SYNTHESIS AND STRUCTURAL FEATURES OF 1,3,2,5-DIOXABORAPHOSPHORINANE COMPLEXES WITH Pt(II) AND Pd(II) SALTS

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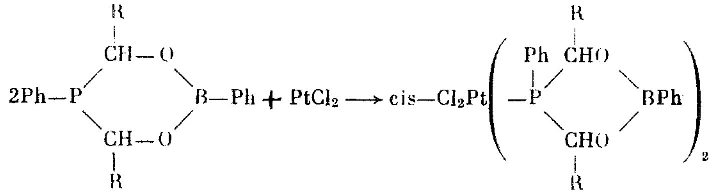
UDC 543.422.25:542.91:541.49:547.
1'127'118:546.922'131:546.982'131

Complexes of composition L_2MCl_2 [M = Pt, R = H (I), Me (II), Ph (III)] and $LMCl_2$ [M = Pd, R = H (IV)] are prepared by reaction of 4,6-R_2-2,5-diphenyl-1,3,2,5-dioxaboraphosphorinanes (L) with MCl_2. Far-IR and ^{31}P NMR spectroscopy are used to demonstrate that I is cis whereas II and III are trans complexes in the solid. The conformational behavior of I is studied by ^{31}P and ^{1}H NMR. The asymmetric form of I exhibits anomalous stability.

1,3,2,5-Dioxaboraphosphorinanes have three nucleophilic centers (P and O atoms). The effective negative charge of the O atoms is increased owing to the low electronegativity of the B atom whereas the nucleophilicity of the P atom is reduced owing to $n{-}\sigma^*$ interaction of its nonbonded electron pair and the C—O bond [1]. Therefore, electronic and geometric effects compete during complexation of this class of phosphines. It has been proposed that the O atoms are involved in complexation of 1,3,2,5-dioxaboraphosphorinanes with Cu(I) and Ag(I) salts and has been noted that the reaction occurs stereospecifically [2]. It seemed interesting to study complexes of these P,B-containing compounds with transition metals from other groups. Hence, the steric demands of the ligand take on special meaning in square-planar Pt(II) and Pd(II) complexes.

The reaction of 4,6-R_2-2,5-diphenyl-1,3,2,5-dioxaboraphosphorinanes with $PtCl_2$ occurs smoothly in CH_3CN to form the gray, air-stable, slightly soluble, high-melting (1:2 (metal: ligand) complexes I-III.



R = H (I), Me (II), Ph(III).

The IR spectra of I-III contain absorption bands (AB) corresponding to vibrations of the heterocyclic fragments in the range 4000-700 cm^{-1} and to Pt—Cl stretches in the far-IR (700-200 cm^{-1}). Two Pt—Cl AB at 322 and 295 cm^{-1} are observed in the IR spectrum of I whereas one at 344 cm^{-1} is seen in the spectra of II and III. Therefore, I exists as the cis and II and III as the trans isomers in the solid [3].

Additional confirmation of the configuration of the complexes comes from the ^{31}P NMR. The chemical shifts (CS) in DMF of I-III range from 27 to 4 ppm. This is characteristic for 4-coordinate phosphines. However, the direct spin—spin coupling constants (SSCC) of the ^{31}P and ^{195}Pt nuclei differ substantially. For I, $^{1}J_{PtP}$ is 3470 Hz, indicative of cis phosphines [3]. The spectrum of II has a multiplet from 22.7 to 21.3 ppm with multiplet satellites. The average $^{1}J_{PPt}$ is 2450 Hz. The presence of a multiplet can be explained by the existence of three stereoisomeric forms of the ligand [4]. The size of the constants is indicative of trans ligands [3]. Heating in DMF partially (~25%) converts III to the cis isomer. This is suggested by the appearance in the ^{31}P NMR of two signals at 27.2 and 4.2 ppm and SSCC of ^{31}P and ^{195}Pt of 3531 and 2577 Hz, respectively. The decrease of the fraction

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Institute of Organic and Physical Chemistry, Kazan' Scientific Center, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 10, pp. 2309-2312, October, 1991. Original article submitted November 6, 1990.

