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Theoretical study of oxidative additions to platinum metal complexes: VII. Mechanisms of methane activation by 16- and 14-electron platinum(II) and palladium(II) chlorophosphine complexes

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Abstract

Stationary points of the MP2//MP2 and B3LYP//B3LYP potential energy surfaces were studied for two model systems: methane-trans-dichlorobisphosphineplatinum(II) and methane-trans-dichlorobisphosphinepalladium(II). The points correspond to the products and transition states of the oxidative addition reactions and of metathesis of C-H bonds of methane and M-Cl bonds of the complexes with their participation, i.e., to 14-electron $MCl_2(PH_3)$ species and their η^3 complexes with methane, and also to the products and transition states of oxidative additions and metathesis of the C-H and M-Cl bonds involving $[MCl_2(PH_3)]$ complexes. The electron correlation for all the complexes was considered within the framework of Møller-Plesset (MP2) and coupled cluster [CCD, CCSD(T)] methods and density functional (B3LYP) theory. Corrections for the energy of zero vibrations of the complexes and enthalpies and entropies of the reactions were calculated. The complexes $[PdCl_2(PH_3)]$ and especially $[PtCl_2(PH_3)]$ tend to activate methane by the scheme of oxidative addition to a greater extent as compared to the metathesis of the C-H and M-Cl bonds.
