COMPLEXES OF CYCLIC AMINOMETHYLPHOSPHINES WITH Pt(II), Pd(II), Cu(I), AND Ag(I) SALTS


1,3,5-Diazaphosphorinanes and 1,5,3,7-diazadiphosphacyclooctanes form complexes with Pt(II), Pd(II), Cu(I), and Ag(I) salts. Platinum and palladium are coordinated through phosphorous atoms. In the case of 1,3-diphenyl-5-p-toluidenomethyl-1,3,5-diazaphosphorinane complex formation with platinum and palladium is accompanied by formation of a new polydentate ligand, p-tolylbis-(1,3-di-p-tolyl-1,3,5-diazaphosphorinane-5-yl)methylamine, where the metal is also bonded to phosphorus atoms.

Keywords: 1,3,5-diazaphosphorinanes, 1,5,3,7-diazadiphosphacyclooctanes, complexes, platinum, palladium, ring conformation.

Functionally substituted phosphines have several coordination centers and are able to undergo different conversions in the process of complex formation. Aminomethyl derivatives of phosphines containing a P-C-N moiety possess these qualities. Moreover, published data on their chemical properties and structure and the possibility of using a number of physicochemical methods for this class of compounds make it possible to draw conclusions regarding the structure of their complexes in solution and in the solid state. It has been shown previously [1, 2] that heterocycles with a P-C-N moiety, containing a PhCH₂ group at the nitrogen atoms, exist in a conformational equilibrium in which there is a form with axial orientation of the substituent at the nitrogen atom and equatorial at the phosphorus atom. In complexes of cyclic aminomethylphosphines with BH, the number of added borane

*Deceased.
molecules depends on the conformational composition of the heterocycles [3]. We have
described previously [4] a method for synthesis of the complex trans-(PhP(CH₂NRCH₂)₂PPh)-
PtCl₂, where R = C₆H₄Me-p. It appeared that replacing the tolyl groups by benzyl at the
nitrogen atoms in 1,5,3,7-diazadiphosphacyclooctanes leads to a change in the configura-
tion of the central atom in the complex with PtCl₂:

\[
\begin{align*}
R & \quad \text{PhP} \quad \text{PPh} + \text{MCl₂} \rightarrow \\
\text{M} & = \text{Pt}, \quad \text{R} = \text{CH₃Ph} (1) \\
\text{M} & = \text{Pd}, \quad \text{R} = \text{C₆H₄Me-p} (2), \text{CH₂Ph} (3).
\end{align*}
\]

The \(^{3}P\) NMR spectra of solutions of the cis-(PhP(CH₂NRCH₂)₂PPh)PtCl₂ complex (1) display
one signal with a chemical shift (CS) of -26 ppm and SSCC with the platinum of 2929 Hz.
The occurrence of one signal and its significant displacement compared with the CS of the
original ligand (-50 ppm) indicate coordination of the platinum through a phosphorus atom
and the SSCC \(^1J_{P-Pt}\) value is characteristic of a cis complex (see [4], \(R = \text{C₆H₄Me-p}, \delta =
13\) ppm, \(^1J_{P-Pt} = 2297\) Hz). The IR spectra of crystalline complex 1 (dark-brown crystals)
also indicate a cis configuration of the Pt atom: \(\nu(Pt-Cl)_{cis} = 315, 326\) cm\(^{-1}\) (two bands),
in contrast with \(\nu(Pt-Cl)_{trans} = 313\) cm\(^{-1}\) (one band) [5]. No further Pt-P-Pt interaction is
observed in the \(^{3}P\) NMR spectra which makes it possible to rule out the dimeric structure
of a binuclear cluster-type complex. Moreover, a binuclear cis,cis complex should experi-
ence strong steric interactions. The difference in structure of the 1,5,3,7-diazadiphos-
phacyclooctane complexes with PtCl₂ when \(R = \text{C₆H₄Me-p}\) and CH₂Ph may be explained either
by a difference in the conformational composition of the heterocycles (the orientation of
substituents) or by conformational features of the heterocycles [6].

Differences in the configuration of the central atom have not been noted in the 1,5,3,
7-diazadiphosphacyclooctane complexes with PdCl₂.

The IR spectra of the crystalline complexes 2 (pale-yellow crystals) and 3 (orange
crystals) contain double \(\nu(Pd-Cl)\) bands, 289, 303 cm\(^{-1}\) for 2 and 293, 316 cm\(^{-1}\) for 3, which
indicates a cis configuration for the Pd-Cl bonds. The occurrence of one signal each in the
\(^{3}P\) NMR spectra and the size of the CS (2.37 ppm for 2 and -9.6 ppm for 3) suggest co-
ordination of the Pd through phosphorus atoms. Data from elemental analysis, the IR spec-
tra of the crystals, and also the ratio of integral intensities of all types of protons
in the PMR spectra reveal no change in the structure of the ligand.

A cis complex with coordination of the metal through a phosphorus atom is formed by
interaction of 1,3,5-triphenyl-1,3,5-diazaphosphorinane with PdCl₂. The metal is bonded
to two ligand molecules:

\[
\begin{align*}
\text{Ph} & \quad \text{2PhP} \quad \text{CH₅ + PdCl₂} \rightarrow \text{cis-} \\
\text{2PhP} & \quad \text{CH₅} \quad \text{Ph}
\end{align*}
\]

The IR spectra of the crystalline complex 4 (orange crystals) have \(\nu(Pd-Cl)\) bands at
302 and 277 cm\(^{-1}\) and the \(^{3}P\) NMR spectra have a signal with a CS of 1.37 ppm.

Of special interest are cases when changes occur during synthesis of the complexes
which are uncharacteristic of the free ligands. For example, reactions are known for 1,3,5-
diazaphosphorinanes with an aminomethyl radical at the P atom which leads to tris(amino-
ethyl)phosphines and 1,1'-diaza-3,3'-diphosphetidines [7, 8].