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Direct synthesis of cyclic and polymeric phosphazenes bearing diphenylphosphine groups and their complexes with $[W(CO)_5]$ fragments

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Abstract

The reactions of the cyclotriphosphazenes $[N_3P_3Cl_6]$ or $[N_3P_3(O_2C_{12}H_8)_2Cl_2]$ with the phenolic phosphine $PPh_2(C_6H_4\text{-}OH)$ in the presence of Cs_2CO_3 give, respectively, the cyclic phosphazene phosphines $[N_3P_3(OC_6H_4PPh_2)_6]$ (**1**) and $[N_3P_3(O_2C_{12}H_8)_2(OC_6H_4PPh_2)_2]$ (**2**), very pure and in high yield. The similar reaction with the linear polyphosphazene $\{[NP(O_2C_{12}H_8)]_{0.65}[NPCl_2]_{0.35}\}_n$ in THF gives the diphenylphosphine polymer $\{[NP(O_2C_{12}H_8)]_{0.65}[NP(OC_6H_4PPh_2)_2]_{0.35}\}_n$ (**3**). The phenolic tungsten pentacarbonyl complex $\{W(CO)_5[PPh_2(C_6H_4\text{-}OH)]\}$ reacts in the same way with those cyclic and polymeric phosphazenes to give the corresponding complexes $\{N_3P_3[OC_6H_4PPh_2\text{-}W(CO)_5]_6\}$ (**4**), $[N_3P_3(O_2C_{12}H_8)_2(OC_6H_4PPh_2\text{-}W(CO)_5)_2]$ (**5**), and $\{[NP(O_2C_{12}H_8)]_{0.65}[NP(OC_6H_4PPh_2\text{-}W(CO)_5)_2]_{0.35}\}_n$ (**6**). © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Cyclophosphazenes; Polyphosphazenes; Phenolic phosphine; Macromolecular complexes; Carbonyls; Cesium carbonate

1. Introduction

Transition metal polymeric complexes are interesting for many reasons, including their potential technological importance [1]. The metal-containing polymers that consist on a polymeric main chain with a pendant complex of a ML_n fragment attached through a spacer (Fig. 1) are of interest for their relevance to catalysis [2,3], and other possible applications [4]. A number of polymeric complexes of this type are known where the main chain is a linear polyphosphazene $[\text{-}N{=}PR_2]_n$ [5]. Among those, there are a few that bear transition metal–phosphine complexes [6,7] (i.e. $L{=}PPh_2$), some of which have been found to exhibit useful catalytic properties [8].

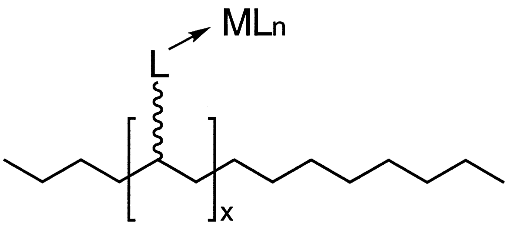

Fig. 1. A linear polymer with a metal–ligand complex attached through a spacer.

The most common synthetic route to these polymeric complexes, starting from a chlorophosphazene precursor, involves the multistep preparation of the polymer bearing the PPh_2 group (reactions (i)–(iii) in Scheme 1), followed by a substitution reaction with a transition metal complex having a labile ligand S (reaction (iv) in Scheme 1). However, this method involves several difficulties. Thus, in step (iii) some of the PPh_2 sites are quaternized by the BuBr formed in the lithiation step [9], and the substitution reaction (iv) may be complicated by crosslinking caused by the coordination to the same metal center of two PPh_2 groups from different chains, giving rise to insoluble materials [7].

Searching for other alternatives, we tried to introduce a complex directly into the phosphazenes by means of the replacement reaction indicated by (v) in Scheme 1.

We chose the fragment $W(CO)_5$ because it is easily coordinated to a PPh_2 groups to give very stable complexes, and because it has a potential interest as a chromophore for second harmonic generation [10].

