

PC I-2

High Oxidation-State Transition-Metal Complexes Prepared with Laser-Ablation and Isolated in Matrix: Simplest Carbene and Carbyne Hybrides, C-H Insertion, Photo-Chemistry, Agostic Interaction, α -Hydrogen Migration, and Ligand Effects

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A new generation of simple methyldene complexes has been prepared from reactions of excited Group 4, 5, and 6 transition metal atoms with methyl halides and methane in solid argon. These $\text{CH}_2=\text{MHX}$ ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$) and $\text{CH}_2=\text{MH}_2$ methyldene complexes exhibit the agostic bonding effects of CH_2 and MH_2 distortion. The reactions proceed through the CH_3-MX insertion product followed by α -H transfer on an excited potential energy surface. The higher valence of Group 6 metals sustains a second α -H transfer to form the $\text{CH}^\ominus\text{MH}_2\text{X}$ ($\text{M} = \text{Mo}, \text{W}, \text{X} = \text{H}, \text{F}, \text{Cl}, \text{Br}$) methylidyne complexes, and electron capture by Group 5 $\text{CH}_2=\text{MHX}$ ($\text{M} = \text{Nb}, \text{Ta}, \text{X} = \text{H}, \text{F}$) methyldene complexes gives rise to the analogous $\text{CH}^\ominus\text{MH}_2\text{X}^-$ methylidyne anion complexes. These simple organometallic complexes are identified by matrix infrared spectra through isotopic substitution and by comparison with vibrational frequencies calculated by DFT. Periodic trends in agostic interactions are illustrated for different metals and halogen substituents. Complementary investigations for Group 3 and for Groups 7, 8, and 9 transition metals and for early lanthanide and actinide metals are also discussed.