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 [(CH₃)Pt(L)]⁺ with L = pyridine (py), 2,2′-bipyridine (bipy), and 1,10-phenanthroline (phen). These [(CH₃)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 [(CH₃)Pt(py)]⁺ bearing a monodentate nitrogen ligand. The cationic complexes [(CH₃)Pt(bipy)]⁺ and [(CH₃)Pt(phen)]⁺ also bring about activation of methane, though at a lower rate, whereas the bipyridine complex [(CH₃)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