Ti- and V-(C₆H₆)₂ sandwich complexes seeded in helium supersonic beams have been studied by pulsed field ionization zero electron kinetic energy photoelectron spectroscopy and theoretical calculations. The electronic states of the neutral and ionic complexes have been determined by comparison of experimental and simulated spectra. The ground electronic states of the neutral Ti- and V-(C₆H₆)₂ complexes are determined to be ¹A₁g and ²A₁g, respectively. In these states, the sandwich complexes have η⁰-binding between the metal and each benzene ring and are in an eclipsed D₂h configuration. Ionization of these neutral states causes the benzene rings to pucker slightly and leads to Jahn-Teller distorted D₂h sandwich ions. The Ti⁺- and V⁺-(C₆H₆)₂ ions are in the ²B₉g and ³B₉g electronic states. The ionization energies of Ti- and V-(C₆H₆)₂ are measured to be 5.731(3) and 5.784(5) eV, and the symmetric metal-benzene stretching frequencies in these corresponding ions are 228 and 231 cm⁻¹.