

Theoretical Studies on Monovalent Group 13 and Divalent Group 14 Carbenoids, Metallatranes and Model Systems for Dinitrogen Reduction

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By

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Summary

A comparison of the ligand properties of the group 14 carbenoids (MNHCs, CAASis and CAAGes) considered in this study reveals that the MNHCs exhibit substantially higher electron donation ability compared to those of the CAASis/CAAGes. Since the primary interaction involved in the activation of σ -bonds by group 14 carbenoids is the transfer of electron density from the lone pair localized at the ene (C, Si and Ge) center to the σ^* -antibonding orbital therefore, the MNHCs are expected to perform better than those of the CAASis/CAAGes.

All the group 13 and 14 carbenoids considered in our work exhibit suitable ligand properties for their application in different small molecule activation process. Infact, the barrier heights obtained the group 13 and 14 carbenoids are comparable or lower than those of the experimentally evaluated systems (CAAC, DAC, Roesky's Al(I) and Power's Ga(I) carbenoid), indicating they may be considered as an suitable platform for the activation of different enthalpically strong bonds. However, the nucleophilic borylenes which computes substantially lower barrier heights as well as exergonic reaction free energies for different σ -bond activation process may outperform all other 13 and 14 carbenoids considered in our work.

The extent of the transannular M...Z interaction which is present in the metallatranes considered in this study depends to a large extent on the size and polarizability of the group 13 element (Z group). Furthermore, it should be noted that the strength of the transannular interaction plays a decisive role in governing the reactivity of the TM center in metallatranes. The EDA-NOCV analysis on few representative systems nicely captures the relative σ -donation and π -acceptance abilities of different ligands to metallatranes, as well as highlights the importance of the Lewis acidic group 13 center in promoting the binding of inert ligands, like N₂, to transition metal centers. We believe that our findings could contribute to the design of novel organometallic platforms for the binding and functionalization of a variety of ligand systems.

Furthermore, the complexes considered in our study (**[1a']**–**[1f']** and **[1a'']**–**[1f'']**) for dinitrogen reduction resection (NRR) were found to be capable of dinitrogen functionalization as reflected in the thermodynamic feasibility of several key steps (binding of nitrogen, formation of the diazenido and nitride complex etc.). One of the major advantages of these proposed complexes is that they are unlikely to generate hydrazine during the NRR. In addition, both the catalysts (**[1c'']**–**[1f'']**) are likely to serve as potential candidates for the NRR, which is evident not only

from the calculated highly exergonic reaction free energies of the different steps but also from the moderate barrier heights for the different TSs involved. Therefore, we hope that if one is successful in synthesizing the proposed vanadium complexes, then they may serve as a suitable platform for reducing dinitrogen to ammonia.