LiBH<sub>4</sub> solutions in diethyl ether or tetrahydrofuran react with N-methylmorpholine, N-methylimidazole or piperidine not only with the formation of adducts LiBH<sub>4</sub>(L)<sub>n</sub> (n = 1 or 3) but also with formation of amine boranes BH<sub>3</sub>(L). While LiBH<sub>4</sub> and N-methylimidazole form the 1 : 3 adduct 1, N-methylmorpholine produces the 1 : 1 adduct 2. In both cases the adducts contain hexacoordinated Li atoms. In 1 the Li atom is coordinated to three N atoms and three H atoms. However, in compound 2 the molecules are connected in the solid state with one another to form a two-dimensional polymer built from dimeric units (LiBH<sub>4</sub>)<sub>2</sub> that are connected to adjacent dimeric units via the O and N atoms of the N-methylmorpholine ligand. Each of the Li atoms in 2 is connected to four H atoms via Li–H–B hydrogen bridges and an O and an N atom. The reaction of LiBH<sub>4</sub> with piperidine leads to the compound (LiBH<sub>4</sub>)<sub>6</sub>(HNC<sub>5</sub>H<sub>10</sub>)<sub>16</sub>, 3, which consists of two independent LiBH<sub>4</sub>(HNC<sub>5</sub>H<sub>10</sub>)<sub>3</sub> molecules and two others of composition (LiBH<sub>4</sub>)<sub>2</sub>(HNC<sub>5</sub>H<sub>10</sub>)<sub>5</sub> containing penta- and hexacoordinated Li atoms.

**Key words:** Lithium Tetrahydridoborate Complexes, N-Methylmorpholine, N-Methylimidazole, Piperidine, X-Ray Crystal Structure Determination