Reactions of Laser-Ablated Metal Atoms

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Laser-ablated boron atoms react with methyl fluoride in an argon stream to form two major products, CH2BF and CHBF. In similar reactions of boron with methyl chloride and methyl bromide, both CH2BX and CHBX are also observed, as well as the primary insertion products, CH3BCI and CH3BBr, respectively. Infrared spectra of isotopic combinations of B and CH3X and density functional theory frequency calculations provide evidence for the product identification. Both products form via insertion into the C-X bond followed by loss of one or two H atoms for all reactions. Comparisons are made with the products of the reactions of B with C2H6, CH3NH2, and CH3OH, all of which are isoelectronic with CH3F. The calculations not only predict the vibrational frequencies exceptionally well, but also predict that there is no dative bonding in either CH2BX or CHBX, despite the empty p-orbital on B and the filled p-orbitals on the halogen atom.
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ACCOMPLISHMENTS

Research under Air Force support in the final year has involved reactions of laser-ablated metal atoms and hydrogen.

Reactions of laser-ablated ruthenium atoms with carbon monoxide and hydrogen in solid argon produce the unsaturated ruthenium carbonyl dihydride $H_2Ru(CO)_2$ and the hydrogen complexes $(H_2)_xRuCO$ ($x=1,2$). The observed absorption bands of the reaction products are identified by isotopic substitution and reproduced well by density functional theory calculations of vibrational fundamentals. The growth of bands due to $H_2Ru(CO)_2$ and $(H_2)RuCO$ during annealing in solid argon indicates that ruthenium monocarbonyl is coordinated with $H_2$ to form the dihydrogen complex $(H_2)RuCO$, while $H_2Ru(CO)_2$ is formed from the $(H_2)RuCO$ complex inserting into $(H_2)$ upon coordinating with another CO.

Infrared spectra of representative $LnH_{1.4}$ lanthanide hydride molecules are observed in solid argon following reactions of the laser-ablated metal atoms with $H_2$. The $LnH_2$ dihydride is
the major product. Spectra of isolated molecular EuH$_2$ and solid stoichiometric EuH$_2$ reveal close correspondence lending support to the molecular assignment, and by extrapolation, providing benchmark infrared frequencies for other lanthanide hydride solids based on their respective molecular vibrational modes.

Laser-ablated boron atoms react with methyl fluoride in an argon stream to form two major products, CH$_2$BF and CHBF. In similar reactions of boron with methyl chloride and methyl bromide, both CH$_2$BX and CHBX are also observed, as well as the primary insertion products, CH$_3$BCl and CH$_3$BBr, respectively. Infrared spectra of isotopic combinations of B and CH$_3$X and density functional theory frequency calculations provide evidence for the product identification. Both products form via insertion into the C-X bond followed by loss of one or two H atoms for all reactions. Comparisons are made with the products of the reactions of B with C$_2$H$_6$, CH$_3$NH$_2$ and CH$_3$OH, all of which are isoelectronic with CH$_3$F. The calculations not only predict the vibrational frequencies exceptionally well, but also predict that there is no dative bonding in either CH$_2$BX or CHBX, despite the empty p-orbital on B and the filled p-orbitals on the halogen atom.

PERSONNEL SUPPORTED

Xuefeng Wang and Stephen Willson

PUBLICATIONS


INTERACTIONS

