

Activation of Hydrogen under Ambient Conditions and Unusual Metal Hydride Reactivity by Main Group Molecules

Major Goals

The major goals as indicated by the title are the detailed understanding of the interactions of main group compounds with small molecules such as H₂, NH₃, CO, C₂H₄ and related species as well as the development of catalysts based on inexpensive main group (13 or 14) elements such as aluminum or silicon. A key feature of the compounds studied is the existence of Lewis acidic and basic sites at the main group element such that the small molecules become activated in a synergistic manner under relatively mild conditions.

What was Accomplished

Our initial investigation concerned a follow-up to our work in the previous period and involved the generation and trapping of a low-valent germanium hydride radical and its reactivity.¹ The generation of the radical involved the photolysis of the germylene Ge(Ar^{Prⁱ4})₂ (Ar^{Prⁱ4} = C₆H₃-2,6-(C₆H₃-2,6-Prⁱ₂)₂) afforded Ge(H)Ar^{Prⁱ4}. This is a result of the insertion of the Ge(I) radical intermediate (i.e., ·GeAr^{Prⁱ4} from cleavage of a Ge-C bond) into a C-H bond.

In related work involving a heavier congener tin-hydride {Ar^{Prⁱ6}Sn(μ-H)}₂. We showed that this low-valent Sn(II) hydride reacted with molybdenum carbonyl Mo(CO)₆ to yield Mo(CO)₅{SnAr^{Prⁱ6}(H)} (**1**).² This species effects rapid hydrostannylation of carbon dioxide to

yield $\{\text{Mo}(\text{CO})_5(\text{SnAr}^{\text{Pr}^i_6})(\kappa^2\text{-O,O}'\text{-O}_2\text{CH})\}$ which has a bidentate formate ligand. Reaction of this species with pinacolborane (HBPin, Pin = pinacolato) in benzene regenerated **1** in quantitative yield. We showed also that the Sn(II) hydride $\{\text{Ar}^{\text{Pr}^i_6}\text{Sn}(\mu\text{-H})\}_2$ reacts with two equivalents of the tungsten carbonyl THF complex $\text{W}(\text{CO})_5(\text{THF})$ to yield the divalent tin hydride transition metal species $\text{W}(\text{CO})_5\{\text{SnAr}^{\text{Pr}^i_6}(\text{H})\}$.³ It was found that this compound readily inserted an ethylene or propylene molecule into the Sn-H bond to give $\text{W}(\text{CO})_5\{\text{SnAr}^{\text{Pr}^i_6}(\text{Et})\}$ or $\text{W}(\text{CO})_5\{\text{SnAr}^{\text{Pr}^i_6}(\text{Pr}^n)\}$ it was also shown that it reacted with Lewis bases to yield a Lewis acid-base complex. In an effort to develop more reactive divalent organotin species, we synthesized a bidentate biscarborane ligand bc (bc = 1,1'-orthocarborane) tin derivative (bc)Sn·THF and $[\text{Sn}(\text{bc})]_2\text{KCl}$.^{4,5} Reactivity studies on these species are currently in hand.

Further studies of low-valent germylene/iron species of the formula $\text{ArGeFeCp}(\text{CO})_2$ (Ar = Ar^{Me_6} ($-\text{C}_6\text{H}_3\text{-2,6-(C}_6\text{H}_2\text{-2,4,6-Me}_3)_2$), $\text{Ar}^{\text{Pr}^i_4}$ ($\text{Ar}^{\text{Pr}^i_4} = \text{C}_6\text{H}_3\text{-2,6-(C}_6\text{H}_3\text{-2,6-Pr}^i_2)_2$), Cp = $\eta^5\text{-C}_5\text{H}_5$) in which the divalent germanium atoms have an empty 3p valence orbital, were undertaken. The complexes react readily with ammonia to form the insertion products $\text{ArGe}(\text{NH}_2)\text{FeCp}(\text{CO})_2$.⁶ They also react readily with water to give $\text{ArGe}(\text{OH})(\text{H})\text{FeCp}(\text{CO})_2$ via insertion of the germanium into an O-H bond. It was also demonstrated that the diorgano germylene $\text{Ge}(\text{Ar}^{\text{Me}_6})_2$ reacted with azobenzene at room temperature to cleave the N=N double bond and give Ge(IV) diamido products.⁷

In work on heavier group 14 element (M = Ge, Sn, or Pb) triple bonded species $\text{ArM}\equiv\text{MAr}$ (Ar = $\text{Ar}^{\text{Pr}^i_4}$ or $\text{Ar}^{\text{Pr}^i_6}$) it was shown that they reacted readily with the molybdenum carbonyl multiple bonded dimeric compounds $[(\text{CO})_2\text{CpMo}\equiv\text{MoCp}(\text{CO})_2]$ (Cp = $\eta^5\text{-C}_5\text{H}_5$) in

THF to yield the mixed metal products $\text{Ar}^{\text{Pr}^i}_4\text{M}\equiv\text{MoCp}(\text{CO})_2$ ($\text{M} = \text{Ge}$ or Sn) or $\text{Ar}^{\text{Pr}^i}_4\text{M}-\text{MoCp}(\text{CO})_3$. Such metathetical exchanges of heavier main group and transition metal triple bonded species had not been previously described in the literature.⁸

Work on low-valent organoaluminum(I) species having two empty valence 3p orbitals as well as a lone pair in the valence shell was initiated to investigate their reactivity. Thus, reduction of the Al(III) iodide $\text{AlI}_2\text{Ar}^{\text{Pr}^i}_8$ ($\text{Ar}^{\text{Pr}^i}_8 = -\text{C}_6\text{H}-2,6-(\text{C}_6\text{H}_2-2,4,6-\text{Pr}^i_3)_2-3,5-\text{Pr}^i_2$) with Na/NaCl in hexanes gave a dark red solution from which the alane diyl monomer $:\text{AlAr}^{\text{Pr}^i}_8$ was isolated in ca. 30% yield as yellow-orange crystals. X-ray diffraction studies showed that the aluminum atom was one-coordinate and readily reacts with hydrogen under ambient conditions to give the aluminum hydride $\{\text{AlH}(\mu\text{-H})\text{Ar}^{\text{Pr}^i}_8\}_2$.⁹

References

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