In this paper we describe the preparation of cyclic and

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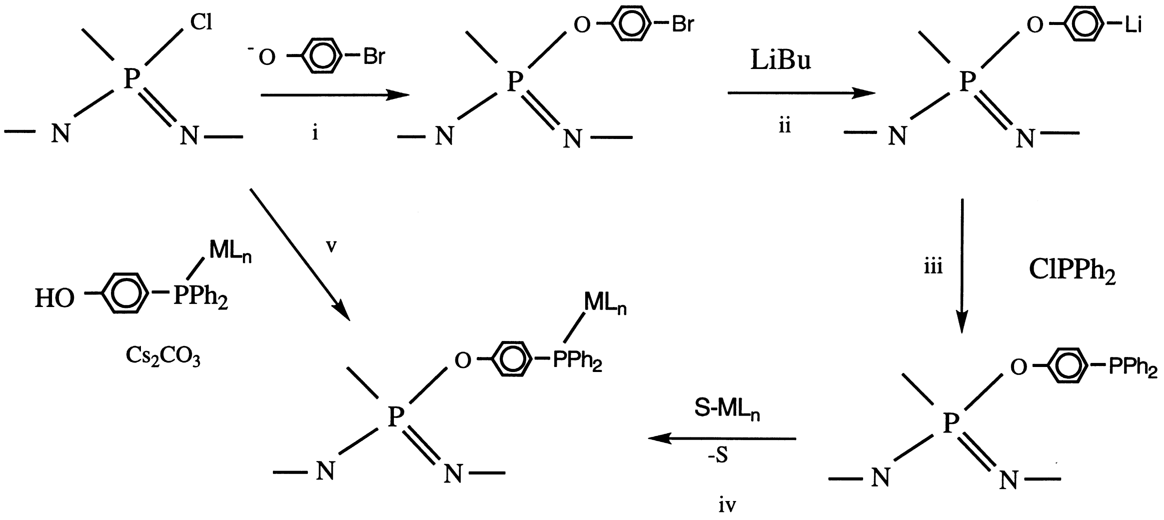


Scheme 1.

polymeric phosphazenes bearing diphenylphosphine groups and their $[W(CO)_5]$ complexes by this direct route, consisting on the reaction of a phenolic phosphine $PPh_2(C_6H_4\text{-}OH)$ or its complex $\{W(CO)_5[PPh_2(C_6H_4\text{-}OH)]\}$ with cyclic or polymeric chlorophosphazenes in the presence of Cs_2CO_3.

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 acetone used as solvent was predistilled from $KMnO_4$, and distilled twice from anhydrous $CaSO_4$. 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 4-hydroxy-phenyl diphenylphosphine ($HO\text{-}C_6H_4\text{-}PPh_2$) [11] was synthesised by reacting the known [12] $(CH_3O)(CH_3)_2C\text{-}O\text{-}C_6H_4\text{-}Li$ with $PClPh_2$ followed by deprotection with aqueous HCl (see Experimental). The hexachlorocyclotriphosphazene $[N_3P_3Cl_6]$ (Fluka) was purified from hot petroleum ether and dried in vacuum. The cyclic $[N_3P_3(O_2C_{12}H_8)_2Cl_2]$ was prepared as described elsewhere [13]. The polymer $[NPCl_2]_n$ was prepared by heating the melted $[N_3P_3Cl_6]$ as described by Allcock et al. [14].

The IR spectra were recorded with a Perkin-Elmer FT Paragon 1000 spectrometer. NMR spectra were recorded on Bruker AC-200 and AC-300 instruments, using $CDCl_3$ as solvent unless otherwise stated. ^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 240 microanalyzer. The chlorine, phosphorus and tungsten analyses were performed by Galbraith Laboratories. Gel-permeation chromatography (GPC) was measured with 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 was 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. Thermal gravimetric analyses were performed on a Mettler TA 4000 instrument. The polymer samples were heated at a rate of 10°C/min from ambient temperature to 800°C under constant flow of nitrogen.

2.2. Preparation of $PPh_2(C_6H_4OH)$

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 triethylamine 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 and stirred overnight. Then, 20% aqueous HCl (36 ml) was added and, after stirring for 3 h, the mixture was extracted with diethyl ether (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 and filtered through a column of silica-gel. Evaporation of the solvent gave a white product that was crystallized from CH_2Cl_2/petroleum ether to give $PPh_2(C_6H_4OH)$ as white microcrystals. Yield: 6 g (46%). ^1H NMR 7.4–6.7 (m br, 14H, aromatic rings); 5.3 (s br, 1H, OH). ^{13}C NMR 157.4 s, 136.5 (d, $J_{PC}=21.6$), 128.5 (d, $J_{PC}=8$), 116.4 (d, $J_{PC}=8.3$) [P–C_6H_4]; 138.2 (d, $J_{PC}=9.2$), 134.1 (d, $J_{PC}=19.3$), 129.1 (d, $J_{PC}=10.6$), 129.0, [PPh_2]. ^{31}P NMR −6.6. Found: C, 77.3; H, 5.5%. Calc. for $C_{18}H_{15}OP$: C, 77.7; H, 5.4%.

