**, **2** and **3**, the value is near 93 ppm. Consistently, the ^{31}P NMR of the polymer **4** showed three peaks at 92.1(PPh_2), −6.4 $[NP(O_2C_{12}H_8)]$ and −23.6 $[P(OC_6H_4PPh_2Mn(CO)_2(C_5H_4-CH_3)]$, and the intensity of the latter two were in accord with the ratio of the units present in the proposed formula. By comparing the chemical shift of the phosphorus of the phosphazene rings in $\{N_3P_3[OC_6H_4PPh_2]_6\}$ (8.8 ppm) $\{N_3P_3(O_2C_{12}H_8)_2\ [OC_6H_4PPh_2]_2\}$ (25.8 for the $NP(O_2C_{12}H_8)$, and 10.0 for the $NP[OC_6H_4PPh_2]_2$) [8], with those in **2** (8.0) and **3** (25.7 and 9.7, respectively), it can be noticed how they are sensitive to the presence of the coordinated metallic fragment. This has been repeatedly observed in cyclic and polymeric phosphazenes having pendant complexes with other ligands, such as OC_6H_4-CN [18], or OC_5H_4N [9,19,20]. This effect is also noted in the chemical shifts of the phosphorus atoms baring the groups $OC_6H_4PPh_2-Mn(CO)_2(\eta^5$-$C_5H_4Me)$ in polymer **4**, that are 1.6 ppm lower than in the free phosphine polymer $[\{NP(O_2C_{12}H_8)\}_{0.6}\{NP[OC_6H_4PPh_2]_2\}_{0.4}$ [8].

The ^1H NMR of all the Mn complexes showed the $(C_5H_4CH_3)$ ring as two multiplets at 4.2 and 4.0, and a singlet at 1.9 (CH_3). In the case of the polymer **4**, those peaks appeared at slightly lower frequencies (3.9, 3.7 and 1.8 ppm). This is usually observed by comparing the NMR signals of different groups when free and when pendant from long spyro-phosphazene copolymeric chains [9]. On the other hand, the relative intensities of those signals with those of the aromatic protons (broad signals between 7.5 and 6.7 ppm) gave a ratio of 0.62/0.38 for the two phosphazene units in the copolymer, very close to the idealized value given in the proposed formula. The ^1H spectra of polymer **4** also showed the presence of PTHF (peaks at 3.4 and 1.6) the intensity of which corresponded to an amount of 0.5 OC_4H_8 units per NP unit, representing 6.4% in weight.

The ^{13}C NMR of the models **2** and **3** and the polymer **4**, showed the two carbonyls $Mn(CO)_2$ as a doublet at 234 ppm with a coupling constant $^{13}C-^{31}P$ of 24 Hz, and the $(C_5H_4CH_3)$ ring as four singlets at nearly 100, 84, 82 and 14 (CH_3) ppm. Other peaks in the ^{13}C NMR spectra corresponded to the $O_2C_{12}H_8$ rings (148.6, 130.4, 130.3, 129.3, 126.8, 122.5) [11], and to the $OC_6H_4-PPh_3$ units (in Table 1 are given the assignments, that may be useful for the characterization of similar phosphazenes with transition metal phosphine complexes). As can be noticed, some peaks of the two types of aromatic rings may interfere, as happens in the polymer **4**, where some assignments may be ambiguous, specially those near the 130 ppm region. However, the data in Table 1 clearly show that, in agreement with a general rule noted by us [21], when the phenol $HOC_6H_4-PPh_2Mn(CO)_2(C_5H_4CH_3)$ is transformed into $NP-OC_6H_4-PPh_2Mn(CO)_2(C_5H_4CH_3)$ groups pendant from cyclic or polymeric phosphazene units, the chemical shift of the C1 carbon of the OC_6H_4- ring is shifted approximately 5 ppm to lower frequencies, that of the C4 increases by nearly the same amount, that of C2 also increases, and that of the C3 remains almost unaffected. On the other hand, the carbons of the $P(C_6H_5)_2$ rings shift very little upon the coordination of a metallic fragment to the phosphorus atom, although a large increase in the $^{13}C-^{31}P$ coupling constant (from 10 to 40 Hz) is clearly observed.

