

**SYNTHESIS, STRUCTURE AND HR NMR STUDIES OF  
CYCLOPHOSPHAZENE DERIVATIVES****Krystyna Brandt, Katarzyna Placha, Teobald Kupka<sup>1</sup> and Zbigniew Jedliński**

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In this work we would like to report our initial steps, dealing with synthesis and structure determination of several new ligands: ANSA and SPIRO-derivatives of hexachlorocyclotriphosphazene. These macromolecular compounds are potential ligands which can form inclusion complexes [1] with a number of metal ions, both alkaline and transition ones.

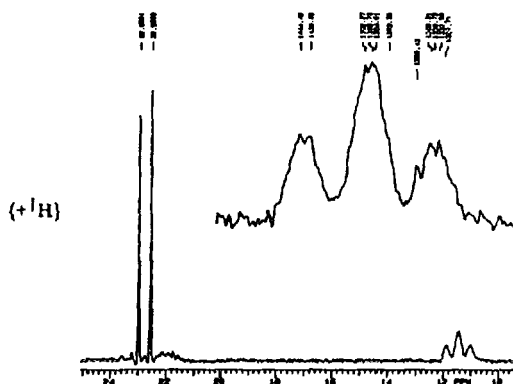
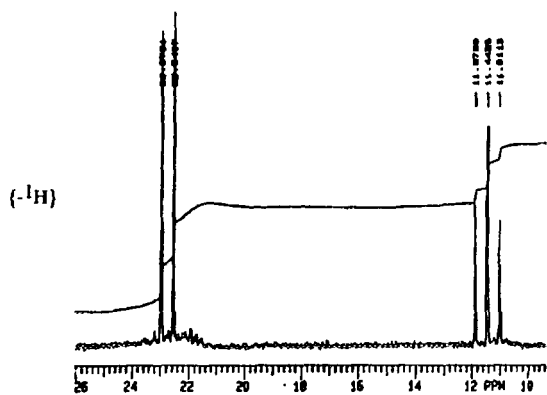
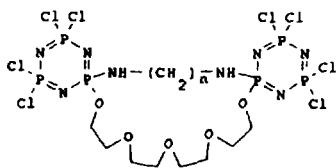
In our recent paper [2] we reported on synthesis and separation of the final products from a raw reaction mixture (chromatographic methods). Both raw reaction mixtures and purified products were analyzed using HR NMR (121 MHz P-31 spectra recorded with Varian VXR-300 NMR). Additionally, IR, mass spectra and elemental analyzes were used to resolve the molecular structure. P-31 NMR spectra were also used to determine the yield (or relative content) of various phosphorus species in crude reaction mixture. Proton and carbon NMR spectra of some final products were recorded, too.

X-ray studies on selected products are in progress. Also, initial semi empirical calculations (PM3 with the MOPAC 6.0 package) on hexachlorocyclotriphosphazene were performed. Geometry optimization (with respect to minimal energy) resulted in a fairly planar six membered ring (P-N-P-N dihedral angle of about 0.1 and P-N and Cl-P bond lengths of 1.6395 and 2.0236 Å, respectively and dipole moment of 0.005 D). The calculated heat of formation (HF = -192.7 kcal/mol) is also reasonable and indicates a fairly stable compound. The bond lengths are in good agreement with some X-ray data [3] in cyclophosphazenes (P-N of 1.54 to 1.65 and P-Cl of 1.98 to 2.01 Å).

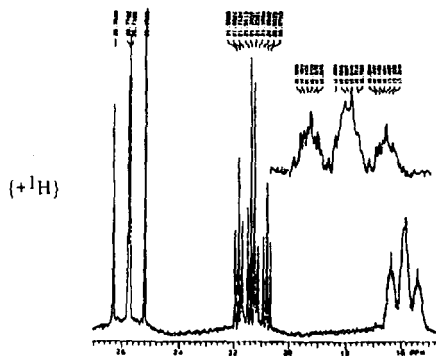
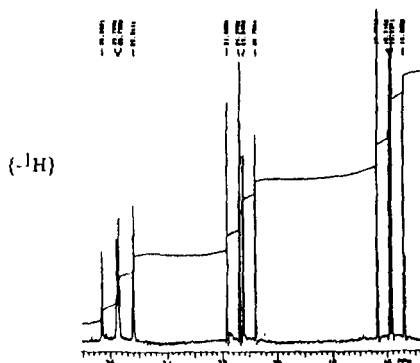
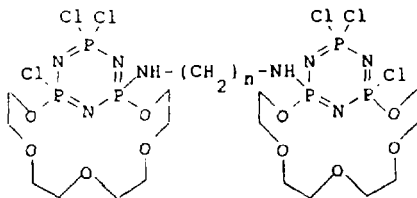
Below are examples of phosphorus NMR spectra at 121 MHz decoupled ( $-^1\text{H}$ ) and coupled with protons ( $+^1\text{H}$ ) in case of two newly obtained products.

## REFERENCES

1. J. -M. Lehn, "From Coordination Chemistry to Supramolecular Chemistry", [in "Perspectives in Coordination Chemistry", A. F. Williams, C. Floriani and A. E. Merbach [Eds.], Verlag Helvetica Chimica Acta, Basel 1992, pp. 447-462.
2. Z. Jedliński, J. Drozd, K. Brandt and T. Kupka, "Novel Synthetic Approach to Reactive Carbonyl-Containing cyclophosphazenes with Direct P-C Bond", in preparation.
3. M. Veith and M. Kross, J. Mol. Struct., 243, 189-209 (1991).



Widmo 3. <sup>31</sup>P NMR produktu syntezy: BINO[1,*n*]+GTE  
(*n*=12)



Widmo  $^{31}\text{P}$  NMR produktu syntezy: ANSA+diamina