Introduction to the Scientific Community – Inorganic Chemistry

An Ambiphilic Germylene as Non-Innocent Ligand for a Ni^0-Complex

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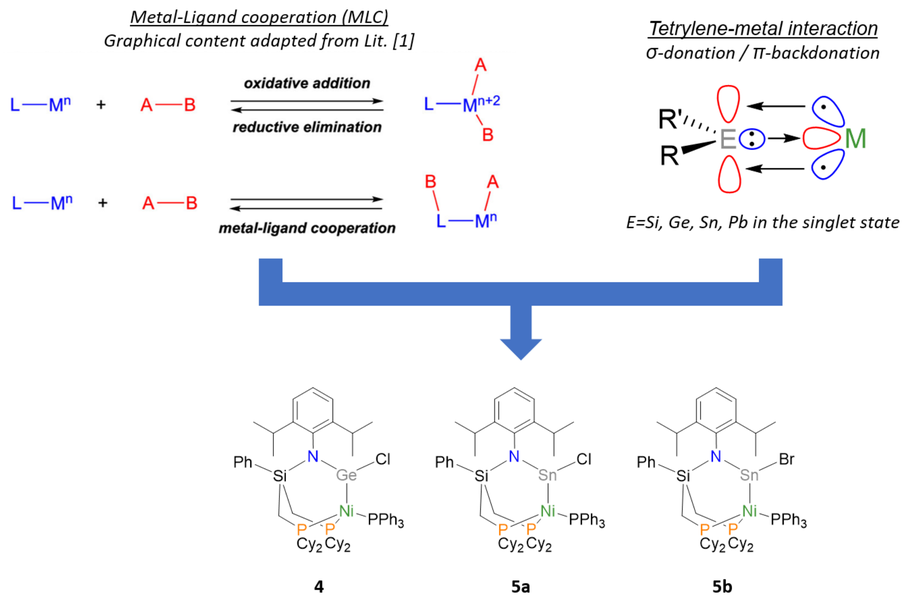
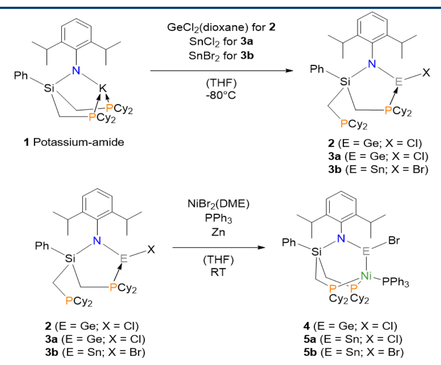
Introduction

The search for cheaper and environmentally benign catalysts is a major driving factor in organometallic research. In this context, Metal-ligand cooperation (MLC) has the potential to increase the catalytic activity of transition metal (TM) complexes.[1] The term MLC describes the active participation of the ligands in bond activation. Recently, ligands based low-valent heavy group 14 elements were successfully used in MLC-active complexes.[2] This year, *Hadlington et al.* presented an MLC-active Ni^0-based complex, featuring a germylene ligand stabilised by a chelating phosphine arm.[3] Based on the work of *Hadlington*, the incorporation of an additional stabilising phosphine group is targeted. In this poster, the synthetic pathways to access the three tetrylenes **2**, **3a** and **3b**, and their respective Ni-complexes **4**, **5a** and **5b** is presented. The successful syntheses were confirmed using ^1H- and ^{31}P-NMR spectroscopy, LIFDI-MS and Single-Crystal-XRD.

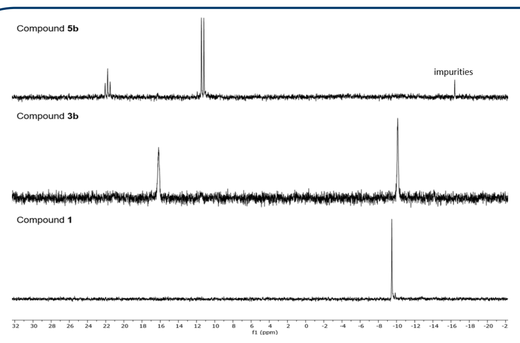


Synthesis of the Ni-complex

Synthetic access to Ni^0-complexes **4**, **5a** and **5b**, through a two-step reaction utilising the potassium-amide **1** as starting material.



