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(C₆H₆) and M(C₆H₆)₂ complexes are identified by benzene isotopic studies (C₁₂H₁₀, C₁₃C₆H₆, C₁₅D₆). 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(C₆H₆) and M(C₆H₆)₂ products have C₅ₗ and D₅h 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 C₆₀ give similar product complexes.