

# Ligand Effects in Amide-Based Low Valent Main Group Element and Transition Metal Compounds

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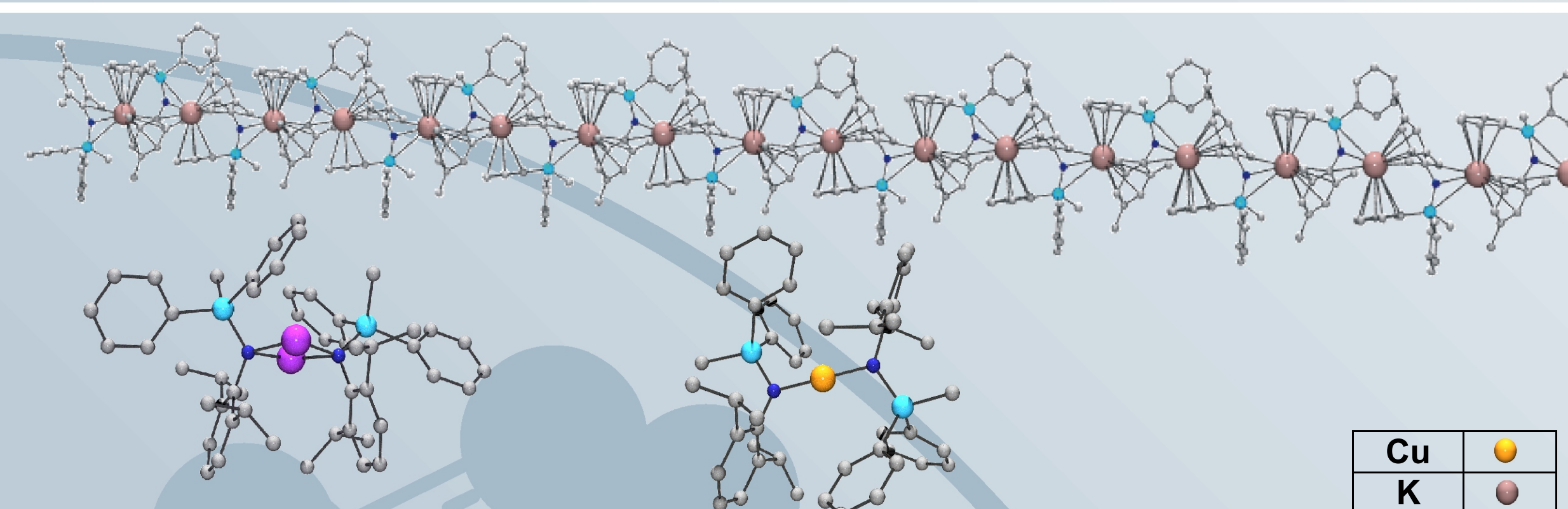
## INTRODUCTION

Silicon substituted amide-based ligands are well-known in literature and have played an enormous role in the preparation and stabilization of low coordination main group element and transition metal compounds.[1] Amongst others this miscellaneous class of compounds finds widespread use in the preparation of metalloid cluster compounds.[2] In contrast to already known ligand systems we introduced additional aryl groups at the nitrogen and the silicon atom to explore the coordination chemistry of the products. Ligands of the type L'H (MesN(H)SiMePh<sub>2</sub>, Mes=2,4,6-trimethylphenyl) and L\*H (DippN(H)SiMePh<sub>2</sub>, Dipp=2,6-diisopropylphenyl) were isolated in good yields and converted to accordant monomers, dimers and coordination polymers.

## ALKALIMETAL DERIVATIVES - DIMERS VS. COORDINATION POLYMERS

The first step of converting the ligand consisted of metallating the system with lithium or potassium, respectively. The products proved enhanced stabilization due to the additional aryl group introduced, observable when analyzing the crystal structures. Interestingly, the lithium and the potassium derivative show quite different constitution: The first one yields a dimer with a quadrangular [Li-N]<sub>2</sub> 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.

