The alkali and alkaline earth phosphanides have already been intensively studied, nonetheless there are only a few reports on the alkali metal diphosphanides, on their structural properties and their synthetic use as building blocks for the synthesis of phosphorus-rich compounds and, in particular, transition-metal complexes. This study extends the so far small family of lithium diphosphanides with the series of \( \text{Li}(\text{LnP}-(\text{SiMe3})_{n-2})_{2}\text{Bu2} \), where \( \text{L} = \text{THF}, n = 0–3; \text{L} = \text{TMEDA or 12-crown-4}, n = 2 \). The coordination numbers of the Li ions are in the range of two to eight in the investigated compounds. There is a clear correlation between the Li–P distance and the coordination number of the Li atom. The higher the coordination number of the Li atom, the longer the Li–P distance is. Coordination numbers of four or higher lead to ionic structures. The influence of the space requirement of the phosphorus substituents on the Li–P bond length should also be taken into account especially in the case of coordination number two. Eight-membered ring structures are realized when the formation of four-membered rings is prevented by sterically demanding substituents. This work is a contribution to the fine tuning of structures by donor molecules and substituents [1].


**Keywords**: Lithium, phosphorous ligand, covalent bond - ionic interaction