

Ligand effects in Low Coordination Chemistry - Structures, Properties, and Reactivity

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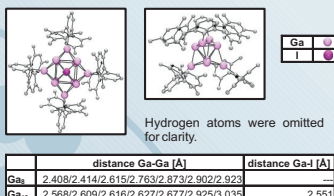
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Introduction

The outstanding success of terphenyl- and amide-based ligands in low coordination main group and transition metal chemistry [1,2] and spectacular findings in these fields inspired the synthesis of according sterically encumbering building blocks. Amongst others these miscellaneous classes of compounds find widespread use in the preparation of metalloid cluster compounds. [3,4] Exciting new compounds stabilized by terphenyl (L^*H , 2,6-Mes₂(C₆H₄), Mes=2,4,6-trimethylphenyl) and amide-based ($L'H$, MesN(H)SiMePh₂ and $L''H$, DippN(H)SiMePh₂, Dipp=2,6-diisopropylphenyl) ligands were isolated in good yields and examined by X-ray-diffraction and multinuclear NMR spectroscopy.

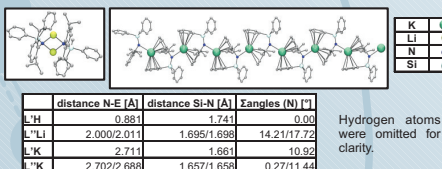
Ga₈ and Ga₁₃ Clusters

Only few group 13 element metalloid clusters are known in literature, most of which are charged. [5] Using the terphenyl-based ligand L^*H two neutral gallium clusters could be isolated and characterized. While the Ga₁₃ cluster is build up based on an inner cubic unit of eight gallium atoms, the Ga₈ derivative shows a tetrahedral substructure. The first bears additional five gallium atoms centered above five of the six surfaces of the cube and is substituted by an additional iodine atom. This provides the opportunity to investigate further reactivity chemistry. The latter bears four atoms centered above the four surfaces of the tetrahedron.



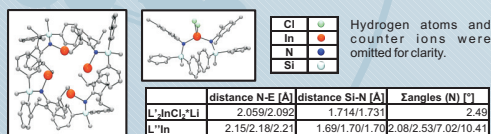
Alkalimetal Derivatives - Dimers vs. Coordination Polymers

Products stabilized by amide-based ligand systems $L'H$ and $L''H$ showed an interesting diversity in steric properties. Enhanced stabilization due to the additional aryl groups of the ligand was observed. E.g., the lithium and the potassium derivative show quite different constitutions: The first one yields a dimer with a quadrangular [Li-N]₂ core and little interaction between the metal center and the aryl groups at the ligand, the latter leads to formation of a coordination polymer through aryl-K complexation.



Indium Derivatives

The steric difference of the two amide-based ligands $L'H$ and $L''H$ can be observed looking at the miscellaneous range of derivatives, e.g. the indate analogs. When using $L'H$ as starting material, the indate ($[L^*InCl_2]^+Li(OEt)_2^-$) can be isolated and characterized. In case of using $L''H$, a one-to-one conversion of the ligand system and InCl leads to formation of a cluster-like tetrameric substructure $[L''In]_4$.



Conclusion & Outlook

A wide range of structurally extremely interesting main group element compounds was isolated and characterized by spectroscopic methods. In future investigations, NMR studies will be conducted in order to study the effects of the variation of the central atoms and the ligand systems. Computational studies based on DFT and CC2 functionals will yield information on bonding, steric properties and stabilities.

Notes & References

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