Inorganica Chimica Acta, 90 (1984) L61–L63

Synthesis and Characterization of the First Dispirodiansabino-Cyclotriphosphazene and of the Second Spiroansa-Cyclotriphosphazene Described in the Literature

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Received July 23, 1984

The reactions of difunctional reagents with hexachlorocyclotriphosphazene, $N_3P_3Cl_6$ can give rise in principle to three types of structures (i) SPIRO (both functional groups attached to the same phosphorus atom), (ii) ANSA (the two functional groups attached to different phosphorus atoms in the same molecule), and (iii), BINO or CROSS-LINKING (each functional group attached to different phosphazene rings).

SPIRO derivatives are now well documented crystallographically [1–8]. One example of BINO has been reported, *e.g.* $N_3P_3Cl_5[HN{-}(CH_2)_4{-}NH]Cl_5P_3N_3$ [9]. The first ANSA structure has been ascribed spectroscopically [10] and crystallographically [11] to the product, $N_3P_3Cl_3(CH_3)[HN{-}(CH_2)_3{-}O]$, of the reaction of monomethylpentachlorocyclotriphosphazene, $N_3P_3Cl_5(CH_3)$, with 3-amino-1-propanol.

Moreover, few merged structures were very recently ascribed to (i) the product $N_3P_3Cl_4[HN{-}(CH_2)_3{-}N][(CH_2)_4{-}NH]Cl_5P_3N_3$ of the reaction of $N_3P_3Cl_6$ with spermidine, $H_2N{-}(CH_2)_3{-}NH{-}(CH_2)_4{-}NH_2$ (SPIROBINO) [12] (ii) the product $N_3P_3Cl_4[HN{-}(CH_2)_3{-}N](CH_2)_4[N{-}(CH_2)_3{-}NH]\cdot Cl_4P_3N_3$ of the reaction of $N_3P_3Cl_6$ with spermine, $H_2N{-}(CH_2)_3{-}NH{-}(CH_2)_4{-}NH{-}(CH_2)_3{-}NH_2$ (DISPIROBINO) [13] and (iii) the product $N_3P_3Cl_2[O{-}(CH_2)_3{-}O]_2$ of the reaction of $N_3P_3Cl_6$ with 1,3-dihydroxypropane (SPIROANSA) [6].

This paper reports the synthesis and characterization of a second SPIROANSA structure (**I**) and of the first DISPIRODIANSABINO cyclophosphazene (**II**).

Conclusive evidence for the existence of **I** and **II** were essentially obtained by ^{31}P NMR spectroscopy. The ^{31}P spectrum (Brucker WH 90) of the starting material, *e.g.* the ANSA-$N_3P_3Cl_3(CH_3)[HN{-}(CH_2)_3{-}O]$ is presented in Fig. 1 [10]. We added 1,3-diaminopropane (1:2) (half of the diamine being used for trapping HCl) in the NMR tube containing 58 mg of the ANSA material in $CDCl_3$ and 1 hour later a new ^{31}P spectrum was recorded, which is presented in Fig. 2.

Comparison of Figs. 1 and 2 shows that the PCl_2 doublet of doublets around 24.5 ppm of the ANSA starting material has vanished and that the expected doublet of sharp doublets around 11.4 ppm

