Diborane was isolated and characterised as early as in 1912. The observation that it slowly reacts with ethylene at 100°C in the gas phase to give triethyl borane was made in 1948. However, the observation that the addition of the $\text{B-H}$ bond in diborane to olefins is facile in ether solvents was made only in 1956. The historical account reveals that this discovery of the powerful catalysis by ether solvents was delayed as diborane was not generated in ether solvents in the presence of olefins prior to 1956. It is now well established that the diborane reacts with Lewis bases (e.g., ether solvents, dimethyl sulfide, amines, etc.) to give the corresponding $\text{BH} - \text{Lewis base complexes}$ which hydroborate olefins more readily than the parent diborane. Many such $\text{BH} - \text{Lewis base complexes}$ are now commercially available (eq.1).

$$\text{B}_3\text{H}_6 + \text{LB} \rightarrow 2\text{BH}_3 \cdot \text{LB}$$

$$\text{LB} = \text{THF}, \text{Me}_2\text{S}, R_3\text{N}(R=\text{H or alkyl}) \text{ etc.}$$

Our preliminary experiments revealed that the $\text{Hg(OOCCH}_3)_2/\text{NaBH}_4$ system or the $\text{CH}_3\text{COOH/NaBH}_4$ system in THF hydroborates olefins at room temperature. The reaction is relatively slow compared to $\text{BH}_3 \cdot \text{THF}$ and only one equivalent of 1-alkene reacts in 12 h at room temperature. Many literature reports indicate that the stronger the Lewis-base borane
complex, the slower is the hydroboration. In some instances, the stronger complexing ability of Lewis bases can be utilized for achieving controlled hydroboration. For example, ClBH₂·OEt₂ gives the corresponding dialkyl chloroborane with 1-butene in diethylether but in the presence of 1 to 2 equivalents of THF the hydroboration can be stopped at the monoalkyl-chloroborane stage (eq.2,3).

\[
\begin{align*}
\text{ClBH}_2\cdot\text{OEt}_2 &\rightarrow \text{C}_2\text{H}_5\text{CH} = \text{CH}_2 & \rightarrow \text{C}_2\text{H}_5\text{CH} \cdot \text{CH} \cdot \text{BCl} \\
\text{ClBH} &\cdot\text{OEt} &\rightarrow \text{C}_2\text{H}_5\text{CH} \cdot \text{CH} \cdot \text{BCl} \\
\text{1 to 2 eq. THF} &
\end{align*}
\]

It has been suggested that stronger complexation by THF prevents further hydroboration. It was of interest to investigate the utilization of the RCOOH/NaBH₄ system for selective and controlled hydroborations.

As mentioned above, diborane reacts with ether solvents and other Lewis bases to form BH₃ Lewis base complexes which then hydroborate olefins. The reactivity is dependent on the stability of such complexes. However, the mechanism of this important reaction and the role of the Lewis base in the transition state of the reaction are not clearly understood and differences of opinion exist. It was also of interest to investigate this problem.

Since several monographs and detailed reviews have been published covering hydroboration and other reactions of BH₃-Lewis base complexes and also the reactions of organoboranes, only the reports...
closely related to the present investigations will be discussed under the 'introduction and results and discussion' sections in Chapters 1-3.

REFERENCES