In the case of polymer **4**, the spectrum was rather broad, and the peaks at 130–129 corresponding to the C6, C4 and C1 carbons of the $O_2C_{12}H_8$ rings are hidden

Table 1
^{13}C NMR data for the $O-C_6H_4-PPh_2$ groups in phosphazenes [a]

	OC_6H_4P C_1	OC_6H_4P C_2	OC_6H_4P C_3	OC_6H_4P C_4	$(C_6H_5)_2P$ C_1	$(C_6H_5)_2P$ C_2	$(C_6H_5)_2P$ C_3	$(C_6H_5)_2P$ C_4	Ref
$HO-C_6H_4-PPh_2$	157.4	116.4 (8)	136.5 (21.5)	128.5 (8)	138.2 (9)	134.1 (19)	129.1 (10.5)	129	8
$N_3P_3(O-C_6H_4-PPh_2)_6$	151.6	121.8 (broad)	135.7 (20.5)	134.6 (12)	137.6 (11)	134.2 (19.5)	129.2 (7)	129.5	8
$N_3P_3(O-C_6H_4-PPh_2W(CO)_6)_6$	152.4	121.4 (10)	135 (13)	132.7 (34)	136 (40)	133.5 (12)	129.4 (10)	131.2	8
$HO-C_6H_4-PPh_2Mn(CO)_2$ $(\eta^5-C_5H_4Me)$ (**1**)	157.3	115.8 (9)	135.6 (11)	129.3 (not seen)	139.4 (40)	133.2 (9)	128.7 (7.5)	129.9	This work
$N_3P_3(O-C_6H_4-PPh_2-$ $Mn(CO)_2(\eta^5-C_5H_4Me))_6$ (**2**)	151.8	121 (8)	135 (11.5)	135.9 (40)	138.7 (40)	133.3 (10.5)	128.8 (9)	130.1	This work
$N_3P_3(O_2C_{12}H_8)_2(O-C_6H_4-PPh_2-$ $Mn(CO)_2(\eta^5-C_5H_4Me))_2$ (**3**)	152.1	121.4	135.1 (11.5)	136.5 (40.5)	138.9 (40.5)	133.4 (10.5)	128.8 (9)	130.1	This work
$\{[NP(O_2C_{12}H_8)]_{0.65}$ $[NP(O-C_6H_4-PPh_2]_{0.35}\}_n$	152	121.7 (broad)	135.2 (19)	(hidden)	138 (broad)	134.1 (19)	129 (broad)	129 (broad)	8
$\{[NP(O_2C_{12}H_8)]_{0.65}$ $[NP((O-C_6H_4-PPh_2-W(O)_5)_2]_{0.35}\}_n$	152	121 (broad)	134 (broad)	(hidden)	136 (broad)	133. (broad)	129	131 (broad)	8
$\{[NP(O_2C_{12}H_8)]_{0.6}[NP((O-C_6H_4PPh_2-$ $Mn(CO)_2(\eta^5-C_5H_4Me))_2]_{0.4}\}_n$ (**4**)	153	121	134 (broad)	(hidden)	139 (broad)	133 (broad)	129 (broad)	130 (broad)	This work

[a] δ in ppm, J in Hz, $CDCl_3$ as solvent.

under the intense signals of the C3 and C4 of the $P(C_6H_5)_2$ groups (see Table 1). The ^{13}C NMR spectra of polymer **4** also confirmed the presence of PTHF (71.3, 27.2 ppm).

The thermal stability of the polymeric complex **4**, as measured by TGA at a heating rate of 10 °C min^{-1}, was only moderate. Surprisingly, the initial loss of weigh below 150^{a}C expected for the depolymerization of PTHF (6%) and evaporation of the resulting THF, was reduced to 1.25% between 0 and 250 °C. A first important loss (22%) was centered at 350 °C, followed by another one of 36% at 450 °C. At 800 °C the residue was of the order of 41%. The loss of 350 °C is probably due to the volatilisation of organic molecules arising from the organometallic ligands, while the loss at higher temperature correspond to the formation of volatiles after the decomposition of the aryloxypolyphosphazene units to give a crosslinked pyrolitic residue [22].

The DSC curve for **4**, scanned from −50 to 250 °C, showed a clear heat capacity jump corresponding to a glass transition with $T_g = 128$ °C ($\Delta C_p = 0.16$ J g^{-1} K^{-1}). This T_g is higher than that of the free phosphine polymer $[\{NP(O_2C_{12}H_8)\}_{0.6}\{NP[OC_6H_4PPh_2]_2\}_{0.4} \cdot 0.7[OC_4H_8]_n$ ($M_w = 800.000$, $T_g = 96$ °C), made by the same method [14], a difference due to the presence of voluminous transition metal-ligand fragments in **4** [23–25] (for the similar phosphine polymer with higher M_w the value is 115 °C, and for its $W(CO)_5$ complex is 127 °C [8]).

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