

# Novel Contributions to Low Valent Main Group Chemistry - From Molecules Towards Clusters

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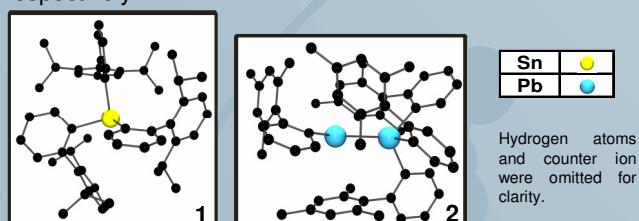
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## Introduction

Starting with the boron hydride characterization by Lipscomb [1] and the first extended definition of metal atom clusters by Cotton [2], a number of main group element clusters has been synthesized and characterized. Among this interesting class of compounds metalloid clusters take a special position due to their exceptional intermediate state between elemental metal and molecular compound [3].

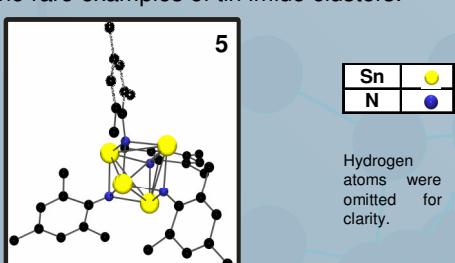
## Plumbylplumbylene and Stannylyl Anion

Two interesting new compounds 1 and 2 containing elements of main group 4 showing unusual bonding behaviour could be identified by X-ray diffraction and NMR spectroscopy. Starting from  $\text{SnCl}_2$  or  $\text{PbCl}_2$  and employing the biphenyl-ligands  $\text{C}_6\text{H}_5\text{-2-Dipp}$  and  $\text{C}_6\text{H}_5\text{-2-Mes}$ , sterically crowded stannylyl anion 1 (lithium counter ion not shown) and plumbylplumbylene 2 were obtained, respectively.



## Tin Based Imidocubane

By reduction of  $\text{Ph}_2\text{MeSiN}(\text{Mes})\text{SnCl}$  with  $\text{CsK}$ , crystals of compound 5 were obtained. Reductive conditions lead to decomposition of the ligand system  $\text{Ph}_2\text{MeSiN}(\text{Mes})\text{H}$  and to formation of the tin tetrahedron based imidocubane 5 - one of the rare examples of tin imido clusters.

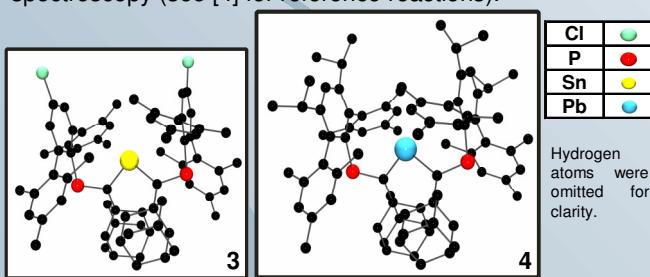


## Conclusion and Outlook

A series of low valent main group element compounds containing elements of group 13 and 14 was synthesized and characterized by X-ray diffraction and multinuclear NMR spectroscopy. Further work will include computational characterization and ongoing reactions in order to enlarge the number of cluster compounds known in literature. In addition, further variation of the ligand system will lead to new structural possibilities.

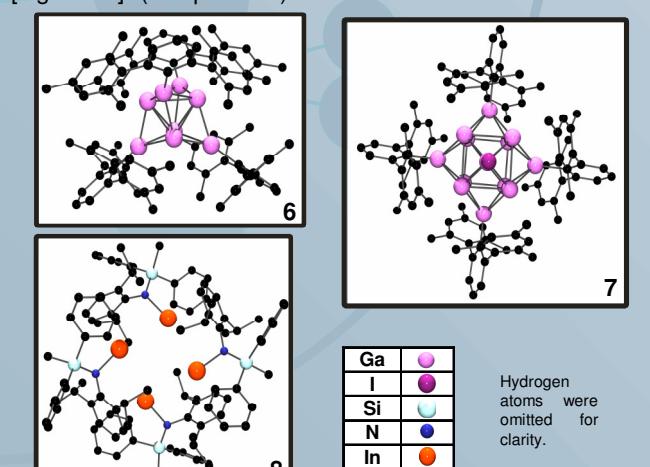
## Adamantane-Stabilized Tetrylenes

By conversion of germylenes, stannylenes and plumbylenes with phospha-alkyne ada-CP (ada = adamantane), compounds of type 3 and 4 were synthesized. A range of intermediate products (3- or 4-membered ring systems) was identified by NMR spectroscopy (see [4] for reference reactions).



## Gallium and Indium Clusters

Only few group 13 element metalloid clusters are known in literature, most of which are charged [3]. Employing the terphenyl-based ligand  $\text{C}_6\text{H}_4\text{Mes}_2$ , two new, neutral gallium clusters  $\text{Ga}_8$  and  $\text{Ga}_{13}$  (compounds 6 and 7) were isolated and characterized. These feature capped tetrahedral and cubane core structures. In case of In, a one-to-one conversion of the ligand system  $\text{Ph}_2\text{MeSiN}(\text{Dipp})\text{Li}$  with  $\text{InCl}$  lead to formation of a cluster-like tetrameric substructure [ $\text{Ligand-In}$ ]<sub>4</sub> (compound 8).



## References

- [1] Dicerson, R.E.; Lipscomb, W.N. *J. Chem. Phys.* **1957**, 212.
- [2] Cotton, F.A. *Q. Rev. Chem. Soc.* **1966**, 389.
- [3] Driess, M.; Nöth, H. *Molecular Clusters of the Main Group Elements*, 1st ed.; Wiley-VCH: Weinheim, **2004**.
- [4] Meiners, F.; Saak, W.; Weidenbruch, M. *Chem. Comm.* **2001**, 215.