Sexidentate Phosphorus-Containing Macrocyclic Ligands.
Synthesis of 1,10-Dipropyl-4,7,13,16-Tetraphenyl-1,10-Diaza-4,7,13,16-Tetraphospha-cyclooctadecane

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Received July 30, 1982

Macrocyclic polyphosphanes are currently under active investigation as stereochemically versatile and strongly-binding ligands toward soft transition metals [1–3]. We recently reported the synthesis and coordination behaviour of 18-membered potentially sexidentate macrocycles containing four phosphane groups and two ethereal or thioethereal groups, named [18]aneP_4O_2 and [18]aneP_4S_2, respectively [2, 3]. Five diastereoisomers are expected and have been isolated, due to the high racemization energy of tertiary phosphanes (Fig. 1). They display a markedly different coordinative behaviour according to the absolute stereochemistry at the phosphorus atoms and to the nature of E, as far as coordination number and geometry of their metal complexes are concerned.

TABLE I. Physical Data for Some [18]aneP_4O_2 Isomers.

Isomer	M.p. (°C)	$^{31}P\{^1H\}$ Chemical Shifts (ppm) in $CDCl_3$
(a)	oil	22.37; 22.43; 23.72; 23.96
(b)	oil	22.09
(c)	136–8	22.73
(d)	141–2	23.93

As a part of a continuing study on polyphosphane macrocycles we have synthesized the title ligand containing four phosphane and two tertiary amino groups: [18]aneP_4N_2, E = N-Pr. Marked differences in ligating ability of this macrocycle with respect to [18]aneP_4O_2 and [18]aneP_4S_2 are expected, due to different donicity and steric requirements of the tertiary amino group and ethereal or thioethereal groups.

The ligand [18]aneP_4N_2 has been prepared by adding 2,2′-dichlorodiethylpropylamine to the stoichiometric amount of the bis-potassium salt of 1,2-bis(phenylphosphino)ethane suspended in tetrahydrofuran at room temperature. Work up of the reaction mixture has led so far to the isolation of four diastereoisomers in the pure state. Physical data are reported in Table I.

Heating of each of the four diastereoisomers in boiling *m*-xylene (140 °C) leads, in about two hours, to the same equilibrium mixture of the five diastereoisomers as shown by ^{31}P NMR spectroscopy. The equilibrium spectra contain the signals of the four isomers and a further signal at 23.64 ppm, which can safely be attributed to the so far non-isolated diastereoisomer. The NMR estimated amounts of

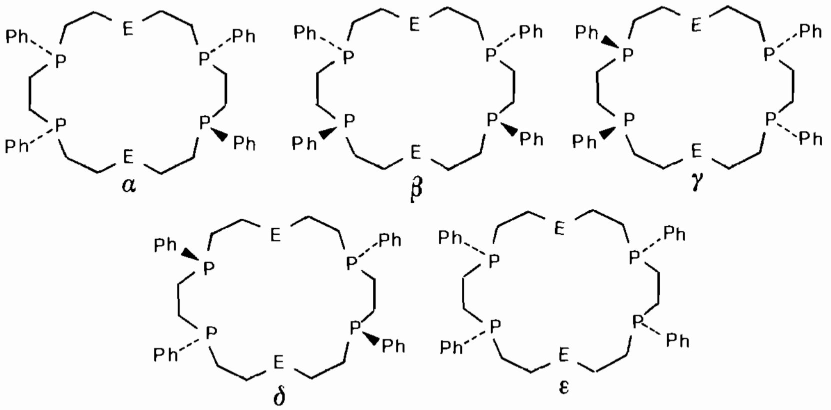

Fig. 1. The five diastereoisomers of [18]aneP_4E_2; E = O, S, N-Pr.

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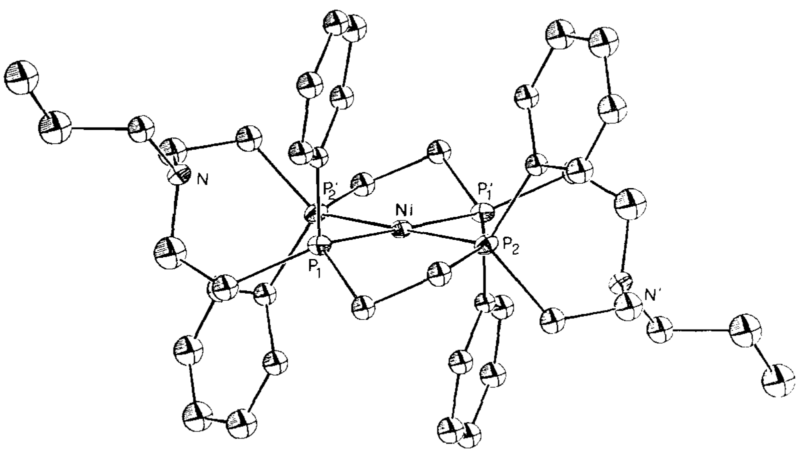

Fig. 2. The structure of $[Ni(d\text{-}[18]aneP_4N_2)]^{2+}$ cation. Bond lengths: Ni–P(1) = 2.234(3); Ni–P(2) = 2.273(3) Å.

each isomer are approximately the statically predicted ones.