2.3. Preparation of $\{W(CO)_5[PPh_2(C_6H_4\text{-}OH)]\}$

To a solution of $PPh_2(C_6H_4OH)$ (1.6 g, 5.74 mmol) in methanol (20 ml) was added a solution of $[W(MeOH)(CO)_5]$ obtained by irradiating with UV light $[W(CO)_6]$ (2.0 g, 5.7 mmol) in methanol (90 ml) until the carbonyl band at 1982 cm^{-1} was no longer observed (≈4.5 h). The mixture was stirred at room temperature overnight and filtered. The volatiles were removed in vacuo to give $\{W(CO)_5[PPh_2(C_6H_4\text{-}OH)]\}$ as a yellow solid that was washed with hexane and dried in vacuo. Yield 2.9 g., 85%. IR (CH_2Cl_2, cm^{-1}): ν(CO): 2071 m, 1977 w, 1937 s. ^1H NMR 7.5–6.8 (m.br.,14H, aromatic rings); 5.7 (s.br., 1H, OH). ^{13}C NMR 198 br., 199 br, [$W(CO)_5$]; 158, 136 (d, $J_{PC}=13.8$), 116.4 (d, $J_{PC}=11$) [P–C_6H_4]; 133.4 (d, $J_{PC}=11.9$), 130.9, 129.3 (d, $J_{PC}=9.7$) [PPh_2]. ^{31}P NMR 19.5 ($J_{PW}=243$ Hz). Found: C, 45.8; H, 2.3%. Calc. for $C_{23}H_{15}O_6PW$: C, 45.9; H, 2.5%.

2.4. Preparation of $[N_3P_3(OC_6H_4PPh_2)_6]$ **(*1*)**

A mixture of $[N_3P_3Cl_6]$ (0.3 g, 0.86 mmol), $PPh_2(C_6H_4\text{–}OH)$ (1.45 g., 5.21 mmol) and Cs_2CO_3 (3.36 g, 10.31 mmol) in acetone (30 ml) was refluxed for 0.5 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 $[N_3P_3(OC_6H_4PPh_2)_6]$ as a white solid. Yield 1.4 g, 91%. IR(nujol): ν(PN)-region: 1212 m, 1187 m, 1160 s. ^1H NMR 7.6–6.9 (m br, aromatic rings). ^{13}C NMR 151.6, 135.7 (d, $J_{PC}=20.6$), 134.6 (d, $J_{PC}=12$), 121.8 br [P–C_6H_4]; 137.6 (d, $J_{PC}=11$), 134.2 (d, $J_{PC}=19.5$), 129.5, 129.2 (d, $J_{PC}=7$) [PPh_2]. ^{31}P NMR 8.8 (s, 3P, P_3N_3); −6.4 (s, 6P, PPh_2). Found: C, 71.3; H, 4.5; N, 2.0%. Calc. for $C_{108}H_{84}N_3O_6P_9$: C, 72.1; H 4.7; N, 2.3%.

2.5. Preparation of $[N_3P_3(O_2C_{12}H_8)_2(OC_6H_4PPh_2)_2]$ **(*2*)**

A mixture of $[N_3P_3(O_2C_{12}H_8)_2Cl_2]$ (0.5 g., 0.87 mmol), $PPh_2(C_6H_4\text{–}OH)$ (0.485 g., 1.74 mmol) and Cs_2CO_3 (1.135 g., 3.48 mmol) in acetone (40 ml) was refluxed for 0.5 h. The solvent was removed in vacuo and the residue was extracted with CH_2Cl_2 (4×25 ml). The solution was filtered and evaporated to dryness to give $[N_3P_3(O_2C_{12}H_8)_2(OC_6H_4PPh_2)_2]$ as a white solid. Yield 0.75 g, 81%. IR(nujol): ν(PN)-region: 1243 m, 1171 s, br. ^1H NMR 7.6–6.9 (m, br, aromatic rings). ^{13}C NMR 151.9 (d, $J_{PC}=7$), 135.8 (d, $J_{PC}=20.6$), 134.5, 122.0 m. [P–C_6H_4], 137.7 (d, $J_{PC}=10.6$), 134.3 (d, $J_{PC}=19.5$), 129.5, 129.2 (d, $J_{PC}=7$) [PPh_2]; 148.6 m, 130.4, 130.2, 129.1, 126.7, 122.4 ($O_2C_{12}H_8$). ^{31}P NMR 25.8 [d, 2P, $P(O_2C_{12}H_8)$]; 10.0 [dd, 1P, $P(OC_6H_4\text{–}PPh_2)_2$]; −6.1 (s, 2P, PPh_2). Found: C, 67.8; H, 4.5; N, 3.9%. Calc. for $C_{60}H_{44}N_3O_6P_5$: C, 68.1; H, 4.2; N, 4.0%.

