O-COMPLEXES OF 1,3,2,5-DIOXABORAPHOSPHORINANES WITH COPPER(I) AND SILVER(I) SALTS

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1,3,2,5-Dioxaboraphosphorinanes interact stereospecifically with Cu(I) and Ag(I) salts to form the corresponding O-complexes. The three-dimensional structure of the ligands has been established from <sup>31</sup>P NMR and <sup>1</sup>H NMR data.

Functionally substituted phosphines have a number of features which gives them a special place amongst phosphine ligands in coordination chemistry: they include the presence of 1) heteroatoms other than phosphorus with unshared electron pairs, 2) functional groups forming bonds with a metal by using its valence electrons, 3) heteroatoms with a vacant orbital (a boron atom, for example), high lability of the P-C bonds, and the stereoisomerism characteristic of cyclic phosphines. At present there are only scattered publications on the coordination chemistry of functionally substituted phosphines.

In this connection 1,3,2,5-dioxaboraphosphorinanes and their analogs may be considered as potential ligands possessing all these features. In fact, the composition and structure of complexes based on 1,3,2,5-dioxaboraphosphorinanes depend on the ligand-metal ratio, substituents in the ligand and its three-dimensional structure, on the solvent, and the acceptor properties of the metal.

Synthesis of the complexes is carried out by addition of Cu(I) and Ag(I) salts to a solution of the ligand. Thus, 2,5-diphenyl-1,3,2,5-dioxaboraphosphorinane (I) and silver nitrate may give complexes of composition MP and MP<sub>3</sub> depending on the experimental conditions for the reaction. Addition of silver nitrate to a dilute solution of (I) in chloroform yields {0-2,5-diphenyl-1,3,2,5-dioxaboraphosphorinane}silver(I), nitrate (II). A saturated solution gives an 85% yield of tris{0-2,5-diphenyl-1,3,2,5-dioxaboraphosphorinane}silver(I) nitrate (III). Compound (II) is converted into (III) by treatment with two moles of (I).



Complexes (II) and (III) are white crystalline substances, each having one chemically shifted signal in its <sup>31</sup>P NMR spectrum of -28.4 ppm (acetonitrile) and -30.9 ppm (acetonitrile) respectively. Elemental analysis and the ratio of integral proton intensities in the PMR spectra agree with the theoretical values. The chemical shifts of complexes (II) and (III) in their <sup>31</sup>P NMR spectra attract attention in that they are only slightly different from the chemical shift of ligand (I) (-42 ppm), which suggests that there is no P-Ag coordination bond. Usually formation of a P-Ag bond produces a weak-field displacement of the signal [1].

When silver nitrate is dissolved in bis(oxymethyl)phenylphosphine the chemical shift changes from -20 to 0 ppm, which probably indicates coordination at the phosphorus atom. In that case the bis(oxymethyl)phenylphosphine is acting as a phosphine ligand and not as a bidentate chelate. The resulting complex reacts with phenylboric acid giving compound (III). In addition the metal atom migrates from the phosphorus atom to the oxygen atom of the heterocycle. A similar migration of metal coordination is explained by the reduced nucleophilic nature of the P atom in (I) compared with tertiary phosphines [2].

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Com- pound	δ "p (solvent)	٥ 'Ħ (solvent)	<sup>2</sup> J <sub>pH</sub> , Hz
(V) (1X) (VI) (X) (VII) (XI) (VIII) (XII)	$\begin{array}{c} -26, -27, -33\\ -25 (MeCN)\\ -30 (CHCl_3, THF)\\ -26, -29, -32\\ -25.7 (MeCN)\\ -35 (CHCl_3)\\ -13,2 -19, -25\\ -13 (MeCN)\\ -14, -19, -25\\ 14,6 (MeCN, DMF)\\ -23,6 (CHCl_3) \end{array}$	$\begin{array}{cccc} 5.13 & (CD_{3}CN) \\ 5.03 & (CDCI_{3}) \\ - \\ 4.72 & (CDCI_{3}) \\ 6.40 \\ 5.7 & (DMF)^{3} \\ 6.1 \\ 5.97 & (CDCI_{3}) \\ 5.8 \\ 5.3 & (CDCI_{3})^{\dagger} \\ 6.20 \\ 5.82 & (CDCI_{3}) \\ 6.27 \\ 5.95 & (CDCI_{3}) \end{array}$	Multiplet 11 Multiplet 0 5.8 15,4 0 11 5 14 0 9,6 0 9,6

