Russian Journal of General Chemistry, Vol. 71, No. 7, 2001, pp. 1036–1037. Translated from Zhurnal Obshchei Khimii, Vol. 71, No. 7, 2001, pp. 1101–1102.
Original Russian Text Copyright © 2001 by Yaroshevskaya, Polovnyak, Gurevich.

Reaction of $CoS_4C_4Ph_4$ with (3-Indolyl)phosphonites by ESR Data

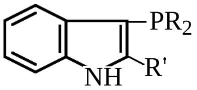
V. A. Yaroshevskaya, V. K. Polovnyak, and P. A. Gurevich

Kazan State Technological University, Kazan, Tatarstan, Russia

Received February 7, 2000

Abstract—The reactions of the Co(II) bis-α-dithioketone complex with excess (3-indolyl)phosphonites in acetone and in solvent-free conditions were studied by ESR spectroscopy. It was shown that initially one molecule of the P(III) derivatives enters in the axial position and further the second molecule enters *trans* to the first one.

The square-planar low-spin Co(II) bis-α-dithioketone complex $CoS_4C_4Ph_4$ was obtained by the procedure in [1] and used as indicator system in studies on complex formation of (3-indolyl)phosphonites **I**–**IV** [2].



I–IV

R = OEt (**I**), OPr (**II**), OPh (**III**), NEt_2 (**IV**); R' = H (**I–III**), Me (**IV**).

The complex formation reactions were performed both in acetone and with no solvent, using excess compounds **I**–**IV**. The reaction kinetics were studied at various temperatures (290–400 K).

The rate of ligand insertion depends on the nature of substituents on the phosphorus atom and decreases in the order $P(OEt)_3 \geq IndP(OEt)_2 > IndP(OPr\text{-}i)_2 > IndP(OPh)_2 > IndP(NEt_2)_2$ (Ind is 3-indolyl).

Figure 1 depicts the ESR spectra for the resulting adduct of the Co(II) complex with compound **I** at 290 K. The spectra are described by the isotope spin Hamiltonian.

$$H = g\beta H_0 S_z + A I_z S_z + \alpha I S_z.$$

Here A and α are the hyperfine coupling constants of ^{59}Co and ^{31}P, respectively. The spectra contain a number of lines. Apart from the eight lines of the hyperfine structure produced by coupling of the unpaired electron with ^{59}Co (I 7/2), an additional hyperfine structure is observed, arising from coupling of the unpaired electron with one ^{31}P nucleus (I 1/2) (adduct **A**) or with both equivalent ^{31}P nuclei (adduct **B**).

The ESR spectra show that adducts **A** and **B** are monomers. As seen from the table, the spectral parameters depend on the nature of the phosphorus-containing substituent. The values of the g factors suggest that the metal–phosphorus bond is covalent.

The resulting data allow us to propose the following scheme of the insertion of (3-indolyl)phosphonites **I**–**IV** into the internal sphere of the square-planar

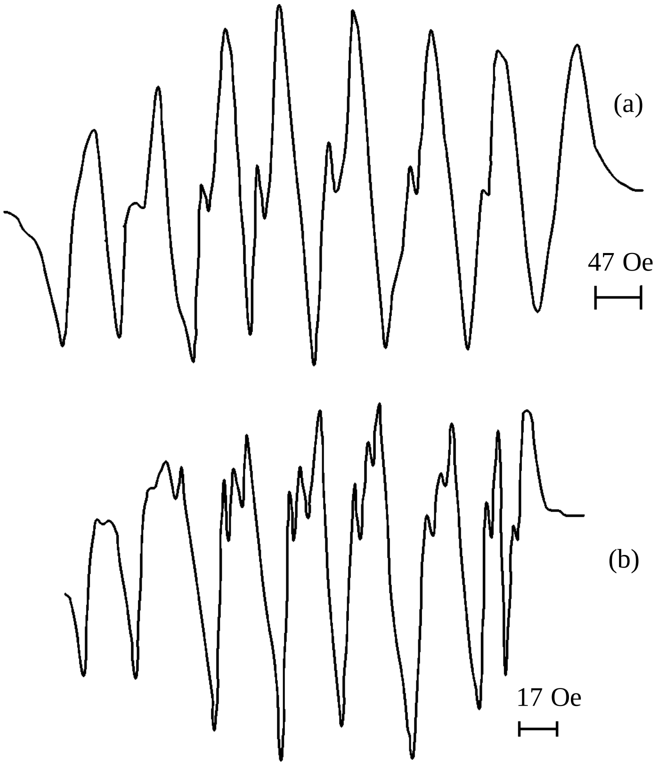


Fig. 1. ESR spectra of the adducts of the cobalt(II) α-dithioketone complex with excess $IndP(OEt)_2$ in acetone (290 K). (a) Adduct **A** and (b) adduct **B**.

