COMPLEXES OF 1,3,5-TRIPHENYL-1,3,5-DIAZAPHOSPHORINANE WITH Pt(II), Co(II), Ni(II), AND Cu(I) SALTS

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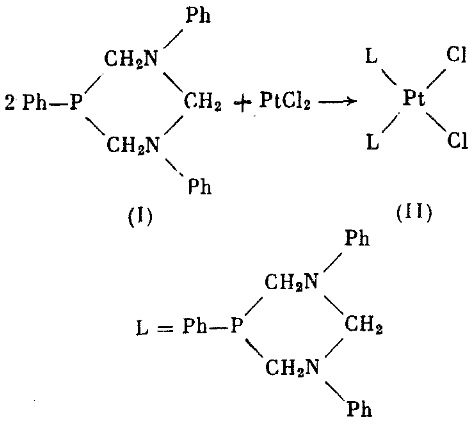
UDC 542.91:541.49:547.1'118

1,3,5-Triphenyl-1,3,5-diazaphosphorinanes form 2:1 complexes with Pt(II), Co(II), Ni(II), and Cu(I). ^{31}P NMR spectroscopy indicated that Pt, Co, and Ni are coordinated at the phosphorus atoms, while Cu(I) is coordinated at the nitrogen atoms.

1,3,5-Diazaphosphorinanes and 1,5,3,7-diazadiphosphacyclooctanes are ligands with several potential sites for metal coordination. The complexation of 1,5,3,7-diazadiphosphacyclooctane with molybdenum carbonyl has been described by Markl et al. [1]. In this case, the coordination occurs at the phosphorus atoms.

We have synthesized complexes of 1,3,5-triphenyl-1,3,5-diazaphosphorinane (I) with Pt(II), Co(II), and Ni(II) chlorides and cuprous iodide. The reaction was carried out in acetonitrile. The determination of the composition and several conclusions concerning the structure of these complexes in solution were obtained using NMR and IR spectroscopy. In all cases, 2:1 ligand-metal complexes were obtained.

Thus, $PtCl_2$ complexes with (I) to give a dark red-brown crystalline product, which gives transparent crystals with a gray metallic shine upon slow crystallization from acetonitrile.


(I) (II)

The PMR and IR spectra show the invariance of the structure of the starting ligand. The ^{31}P NMR spectrum has one signal at −20.32 ppm ($^1J_{P-Pt}$ = 3460 Hz), which indicates the equivalence of the phosphorus atoms and the coordination of platinum at the phosphorus atoms in both ligands. The $^1J_{P-Pt}$ coupling constant is characteristic for the cis configuration of the complex [2].

Under analogous conditions, anhydrous $CoCl_2$ complexes with (I) form dark gray complex (III), while $NiCl_2$ complexes with (I) form bright red complex (IV)

$$\underset{(I)}{2L} + MCl_2 \longrightarrow \underset{(III),\,(IV)}{L_2MCl_2}$$

M = Co (III), Ni (IV).

The ^{31}P NMR spectra of complexes (III) and (IV) in chloroform have one broad signal at −1.56 and −16.7 ppm, respectively. The strong downfield shift of these signals in comparison with the signal of the starting ligand (−61 ppm [3]) indicates coordination of the metal at the phosphorus atoms in both ligands. An analogous shift was observed in our

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A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Branch, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 1, pp. 209-211, January, 1991. Original article submitted April 16, 1990.

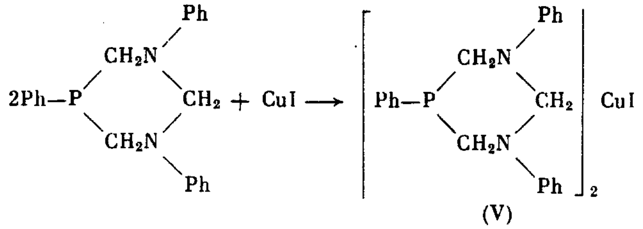
0568-5230/91/4001-0191$12.50

TABLE 1. Physical Indices for L_2MX (II)-(V)

Compound	Yield, %	Mp, °C	$\delta\,^{31}P$ (solvent)	Found/Calculated, %				
				C	H	N	P	Cl
(II)	70	200–202	–20,3 (CH_3CN)	54,08 54,19	4,71 4,52	6,14 6,02	6,96 6,67	7,78 7,63
(III)	52	128–132	–1,56 (CH_3CN)	63,49 63,48	5,66 5,30	7,56 7,05	8,04 7,81	8,33 8,94
(IV)	50	188–189	–16,7 ($CHCl_3$)	62,96 63,48	5,62 5,30	7,15 7,05	7,89 7,81	9,57 8,94
(V)	40	182–183	–40 DMF	59,02 58,98	5,15 4,92	6,86 6,55	7,40 7,25	