TABLE 1. <sup>31</sup>P and <sup>1</sup>H NMR Characteristics of Complex (IX)-(XII) and of Ligands (V)-(VIII)

\*R,R-stereoisimer (VII) ( $\delta^{31}P = -13 \text{ ppm}$ ) [6]. †R,R-stereoisomer (VIII) ( $\delta^{31}P = -14 \text{ ppm}$ ) [7].

Compound (I) interacts with cuprous iodide in chloroform or pyridine and, regardless of the solvent or metal-ligand ratio, the ligand gives complex (IV) of composition  $P_2CuI$ .

$$2PhP \underbrace{\stackrel{-O}{-O}}_{-O} BPh + Cul \underbrace{\stackrel{C_{s}H_{s}N}{-CHCl_{s}}}_{CHCl_{s}} \left\{PhP \underbrace{\stackrel{-O}{-O}}_{-O} BPh\right\}_{2}Cul$$
(IV)

Compound (IV) is a white crystalline substance ( $\delta^{31}P = -39.2 \text{ ppm (CHCl}_3)$ ) which gives qualitative reactions for Cu(I) and I. Elemental analysis and the ratio of integral proton intensities in the PMR spectra correspond to the attributed structure. In the PMR spectra the methylenic protons of the heterocycles appear as a singlet with a chemical shift of 4.8 ppm. The molecular weight of (IV) in benzene determined by ebullioscopy is 730, the theoretical values is 703.

When copper(I) iodide is dissolved in bis(oxymethyl)phenylphosphine the <sup>31</sup>P NMR spectra show a slight weak-field shift (from -20 to -13 ppm), which suggests that copper, unlike silver(I), is coordinated with oxygen atoms, and the phosphorus-containing diol acts as a bidentate chelating ligand. The copper complex of bis(oxymethyl)phenylphosphine reacts with phenylboric acid to give compound (IV). The occurrence of only one signal in the <sup>31</sup>P NMR spectra, the similarity of its chemical shift with that of the original compound (I), and the equivalence of the CH<sub>2</sub> groups in the PMR spectra indicate that there is no P-Cu coordination bond and that the heterocycles are bound symmetrically to the Cu atom.



The reaction of tributylammonium 2,5-diphenyl-1,3,2,5-dioxaborataphosphorinane, containing a four-coordinate boron atom, with copper(I) iodide in pyridine occurs with cleavage of benzene from the boron atom and formation of complex (IV). A similar reaction has been observed previously [3, 4].



Isocyanides are known to form stable complexes with an ionic structure with Cu(I). When (IV) interacts with t-butylisocyanide two phosphine ligands are displaced and tetra(t-butylisocyanide)copper(I) iodide is formed:

 $(IV) + 4 C = NBu - t \rightarrow 2 (I) + [(t - BuNC)_4Cu]^+I^-$ 

Compound (I) exists in solution in the form of a mixture of two conformers with different orientations of the phenyl at the phosphorus atom, the equilibrium being almost completely shifted in favor of the conformer with axial orientation of the substituent (96%). This is due to interaction of the heteroatoms in the P-C-O-B bond system [5]. For this conformation of the heterocycle, complex formation should take place from the side with the lower screening.



The conformational equilibrium of (IV) should also be displaced to the side of the conformer with axial orientation of the phenyl at the phosphorus atom, since Cu(I) acts in the same direction as the boryl group, increasing the acceptor character of the C-O bond and, consequently, stabilizing the conformer with an axial substituent at the phosphorus atom. The existence of (IV) predominantly in this conformation is supported by the similar chemical shifts of (I) and (IV) in the <sup>31</sup>P NMR spectra. Moreover, in the PMR spectra of complex (IV) the CH<sub>2</sub>-group protons show up as a singlet similar to that of the CH<sub>2</sub>-group protons of the original ligand (I) [5].