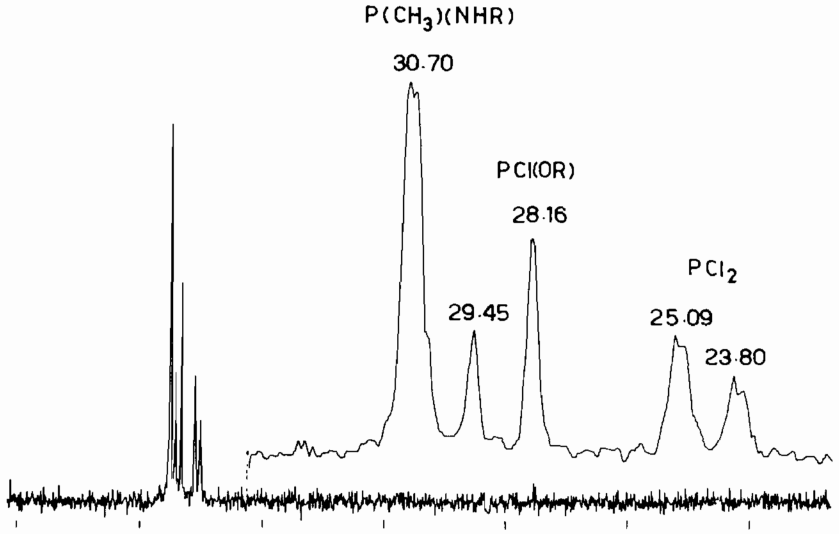

Fig. 1. ^{31}P NMR spectrum (BRUCKER WH 90) of the ANSA starting material. Chemical shifts (in ppm versus 85% H_3PO_4) are defined as positive in low field direction.

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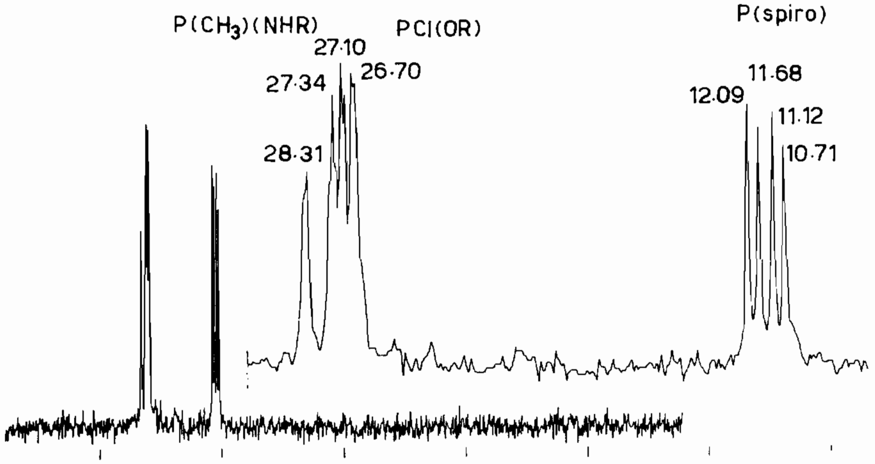

Fig. 2. ^{31}P NMR spectrum (BRUCKER WH 90) of (I). Chemical shifts (in ppm versus 85% H_3PO_4) are defined as positive in low field direction.

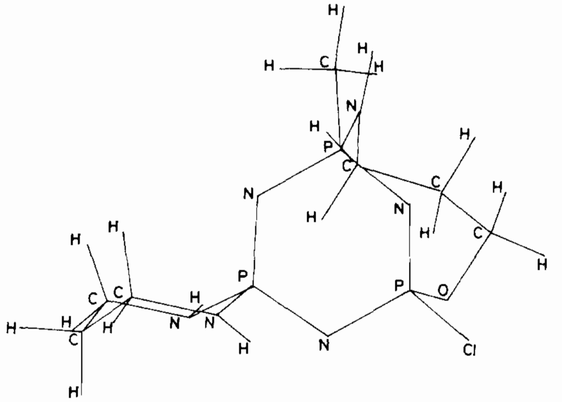

Fig. 3. A perspective view of (I).

is revealed, and may be assigned unambiguously to a SPIRO loop-bearing phosphorus atom [2, 3, 12, 13] in an ABC-type cyclotriphosphazene. The infrared spectrum of this new compound (I) reveals a unique P–Cl band at 555 cm^{-1}, assigned to (I) the SPIROANSA structure which is visualized in Fig. 3.