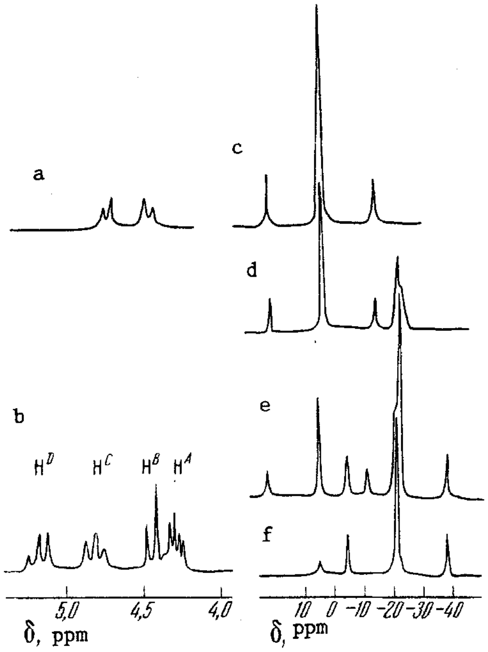


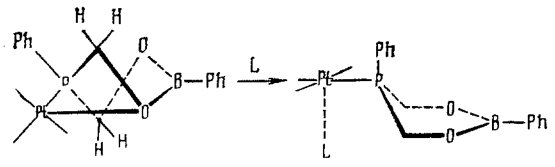
Fig. 1. NMR spectra of bis(2,5-diphenyl-1,3,2,5-dioxaboraphosphorinane)-Pt(II) dichloride (I): PMR of I in DMF-d_7 (a), PMR of I in CD_3CN (b), ^{31}P NMR of I in DMF (c), ^{31}P NMR of I in CH_3CN at 50°C after 15 days, 5 days, and immediately after dissolution, respectively (d-f).

of the cis isomer in solution in the order I, III, II is consistent with the increasing steric demands of the substituents in the 4,6-positions of the P,B-containing heterocycles.

Bonding of the boryl group to Pt is also consistent with the data obtained. Formation of such bonds should have a considerable influence on the conformational behavior of the 1,3,2,5-dioxaboraphosphorinanes. The CS in the ^{31}P NMR spectra of I depended on the solvent. In DMF, it was 4.2 ppm ($^1J_{PPt}$ = 3470 Hz) whereas in low-boiling and less polar CH_3CN it was −22.7 ppm ($^1J_{PPt}$ = 3450 Hz). A signal with CS 4.0 ppm ($^1J_{PPt}$ = 3470 Hz) appeared and slowly increased in a CH_3CN solution of I thermostatted at 50°C. The half-life of the conversion was ≈240 h (Fig. 1). Complex I was isolated from the solutions after removal of solvents. Its melting point and spectral characteristics were unchanged, consistent with a reversible conversion.

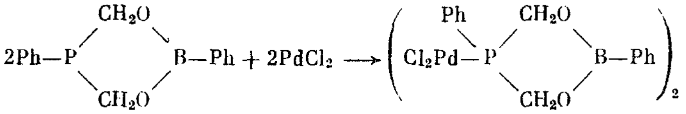
The methyl protons of the ring in PMR spectra of I in DMF appear as two doublets with SSCC $^2J_{HH}$ = 13.2 Hz and $^2J_{PH}$ = 0 Hz. This indicates that the heterocycle has predominantly the chair conformation. The low values of $^2J_{PH}$ is characteristic of a dioxaboraphosphorinane with an axial phenyl on the P atom [5]. In such a conformation, the metal cannot interact intramolecularly with the boryl group.

The spectrum of the methylene protons of I in acetonitrile appears as an ABCDX system (Fig. 1). Consequently, the heterocycle has an asymmetric conformation. The small SSCC $^2J_{PH}$ = 6 Hz and $^2J_{PH}$ = 0 Hz ($^2J_{HH}$ = 13.5 Hz) correspond to a dihedral angle of 40-60° between the Pt—P—C and P—C—H planes [5]. The signals of H^C and H^D are shifted by 0.5 ppm to weak field relative to H^A and H^B. The values $^2J_{PH^C}$ = 13.3 Hz and $^2J_{PH^D}$ = 15.5 Hz ($^2J_{H^CH^D}$ = 15 Hz) are consistent with an increase of the corresponding dihedral angles to 140-180° [5]. Therefore, the ligands probably have a distorted "twist" conformation. The stability of such a conformation can be explained by an electrostatic interaction of the metal with axial O atoms. The Pt—O bond is unstable and decomposes in polar solvents.



L = solvent

The ligand 2,5-diphenyl-1,3,2,5-dioxaboraphosphorinane reacts differently with $PdCl_2$. The 1:1 complex is formed even with an excess of ligand



(IV)

Crystalline IV exhibits AB of skeletal vibrations of the heterocycle in the IR spectra and AB of Pd–Cl and Pd–P stretches in the far-IR region. The ^{31}P NMR of IV in DMF has a single signal in the range characteristic of four-coordinate P. The methylene protons of the ring appear as two doublets with $^2J_{HH}$ = 15 Hz and $^2J_{PH}$ = 0 Hz in the PMR in slightly basic chloroform. Forms with Pd–O bonds probably are absent in solution. The heterocyclic ligand exists primarily in the chair conformation with an equatorial Pd–P bond.

The low electrical conductivity of acetonitrile solutions of I-IV enables charged structures to be eliminated.

