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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.

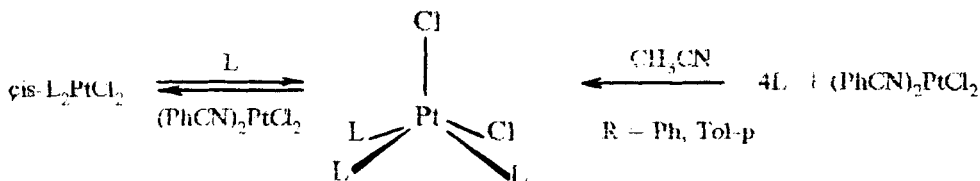
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Structure and reactivity of square-planar phosphine complexes are greatly depended from the repulsion of the $P(\alpha C\equiv)$ units and neighbouring ligands. The conformational behaviour of heterocyclic phosphines (in particular 1,3,5-diazaphosphorinanes) 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 its 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 its 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.