Introduction to the Scientific Community – Inorganic Chemistry

Improvement of the synthesis of $Ga_4(TMP)_4$ and its application as ligand in *Hume-Rothery* inspired cluster chemistry

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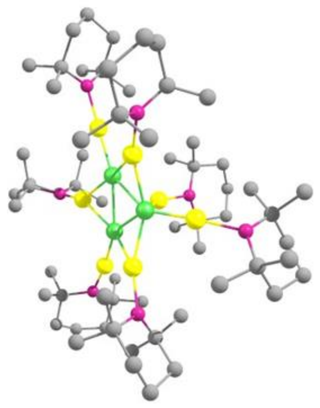
Introduction

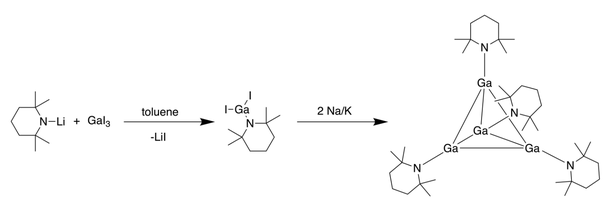
Monitoring heterogenous catalyst especially under catalytic reaction conditions is very challening and commonly limited to standard surface analytic techniques. An alternative approach to follow catalytic processes on a molecular level, might be using molecular models. The advantage is that these molecular compounds can be analyzed by ^{1}H-NMR, LIFDI-MS and other solution based molecular analytic techniques. The *Hume-Rothery* inspired cluster $[(GaTMP)_3Ni_3(\mu_2\text{-}GaTMP)_3(\mu_3\text{-}GaTMP)]$ might be interesting as a model catalyst for the semihydrogenation of alkyenes. When $GaCp^*$ was used as ligand, an undesired transmetallation from $GaCp^*$ to $NiCp^*$ was observed, thereby the reactive Ni^0 sites were deactivated and potential substrate interactions are suppressed. To avoid transmetallation $Ga_4(TMP)_4$ (**Ga_4**) is used as ligand. In this poster we present a new synthetic approach with GaI_3 as starting material to obtain **Ga_4** and the improvement via sonochemical 'GaI' in different solvents and reactants (LiTMP and KTMP) was investigated.



Molecular structure of $[(GaTMP)_3Ni_3(\mu_2\text{-}GaTMP)_3(\mu_3\text{-}GaTMP)]$, the open and accessible Ni^0 sites are displayed by green nickel atoms, the yellow atoms represents the gallium, which is connected with the TMP (purple nitrogen atoms and grey carbon atoms).

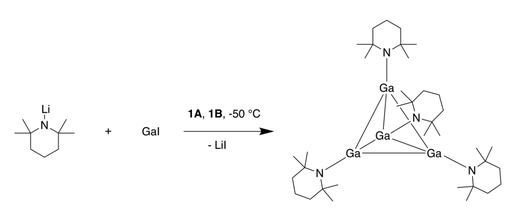
Synthesis of $Ga_4(TMP)_4$

New synthetic approach for the preparation of **Ga_4**, where $GaTMPI_2$ (**Ga_1**) should be obtained as intermediate. After reduction with Na/K the **Ga_4** cluster should be obtained.



New synthetic approach for preapation of **Ga_4**.

Improvement of the synthesis for **Ga_4** via sonochemical 'GaI' in different solvents (1A toluene/ 1B Et_2O).[1]

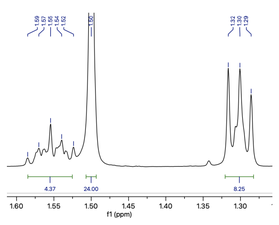


Synthetic access to **Ga_4** with LiTMP and 'GaI' .

Characterization of the intermediate

Elemental analysis of the intermediate, compared to the theoretical values of **Ga_1** and $GaITMP_2$ (**Ga_2**)

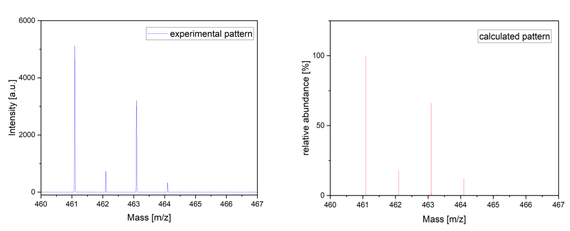
	%C	%N	%H
$[C_9H_{18}GaI_2N]$ (**Ga_1**)	23.31	3.02	3.91
$[C_{18}H_{36}GaIN_2]$ (**Ga_2**)	45.31	5.87	7.61
Found	44.14	5.69	7.53



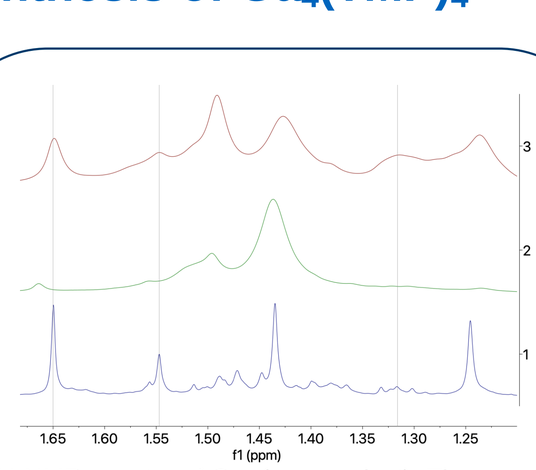
^{1}H-NMR spectrum of **Ga_2**

Chemical shifts and integrals differ only minimal from the $GaXTMP_2$ (X = Cl, Br) compounds in literature[2]

LIFDI-MS of **Ga_2**, the isotopic pattern can be assigned to $GaITMP_2$-Me (fragmentation of one methyl group occurs)



Results of the sonochemical synthesis of $Ga_4(TMP)_4$



^{1}H-NMR spectra of **Ga_4** (raw product). The gray lines represent the chemical shifts of **Ga_4**.

- 1 (blue): Excess of LiTMP + Et_2O before extraction
- 2 (green): Excess of 'GaI' + Et_2O after extraction
- 3 (red): Excess of 'GaI' + Et_2O bfefore extraction

With an excess of LiTMP in Et_2O the formation of **Ga_4** could be observed by ^{1}H-NMR but no product could be isolated.

For KTMP as reactant, no conversion to **Ga_4** could be observed in Et_2O and toluene.

Conclusion

For the new synthesis route $GaTMPI_2$ should be obtained as an intermediate, but it was shown by ^{1}H-NMR, LIFDI-MS and CHNS-analysis that $GaITMP_2$ was formed instead. Therefore, the new synthesis route could not be successfully carried out, because the reduction of $GaITMP_2$ with Na/K does not lead to **Ga_4**. In addition, it could be shown that the synthesis over the sonochemically route is strongly dependent from the solvent. Here, an excess of LiTMP in Et_2O was the most promissing approach. The reaction with KTMP proceeds even worse, presumably due to the strong basicity of KTMP. The synthesis procedure can be further optimized by the use of a non-coordinating solvent, which cannot be deprontonated by KTMP. The synthesis of low valent group 13 amides is a huge challenge, therefore new approaches have to be investigated.

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[1] A. Seifert, G. Linti, *Eur. J. Inorg. Chem.* **2007**, *32*, 5080-5086.
[2] G. Linti, R. Frey, K. Polborn, *Chem. Ber.* **1994**, *127*, 1387-1393.