EXPERIMENTAL

The ^1H and ^{31}P NMR spectra were recorded on a Bruker WM-250 spectrometer at working frequencies (MHz) νH 250 and νP 101. IR spectra were taken on a UR-20 spectrometer as mineral oil mulls. Far-IR spectra were recorded on a Bruker IR-Fourier-spectrometer in the range 700-100 cm^{-1} in polyethylene.

Bis(2,5-diphenyl-1,3,2,5-dioxaboraphosphorinane)Pt(II) Dichloride (I). The compound $PtCl_2$ (0.78 g, 0.003 mole) was added to 2,5-diphenyl-1,3,2,5-dioxaboraphosphorinane (1.5 g, 0.006 mole) in acetonitrile (10 ml). The reaction mixture was stirred until the slightly exothermic reaction subsided. The gray crystals of I that formed after 5 h were filtered off. Yield (I): 1.9 g (81%), mp 237-239°C. An analytical sample was obtained by recrystallization from acetonitrile, mp 240°C. IR spectrum (ν, cm^{-1}): 322 and 295 (polyethylene). ^{31}P NMR spectrum (δ, ppm): 4.2 ($^1J_{PtP}$ = 3470 Hz, DMF), –22.7 ppm ($^1J_{PtP}$ = 3450 Hz, CH_3CN). ^1H NMR spectrum (δ, ppm, J, Hz): 8.2-7.2 m (10 H, Ar–H), 4.6 d (2H, $^2J_{PH}$ = 13.1, H), 4.35 d (2H, $^2J_{HH}$ = 13.1, H) (in DNMF-d_7); 7.8-7.2 m (10H, Ar–H), 5.20 dd (1H, $^2J_{H}D_{H}C$ = 15.0, $^2J_{PH}D$ = 15.5 H^D), 4.84 dd (1H, $^2J_{H}C_{H}D$ = 15, $^2J_{PH}C$ = 13.3, H^C), 4.50 d (1H, $^2J_{H}B_{H}A$ = 13.5, $^2J_{PH}B$ = 0, H^B), 4.33 dd (1H, $^2J_{H}A_{H}B$ = 13.5 $^2J_{PH}A$ = 6.0, H^A) (CD_3CN). Electrical conductivity $\Lambda = 3.4\ \Omega^{-1}/(cm^2 \cdot mole^{-1})$ (CH_3CN); $\Lambda = 6.0\ \Omega^{-1}/(cm^2 \cdot mole^{-1})$ (DMF) at C = 0.001 M. Found: C, 43.25; H, 3.65; P, 8.09; Cl, 9.34%. $C_{28}H_{28}B_2Cl_2O_4P_2Pt$. Calculated: C, 43.19; H, 3.60; P, 7.97; Cl, 9.13%.

Bis(4,6-dimethyl-2,5-diphenyl-1,3,2,5-dioxaboraphosphorinane)Pt(II) Dichloride (II). This was prepared analogously to I. Yield (II): 42%, mp 242-246°C. IR spectrum (ν, cm^{-1}): 344 (polyethylene). ^{31}P NMR spectrum (δ, ppm): 22.7, 21.8, 21.3, 20.4, average $^1J_{PtP}$ = 2450 Hz (DMF). PMR spectrum (δ, ppm): 8.04-7.32 m (10H, Ar–H), 5.50-5.20 m (2H, –CH=), 1.6-1.40 m (6H, CH_3) (DMF). $\Lambda = 3.4\ \Omega^{-1}/(cm^2 \cdot mole^{-1})$ at C = 0.001 M in CH_3CN. Found: C, 45.80; H, 4.20; P, 7.53; Cl, 8.66%. $C_{32}H_{36}B_2Cl_2O_4P_2Pt$. Calculated: C, 46.10; H, 4.32; P, 7.44; Cl, 8.40%.

Bis(2,4,5,6-tetraphenyl-1,3,2,5-dioxaboraphosphorinane)Pt(II) Dichloride (III). This was prepared analogously to I. Yield (III), 61%, mp 355-356°C. IR spectrum (ν, cm^{-1}): 344 (polyethylene). ^{31}P NMR (δ, ppm): 27.2 ($^1J_{PtP}$ = 2577 Hz), 4.24 ($^1J_{PtP}$ = 3531 Hz) in the ratio 3:1 (DMF). $\Lambda = 3.0\ \Omega^{-1}/(cm^2 \cdot mole^{-1})$ at C = 0.001 M in acetonitrile. Found: C, 57.17; H, 4.12; P, 5.74; Cl, 7.00%. $C_{52}H_{44}B_2Cl_2O_4P_2Pt$. Calculated: C, 57.67; H, 4.07; P, 5.73; Cl, 6.56%.

