ANION PHOTOELECTRON SPECTROSCOPIC AND DFT STUDIES OF M-C_nH_n COMPLEXES OF Nb AND Y

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We report mass spectra, anion photoelectron spectra and density functional theory (DFT) calculations of products of the reactions of ethylene with the early second transition series metals, niobium and yttrium. Gas phase metal atoms and clusters were prepared in a 103 cm long flowing afterglow ion-molecule reactor equipped with a DC discharge source containing a Nb or Y metal rod as the cathode. The anionic reaction products were mass-selected, and their 488 nm photoelectron spectra were obtained at an instrumental resolution of about 5 meV (40 cm^{-1}), enabling the measurement of vibrational frequencies in both the anionic and neutral metal-ligand complexes. Upon reaction of C_2H_4 with niobium, two isomers of $NbC_2H_2{}^-$ were observed. Based on the comparison of the measured and calculated electron affinities, vibrational frequencies, geometry changes upon photodetachment, and excited state energies, we conclude that one isomer is a C_{2v} Nb-acetylene π-complex with a $^4A_2$ ground state for the neutral molecule and a $^3A_2$ ground state for the anion. Possible assignments for the other $NbC_2H_2{}^-$ isomer, which exhibits an unusual combination of a low vibrational frequency with a large deuterium shift, are discussed. Reaction with three C_2H_4 molecules in the plasma yields $NbC_6H_6{}^-$. Comparison of the measured spectroscopic properties with our DFT predictions indicates that this complex has a C_{6v} Nb-benzene half-sandwich structure, with a $^2A_1$ ground state for the neutral molecule and a $^3A_1$ ground state for the anion. These results are compared with similar experiments and DFT calculations for reactions of ethylene with yttrium.