The properties of heterocyclic ligands of the 1,3,2,5-dioxaboraphosphorinane series are determined to a considerable extent by interaction of the heteroatoms in the P-C-O-B system and the nature of substituents in the 4, 6-position of the ring [2]. For (I) the donor properties of the phosphorus atom and the acceptor properties of the boron atom are diminished owing to intramolecular interactions of these heteroatoms. The presence of a strong acceptor in the 4,6-position (CCl<sub>3</sub>) leads to an even greater decrease in donor properties, not only of the phosphorus atom, but also of the oxygen atoms. Thus, 2,5-diphenyl-4,5-di(trichlorome-thyl)-1,3,2,5-dioxaboraphosphorinane does not form complexes with copper(I) iodide.

When the substituents in 1,3,2,5-dioxaboraphosphorinanes are donors or weak acceptors, complexes are formed with copper(I) salts, although stable crystalline compounds have been obtained only in the presence of pyridine. In every case copper forms complexes with one molecule of the phosphorus ligand but the number of pyridine molecules varies from one to three.



R = Ph, R' = Ph (VII); x = 1, y = 2 (XI); R = Ph, R' = CBu<sub>s</sub> (VIII); x = 0, y = 1 (XII).

The synthesis and three-dimensional structure of ligands (V)-(VIII) have been described in [5, 6]. The composition of the complexes was determined by elemental analysis, IR spectra, and integral proton intensities in PMR spectra. All the complexes give qualitative reactions for copper and iodine.

Ligands (V)-(VIII) exist as three stereoisomers, their relative proportions in solution being given by the ratio of intensities of their <sup>31</sup>P NMR signals. The <sup>31</sup>P NMR spectra of the complexes contain only one signal and its chemical shift is close to that of one of the stereoisomers of the original ligand (Table 1). The signals of compounds (IX)-(XII) lie in the range characteristic for tertiary phosphines, indicating that coordination occurs through oxygen and not phosphorus.

In the PMR spectrum of (IX) in  $CHCl_3$  the methine ring protons are recorded as a symmetrical doublet of quartets ( ${}^2J_{\rm HH}$  = 7 Hz,  ${}^2J_{\rm PH}$  = 11 Hz). These data suggest an R,S-configuration for the carbon atoms in the 4,6-position of the heterocycle and an axial orientation for the phenyl at the P atom:



It has been shown previously [7] that in complex (X) the ligand occurs in the form of the R,S-steroisomer with equatorial orientation of the phenyl at the P atom.

The chemical shift in the <sup>31</sup>P NMR spectra of (XI) is equal to the chemical shift of the ligand in a twist conformation with R,R-configuration of the  $\alpha$ -carbon atom [6]. In the PMR spectra of complex (XI) the methine ring protons are recorded as a doublet and a singlet ( $\delta = 6.1$  ppm, <sup>2</sup>J<sub>PH</sub> = 0 Hz;  $\delta = 5.97$  ppm, <sup>2</sup>J<sub>PH</sub> = 9 Hz), indicating an R,R-configuration for the heterocycle. In that event the Cu atom may form a bond only with one oxygen atom:



Saturation of the empty orbitals of copper(I) is attained by addition of two molecules of pyridine. Moreover, the presence of acceptor substituents at the 4,6-position and of a Cu atom at the O atom increases the acceptor properties of the B atom, leading to formation of a pyridine complex with the B atom. The ligand in (XII) also occurs in the R,R-configuration [7]. However, in this case a pyridine complex is not formed with the B atom due to the steric requirements of the 1,1-dibutylamyl radical.

It should be noted that replacing the  $CHCl_3$  solvent with acetonitrile leads to a shift in the <sup>31</sup>P NMR signal and, in addition, the proton chemical shifts and spin-spin coupling constants in the PMR spectra of complexes (IX)-(XII) vary slightly. The complexes may be isolated in an unchanged form from all the solutions and completely retain their spectroscopic characteristics. This may be explained by a change in the position of the conformational equilibrium of the corresponding stereoisomer of the ligand or conversion of the 0, 0-complex into an 0-complex with increase in basicity of the solvent. Thus, heterocyclic P, B-containing ligands of the 1,3,2,5-dioxaboraphosphorinane series form complexes with silver(I) and copper(I) salts. The composition and structure of the complexes in solution depend on the characteristics of substituents in the heterocycle. Co-ordination takes place through the oxyboryl fragment. One of the stereoisomers of the original ligand is retained in the complexes.

