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Theoretical Study of Oxidative Addition to Platinum Metal Complexes. II. New Approach to Thermodynamics of Methane Reaction with 16-Electron Square-Planar Complexes of Rhodium(I), Palladium(II), Iridium(I), and Platinum(II)

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Abstract

The geometries and thermodynamic parameters of reagents and diastereomeric products of oxidative addition of methane to square-planar complexes of rhodium(I), palladium(II), iridium(I), and platinum(II) $[MX_nL_{4-n}]_q$ (where M is Rh or Ir, X is Cl, L is PH_3 , $n = 1-3$, and $q = 2 - n$; M is Pd and Pt, X is Cl, L is PH_3 , $n = 1-3$, and $q = 2 - n$; M is Pd, X is F, Cl, Br, I, Me, SiH_3 , and SnH_3 , L is PH_3 , NH_3 , and AsH_3 , $n = 2$, and $q = 0$) were calculated by the nonempirical MO method. The trans effect order of the ligands, similar for all metals under study was refined: $H > Me \approx SH_3 \approx SnH_3 > Cl > AsH_3 \approx PH_3 > NH_3$. The M-Y bond under the influence of trans hydride or methyl ligand becomes weaker in the following order: M-H, M-C, M-Si, M-Sn \gg M-P, M-As $>$ M-Cl $>$ M-N. A simple procedure to predict the relative stability of diastereomeric products of oxidative addition of alkanes to the planar complexes of the corresponding metal was developed. The energy of methane addition to the planar metal complexes was calculated by the general procedure involving three components: (a) the deformation energy of the planar complex into a butterfly-like carbene complex by bending one of the ligands under the coordination plane (E_{def}), (b) the energy of singlet-triplet rearrangement of metal carbene (E_{s-t}), and (c) the algebraic sum of dissociation energies of the Me-H, M-H, and M-Me bonds (ΣE_b). The relationship between E_{def} and structural parameters of the metal complex was established. The relationship of E_{s-t} with the ligand composition and the nature of complex-forming metal is qualitatively described by the crystal field theory. The spectrochemical series of studied ligands was refined: $I < Br < AsH_3 \approx Cl \approx < PH_3 < NH_3 \approx SnH_3 < F < SiH_3 < Me$. The strength of bonds formed by a metal with hydride and methyl ligands decreases in the following order: $Ir > Rh \gg Pt > Pd$. The theoretical and experimental data on the oxidative addition of alkanes to the platinum metal complexes were generalized and, as a result, the composition and structure of new metal complexes, which are effective activators of alkanes, were predicted.