2.6. Preparation of $\{[NP(O_2C_{12}H_8)]_{0.65}[NP(OC_6H_4PPh_2)_2]_{0.35}\}_n$ **(*3*)**

A mixture of $[NPCl_2]_n$ (0.91 g, 7.86 mmol), 2,2′-$HOC_6H_4\text{–}C_6H_4OH$ (0.95 g, 5.11 mmol) and K_2CO_3 (2.82 g, 20.44 mmol) in THF (140 ml) was refluxed with mechanical stirring for 10 h. Then, the phosphine $[PPh_2(C_6H_4OH)]$ (1.57 g, 5.66 mmol) and Cs_2CO_3 (1.84 g, 5.66 mmol) were added, and the refluxing was continued for another 15 h. The resulting mixture was poured into water (1.5 l) to give a precipitate that was washed twice with water (1 l) and extracted with THF (300 ml). The resulting solution was filtered through celite and Na_2SO_4 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 white solid that was dried in vacuo, first at room temperature and then at 70°C for 3 days. Yield: 1.4 g (49.5%). The isolation procedure was carried out under the laboratory atmosphere. IR(nujol): ν(PN)-region: 1246 s, 1198 vs. ^1H NMR δ 7.4–6.6 (m, br, 16H, aromatic rings). ^{13}C NMR: 152 br, 135.2 (d, $J_{PC}=19.3$), 121.7 br [P–C_6H_4]; 138 br, 134.1 (d, $J_{PC}=19.2$), 129 br, [PPh_2]; 149 br, 129.6 br, 125.6 br, 123 br, [$O_2C_{12}H_8$]. ^{31}P NMR −5.6 [m, $P(O_2C_{12}H_8)$]; −6.1 (s, PPh_2); −22.0 [m, $P(PPh_2)_2$]. Found: C, 67.2; H, 4.3; N, 3.9%. Calc. for $C_{20.4}H_{15}NO_2P_{1.7}$: C, 68.3; H, 4.2; N, 4.2%, Chlorine content: 0.07%. M_w(GPC): 160 000 ($M_w/M_n=266$) (see text). T_g(DSC): 115°C ($\Delta Cp=0.21$ J $g^{-1}K^{-1}$). TGA: −50.7% (500°C). Residue at 800°C: 38%.

The product had traces (less than 2% in weight) of PTHF (weak signals in the ^1H NMR at 3.4 and 1.6). The freshly prepared polymer had ≈8% of the PPh_2 groups oxidized to $Ph_2P{=}O$ (weak signal at 28.5 in the ^{31}P NMR), a fraction that increases on standing, specially during handling in solution.

2.7. Preparation of $\{N_3P_3[OC_6H_4PPh_2\text{-}W(CO)_5]_6\}$ **(*4*)**

A mixture of $[N_3P_3Cl_6]$ (0.11 g, 0.33 mmol), $\{W(CO)_5[PPh_2(C_6H_4\text{–}OH)]\}$ (1.2 g, 1.99 mmol) and

Cs_2CO_3 (1.3 g, 3.96 mmol) in THF (20 ml) was refluxed for 1 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$\{N_3P_3[OC_6H_4PPh_2–W(CO)_5]_6\}$ as a yellow solid. Yield 1.05 g, 85%. IR: ν(CO) (CH_2Cl_2): 2071 m, 1980 w, 1937 s, br. ν(PN)-region (nujol): 1220 m, 1191 m, 1165 s. ^1H NMR 7.5–7.0 (m br, aromatic rings). ^{13}C NMR 199.5 {d, $J_{PC(trans)}=22$, 6CO}; 197.7 {d, $J_{PC(cis)}=7$, $J_{WC}=126$, 24CO}[$W(CO)_5$]; 152.4, 135 (d, $J_{PC}=13$), 132.7(d, $J_{PC}=34$), 121.4 (d, $J_{PC}=10$) [$P–C_6H_4–$]; 136 (d, $J_{PC}=40$), 133.5 (d, $J_{PC}=12.1$), 131.2, 129.4 (d, $J_{PC}=10$) [PPh_2]. ^{31}P NMR 20.5 (s, 6P, $PPh_2–W$, $J_{PW}=244$ Hz); 7.6 [s, 3P, P_3N_3]. Found: C 44.7; H, 2.3; N, 0.9%. Calc. for $C_{138}H_{84}N_3O_{36}P_9W_6$: C, 44.3; H, 2.3; N, 1.1%.

