

A QUANTUM CHEMICAL STUDY OF THE STRUCTURE AND CHEMISTRY OF HZnCH<sub>3</sub>, A TRANSITION METAL COMPOUND WITH 4s<sup>2</sup> RECOUPLED PAIR BONDING

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A structure was recently reported by Flory et al.<sup>a</sup> for methyl zinc hydride, HZnCH<sub>3</sub>, a molecule that may be formed via the direct insertion of Zn into one of the CH bonds of methane. The experiments were not able to demonstrate the formation pathway conclusively. The structures, bond energies, and other properties of HZnCH<sub>3</sub>, ZnH, and ZnCH<sub>3</sub> were determined with high level coupled-cluster theory and multireference configuration interaction calculations in order to better understand the nature of the chemistry of HZnCH<sub>3</sub>. The Zn–H and Zn–C bonds in HZnCH<sub>3</sub>(*X*<sup>1</sup>*A*<sub>1</sub>) were found to be formed through recoupling the 4s<sup>2</sup> pair of Zn(<sup>1</sup>S) in a manner that is very similar to the bonding in HBeCH<sub>3</sub> and other compounds where the 2s<sup>2</sup> pair of Be is recoupled. Various formation pathways were characterized, such as the analogous family of exchange reactions H + CH<sub>4</sub> → CH<sub>3</sub> + H, Zn + CH<sub>4</sub> → ZnCH<sub>3</sub> + H, and Be + CH<sub>4</sub> → BeCH<sub>3</sub> + H. Direct insertion may involve an intersystem crossing from the Zn(<sup>3</sup>P) + CH<sub>4</sub> triplet surface to the singlet surface, which has been explored.

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<sup>a</sup>M. A. Flory, A. J. Apponi, L. N. Zack, and L. M. Ziurys, *J. Am. Chem. Soc.* **132**, 17186 (2010).