TU Clausthal

Heterobimetallic Alkali and Alkaline Earth Phenolates

Introduction

The preparation of heterobimetallic compounds of the alkali metals has led to an array of different applications. Heterobimetallic compounds are used as polymerizationn initiators, catalysts and as superbases for the selective deprotonation of a large variety of substrates, including non-acidic protons such as in toluene. Heterobimetallic compounds can also be utilized as precursors for metal-organic chemical vapor deposition (MOCVD) to prepare semiconductors and superconductors. The mixed metals have lower melting points and an increased volatility to aid in these MOCVD processes.

Previous Work

Diphenylphenol (2,6-diphenylphenol, Odpp) has been used for the synthesis of heterobimetallic alkali and alkaline earth phenolates such as [Na{Ba(Odpp)3}]·PhMe (Figure 1) exhibiting extensive metal-π-interactions, as many other heterobimetallic compounds.

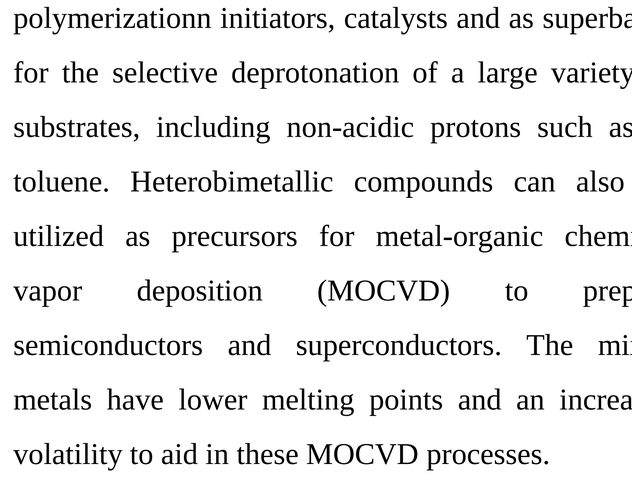


Figure 1: Crystal structure of **[Na{Ba(Odpp)$_3$}]·PhMe**. For clarity, the hydrogen atoms and toluene solvate are not shown

Target Compounds

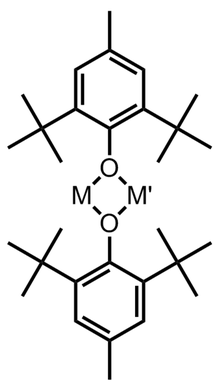


Figure 2: Proposed structure of **[MM'(BHT)$_2$(thf)$_x$]**.

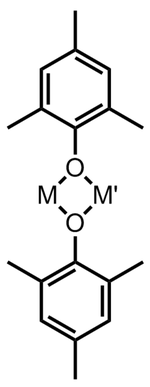


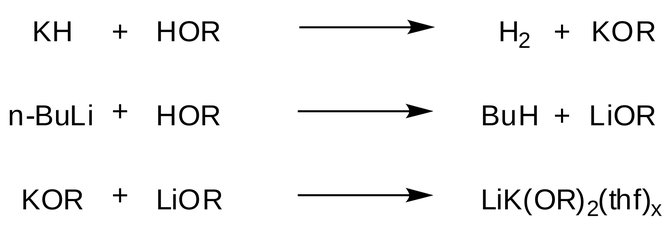
Figure 3: Proposed structure of **[MM'(OMes)$_2$(thf)$_x$]**.

Objective

The preparation of heterobimetallic compounds using aryloxides not capable of π-interactions. These aryloxides are 2,6-di-tert-butyl-4-methylphenol (BHT) and 2,4,6-trimethylphenol (OMes).

Synthesis

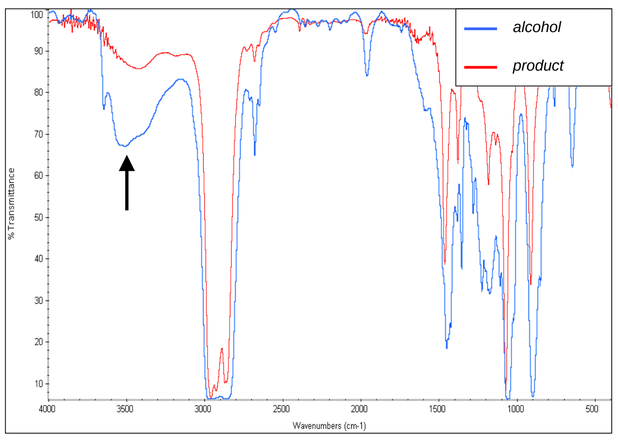
Schlenk line techniques were used to perform all reactions. The starting materials NaH, KH, n-butyllithium, 2,6-di-tert-butyl-4-methylphenol and 2,4,6-trimethylphenol are commercially available. THF as a solvent was used for all reactions



- Sodium/potassium hydride and aryl alcohol afford sodium/potassium aryloxide.
- Butyllithium and alcohol form lithium aryloxide.
- Target compound is anticipated to form by combining LiOR with Na/KOR

Results

The IR-spectrum shows that the ligand is mostly deprotonated and that the metal-aryloxides were formed.



The peak at ν = 3300cm^{-1} indicates presence of alcohol. This peak is very strong in the educt spectrum (blue) and very weak in the product spectrum (red), indicating the formation of target compounds.

Conclusion

Difficulties in growing X-ray quality crystals of target compounds:

- Very soluble in thf
- Very low solubility in hexane and toluene, suggesting the presence of THF adduct and formation of aggregates in their absence.

Possible solutions:

- Increase solubility in toluene or hexane by adding THF
- Layering THF-solution with hexane
- Introduce alternative set of donors
- Sublimation

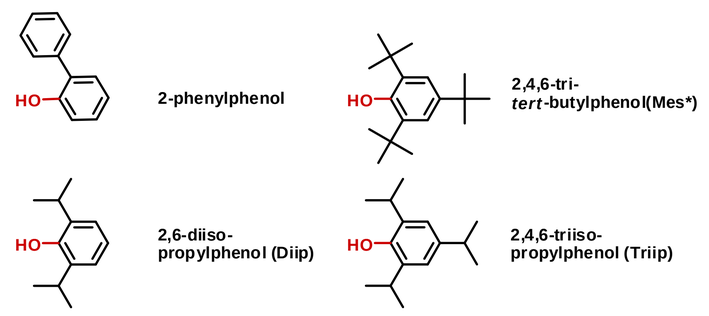
Future Work

A new route will be employed in the future: mild solid state reactions at temperature of ~220°C :

- Fill Carius tubes with the air-sensitive educts in dry-box
- Vacuum tubes at pressure less than 40 mtorr
- Place tubes in oven and heat until reactants melt expected reaction time: about 5 days at ~220°C
- After recrystalization we anticipate X-ray quality crystals.

Extend to include other metal-combinations: Mg, Ca, Sr, Ba, Rb, Cs and Zn.

Expand to other ligands.



References

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[2] K. Ruhlandt-Senge et al., Chem. Eur. J. **2007**, 13, 1921-1928.

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