2.8. Preparation of $\{N_3P_3(O_2C_{12}H_8)_2[OC_6H_4PPh_2\text{-}W(CO)_5]_2\}$ *(**5**).*

A mixture of $[N_3P_3(O_2C_{12}H_8)_2Cl_2]$ (0.15 g., 0.26 mmol), $[W(CO)_5[PPh_2(C_6H_4–OH)]\}$ (0.32 g., 0.53 mmol) and Cs_2CO_3 (0.34 g., 1.04 mmol) in THF (30 ml) was refluxed for 45 min. 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$\{N_3P_3(O_2C_{12}H_8)_2[OC_6H_4PPh_2–W(CO)_5]_2\}$ as a yellow solid. Yield 0.3 g, 68%. IR: ν(CO) (CH_2Cl_2): 2071 m, 1981 w, 1938 s, br. ν(PN)-region (nujol): 1229 m, 1173 s br. ^1H NMR 7.6–7.0 (m br, aromatic rings). ^{13}C NMR($CDCl_3$): 199.5 {d, $J_{PC(trans)}=22$, 2CO}; 197.7 {d, $J_{PC(cis)}=7$, $J_{WC}=126$, 8CO} [$W(CO)_5$]; 152.9 (d, $J_{PC}=7$), 135.3 (d, $J_{PC}=13$), 132.6 (d, $J_{PC}=42$), 121.9 m, [OC_6H_4]; 135.7 (d, $J_{PC}=41$), 133.4 (d, $J_{PC}=12$), 131.1, 129.3 (d, $J_{PC}=10$) [PPh2]; 148.6 m, 130.4, 130.3, 129.1, 126.9, 122.4, [$O_2C_{12}H_8$]. ^{31}P NMR 25.6 [d, 2P, $P(O_2C_{12}H_8)$]; 20.7 (s, 2P, PPh_2, $J_{PW}=244$); 9.6 [dd, 1P, $P(OC_6H_4–PPh_2–W)_2$]. Found: C, 49.3: H, 2.7; N, 2.3%. Calc. for $C_{138}H_{84}N_3O_{36}P_9W_6$: C, 49.3; H, 2.6; N, 2.5%.

2.9. Preparation of $\{[NP(O_2C_{12}H_8)]_{0.65}[NP(OC_6H_4PPh_2\text{-}W(CO)_5)_2]_{0.35}\}_n$ *(**6**)*

A mixture of $[NPCl_2]_n$ (0.57 g, 4.96 mmol), 2,2′-HO-C_6H_4-C_6H_4-OH (0.6 g, 3.23 mmol) and K_2CO_3 (1.8 g, 12.9 mmol) in THF (130 ml) was refluxed with mechanical stirring for 6 h. Then, the complex $[W(CO)_5[PPh_2(C_6H_4\text{-}OH)]\}$ (3 g, 4.98 mmol) and Cs_2CO_3 (2.1 g, 6.44 mmol) was added, and the reaction was continued for another 16 h The resulting mixture was poured into water (1.5 l) to give a precipitate that was washed twice with water (1 l) and extracted with THF (200 ml). Some material remained undissolved. The extracts were 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 room temperature, for one week. Yield 0.6 g, 24%. The isolation operations were carried out under the laboratory atmosphere. IR: ν(CO) (CH_2Cl_2): 2071 m, 1981 w, 1936 s, br (in THF: 2070, 1978, 1938). ν(PN)-region (nujol): 1246 m, 1197 s. ^1H NMR 7.8–6.2 (m br, aromatic rings). ^{13}C NMR: 197.8 m, br [WCO_5]; 152 br, 134 br, 121 br. [$P–C_6H_4$]; 136 br, 133 br, 131 br, 129 [PPh_2]; 149 br, 130 br, 126 br, 123 br, [$O_2C_{12}H_8$]. ^{31}P NMR 20.0 (s., $PPh_2–W$, $J_{PW}=244$); −5.0 [m, $P(O_2C_{12}H_8)$]; −23.5 [m, $P(OC_6H_4–PPh_2–W)_2$]. Found: C, 50.1; H, 2.6; N, 2.4; P, 9.9; W, 22.4%. Calc. for $C_{23.9}H_{15}NO_{5.5}P_{1.\ 7}W_{0.7}$: C, 49.0: H, 2.6; N, 2.6; P, 9.0; W, 21.9%. Chlorine content: 0.04%. M_w(GPC): 1 700 000 ($M_w/M_n=4$). T_g(DSC): 127°C. ($\Delta Cp=0.08$ J g^{-1} K^{-1}). TGA: −14% (150–380°C), −24% (470°C). Residue at 800°C:56%.

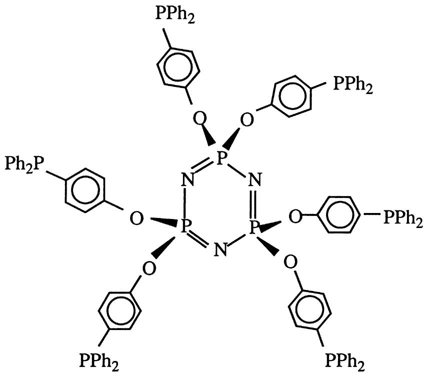
The polymer had ≈7% of the PPh_2 groups oxidized to $Ph_2P{=}O$. (weak signal at 28.5 in the ^{31}P NMR).