Concerning the correlation between phosphane configuration of diastereoisomers and NMR spectra, inspection of Fig. 1 shows that the sole α-isomer has four unequivalent phosphorus atoms, thus requiring four ^{31}P NMR signals. On the contrary, all the four remaining isomers have equivalent phosphane groups and each isomer should display only a lone signal.

Our previous studies on the diastereoisomers of $[18]aneP_4O_2$ and $[18]aneP_4S_2$ confirmed such a behaviour [2, 3]. They also showed that, within the isomeric ^{31}P NMR pattern, higher-field signals are indicative of *cis*-phosphane configuration in the $P(Ph)CH_2CH_2P(Ph)$ moieties whereas lower-field signals are indicative of *trans*-configuration. The (a) isomer, therefore, should be assigned the 4RS, 7RS, 13RS, 16SR phosphane configuration (α-isomer of Fig. 1). Isomers (b) and (c), both of which have a lone lower-field signal, are tentatively assigned one of the two phosphane configurations 4RS, 7RS, 13SR, 16SR or 4RS, 7RS, 13RS, 16RS. Finally, isomer (d), which has a lone high-field signal, is tentatively assigned one of the two configurations 4RS, 7SR, 13RS, 16SR or 4RS, 7SR, 13SR, 16RS.

In order to test these hypotheses of structural assignments, the X-ray crystal structure of $[Ni(d\text{-}[18]aneP_4N_2)][BPh_4]_2\cdot 2Me_2CO$ was determined. Crystals are monoclinic, space group $P2_1/n$ with a = 25.275(5), b = 13.089(3), c = 13.060(3) Å, β = 102.94(5)°; U = 4210.8 Å^3, Z = 2, F(000) = 1628, μ(Mo-Kα) = 3.0 cm^{-1}, D = 1.205 g/cm^3. Intensity data [3142 independent observed reflections in the range $3° \leqslant 0 \leqslant 25°$] were collected on a Philips PW 1100 diffractometer with monochromatic MoKα radiation. The structure was solved by the heavy atom technique and refined by least-squares cycles to a conventional R factor of 0.101.

The structure of $[Ni(d\text{-}[18]aneP_4N_2)][PBh_4]_2\cdot 2Me_2CO$ consists of $[Ni(d\text{-}[18]aneP_4N_2]^{2+}$ cations, $[BPh_4]^-$ anions and lattice Me_2CO molecules. Stereoisomer (d) has a *meso*-centrosymmetric configuration 4RS, 7SR, 13SR, 16RS, the phenyl groups of two adjacent phosphorus atoms being in the *cis*-position. It corresponds to the γ-isomer of Fig. 1. This X-ray result strongly supports the proposed configurational assignments of the remainig isomers based on ^{31}P NMR spectra. The nickel atoms lie in crystallographic centres of symmetry and are coordinated square-planarly by the four phosphorus atoms (Fig. 2). The average Ni–P bond distance is 2.25 Å, in agreement with the usual values found in square planar nickel(II) complexes. The 'bite' angle P_1–Ni–P_2 is 84.1(0.1)°. The two nitrogen atoms of the ligand are not coordinated to the nickel atom, the metal to nitrogen intramolecular distance being 4.141(3) Å. Towards nickel(II), γ-$[18]aneP_4N_2$ behaves as a quadridentate ligand in much the same way as γ-$[18]aneP_4O_2$ and γ-$[18]aneP_4S_2$ [2, 3]. With the γ-isomers, lack of coordination of the E atoms is not to be ascribed directly to an intrinsic low donicity of such atoms since the rest of the isomers do behave as quinque- and sexi-dentate ligands. Rather, to steric incompatibility of $P–CH_2$-CH_2–E–CH_2CH_2P moieties to both facial and meridional coordination if a planar of pseudoplanar arrangement of the four phosphorus atoms occurs around the metal ion. On the other hand, the higher donicity of phosphanes with respect to ethers, thioethers and amines favours coordination of all the four phosphorus atoms to nickel(II) ions.

Studies are in progress in order to isolate all the isomers of the $[18]aneP_4N_2$ and to characterize their metal complexes.

Acknowledgments

Thanks are expressed to Mr. P. Innocenti for NMR spectra and to Mr. G. Vignozzi for microanalyses.

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