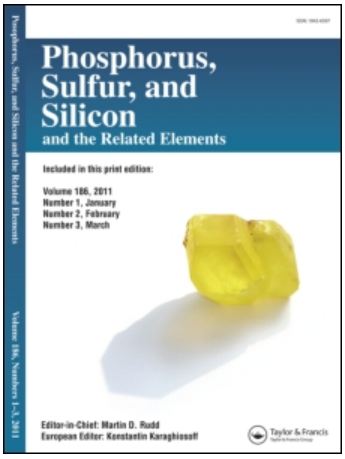

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1,3,5-Diazaphosphorinanes on the Pt-Group Metal Templates. Conformational Behaviour of the Heterocyclic Ligands and Stabilization of Unusual Coordination of Pt(II) Ion

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1,3,5-DIAZAPHOSPHORINANES ON THE Pt-GROUP METAL TEMPLATES. CONFORMATIONAL BEHAVIOUR OF THE HETEROCYCLIC LIGANDS AND STABILIZATION OF UNUSUAL COORDINATION OF Pt(II) ION.

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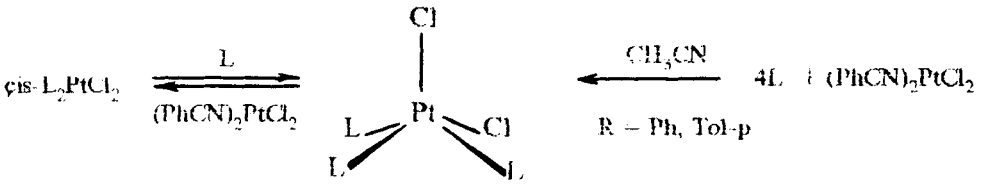
Structure and reactivity of square-planar phosphine complexes are greatly depended from the repulsion of the $P(\alpha C\equiv)_3$ units and neighbouring ligands. The conformational behaviour of heterocyclic phosphines (in particular 1,3,5-diazaphosphorinanes) on the metal templates determines the special features of structures of the corresponding complexes.

It has been shown that 1,3,5-diazaphosphorinanes formed cis-P-complexes of Pt(II) and Pd(II). X-ray analysis of the obtained complexes demonstrated that the phosphine ligands possess chair conformation with diaxial orientation of aryl substituents on P and N atoms. This conformation is stabilized by attractive dispersion interaction of diaxial aryl groups. It has been shown on the base of NMR ^1H data that the less sterically demanded conformer with equatorial orientation of P-M bonds predominates in solutions of all complexes.

The phosphine Pt(II) complexes L_2PtCl_2 in the presence of free ligand excess formed 5-coordinated species L_3PtCl_2. The physical properties and behaviour of L_3PtCl_2 in solutions are probably determined by the ligand sterical demands.



In the solid state the complex L_3PtCl_2 (R=Tol-p) has usual yellow color and it NMR ^{31}P spectrum appears as A_2B spin system. At the same time complex L_3PtCl_2 (R=Ph) has unusual deep red color and it NMR spectrum is consistent with fast cis- to trans- L_2PtCl_2 isomerization catalyzed by free phosphine. Thus, isolated complex L_3PtCl_2 (R=Ph) is probably a low stable intermediate of cis-trans isomerization.