3. Results and discussion

Following the method described earlier for the synthesis of other aryloxi phosphazenes [15], the hexachlorocyclotriphosphazene $[N_3P_3Cl_6]$ was reacted with six equivalents of the phosphine phenol $PPh_2(C_6H_4OH)$ in refluxing acetone in the presence of Cs_2CO_3 to give, in only 1/2 h, the hexaphosphine derivative $[N_3P_3(OC_6H_4PPh_2)_6]$ (**1**) (Chart 1), that was obtained analytically and spectroscopically pure, in 90% yield. The very short reaction time required to obtain **1** is rather surprising taking into account the size of the PPh_2 groups [16,17]. This compound had been previously prepared [18] starting from $[N_3P_3(OC_6H_4Br)_6]$ using the three step synthesis shown in Scheme 1.

In a similar manner to $[N_3P_3Cl_6]$, the spirocyclic phosphazene [13] $[N_3P_3(O_2C_{12}H_8)_2Cl_2]$ reacted with $PPh_2(C_6H_4OH)$ and Cs_2CO_3 in refluxing acetone to give the new diphosphine $[N_3P_3(O_2C_{12}H_8)_2(OC_6H_4PPh_2)_2]$ (**2**), in ≈80% yield (Chart 1). This reaction is also surprisingly fast, requiring only 1/2 hour for completion.

This observation led us to extend the same technique to synthesize the high molecular weight phosphazene $\{[NP(O_2C_{12}H_8)]_{0.65}[NP(OC_6H_4PPh_2)_2]_{0.35}\}_n$ (**3**) shown in Scheme 2, which is the polymeric counterpart of **2**. As shown in Scheme 2, this random copolymer was obtained by reacting first the poly(dichlorophosphazene) $[NPCl_2]_n$ with 2,2′-dihydroxy-biphenyl (2,2′-HOC_6H_4-C_6H_4OH) and K_2CO_3 in THF [13] to give the partially substituted intermediate $\{[NP(O_2C_{12}H_8)]_{0.65}[NPCl_2]_{0.35}\}_n$ that was subsequently reacted with $PPh_2(C_6H_4OH)$ and Cs_2CO_3. Both steps could be followed by ^{31}P NMR to prove that no crosslinked products were formed in the first step, and that, the mechanism of the second step was non-geminal. The product **3** is only sparingly soluble in THF.



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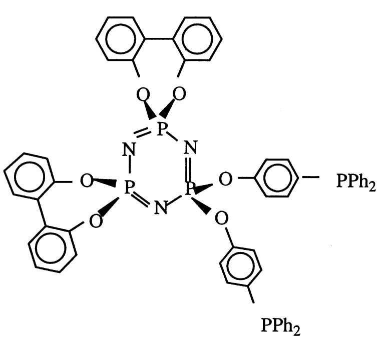

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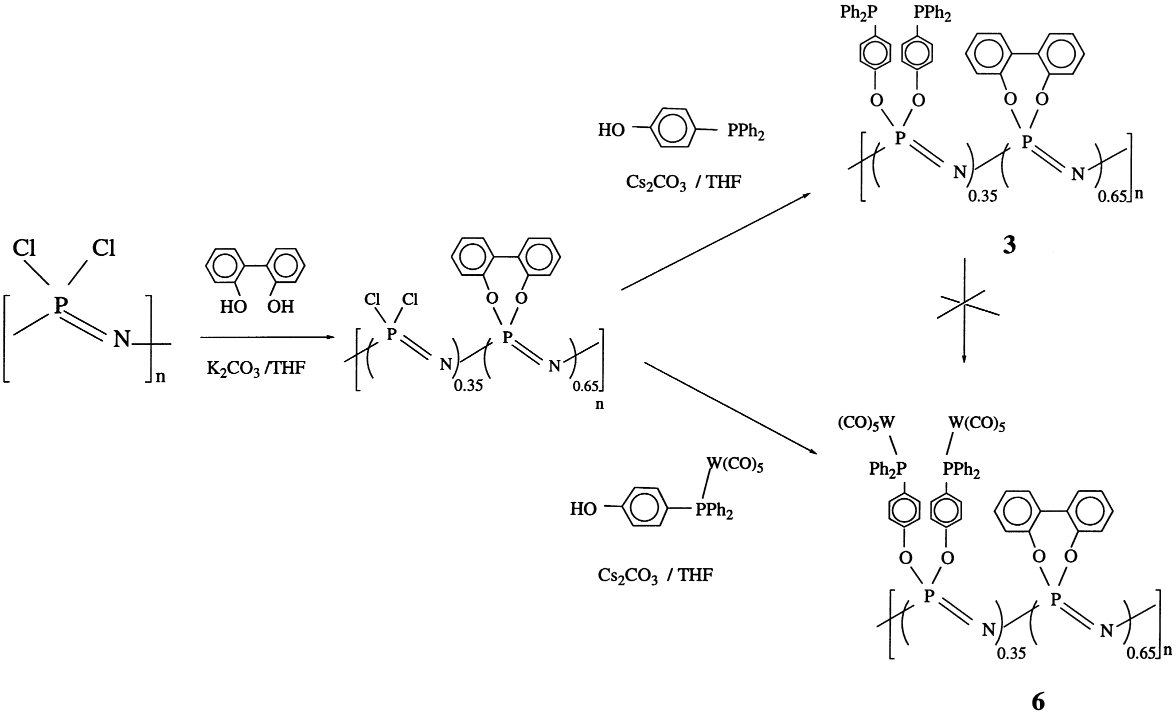
Chart 1.