Based on these results the metallated species were used in order to synthesize a wide range of products containing main group elements and transition metals at the center, e.g. the cuprate [L\*<sub>2</sub>Cu]\*Li(OEt<sub>2</sub>)<sub>3</sub>.



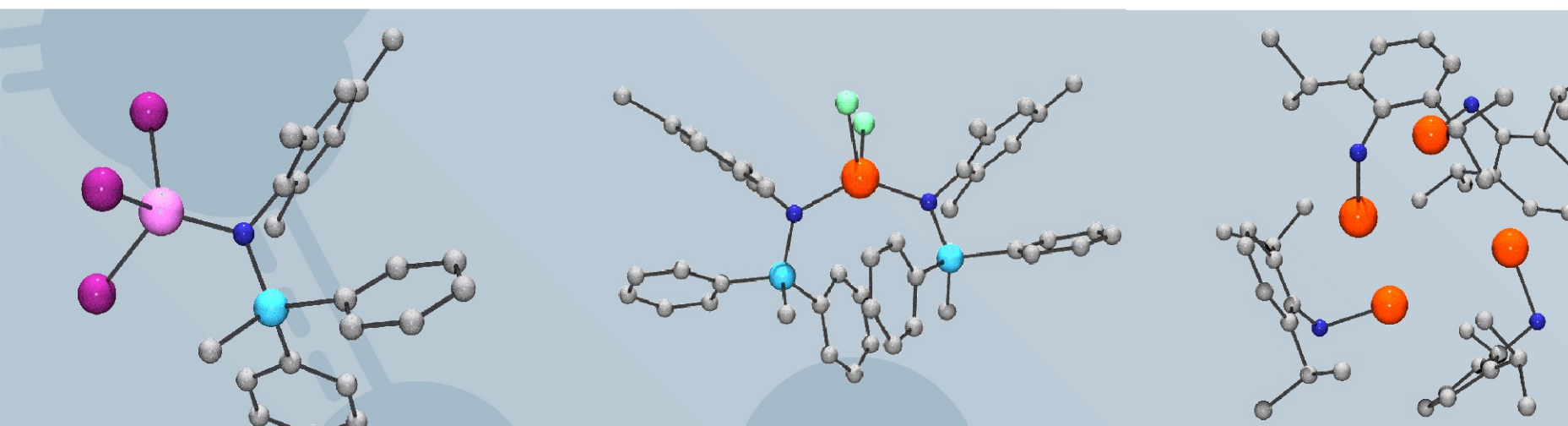
compound	distance N-E [Å]	distance Si-N [Å]	Σangles (N) [°]
L'H	0.881	1.741	0.00
L*Li	2.000/2.011	1.695/1.698	14.21/17.72
L*K	2.711	1.661	10.92
L*K	2.702/2.688	1.657/1.658	0.27/11.44
L* <sub>2</sub> Cu*Li	1.869/1.871	1.686/1.690	0.42/7.34

Cu	●
K	●
Li	●
N	●
Si	●

Hydrogens and counter ions were omitted for clarity.

## GROUP 13 DERIVATIVES

The steric and electronic differences between the two ligand systems is best expressed when looking at their group 13 derivatives. When using L'H as the starting material, the gallate and indate derivatives are obtained, being substituted either by one equivalent of ligand system ([L'Gal<sub>3</sub>]\*Li(OEt<sub>2</sub>)<sub>3</sub>) or by two equivalents ([L<sub>2</sub>'InCl<sub>2</sub>]\*Li(OEt<sub>2</sub>)<sub>2</sub>), respectively. In case of using L\*H, a one-to-one conversion of the ligand system and InCl lead to formation of a cluster-like tetrameric substructure [L\*In]<sub>4</sub>.



