

**New Approach for the Assembly of a Multi - Site Coordinating Polymeric Ligand:  
Synthesis of a Pendant Pyrazolyl Cyclotriphosphazene containing Polymer**

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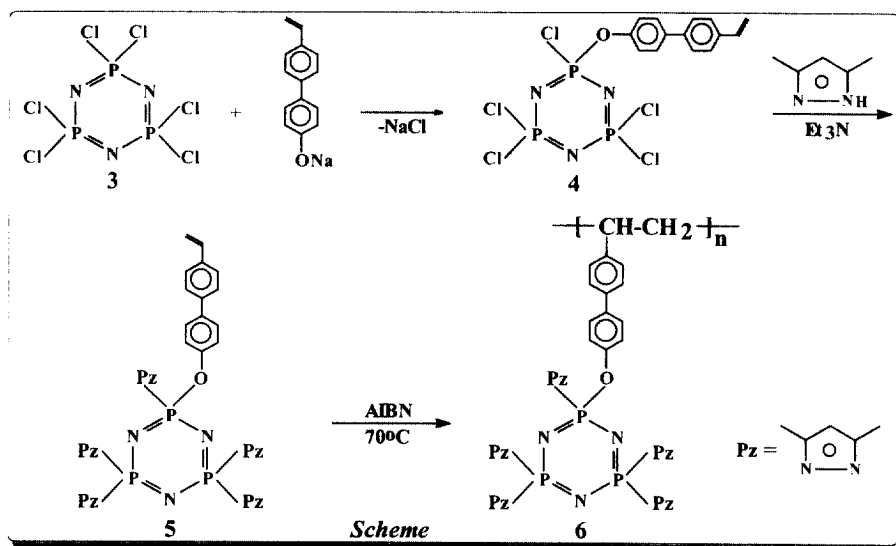
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Received 24 September 1998; revised 23 November 1998; accepted 30 November 1998

**Abstract:** A new multi-site coordinating polymeric ligand, **6**, containing a pendant cyclotriphosphazene moiety has been synthesised in high yield by a simple synthetic procedure

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In recent years there has been a resurgence of interest in solid-phase organic synthesis and in the use of polymer supported reagents or catalysts for organic reactions.<sup>1-2</sup> However, in spite of this renewed interest there are not many attempts reported in the literature on the development of new polymeric supports. The most popular among the traditional solid polymer supports are the divinylbenzene cross-linked polystyrenes<sup>3</sup> (Merrifield and Wang resins). In this account we wish to report the synthesis and characterisation of a new multi-site coordinating polymeric ligand based on pyrazolyl cyclotriphosphazene. Recently it has been shown that pyrazolyl cyclotriphosphazenes,  $N_3P_3(3,5-Me_2Pz)_6$  (**1**) and  $N_3P_3Ph_2(3,5-Me_2Pz)_4$  (**2**) exhibit a diverse coordination behavior with the formation of mono or bi (homo or hetero) metallic systems<sup>4-5</sup>. We have adapted these heterocycles to the polymeric system (Scheme).



Hexachlorocyclotriphosphazene,  $N_3P_3Cl_6$  (**3**) was reacted with the sodium salt of 4-hydroxy-4'-vinyl biphenyl to afford **4**. The remaining chlorine atoms in **4** were substituted by the reaction of 3,5-dimethyl

pyrazole in presence of triethylamine to afford **5**, which was characterised by multinuclear NMR and mass spectroscopy.<sup>6,7</sup> Compound **5** can be readily homopolymerised in dichloroethane using AIBN as the initiator to afford the polymeric ligand, **6**.<sup>6</sup> The invariance of the nature of <sup>31</sup>P NMR spectra (AB<sub>2</sub> type) in **5** and **6** demonstrates that the *multi-site* coordinating pyrazolyl cyclophosphazene moiety remains *unscathed* during polymerisation<sup>7</sup>. While **6** is soluble in organic solvents a cross-linked insoluble version of this polymer can be readily prepared by copolymerising **5** with small amounts of divinyl benzene. Both **6** and its cross-linked analogue have five pyrazolyl units per one pendant group in addition to skeletal nitrogens of the inorganic ring for coordination. These polymers should be able to interact with several types of metal ions leading to a rich array of polymer supported reagents or catalysts. Currently we are carrying out the metallation studies of **6** and its cross-linked analogue.

**Acknowledgements:** We are thankful to Department of Science and Technology and Council of Scientific and Industrial Research (India) for financial support. VC is thankful for a Homi Bhabha Fellowship.

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6. Preparation of **5**: To a solution of **4** (3.00 g, 5.91x10<sup>-3</sup> mol) in benzene (50 ml) was added a mixture of 3,5-dimethyl pyrazole (3.40 g, 3.54x10<sup>-2</sup> mol) and triethylamine (3.60 g, 3.56x10<sup>-2</sup> mol) also dissolved in benzene (50 ml). The reaction mixture was heated under reflux for 6h, allowed to come to room temperature and filtered. Removal of solvent from the filtrate afforded an oil which was flash chromatographed on silica gel using 25% ethyl acetate / 75% benzene as the eluent, to afford **5** which was isolated as a pale yellow crystalline solid (2.70 g, 49.9% yield), m.p.146° C. Preparation of **6**: **5** (2.00 g, 2.48x10<sup>-3</sup> mol) was dissolved in 1,2-dichloroethane (20 ml) along with AIBN (8.1 mg) and taken in a polymerisation tube. After three freeze-thaw cycles the tube was sealed and kept at 70° C for 19h. The tube was then cooled and opened. The contents were poured into an excess (400 ml) of hexane to afford **6** as a powder. It was purified by repeated reprecipitations. Pure **6** was obtained as a white solid. It was dried in vacuum (10<sup>-3</sup> Torr) at 40° C for 24hr. Yield, 1.70 g, 85%.
7. Spectroscopic data for **5** and **6** are given below.  
**5**: C<sub>39</sub>H<sub>48</sub>N<sub>13</sub>OP<sub>3</sub>: FAB Mass: m/z: 806 (M<sup>+</sup>), <sup>31</sup>P NMR (161.9 MHz, CDCl<sub>3</sub>): δ = 3.10 [t, P(OR)(Pz)], 0.41 [d, P(Pz)<sub>2</sub>], <sup>2</sup>J(P-N-P), 65.8 Hz. <sup>1</sup>H NMR (400.0 MHz, CDCl<sub>3</sub>): δ = 7.50 (m, 8H); 6.75 and 5.25 (m, 3H); 5.88, 5.81, 5.76 (s, 5H); 2.38, 2.24, 2.23, 2.09, 2.08, 2.00 (s, 30H)  
**6**: <sup>31</sup>P NMR (161.9 MHz, CDCl<sub>3</sub>): δ = 2.71 [t, P(OR)(Pz)], 0.10[d, P(Pz)<sub>2</sub>], <sup>2</sup>J(P-N-P), 65.5 Hz. <sup>1</sup>H NMR (400.0 MHz, CDCl<sub>3</sub>): δ = 7.50 (m, 8H); 5.70 (broad, 5H); 2.30 (broad, 30H), 1.50 (m, 3H). Intrinsic viscosity<sup>8</sup>: 3.6 cm<sup>3</sup>/g (benzene), indicating a molecular weight of 10,000 - 12,000.
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