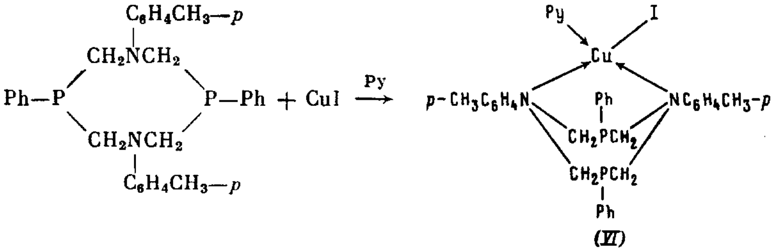
previous work [4]. The ebullioscopic determination of the molecular weight of complexes (III) and (IV) in benzene permitted us to establish the monomeric structure of complexes (III) and (IV) at the boiling point of benzene. The molecular weight was 800 for (III) and 760 for (IV) (theoretical value 794).

The reaction of (I) with cuprous iodide gives a white crystalline compound, which gives qualitative tests for cuprous ions and iodide. The PMR spectra (ratio of the integral intensities of the phenyl and methyl group protons) and IR spectra (retention of the heterocycle ring vibrations) as well as the elemental analysis data indicate the retention of the ligand structure and formation of a 2:1 ligand–metal complex. However, the slight displacement of the ^{31}P NMR spectral signal of this complex (–40 ppm) in comparison with the starting ligand indicates the coordination of copper not at the phosphorus atom but rather at one of the nitrogen atoms in the heterocycle. The low solubility of complex (V) did not permit determination of its molecular weight in solution.



(V)

The conclusion concerning the coordination of copper at the nitrogen atoms was supported by comparison of the chemical shifts of the complexes of 1,5,3,7-diazadiphosphacyclooctanes with Ni(II) and Co(II) described in our previous work [4] and complex (VI), which was obtained by the reaction of 1,5-di-(p-tolyl)-3,7-diphenyl-1,5,3,7-diazadiphosphacyclooctane with CuI in pyridine. Nevertheless, rapid exchange of the phosphorus and nitrogen donor atoms of the ligand in the complex molecule in solution cannot be excluded.



(VI)

The composition of complex (VI) was indicated by elemental analysis, PMR and IR spectroscopy, and its qualitative reactions for cuprous ions and iodine. The ^{31}P NMR spectra have a single signal at –33.7 ppm (the chemical shift of the starting ligand is –50 ppm). On the other hand, coordination of the metal at the phosphorus atoms in 1,5,3,7-diazadiphosphacyclooctanes leads to a signal at 19 ppm [4]. Different coordination of metals in the same ligand is noted in our subsequent communication [5], in which copper is coordinated with bis(hydroxymethyl)phenylphosphine at the oxygen atoms, while silver is coordinated at the phosphorus atom in solution as indicated by ^{31}P NMR spectroscopy.

The specific electrical conductivity of complexes (II)-(VI) determined in acetonitrile and DMF is the range from 10 to 60 $\Omega^{-1}cm^2mole^{-1}$, which permits us to exclude ionic structures for these complexes.

Our detailed study of the complexes in solution and in the crystal state will be continued.

EXPERIMENTAL

General Procedure for the Preparation of Bis(1,3,5-triphenyl-1,3,5-diazaphosphorinane)-MX (MX = $PtCl_2$ (II), $CoCl_2$ (III), $NiCl_2$ (IV), and CuI (V)). A sample of 0.01 mole 1,3,5-triphenyl-1,3,5-diazaphosphorinane (I) was added to a suspension of 0.005 mole MX in 15 ml solvent (acetonitrile for (II)-(IV) or chloroform for (V)). The red-brown (II), black (III), red (IV), and white crystals (V) were filtered off and washed with acetonitrile. The C_6H_5/CH_2 ratio of the integral intensities in the PMR spectra was 15/6. The other physical indices for these compounds are given in Table 1.

[N,N-1,5-Di(p-tolyl)-3,7-diphenyl-1,5,3,7-diazadiphosphacyclooctane]pyridinecuprous iodide (VI). A sample of 0.4 g (0.002 mole) CuI was added to a solution of 1 g (0.004 mole) 1,5-di(p-tolyl)-3,7-diphenyl-1,5,3,7-diazadiphosphacyclooctane in 3 ml pyridine. After standing overnight, the crystals of (VI) were filtered off and washed with acetone. The yield of (VI) was 1.1 g (71%), mp 198-199°C, $\delta^{31}P$ = −33.7 ppm (DMF). The (C_6H_5 + C_6H_4 + C_5H_5N)/CH_2/CH_3 ratio of the integral intensities in the PMR spectra was 23/8/6. Found: C, 56.00; H, 4.90; N, 5.62; P, 8.48%. Calculated for $C_{35}H_{37}CuIN_3P_2$: C, 55.89; H, 4.92; N, 5.59; P, 8.25%.

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