C–H Bond Activation of Methane with Gaseous [(CH₃)Pt(L)]⁺ Complexes (L = Pyridine, Bipyridine, and Phenanthroline)

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Electrospray ionization of solutions of dimethyl(1,5-cyclooctadiene)platinum(II) in methanol with traces of nitrogen-containing ligands L provides gaseous complexes of the type $[(CH_3)Pt(L)]^+$ with L = pyridine (py), 2,2'-bipyridine (bipy), and 1,10-phenanthroline (phen). These $[(CH_3)Pt(L)]^+$ cations are capable of activating the C–H bond in methane as shown by H/D exchange when using CD₄ as a neutral reactant. Most reactive is the complex $[(CH_3)Pt(py)]^+$ bearing a monodentate nitrogen ligand. The cationic complexes $[(CH_3)Pt(bipy)]^+$ and $[(CH_3)Pt(phen)]^+$ also bring about activation of methane, though at a lower rate, whereas the bipyridine complex $[(CH_3)Pt(py)_2]^+$ does not react with methane at thermal conditions. A detailed analysis of the experimental data by means of kinetic modeling provides insight into the underlying mechanistic steps, but a distinction whether the reaction occurs as σ bond metathesis or *via* an oxidative addition cannot be made on the basis of the experimental data available.

Key words: C-H Bond Activation, Electrospray Ionization, Mass Spectrometry, Methane, Platinum