REACTION PRODUCTS OF LASER ABLATED EARLY TRANSITION METALS WITH BENZENE MOLECULES IN CONDENSING ARGON

JONATHAN T. LYON, LESTER ANDREWS, *Department of Chemistry, University of Virginia, Charlottesville, VA 22904-4319.*

Early transition metal atoms, produced by laser ablation, are reacted with benzene vapor diluted in argon during co-deposited onto a low temperature CsI window. The resulting reaction products are trapped and the $M(C_6H_6)$ and $M(C_6H_6)_2$ complexes are identified by benzene isotopic studies (C_6H_6, $^{13}C_6H_6$, C_6D_6). Density Functional Theory (DFT) frequency calculations are used to confirm the assignments. Calculated ground state energies predict these reaction products to be energetically favorable. The $M(C_6H_6)$ and $M(C_6H_6)_2$ products have C_{6v} and D_{6h} symmetries respectively. Based on the observed aromatic C-C breathing mode frequency shifts, the metal-carbon bond strengths are shown to increase down a group (from vanadium to tantalum) and decrease from left to right along a period (from scandium to chromium). These trends indicate that back donation of electrons from the metal d orbitals to the unoccupied π^* orbitals of benzene is the primary electronic interaction responsible for the bonding in these molecules. Analogous experiments in progress with C_{60} give similar product complexes.