

## Theoretical study of oxidative addition to platinum metal complexes: VI. Complex formation of Rh(I), Pd(II), Ir(I), and Pt(II) with tridentate N- and P-donor fac-chelating ligands as a tool for controlling activity of metal complexes in oxidative methane addition

Vedernikov A., Shamov G., Solomonov B.  
Kazan Federal University, 420008, Kremlevskaya 18, Kazan, Russia

---

### Abstract

An approach was formulated to designing tridentate chelating ligands L ensuring stabilization of high-valence platinum metal hydridoalkyl complexes  $[(\text{Me})\text{M}(\text{L})(\text{H})\text{Cl}]$  ( $\text{M} = \text{Rh}, \text{Pd}^+, \text{Ir}, \text{and Pt}^+$ ) and thermodynamically more favorable oxidative methane addition to the corresponding low-valence complexes  $[\text{M}(\text{L})\text{Cl}]$ . The approach is based on diminishing strain in ligand framework and in chelate rings formed by the ligand, on using strong-field ligands, and also on minimizing deformation of metal coordination entity in the course of the reaction with methane. Within the framework of a nonempirical molecular-orbital method full geometry optimization was performed for the  $[\text{M}(\text{L})\text{Cl}]$  and  $[(\text{Me})\text{M}(\text{L})(\text{H})\text{Cl}]$  species containing eight N- and P-donor ligands L fitting to a greater or lesser extent the above-mentioned requirements: tris(iminomethyl)methane, cyclopropane-1,2,3-triamine, 1,3,5-triazacyclohexane, cyclohexane-1,3,5-triamine, 1,4,7-triazacyclonona-2,5,8-triene, cyclonona-1,4,7-triene-3,6,9-triamine, tris(2-phosphavinyl)methane, and cyclonona-1,4,7-triene-3,6,9-triphosphine. By calculations at the MP2 and B3LYP levels with allowance for electron correlation it was found that the energies of the reactions of the  $[\text{M}(\text{L})\text{Cl}]$  complexes with methane vary by almost 38 kcal/mol (for example, from -19 to +19 kcal/mol for  $\text{M} = \text{Pd}^+$ ). A relationship between the deformation of chelate rings, the denticity of ligand L in the  $[\text{M}(\text{L})\text{Cl}]$  species, and the efficiency of the ligand in stabilization of high-valence metal hydridoalkyl complexes was established. The existence of complexes  $[(\text{Me})\text{M}(\text{L}) \cdot (\text{H})\text{Cl}]$  with  $\text{L} = \text{cyclohexane-1,3,5-triamine}$  and  $1,4,7\text{-triazacyclonona-2,5,8-triene}$ , moderately stable at  $\text{M} = \text{Pd}(\text{IV})$  and stable at  $\text{M} = \text{Pt}(\text{IV})$  and  $\text{Ir}(\text{III})$ , and also of stable alkylhydridorhodium(III) complexes was predicted for the first time. Characteristics of the frontier orbitals of complexes  $[\text{M}(\text{L})\text{Cl}]_p$ ,  $[\text{CpMCl}]_q$ , and  $[\text{MCl}_2(\text{PH}_3)_2]_q$  ( $\text{M} = \text{Rh}, \text{Ir}, q = -1, p = 0$ ;  $\text{M} = \text{Pd}, \text{Pt}, q = 0, p = +1$ ) with distorted and undistorted coordination entities were compared.

---