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Complexes of Platinum(II) Chloride with Cyanophosphines

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Abstract — Platinum(II) cyanophosphine complexes PtL_2Cl_2, where L = $P(CN)_3$, $PhP(CN)_2$, or Ph_2PCN, were synthesized. Their properties and mode of coordination were examined.

Platinum(II) complexes have a square-planar structure. In particular, quite stable are acido complexes PtX_4^{2-}, where X is an acid residue. Complexes like PtL_2X_2, where is X is an organoelement ligand, exhibit *cis–trans* isomerism and are quite active in ligand substitution reactions in which the role of leaving invariably belongs to the acido ligand as a result of the *trans*-effect of the organoelement ligand. The PtL_2X_2 complexes, where L is an organic P(III) ligand and X is an acido ligand (Hlg^- or SCN^-), have been thoroughly studied in terms of synthesis, composition, and structure. Much less work has been on complexes with bidentate ligands, ambidentate in particular.

In the latter case, an important problem is intraspherical competition of ambidentate ligands when coordination via different donor atoms is possible. For instance, such a typical ambidentate ligand as thiocyanate can coordinate both via the nitrogen and sulfur atoms. Therewith, the thiocyanate ligand coordinated via the nitrogen and sulfur atoms have much different geometries: linear and angular, respectively. The different modes of coordination of the thiocyanate ligand makes possible stabilization of different geometric isomers of Pt(II): Coordination via the nitrogen atom stabilizes the *trans* isomer, whereas coordination via the sulfur atom, the *cis* isomer. Such a definite picture is observed when the organoelement ligand is monodentate (substituted phosphines, phosphites, amines, etc.). When the organoelement ligand is also ambidentate, the situation becomes unpredictable. We synthesized ambidendate ligands of a new type, substituted cyanophosphines, whose P(III) and N(III) atoms can act as donor centers (Table 1).

Substituted cyanophosphines would be expected to act both as monodentate ligands coordinating via the above donor centers and as bidentate. In the latter case, *cis* coordination of acido ligands would be predetermined.

The following modes of coordination of substituted phosphines are possible: via lone electron pairs (LEP) of N and P and polydentate coordination via N–N and N–P. Here we present the results of an experimental study of the mode of coordination of cyanophosphines in square-planar platinum(II) complexes.

It terms of organophosphorus chemistry, the cyano group in P(III) cyanides plays the role of a pseudohalide, and, therefore, these compounds tend to react similarly to substituted phosphorus halides [1].

With the aim to predict the metal-coordinating center in the P–C≡N ambidentate system, we performed quantum-chemical calculations of the populations and energies of the corresponding molecular orbitals of the free ligands (Table 2) [2].

Taking account of the calculation results and relying on Pearson's principle of hard and soft acids and bases [4], one should expect that the mode of platinum–ligand coordination will vary with cyanide structure.

Thus, $P(CN)_3$ should preferentially coordinate with Pt by its phosphorus atom (I 12.55 eV). The energy of HOMO in Ph_2PCN (phenyl π system) is 9.75 eV, and, therefore, a considerable contribution of phenyl π electrons would be expected.

Evidence for the above reasoning comes from the calculated populations of atomic orbitals in HOMO. Table 3 lists the contributions of atomic orbirals of

Table 1. Properties of ligands

Ligand	bp, °C	δ_P, ppm	ν_{CN}, cm^{-1}
$P(CN)_3$	50–60	–138.3	2180
$PhP(CN)_2$	68–70	–76.0	2190
$Ph_2P(CN)$	110	–36.4	2190
Ph_3P	80	–	–

the P–C≡N fragment into the HOMO of $P(CN)_3$. As seen, the HOMO is mostly contributed by the phosphorus LEP (0.46). At the same time, in Ph_2PCN, the contributions of atomic orbitals of the P–C≡N fragment into HOMO get close to zero, whereas the greatest contribution is from phenyl AOs. We prepared complexes PtL_2Cl_2, where L = $P(CN)_3$, $PhP(CN)_2$, and Ph_2PCN. By the indicator ion (SCN^-) technique [5] the complexes were assigned *trans* configuration.

The reaction of $PtCl_2$ with $P(CN)_3$ gives rise to the complex $[Pt(P(CN)_3)_2Cl_2]$. The CN absorption band in the IR spectrum of this compound is shifted with respect to that of the free ligand (ν 2180 cm^{-1}) to high frequencies (ν 2220 cm^{-1}), which, according to [6], points to platinum coordination by the nitrogen LEP.

The ^{31}P NMR spectrum of $[Pt(P(CN)_3)_2Cl_2]$ displays two doublets at δ_1 –6.0 (J_{PtP} 404 Hz) and δ_2 –4.3 ppm (J_{PtP} 131.1 Hz) (Table 4).

The low coupling constants are presumably associated with the fact that platinum interacts with phosphorus via σ- and π-bond systems [7]. Contrary to expectations, no coordination with phosphorus is observed, probably because the phosphorus LEP resides on a low-lying *s* orbital and is shielded by 3*p* electrons, which prevents its coordination with Pt.

The complex $[Pt(P(CN)_3)_2Cl_2]$ is thermally and hydrolytically stable, whereas the free ligand $P(CN)_3$ readily hydrolyzes to phosphorous acid [8].

The reaction of $PtCl_2$ with Ph_2PCN gives rise to the complex $[Pt(Ph_2PCN)_2Cl_2]$. The IR spectrum of the product contains a ν_{CN} band at 2188 cm^{-1}, and its ^{31}P NMR spectrum shows two doublets at δ_1 66.67 (J_{PtP} 213.8 Hz) and δ_2 2.16 ppm (J_{PtP} 157.6 Hz) (Table 4).