Two-step synthesis to the Ni^0-complexes. (Cy = cyclohexyl)

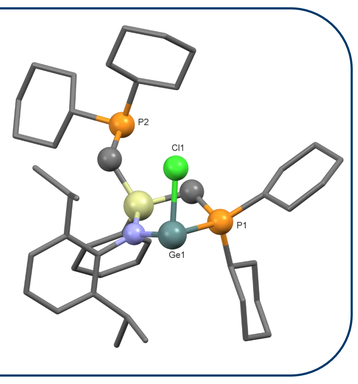


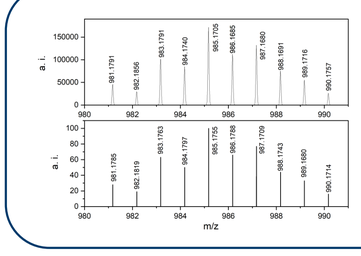
In situ ^{31}P-NMR spectroscopy monitoring the reactions shown above.

Structure of the free ligand

Crystal structure of 2

Ge-P = 2.491(2) Å
Ge-Cl = 2.362(2) Å
Ge-N = 1.931(5) Å
Degree of pyramidalisation at the Ge: **272.24°**



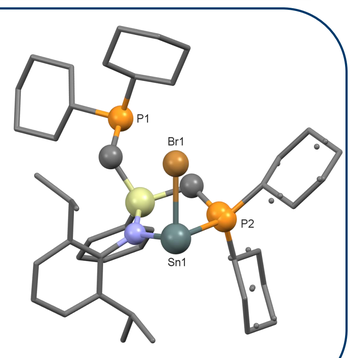


Top: Experimental LIFDI/MS of **2**.

Bottom: Calculated MS spectrum of **2**.

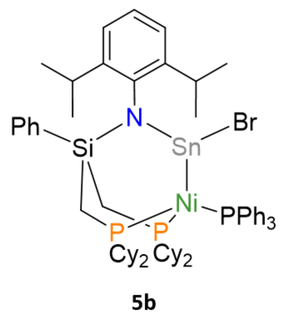
Crystal structure of 3b

Sn-P = 2.68(2) Å
Sn-Br = 2.678(2) Å
Sn-N = 2.13(1) Å
Degree of pyramidalisation at the Sn: **267.5°**

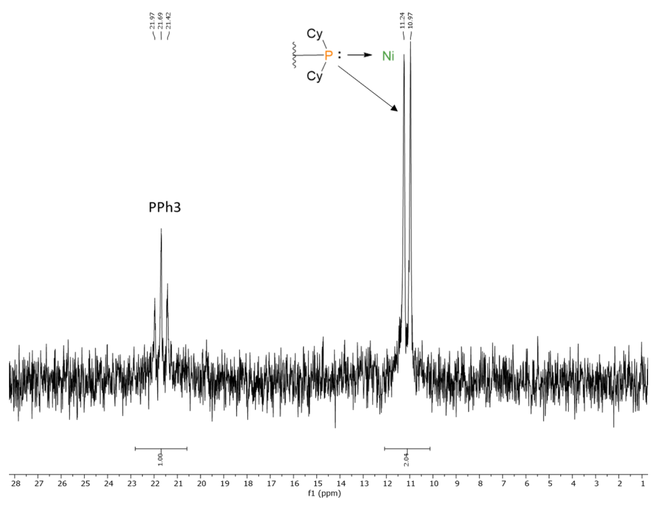


Structure of the complex

- Facile synthetic access
- Orbital interaction allowing MLC
- Tetrylene centre acting as single centre ambiphiles
- Chelating phosphines assure the stability of the structure



5b



^{31}P-NMR spectrum of **5b** showing an integral ratio of 1 : 2.

Conclusion

The presented research describes an efficient and easily scalable synthesis of tetrylene-amide ligands. The SC-XRD measurements revealed the pyramidalised geometry of the tetrylene centres in solid state, indicating the low-valent character in all three ligands. The complexation of the tetrylenes with $NiBr_2$ through a reduction with Zn was successfully monitored by ^{31}P-NMR spectroscopy for all three complexes. The next steps include the isolation and characterisation of the resulting complexes. Further analysis of structure and reactivity could reveal the potential catalytic applications of these complexes.

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[1] M. Rauch, S. Kar, A. Kumar, L. Avram, L. J. W. Shimon, D. Milstein, *Journal of the American Chemical Society* **2020**, *142*, 14513-14521.
[2] J. A. Cabeza, P. García-Álvarez, C. J. Laglera-Gándara, *European Journal of Inorganic Chemistry* **2020**, *2020*, 784-795.
[3] P. M. Keil, T. Szilvási, T. J. Hadlington, *Chemical Science* **2021**, *12*, 5582-5590.