Bis(2,5-diphenyl-1,3,2,5-dioxaboraphosphorinane)Pd(II) Dichloride (IV). The compound $PdCl_2$ (0.30 g, 0.002 mole) was added to 2,5-diphenyl-1,3,2,5-dioxaboraphosphorinane (1.00 g, 0.004 mole) in CH_3CN (15 ml). The yellow crystals that formed were recrystallized from chloroform. Yield (IV): 0.7 g (54%), mp 228-230°C. IR spectrum (ν, cm^{-1}): 313, 297, 278 (Pd–Cl); 176, 166, 156 (Pd–P) (polyethylene). ^{31}P NMR spectrum (δ, ppm): 25.1 (DMF). PMR spectrum (δ, ppm): 8.47-7.86 m (10H, AR–H), 5.18 d (2H, $^2J_{HH}$ = 15.0 Hz, P–C–H), 5.03 d (2H, $^2J_{HH}$ = 15.0 Hz, P–C–H) ($CDCl_3$). $\Lambda = 3.5\ \Omega^{-1}/(cm^2 \cdot mole^{-1})$ at C = 0.001 M in CH_3CN. Found: C, 38.83; H, 3.36; P, 7.74; Cl, 16.46%. $C_{14}H_{14}BCl_2O_2PPd$. Calculated: C, 38.76; H, 3.23; P, 7.15; Cl, 16.38%.

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CRYSTAL STRUCTURE OF THE BENZENE DISOLVATE OF THE CIS ISOMER OF THE 2-CHLOROMETHYL-2-PHENYL-1,3,2-BENZOXAZAPHOSPHOLE DIMER

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The x-ray crystal and molecular structure of the benzene disolvate of the "soluble" diastereomer of the 2-chloromethyl-2-phenyl-1,3,2-benzoxazaphosphole dimer is solved. This diastereomer is the cis isomer.

We discovered during synthesis of the dimers 2R,2R'-1,3,2-benzoxazaphospholes (R, R' = Alk, Ar, OAr) that if R ≠ R' the respective dimers are obtained as a mixture of two diastereomers with the cis and trans configurations for the exocyclic substituents R and R' relative to the plane of the 4-membered 1,3,2,4-diazadiphosphetidine heterocycle. In particular, both diastereomers of the 2-chloromethyl-2-phenyl-1,3,2-benzoxazaphosphole dimer (I) are formed in approximately equal amounts (1:1). However, one of them (Ia) (mp 177-182°C) dissolves with heating in dioxane or benzene whereas the second diastereomer (Ib) (mp 186-189°C) is insoluble in these and the majority of other solvents. Details of the synthesis and properties of dimer I and other dimers of this series will be published separately.

An x-ray structure analysis of crystals of II (mp 103-105°C), the benzene disolvate of the "soluble" diastereomer (Ia) prepared by recrystallization from benzene (II = $Ia \cdot 2C_6H_6$), was carried out in order to determine the molecular structure and relative configuration (cis or trans) of the diastereomers Ia and Ib.

Molecule Ia in the crystal structure of II was found to be the cis isomer (Fig. 1). Therefore, the "insoluble" diastereomer (Ib) is the trans isomer.

The principal bond lengths and angles in Ia are listed in Table 1. Both P atoms in Ia have distorted trigonal-bipyramidal 5-coordination with O^1 and N^2 in the axial positions of P^1; O^2 and N^1 in those of P^2. Atom P^1 deviates slightly from the equatorial plane (defined by N^1, C^1, and C^3) by 0.019(1) Å toward O^1; P^2, from the equatorial plane (defined by N^2, C^2, and C^{15}), by 0.070(1) Å toward O^2. The equatorial bonds P^1–N^1 and P^2–N^2 are significantly shorter than the axial bonds P^1–N^2 and P^2–N^1. Owing to the different hybridization of the C atoms, the bonds P^1–C^1 and P^2–C^2 are slightly longer than P^1–C^3 and P^2–C^{15}. The bond lengths and angles around P and N in Ia are within the range for similar phosphoranes [1-5].

Both chloromethyl substituents of Ia in the crystal structure of II are disordered by rotation around the P^1–C^1 and P^2–C^2 bonds. Each Cl atom occupies two different positions: Cl^1 and $Cl^{1'}$ and Cl^2 and $Cl^{2'}$. The bond lengths and angles involving the lesser occupied positions $Cl^{1'}$ and $Cl^{2'}$ ($Cl^{1'}$–C' and $Cl^{2'}$–C^2 and $Cl^{1'}C^1P^1$ and $Cl^{2'}C^2P^2$) are

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Institute of Physiologically Active Substances, Academy of Sciences of the USSR, Chernogolovka. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 10, pp. 2313-2316, October, 1991. Original article submitted November 6, 1990.

0568-5230/91/4010-2026$12.50