Synthesis of *cis*-bis-P,P′-(triethylammonium-2,2,5-triphenyl-1,3,2,5-dioxaborataphosphorinane)dichloroplatinum(II)

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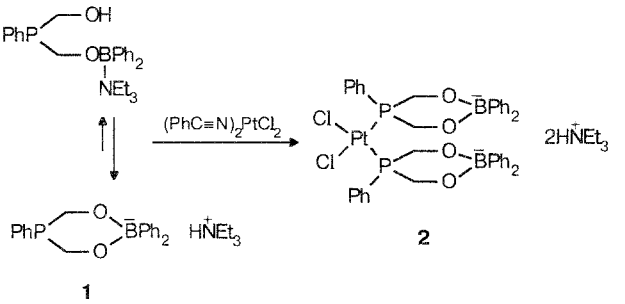
The reaction of triethylammonium 2,2,5-triphenyl-1,3,2,5-dioxaborataphosphorinane with $PtCl_2(PhCN)_2$ gave a complex whose structure was given as *cis*-bis-P,P′-(triethylammonium 2,2,5-triphenyl-1,3,2,5-dioxaborataphosphorinane)dichloroplatinum(II) on the basis of ^1H and ^{31}P NMR, medium- and long-wave IR spectroscopy, and conductometry.

Key words: tautomerism, platinum complexes, ammonium dioxaborataphosphorinane.

The tautomerization of ligands plays an important role in the formation of metallocomplexes.[1] Ligands with active functional groups are brought together on metal matrices, which leads to template transformations.[2] In this connection, metallocomplexes in which the ligands bonded to the central ion are capable of tautomerism are of particular interest. Due to the tautomeric transformations of the ligands, such metallocomplexes may have good solubility both in polar and nonpolar solvents and display interligand tautomerism, changes in the steric and electronic parameters of the ligands may also take place, *etc.* It has been shown previously that triethylammonium 2,2,5-triphenyl-1,3,2,5-dioxaborataphosphorinane (**1**) displays a particular type of tautomerism, *viz.*, ion-complex, element-prototropic, ring-chain tautomerism.[3] An X-ray diffraction study has shown that compound **1** in the crystal exists in an ionic form, and the Ph substituent in the heterocyclic anion at the trivalent phosphorus atom has axial orientation.[4] The tautomeric equilibrium in solution is also shifted to the ionic form.

We have obtained the *cis*-bis-P,P′-(triethylammonium 2,2,5-triphenyl-1,3,2,5-dioxaborataphosphorinane) dichloroplatinum(II) complex (**2**) for the first time by treating **1** with a platinum benzonitrile complex, $PtCl_2(PhCN)_2$, in acetone. Complex **2** is a stable finely crystalline compound. It has two equivalent ligands and the metal atom is coordinated at the phosphorus atoms. The ^{31}P NMR spectrum of compound **2** has only one signal with a chemical shift at −10.68 ppm and a coupling constant $^1J_{P-Pt}$ = 3252 Hz. The long-wave region of the IR spectrum displays absorption at 308 and 282 cm^{-1}. These data correspond to the *cis*-configuration of the complex (with respect to the platinum ion). The presence of the main absorption bands of the original ligand **1**, including those at 2500 and 2700 cm^{-1}, in the IR spectra of crystalline compound **2**, and the absence of absorption of hydroxyl groups of the acyclic form indicate that both ligands have ionic structures. The ^1H NMR spectra of solutions of complex **2** contain signals of the CH_2-group protons of the cycle as a broadened $(AB)_2X$-system of signals. If the temperature is decreased to −30 °C, the signals of these protons collapse into a narrow singlet with a chemical shift at 4.42 ppm. When the temperature is increased, the spectrum changes to the original shape. Evidently, the temperature dynamics observed in the NMR spectra are due to the existence of intracomplex tautomerism.



Experimental

***cis*-Bis-P,P′-(triethylammonium 2,2,5-triphenyl-1,3,2,5-dioxaborataphosphorinane)dichloroplatinum(II) (2).** A solution of ligand **1** (0.40 g, 0.9 mmol) in acetone was poured into a solution of $PtCl_2(PhCN)_2$ complex (0.21 g, 0.45 mmol). After 24 h a portion of the solvent was removed *in vacuo*. The precipitate of complex **2** was filtered off and recrystallized from acetone. The yield of **2** was 0.124 g (24 %), m.p. 141—142 °C (from acetone). Found (%): C, 54.81; H, 6.32; N, 2.65; P, 5.69. $C_{52}H_{70}B_2Cl_2N_2O_4P_2Pt$. Calculated (%): C, 54.92; H, 6.16; N, 2.47; P, 5.45. Molar electric conductivity of solutions at 20 °C, $C = 1 \cdot 10^{-3}$ mol L^{-1}, Λ (MeCN, Ohm^{-1} cm^{-1} mol^{-1}): 41.0 (**1**), 125 (**2**). ^{31}P NMR (MeCN), δ: −10.68 ($^1J_{P-Pt}$ = 3252 Hz). IR (KBr, oil), ν/cm^{-1}: 2654, 2500 (H—N^+); IR (polyethylene, oil), ν/cm^{-1}: 308, 282 (Pt—Cl); IR (MeCN), ν/cm^{-1}: 2628, 2588

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(H—N^+), 1632 (Ph); ^{1}H NMR (CD_3CN, +30°C), δ: 1.22 (t, 18 H, CH_3), 3.00 (q, 12 H, CH_2), 4.49—4.72 (m, 8 H, $-C\underline{H}_2O$), 7.07—8.22 (m, 30 H, $C_6\underline{H}_5$); ^{1}H NMR (CD_3CN, −30°C), δ: 4.42 (s, 8H, $P-C\underline{H}_2-O$).

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