The J_{PtP} constants are much lower than those characteristic of Pt–P coordination (2000–3000 Hz [9]). At the same time, had platinum been coordinated by CN, the ν_{CN} band in the IR spectrum would has been shifted relative to that of the free ligand (ν_{CN} Ph_2PCN 2190 cm^{-1}) [10]. Thus, in the complex $[Pt(Ph_2PCN)_2Cl_2]$ we deal with coordination by the phosphorus LEP. In the long-wave region of the IR spectrum, a band at 305 cm^{-1} is observed, which, too, is assignable to first harmonics of Pt–P stretching vibrations (ν_{PtP}). The shift of the ^{31}P NMR signals is compensated for in part by electron transfer from phenyl substituents to phosphorus, which explains the anomalously low chemical shifts (δ_1 and δ_2) and coupling constants (J_{PtP}).

Table 2. Orbital energies of free ligands (eV)

Orbital	Ligand		
	$P(CN)_3$	$P(CN)_3$ [3]	Ph_2PCN
LEP P	12.55	12.04	10.84
π_{CN}	14.25	13.50	13.50
LEP N	15.28	14.13	14.34
π_{Ph}	–	–	9.75

Table 3. Contributions of atomic orbitals of the P–C≡N fragment into the HOMO of $P(CN)_3$

Atom	Atomic orbital	Ligand $P(CN)_3$	Atom	Atomic orbital	Ligand $P(CN)_3$
P	$3s_\sigma$	0.46	S	$2p_{\pi'}$	0.13
	$3p_\sigma$	0.23	N	$2s_\sigma$	0.06
S	$2s_\sigma$	0.10		$2p_\sigma$	0.13
	$2p_\sigma$	0.21		$2p_\pi$	0.17
	$2p_\pi$	0.10		$2p_{\pi'}$	0.21

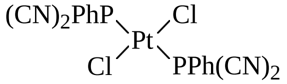
Table 4. ^{31}P chemical shifts of the Pt–P bond

Complex	δ_1, ppm	J_{PtP}, Hz	δ_2, ppm	J_{PtP}, Hz
$[Pt(P(CN)_3)_2Cl_2]$	–6.00	404.0	–4.30	131.1
$[Pt(PhP(CN)_2)_2Cl_2]$	18.80	1373.3	–	–
$[Pt(Ph_2PCN)_2Cl_2]$	66.67	213.8	2.16	157.6

The reaction of $PtCl_2$ with $PhP(CN)_2$ gives rise to the complex $[PtL_2]Cl_2$. The IR spectrum of this complex shows no defined ν_{PtCl} band, implying chlorine resides in the outer rather than inner sphere.

The ν_{CN} band of this complex is shifted to 2213 cm^{-1}. Presumably, platinum is coordinated via CN, since uncoordinated CN group has ν_{CN} 2190 cm^{-1}. In this case, a polymeric product is formed.

Alternatively, coordination by the phosphorus LEP can occur, like in the above two cases.



Two dimers may also be formed with a bridging position of the ligand and one platinum atom coordinated to the other via the donor phosphorus atom and nitrogen. For unambiguous conclusions as the mode of coordination in $PhP(CN)_2$, yet unavailable data on the molecular weight and structure of the product are reuired. This will form the subject of our further research.

EXPERIMENTAL

Quantum-chemical calculations were performed by the semiempirical PM3 method.

The IR spectra were measured on a Bruker IFS-113V spectrometer at 100–4000 cm^{-1} for samples pelleted with KBr or polyethylene.

The NMR spectra were obtained on a Bruker SKhR-100 spectrometer at 36.47 (^{31}P, external reference 85% H_3PO_4) and 90.13 MHz (^1H, external reference TMS). Negative chemical shifts relate to an upfield shift. The accuracy in the chemical shifts was +0.02 ppm.

Complex of platinum(II) chloride with phosphorus tricyanide. A solution of 0.38 g of $P(CN)_3$ and 0.3 g of $PtCl_2$ in methylene chloride was allowed to stand at room temperature for 1 day. The complex $[Pt(P(CN)_3)_2Cl_2]$ formed as a yellow precipitate, decomp. point >300°C. Yield 0.42 g (70%). Found, %: P 12.67; Pt 40.28. $C_6N_6Cl_2P_2Pt$. Calculated, %: P 12.75; Pt 40.32.

Complex of platinum(II) chloride with dicyano(phenyl)phosphine. A solution of 0.38 g of $PhP(CN)_2$ and 0.26 g of $PtCl_2$ in 10 ml of methylene chloride was allowed to stand at room temperature for 1 day. The complex $[Pt(PhP(CN)_2)_2]Cl_2$ formed as a yellow precipitate, decomp. point >350°C. Yield 0.4 g (70%). Found, %: P 12.89; Pt 42.90. $C_{16}H_{10} \cdot Cl_2N_4P_2Pt$. Calculated, %: P 13.18; Pt 42.03.

Complex of platinum(II) chloride with cyanodiphenylphosphine. A solution of 0.40 g of $Ph_2P(CN)$ and 0.32 g of $PtCl_2$ in methylene chloride was allowed to stand at room temperature for 1 day. The complex $Pt(Ph_2PCN)_2Cl_2]$ formed as a yellow precipitate, decomp. point >350°C. Yield 0.34 g (70%). Found, %: C 57.28; P 11.16; Pt 35.43. $C_{26}H_{20}Cl_2 \cdot N_2P_2Pt$. Calculated, %: C 57.14; P 11.35; Pt 35.89.

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