## EXPERIMENTAL

The <sup>1</sup>H and <sup>31</sup>P NMR spectra were recorded on a Bruker WM-250 spectrometer with operating frequencies of  $v_{\rm H}$  = 250 MHz and  $v_{\rm P}$  = 101 MHz. The <sup>1</sup>H NMR spectra were also recorded on a Varian T-60 spectrometer (60 MHz) at 34.5°C. Proton chemical shifts are shown relative to an internal TMS standard and the phosphorus shifts relative to an external standard of 85% orthophosphoric acid. Infrared spectra were measured on a UR-20 apparatus using suspensions in vaseline oil.

 $\frac{\{0-2,5-\text{Diphenyl-1},3,2,5-\text{dioxaboraphosphorinane}\}\text{silver(I) Nitrate (II)}.$  To a solution of 2 g (0.008 mole) 2,5-diphenyl-1,3,2,5-dioxaboraphosphorinane (I) in 30 ml chloroform was added with stirring 1.33 g (0.008 mole) silver (I) nitrate. After 3 h the resulting suspension of grey crystals and an insignificant amount of an undissolved residue of silver nitrate was decanted. The crystals were filtered and washed with chloroform. Yield of (II) 2.3 g (70%), mp 190°C (decomp.),  $\delta^{31}P$  -28.4 ppm (MeCN), ratio of integral proton intensities in PMR spectra C<sub>6</sub>H<sub>5</sub>:CH<sub>2</sub> = 5:2. Found: C 39.30, H 3.41, N 3.65, P 7.98%. C<sub>14</sub>H<sub>14</sub>AgBNO<sub>5</sub>P. Calculated: C 39.44, H 3.29, N 3.29, P 7.28%.

<u>Tris-{0-2,5-diphenyl-1,3,2,5-dioxaboraphosphorinane}silver(I) Nitrate (III)</u>. a) To a solution of 1 g (0.004 mole) (I) in 3 ml chloroform was added 0.66 g (0.004 mole) silver (I) nitrate. The suspension of white crystals with the residue of silver nitrate was decanted. The crystals were filtered and washed with chloroform. Yield of (III) 0.8 g (67%), mp 184°C,  $\delta^{31}P$  -30.9 ppm (MeCN), ratio of integral proton intensities in PMR spectra C<sub>6</sub>H<sub>5</sub>:CH<sub>2</sub> = 5:2.

b) To a solution of 1.2 g (0.005 mole) (I) in 8 ml chloroform we added 1 g (0.0025 mole) (II). There was an exothermic effect and a bulky white precipitate formed. The precipiate was filtered and washed with chloroform. Yield of (III) 1.8 g (81%), mp 184°C,  $\delta$  <sup>31</sup>P -30.5 ppm (MeCN).

c) To a solution of 2.1 g (0.012 mole) bis(oxymethyl)phenylphosphine in 30 ml chloroform was added 0.7 g (0.004 mole) silver(I) nitrate. The reaction mixture was heated to boiling for 15 min. The silver nitrate dissolved and a second liquid layer was formed. The <sup>31</sup>P NMR spectrum of the lower layer was measured ( $\delta$  <sup>31</sup>P 0 ppm). To the reaction mixture we added 1.44 g (0.012 mole) phenylboric acid. The water that seprated was removed. After 3 h (III) was filtered and washed with chloroform. Yield of (III) 2.1 g (55%),  $\delta$  <sup>31</sup>P -30.5 ppm (MeCN), mp 182-184°C. The IR and PMR spectra of compound (III) produced by methods a, b, and c are identical. Found: C 53.71, H 4.69, N 1.52, P 10.18%. C<sub>4.2</sub>H<sub>4.2</sub>AgB<sub>3</sub>NO<sub>9</sub>P<sub>3+--</sub> Calculated: C 53.73, H 4.48, N 1.49, P 9.91%.