The analytical and spectroscopic data for the isolated polymer (**3**) confirmed its composition and revealed that the residual unreacted chlorine was very low (700 ppm). No bands attributable to terminal OH groups were detected in the IR spectrum. The ^{31}P NMR proved the ratio of the $NP(O_2C_{12}H_8)/NP(OC_6H_4PPh_2)_2$ units, and showed that a fraction (less than 8%) of the PPh_2 groups (chemical shift -6.4 ppm) were oxidized to $O{=}PPh_2$ (28.5 ppm). The oxidation was observed to increase with time on standing in the solid state (raising 27% in 2 years), showing that the polymer is air sensitive (it becomes more insoluble and fragmented). On the other hand, two weak signals at 3.4 and 1.6 ppm in the ^{1}H NMR revealed that **3** contained traces of poly tetrahydrofuran (PTHF), which is in accord with previous observations made during the synthesis of poly(2,2′-dioxybiphenyl) phosphazenes in THF as solvent [19].

Rather surprisingly, the GPC chromatogram of **3** was weak and very broad showing several peaks corresponding to M_w ranging from 2×10^6 to 10^3. The estimated M_w was (160 000) but the sample was extremely polydisperse ($M_w/M_n=266$). Although this can be due in part to the low solubility of this polymer, we found no convincing explanation for this unusual behaviour.



Scheme 2.

The DSC curve showed a clear glass transition at 115°C which is in the expected range for a polyspirophosphazene random copolymer [13].

Similarly to the diphenylphosphine phenol, the tungsten carbonyl complex $\{W(CO)_5[PPh_2(C_6H_4\text{-}OH)]\}$ (formed from $[W(MeOH)(CO)_5]$ and $HO\text{-}C_6H_4\text{-}PPh_2$ in methanol at room temperature) reacted very fast with the cyclophosphazenes $[N_3P_3Cl_6]$ or $[N_3P_3(OC_{12}H_8)Cl_2]$ and Cs_2CO_3 to give respectively the phosphine complexes $[N_3P_3\{OC_6H_4\text{-}PPh_2\text{-}W(CO)_5\}_6]$ (**4**) and $[N_3P_3\{OC_6H_4\text{-}PPh_2\text{-}W(CO)_5\}_2(O_2C_{12}H_8)_2]$ (**5**) (Chart 2) in high yield and purity.

Both complexes were fully characterized by the analytical and spectroscopic data given in the Experimental section. Interestingly, the chemical shift of the ring phosphorus atoms in **4** are significantly lower than those of the related hexaphosphine **1**, which is in accord with earlier observations in other polymetallic cyclophosphazene complexes [20–22].

