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An Acyclic Zincgermylene: Rapid H_2 Activation

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Abstract : Probably no other field of inorganic chemistry has undergone such a rapid development in the past two decades than the low oxidation state chemistry of main group elements. This rapid development has only been possible by the development of new bulky ligands. In case of our research group, super-bulky monodentate amido ligands and β-diketiminate ligands have been used to a great success. We first synthesized the unprecedented magnesium(I) dimer $[^{Mes}NacnacMg]_2$ ($^{Mes}Nacnac = [(^{Mes}NCMe)_2CH]$-; Mes = mesityl, which has since been used both as reducing agent and also for the synthesis of new metal-magnesium bonds. In case of the zinc bromide precursor [L*ZnBr] (L*=(N(Ar*)($SiPri_3$); (Ar* = $C_6H_2\{C(H)Ph_2\}_2Me$-2,6,4, the reduction with $[^{Mes}NacnacMg]_2$ led to such a metal-magnesium bond. This [L*ZnMg($^{Mes}Nacnac$)] compound can be seen as an 'inorganic Grignard reagent', which can be used to transfer the metal fragment onto other functional groups or other metal centers; just like the conventional Grignard reagent. By simple addition of (TBoN)GeCl (TBoN = $N(SiMe_3)\{B(DipNCH)_2\}$) to the aforesaid compound, we were able to transfer the amido-zinc fragment to the Ge center of the germylene starting material and to synthesize the first example of a germanium(II)-zinc bond: [:Ge(TBoN)(ZnL*)]. While these reactions typically led to complex product mixture, [:Ge(TBoN)(ZnL*)] could be isolated as dark blue crystals in a good yield. This new compound shows interesting reactivity towards small molecules, especially dihydrogen gas. This is of special interest as dihydrogen is one of the more difficult small molecules to activate, due to its strong (BDE = 108 kcal/mol) and non-polar bond. In this context, the interaction between H_2 σ-bond with the tetrelylene p-Orbital (LUMO), with concomitant donation of the tetrelylene lone pair (HOMO) into the H_2 σ* orbital are responsible for the activation of dihydrogen gas. Accordingly, the narrower the HOMO-LUMO gap of tertelylene, the more reactivity towards H_2 it typically is. The aim of a narrow HOMO-LUMO gap was reached by transferring electropositive substituents respectively metal substituents with relatively low Pauling electronegativity (zinc: 1.65) onto the Ge center (here: the zinc-amido fragment). In consideration of the unprecedented reactivity of [:Ge(TBoN)(ZnL*)], a computational examination of its frontier orbital energies was undertaken. The energy separation between the HOMO, which has significant Ge lone pair character, and the LUMO, which has predominantly Ge p-orbital character, is narrow (40.8 kcal/mol; cf.ΔS-T= 24.8 kcal/mol), and comparable to the HOMO-LUMO gaps calculated for other literature known complexes). The calculated very narrow HOMO-LUMO gap for the [:Ge(TBoN)(ZnL*)] complex is consistent with its high reactivity, and is remarkable considering that it incorporates a π-basic amide ligand, which are known to raise the LUMO of germylenes considerably.

Keywords : activation of dihydrogen gas, narrow HOMO-LUMO gap, first germanium(II)-zinc bond, inorganic Grignard reagent

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