<u>Bis(0,0-2,5-diphenyl-1,3,2,5-dioxaboraphosphorinane)</u> Copper(I) Iodide (IV). a) To a solution of (I) in chloroform or pyridine was added an excess of copper(I) iodide. Formation of a bulky white precipitate was observed. The suspension of crystals was decanted with an unreacted residue of copper(I) iodide. The crystals of (IV) were filtered and washed with chloroform. Yield of (IV) 80%, mp 239°C,  $\delta$  <sup>31</sup>P -39.9 ppm (MeCN), ratio of integral intensities in the PMR spectra C<sub>6</sub>H<sub>5</sub>:CH<sub>2</sub> = 5:2.

b) Similar to method c) for (III), but with 3.1 g (0.018 mole) bis(oxymethyl)phenylphosphine, 1.74 g (0.009 mole) copper(I) iodide, and 2.08 g (0.018 mole) phenylboric acid. The chemical shift of the intermediate complex of copper(I) iodide with two molecules of bis(oxymethyl)phenylphosphine is  $\delta^{31}P = -13$  ppm. Yield of (IV) 5.2 g (85%), mp 237-239°C.

c) To a solution of 1.7 g (0.003 mole) tributylammonium 2,2,5-triphenyl-1,3,2,5-dioxaborataphosphorinane in 15 ml pyridine was added 0.62 g (0.003 mole) copper(I) iodide. After the exothermic reaction was completed the solvent was removed under vacuum. Compound (IV) was crystallized from benzene. Yield 69%, mp 238-239 °C. The IR and PMR spectra of compound (IV) produced by methods a, b, and c are identical. Found: C 48.09, H 4.06, P 8.83%.  $C_{28}H_{28}B_2CuIP_2O_4$ . Calculated: C 47.83, H 3.99, P 8.83%. Molecular weight of (IV) in benzene (ebullioscopy): Found 730, Calculated 703. Interaction of (IV) with t-Butylisocyanide. To a suspension of 2 g of (IV) in 20 ml abs. THF was added 1.5 ml t-butylisocyanide. An exothermic reaction occurred and a precipitate was formed. After 6 h the precipitate was filtered. Yield of {tetra(t-butylisocyanide)-copper(I)} iodide 1.1 g (74%). The filtrate was evaporated. Compound (I) was crystallized from ethyl ether. Yield of (I) 0.9 g (65%), mp 105°C  $\delta$  <sup>31</sup>P -40 ppm (DMF) (cf. [5]).

The synthesis of complexes (X) and (XII) has been described previously [6]. The  ${}^{1}\text{H}$  and  ${}^{31}\text{P}$  NMR spectroscopic data for compounds (V)-(XII) are given in Table 1.

 $\frac{\{0,0-4,6-\text{Dimethy}1-2,5-\text{dipheny}1-1,3,2,5-\text{dioxaboraphosphorinane}\}\text{pyridine Copper(I) Iodide}{(IX).}$  To a solution of 2.5 g (0.009 mole) of (V) in 15 ml pyridine was added 1.74 g (0.009 mole) copper(I) iodide. Pyridine is removed under vacuum when reaction is completed. The residue was crystallized from acetone. Yield of (IX) 4.5 g (89%), mp 127-130°C,  $\delta^{31}P-30$  ppm (CHCl<sub>3</sub>, THF), -25 ppm (MeCN). Ratio of integral proton intensities in PMR spectra C<sub>6</sub>H<sub>5</sub>: CH:CH<sub>3</sub> = 15:2:6. Found: C 45.40, H 4.26, N 2.53, P 5.58%. C<sub>21</sub>H<sub>23</sub>BCuINO<sub>2</sub>P. Calculated: C 45.53, H 4.15, N 2.53, P 5.60%.

 $\frac{\{0-2,4,5,6-\text{Tetraphenyl-1},3,2,5-\text{dioxaboraphosphorinane-2-pyridine}\}\text{dipyridine Copper(I)}}{\text{Iodide (XI).}}$ Similar to (IX). Yield of (XI) 59%, mp 107-110°C,  $\delta^{31}P - 12.7$  ppm (MeCN), ratio of integral proton intensities in PMR spectra (C<sub>6</sub>H<sub>5</sub> + C<sub>5</sub>H<sub>5</sub>N):CH = 35:2. Found: C 58.57, H 4.44, N 5.36, P 3.90%. C<sub>41</sub>H<sub>37</sub>BCuIN<sub>3</sub>O<sub>2</sub>P. Calculated: C 58.92, H 4.43, N 5.03, P 3.77%.

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