

## Synthesis and Structural Characterization of Heterocycle-Tethered Boranes, and NHC Pincer Metal Complexes: Catalysis and DFT Studies

Heterocycle-tethered organoboranes generally dimerize by using the heteroatom present in them. When this does not take place, some interesting molecules or properties are bound to be observed. This is demonstrated in this work as well. Hitherto unknown imidazole, pyrazole and dipyrromethane tethered boranes were synthesized and structurally characterized. While the imidazole tethered boranes dimerize, the pyrazoleborane derivative does not dimerize, instead the interesting  $\text{BF}_2(\text{OMe})$  adduct was isolated as a clear liquid. Consequently, the reactive pyrazolymethylborane adduct gave two new bicycles upon exposure to the air and their structures were established by X-ray diffraction studies. Besides, the precursors of both the heterocycle boranes were structurally characterized.

The reaction between  $\text{H}_3\text{B}\cdot\text{THF}$  and diethyldipyrrolylmethane in THF under refluxing conditions afforded the spiroborane,  $[\{\text{Et}_2\text{C}(\alpha\text{-C}_4\text{H}_3\text{N})_2\}\{\text{Et}_2\text{C}(\alpha\text{-C}_4\text{H}_3\text{N})(\alpha\text{-C}_4\text{H}_4\text{N})\}\text{B}]$  in good yield. The same compound was obtained via the metathesis reaction between the dilithium salt of dipyrromethane and  $\text{BF}_3\cdot\text{OEt}_2$  in THF followed by hydrolysis. This spiroborane contains a 2H-pyrrole moiety and is a carbon acid. Hence, it was treated with bases such as NaH,  $\text{Et}_3\text{N}$ , DMAP and  $^t\text{Bu}_4\text{NOH}$  to give spiroborate anions with the corresponding cations  $[\{\text{Et}_2\text{C}(\alpha\text{-C}_4\text{H}_3\text{N})_2\}_2\text{B}]^-$ . Further, these salts were treated with dilute HCl to give back the protonated spiroborane. The structures of the spiroborane and spiroborates were determined by X-ray method. The spiroborane showed a fast deuterium exchange with  $\text{D}_2\text{O}$  and was studied by multinuclear 2D NMR methods. The X-ray structures of spiroborates showed different shapes of arrangement of tetrapyrrolide-spiroborate anions around their cations.

The new pro-NHC pincer ligand, 1,3-bis(diphenylphosphanylmethyl)hexahydropyrimidine, was synthesized conveniently in a single step in an excellent yield. The NHC pincer complexes  $[(\text{PCP})\text{MCl}]\text{X}$  ( $\text{M} = \text{Pd}$  and  $\text{Ni}$ ;  $\text{X} = \text{Cl}$  and  $\text{BF}_4$ ) were formed readily at room temperature without a base or transmetalation reaction, representing their facile formation of carbene via the double C-H bond activation of the hexahydropyrimidine based NHC precursor. The preliminary catalytic study using palladium complexes was demonstrated with Buchwald-Hartwig C-N couplings in which cross coupled products were formed in very high yields. The mechanism of formation of palladium carbene complexes as analyzed by DFT calculations showed two transition states. In addition, a new pentacoordinated NHC pincer complex  $[\text{NiCl}\{\text{C}(\text{NCH}_2\text{PPh}_2)_2(\text{CH}_2)_3\text{-}\kappa^3\text{P,C,P}\}(\text{Xylyl-NC})]\text{PF}_6$  was synthesized and characterized by both spectroscopic and single crystal X-ray diffraction methods. Complex retains its solid state structure in solution, as shown by VT NMR and UV-vis studies. The bonding nature in the pentacoordinated complex was analyzed by DFT calculations.