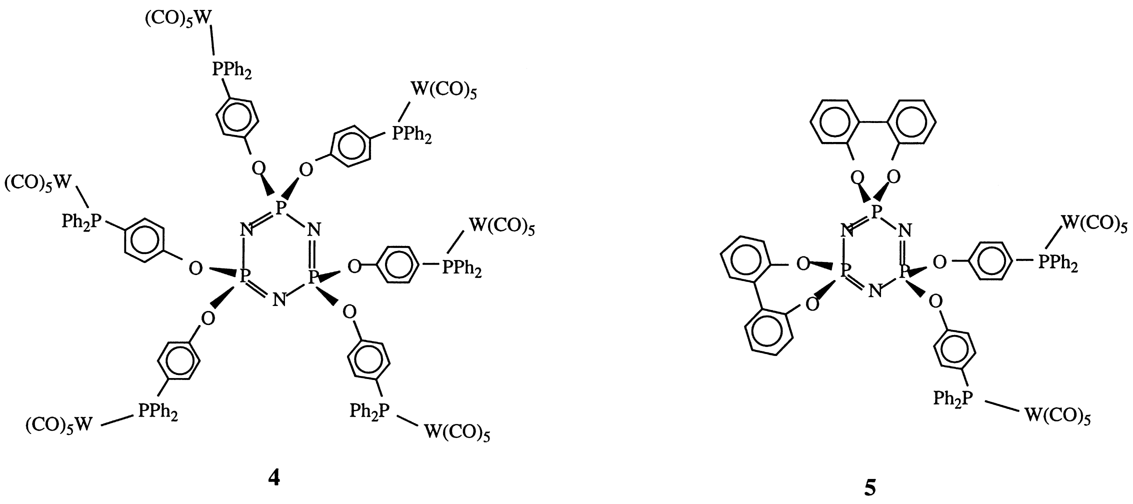
The above reactions were extended to the synthesis of polyphosphazenes carrying diphenylphosphine complexes of $W(CO)_5$. Thus, we found that the polymer $\{[NP(O_2C_{12}H_8)]_{0.65}[NPCl_2]_{0.35}\}_n$ (see Scheme 2), reacts with the phenolic complex $\{W(CO)_5[PPh_2(C_6H_4\text{-}OH)]\}$ in the presence of Cs_2CO_3 to give the very stable and soluble polymeric complex $\{[NP(O_2C_{12}H_8)]_{0.65}[NP(OC_6H_4PPh_2\text{-}W(CO)_5)_2]_{0.35}\}_n$ (**6**). The very low residual chlorine in the final product (below 0.05%) indicated the high efficiency of the substitution reaction, and the analytical purity after several reprecipitation steps from water, methanol and petroleum ether, all conducted under air, showed that the complex is rather stable. However, the yield was only 24%.

The IR (νCO absoptions at 2071 m, 1981 w, and 1936 s, br), ^{13}C NMR (diluted) and ^{31}P NMR spectra clearly showed the presence of the $PPh_2P\text{-}W(CO)_5$ groups. The ^{31}P NMR spectrum allowed a measurement of the ratio of $NP\{OC_6H_4\text{-}PPh_2\text{-}W(CO)_5\}_2$ and $NP(O_2C_{12}H_8)$ groups that was in agreement with the analytical data, and also showed that the product had 7% of the phosphine phosphorus as $Ph_2P{=}O$.

In sharp contrast with the phosphine polymer **3**, the GPC of **6** showed little polydispersity, with a M_w of 1 700 000 and polydispersity index of only 4. The glass transition temperature (127°C) was ≈10°C higher than that of **3**, in accord with the expected increase originated in the incorporation to the polymer of metallic fragments [23]. The ΔCp (0.08) was low, suggesting a high degree of crystallinity. The TGA curve showed two weight losses between 150–380°C (14%) and at 470°C (24%), but the final residue at 800°C was rather high (56%). Although those thermograms measure only the apparent thermal stability (which depends on the heating rate), this type of behaviour suggests that **6** is a rather stable material, although is somewhat easily oxidized by air.

In spite of the presence of $Ph_2P{=}O$ groups in **3** and **6**, and the low yield in the latter, these results open a new route for the preparation of phosphazene–phosphine and their complexes, both cyclic and polymeric, by the direct reaction of a chlorophosphazene and a phenol of the general type $LnM\text{-}Ph_2PC_6H_4\text{-}OH$. The mild conditions required in those reactions might allow the use of moderately stable phenolic complexes. Examples of this type of direct approach to the synthesis of metal-containing high molecular weight phosphazenes are very scarce. Thus, cyclic and polymeric phosphazenes with pendant $[Cr(CO)_3(\eta^6\text{-}C_6H_5O)]$ (also air sensitive) groups have been prepared by reacting the corresponding chlorophosphazenes with the sodium salt $[Cr(CO)_3(\eta^6\text{-}C_6H_5ONa)]$ [24].

Finally, it is worth noting that the reaction of polymer **3** with $[W(MeOH)(CO)_5]$ lead to a brown precipitate different to the soluble complex **6** (Scheme 2). The solid state IR spectrum of this insoluble material showed not only the carbonyl signals expected for the $Ph_2P\text{-}W(CO)_5$ fragments,



4

5

Chart 2.

but also other bands at 2016, 1889 and 1847 that most likely correspond to $W(CO)_4$ fragments. This shows the coordination to the same tungsten atom of two PPh_2 groups, explaining the formation of the insoluble (cross-linked) polymer.

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