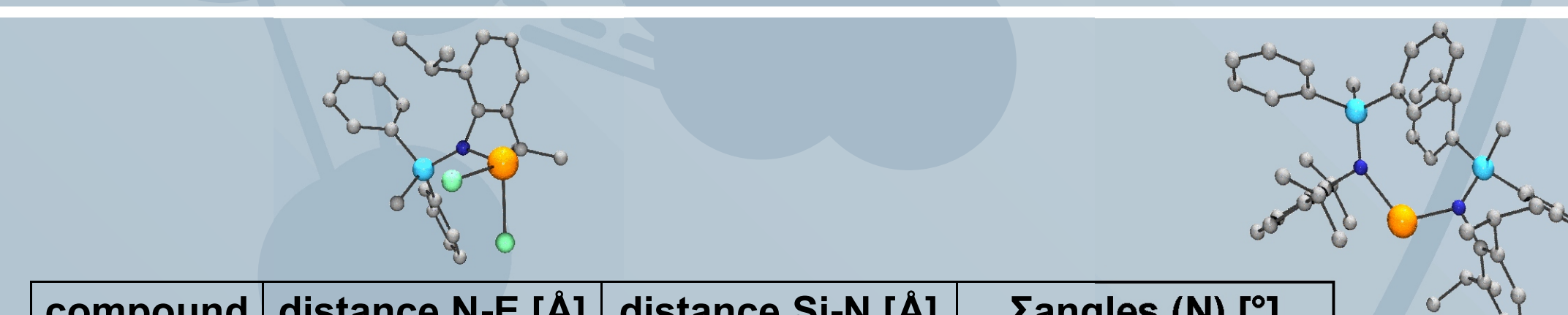
compound	distance N-E [Å]	distance Si-N [Å]	Σangles (N) [°]
P'Gal <sub>3</sub> *Li	1.883	1.730	0.53
P <sub>2</sub> 'InCl <sub>2</sub> *Li	2.059/2.092	1.714/1.731	2.49
P*In	2.146/2.183/2.213	1.686/1.699/1.702	2.08/2.53/7.02/10.41

Cl	●
Ga	●
In	●
I	●
N	●
Si	●

Hydrogens, counter ions and substituents at the N atom were omitted for clarity.

## GROUP 14 DERIVATIVES

Two different classes of compounds could be isolated when reacting L\*H with dichlorides of Ge, Sn and Pb. Depending on the stoichiometry applied during synthesis homoleptic tetrylenes L\*<sub>2</sub>E (E=Ge,Sn,Pb) or heteroleptic derivatives LECl were obtained, the latter as lithium chloride adducts. The products show interesting characteristics in relation to the period of the metal.



compound	distance N-E [Å]	distance Si-N [Å]	Σangles (N) [°]
P* <sub>2</sub> Ge	1.884/1.894	1.748/1.757	2.10/3.19
P* <sub>2</sub> Sn	2.094/2.104	1.733/1.738	0.63/0.93
P* <sub>2</sub> Pb	2.209/2.229	1.702/1.724	0.03/0.17/0.91/0.94
P*SnCl <sub>2</sub> *Li	2.103	1.724	0.03

Cl	●
N	●
Si	●
Sn	●

Hydrogens and counter ions were omitted for clarity.

## CONCLUSION & OUTLOOK

A wide range of main group element and transition metal compounds including the ligand systems MesN(H)SiMePh<sub>2</sub> and DippN(H)SiMePh<sub>2</sub> was isolated and characterized by spectroscopic methods. In future investigations, NMR studies will be conducted to study the effects of the metal in the center of the products. Computational studies using ADF will yield information on bonding, steric properties and stabilities.

## NOTES & REFERENCES

- [1] A. Seifert, G. Linti, Eur. J. Inorg. Chem., 32, 5080 (2006).
- [2] W. Zhang, M. Nishiura, T. Mashiko, Z. Hou, Chem. Eur. J., 14, 2167 (2008).
- [3] P. Wilfling, Michaela Flock, Roland C. Fischer, *unpublished results*.