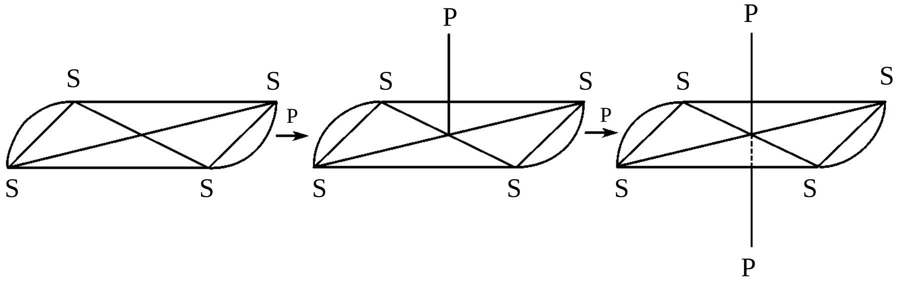


Fig. 2. Scheme of insertion of (3-indolyl)phosphonites **I–IV** into the internal sphere of the square-planar cobalt(II) bis-α-dithioketone complex.

Parameters of the ESR spectra of the adducts of the cobalt(II) bis-α-dithioketone complex with excess (3-indolyl)phosphonites **I–IV** in acetone at 290 K

Adduct	PR_2	$g \pm 0.0005$	$A \pm 0.01$, Oe	$\alpha \pm 0.01$, Oe
A	$P(OEt)_2$	1.0145	23.65	10.51
	$P(OPr)_2$	1.0148	23.68	9.95
	$P(OPh)_2$	2.0158	23.72	9.48
	$P(NEt_2)_2$	2.0117	23.81	7.15
B	$P(OEt)_2$	2.0162	23.60	9.83
	$P(OPr)_2$	2.0170	23.75	9.24
	$P(OPh)_2$	2.0172	23.65	9.02
	$P(NEt_2)_2$	2.0161	23.81	8.85

cobalt(II) bis-α-dithioketone complex, yielding five- and six-coordinate compounds.

We suppose that adducts **A** and **B** of the cobalt(II) bis-α-dithioketone complex with the organophosphorus derivatives studied have the low-spin electron configuration d^7 with the unpaired electron residing on the d_{xy} orbital (the y axis goes between the sulfur atoms and halves the chelate angle [2]). The strong hyperfine coupling between the bis-α-dithioketone complex and ^{31}P nucleus suggests direct coupling between the unpaired electron of the cobalt atom with the phosphorus nucleus and coordination of (3-indolyl)phosphonite via the donor P(III) atom.

EXPERIMENTAL

The ESR spectra were measured on a Bruker spectrometer at ~9000 MHz, reference triethyl phosphite [2].

Diethyl (3-indolyl)phosphonite (I) [4], dipropyl (3-indolyl)phosphonite (II), and diphenyl (3-indolyl)phosphonite (III) were obtained from 0.05 mol of diethyl phosphorochloridite, dipropyl phosphorochloridite, diphenyl phosphorochloridite, diethylamidophosphorous chloride, and (3-indolyl)magnesium chloride in absolute diethyl ether with vigorous stirring (0°C) under argon. The Grignard reagent was obtained from 0.05 mol of magnesium, 0.05 mol of methyl iodide, and 0.05 mol of indole. The reaction mixture was decomposed with aqueous ammonium chloride and hydrochloric acid, which were preliminarily cooled to 0°C. The ether layer was separated, washed with sodium hydrocarbonate, and dried with sodium sulfate. The ether was removed at reduced pressure. Compounds **I** and **II** were purified by distillation, and compound **III**, by reprecipitation into water (pH 6) from ethanol. The physicochemical characteristics of compounds **I–III** are given in [3].

(2-Methyl-3-indolyl) tetraethylphosphonodiamidite (IV) was prepared and purified like compound **I**, yield 42%, bp 146–147°C (0.5 mm), n_D^{20} 1.5620, d_4^{20} 1.0407, δ_P 93 ppm. Found, %: N 14.17; P 10.96. $C_{16}H_{26}N_3P$. Calculated, %: N 14.44; P 10.65.

REFERENCES

1. Schrauzer, G.N., Mayweg, V.P., Finck, N.W., and Heinrich, W., *J. Am. Chem. Soc.*, 1966, vol. 88, no. 20, pp. 4606–4609.
2. Troitskaya, A.D., Yablokov, Yu.V., Ryzhmanova, A.V., Razumov, A.I., and Gurevich, P.A., *Zh. Neorg. Khim.*, 1971, vol. 17, no. 11, pp. 3120–3121.
3. Yaroshevskaya, V.A., Polovnyak, V.K., and Gurevich, P.A., *Zh. Obshch. Khim.*, 2001, vol. 71, no. 7, pp. 1098–1100.