Cold cations of metal-molecular complexes or of small hydrocarbons (aka "carbocations") are produced in a pulsed supersonic molecular beam by laser vaporization or pulsed discharge sources. These ions are mass-selected and studied with infrared photodissociation spectroscopy. Infrared spectra are compared to the predictions of theory (DFT and/or MP2) to elucidate the structures of these ions and, in the case of metal ions, their electronic states. Transition metal (Co, V, Mn, Cu) carbonyls or carbon dioxide complexes are studied in the C-O and CO$_2$ stretching regions. The spectra reveal coordination numbers, ligand vibrational shifts as a function of cluster size, and the occurrence of intracluster reactions. Ligand shifts compared to the predictions of density functional theory provide the spin state on the transition metal cation and how it changes upon progressive ligand addition. Carbocations (C$_2$H$_3^+$, C$_3$H$_5^+$, C$_3$H$_3^+$, protonated benzene, protonated naphthalene) are studied in the C-H stretching and fingerprint regions of the spectrum. Several of these species exhibit more than one structural isomer, allowing investigation of the multiple minima on their potential surfaces. Unusual vibrations are detected for non-classical structures with bridging hydrogens. Protonated naphthalene has spectral lines relevant for the Unassigned Infrared Bands seen in interstellar gas clouds.