COMPLEXES OF 2,5-DIPHENYL-1,3,2,5-DIOXABORAPHOSPHORINANE AND 1,3,5-TRIPHENYL-1,3,5-DIAZAPHOSPHORINANE WITH MOLYBDENUM HEXA-CARBONYL

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The reaction of 2,5-diphenyl-1,3,2,5-dioxaboraphosphorinane (L) and 1,3,5-triphenyl-1,3,5-diazaphosphorinane (L') with molybdenum hexacarbonyl gave, respectively, $Mo(CO)_4L_2$ and $Mo(CO)_5L$ ' complexes.

Keywords: molybdenum hexacarbonyl, phosphorinanes, complexes.

In [1] it was shown that ligands of the dioxaboraphosphorinane series are weaker σ donors than aminomethylphosphines. Thus, the weak σ donor is displaced when the complex of 4,6-dimethyl-2,5-diphenyl-1,3,2,5-dioxaboraphosphorinane with borane is treated with 1,5dibenzyl-3,7-diphenyl-1,5,3,7-diazadiphosphacyclooctane, and 3,7-bis(borane)-1,5-dibenzyl-3,7-diphenyl-1,5,3,7-diazadiphosphacyclooctane is formed. However, the capacity of phosphine ligands for dative bonding due to the d-acceptor character of the P atom has a significant effect on their properties. For a comparison of the d-acceptor properties of the P atoms in functionally substituted phosphines it seemed of interest to study the complexing of boryloxyalkylphosphines and aminomethylphosphines with zero-valence metals.

The reaction of aminomethylphosphines containing two, three, and four phosphorus atoms with molybdenum hexacarbonyl was described in [2-4], and it was shown that under rather severe conditions (refluxing in monoglyme for several days) chelate complexes are formed with the displacement of two molecules of carbon monoxide from $Mo(CO)_6$. To exclude the stabilizing chelate effect we used ligands of the 1,3,2,5-dioxaboraphosphorinane and 1,3,5-diazaphosphorinane series. A complex (2) of two molecules of the ligand with molybdenum tetracarbonyl was obtained in 55% yield in the reaction of excess 2,5-diphenyl-1,3,2,5-dioxaboraphosphorinane (1) with $Mo(CO)_6$ in refluxing acetonitrile:



The structure of 2 was confirmed by the results of elementary analysis and by the presence in the mass spectra of peaks of a molecular ion (m/z = 722), the unbonded ligand, and their fragmentation products. Two signals of equal intensity with chemical shifts (CS) of 3.1 and 1.6 ppm, which are situated in the region characteristic for complexes of tertiary phosphines [5], are observed in the ³¹P NMR spectra. The presence of two signals constitutes evidence for a cis orientation of the phosphine ligands. The character of the absorption of the CO groups in the IR spectra of 2 confirms this conclusion [5]. In the PMR spectra the ratio of the integral intensities of the phenyl and methylene protons also indicates retention of the structure of the ligand.

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The ³¹P NMR spectrum of complex 4 contains one signal with a CS of 6.0 ppm. The characteristic absorption of five carbonyl groups [5] and skeletal vibrations of the ligand at 700-1600 cm⁻¹ are observed in the IR spectra. In addition to peaks of ions M⁺' of the complex (m/z = 570) and the unbonded ligand (m/z = 322), the mass spectra contain peaks of 1,3azaphosphetidine and its complexes. The formation of an azaphosphetidine in the mass spectra was previously noted for diazadiphosphacyclooctanes [6].

Thus, despite the fact that the σ -donor properties of the P atoms are decreased for 1 [7], it displaces two carbonyl groups in Mo(CO)₆, while diazaphosphorinane 3 displaces only one under the same conditions. This fact can evidently be explained by the stronger d-acceptor properties of the P atom in compounds of the 1 type.

EXPERIMENTAL

The ¹H NMR spectra were recorded with a Varian-60 spectrometer (60 MHz) at 34.5°C, and the ^{3 1}P NMR spectra were obtained with a Bruker WM 250 spectrometer with the following operating frequencies: $\delta_{\rm H}$ 250 MHz and $\delta_{\rm P}$ 101 MHz. The IR spectra of suspensions in mineral oil were recorded with a UR-20 spectrometer.

The electron-impact mass spectra were obtained with an MKh-1310 spectrometer operating in a complex with an SM-4 computer. The precise masses were determined automatically with respect to the reference points of perfluorinated kerosene. The relative error in the determination of the masses of the ions was $5 \cdot 10^{-6}$ amu. The ionizing-electron energy was 70 eV, the emission current was 30 μ A, and the input-system temperature was 90°C.

 $\frac{\text{cis-Bis}(2,5-\text{Diphenyl-1},3,2,5-\text{dioxaboraphosphorinane})\text{tetracarbonylmolybdenum(0)}(2).}{\text{solution of 1.55 g (6 mmoles) of 1 and 0.53 g (2 mmoles) of Mo(CO)_6 in 20 ml of MeCN was refluxed for 6 h, after which the solvent was removed in vacuo, and the residue was crystallized from hexane and washed with ether to give 0.8 g (55%) of 2 with mp 88-89°C and <math display="inline">\delta^{31}P$ 1.6 and 3.1 ppm (MeCN); the ratio of the integral intensities of the protons of the phenyl and methylene groups in the PMR spectra was 5:2. Mass spectrum (m/z): 722 (M⁺). IR spectrum (v, cm⁻¹): 1870, 1915, 1930, 1960, 2030 (C=O). Found, %: C 53.55, H 4.04, P 8.44. C_{32}H_{28}B_2MO_8P_2. Calculated, %: C 53.33, H 3.89, P 8.47.

Starting 3 (65%) was isolated from the filtrate after removal of the solvent and treatment of the residue with hexane.

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