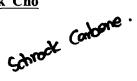


High Oxidation-State Transition-Metal Complexes Prepared with Laser-Ablation and Isolated in Matrix: Simplest Carbene and Carbyne Hybrides, C-H Insertion, Photo-Chemistry, Agostic Interaction, α-Hydrogen Migration, and Ligand Effects

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A new generation of simple methylidene 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 CH2=MHX (X = F, Cl, Br, I) and CH2=MH2 methylidene complexes exhibit the agostic bonding effects of CH2 and MH2 distortion. The reactions proceed through the CH3—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 CH^αMH2X (M = Mo, W, X = H, F, Cl, Br) methylidyne complexes, and electron capture by Group 5 CH2=MHX (M = Nb, Ta, X = H, F) methylidene complexes gives rise to the analogous CH^αMH2X- 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.