This structure contains one remaining labile Cl atom. 43 mg of (I) in $CDCl_3$ were treated as previously in a NMR tube with 15.1 mg of 1,6-diaminohexane, *i.e.* in (2:1 + 1) conditions, half of the diamine being used for trapping hydrogen chloride.

A new ^{31}P NMR spectrum was registered after 2 hours, and is presented in Fig. 4. The doublet of sharp doublets has shifted from 11.4 to 15.8 ppm. Such a high-field shift of about 4 ppm is a characteristic of the building somewhere in the molecule of a BINO bridge [13]. This new compound (II) is also an ABC-type cyclophosphazene whose molecular weight from E.I. [14] and DCI [15] mass spectrometry is equal to 674. Infrared spectrum of **II** does not reveal P–Cl stretching frequency anymore. Thus we may reasonably assign to (II) the DISPIRODIANSABINO structure of Fig. 5. X-ray structures of (I) and (II) are now being determined.

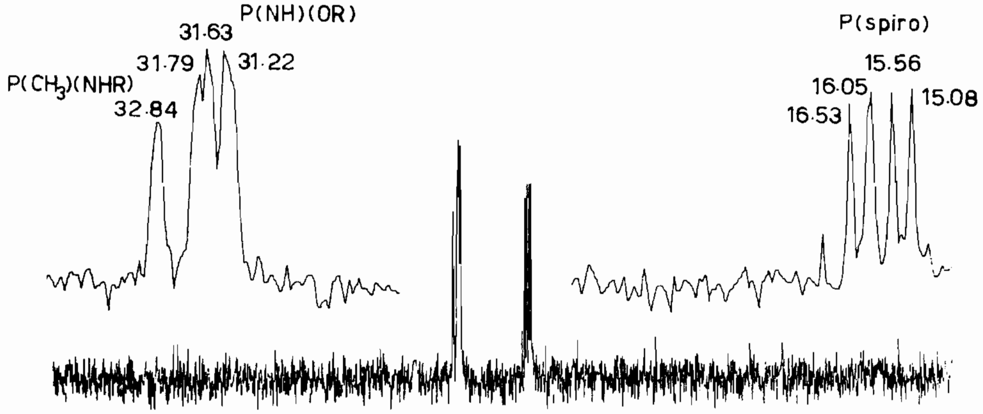

Fig. 4. ^{31}P NMR spectrum (BRUCKER WH 90) of (II). Chemical shifts (in ppm versus 85% H_3PO_4) are defined as positive in low field direction.

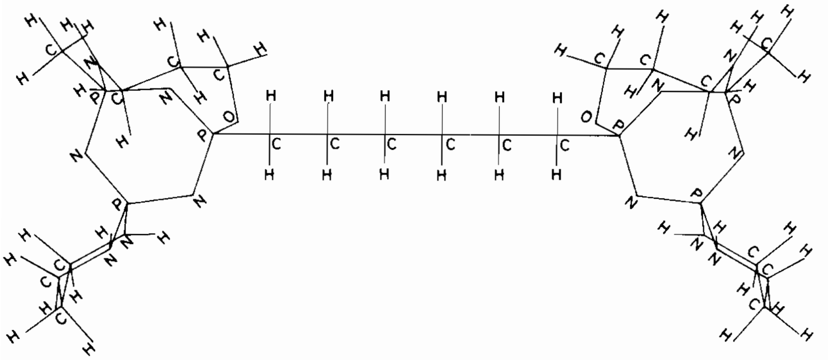

Fig. 5. A perspective view of (**II**).

As a conclusion, we emphasize the high stereospecificity and stereoselectivity of the two reactions described here. It seems from now that any merged chemical containing several SPIRO and/or ANSA and/or BINO moieties may be commonly synthesized in a quantitative manner. This provides the chemist with an interesting project which we propose labelling 'BASIC', *i.e.*, 'BINO-ANSA-SPIRO in cyclophosphazenes' [16].

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