Introduction to the Scientific Community – Inorganic Chemistry

Aryl-Functionalised Germylenes as Ligands in Ni^0-Complexes

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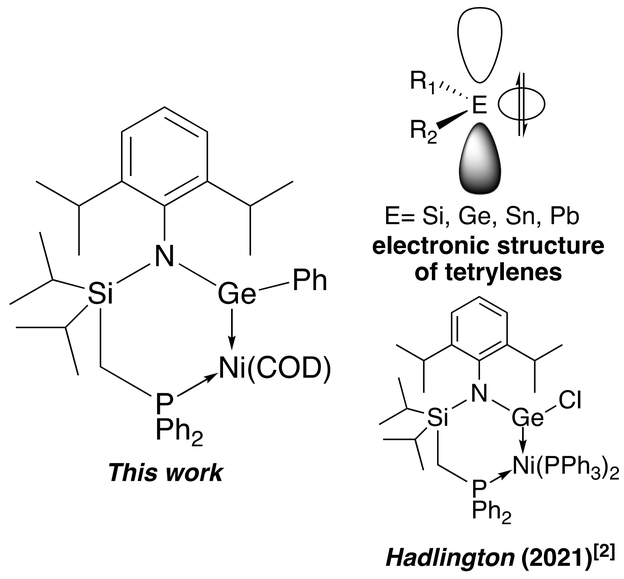
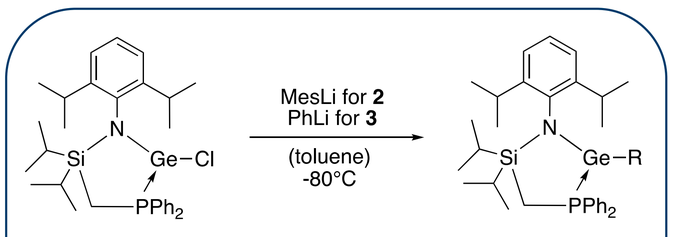
Introduction

The vast use of carbenes has inspired scientists to move towards utilising the heavier group 14 elements in ligand systems. In this regard, tetrylenes can be described as the heavier analogues to carbenes.[1] Besides their transition-metal like reactivity and their ambiphilic character, tetrylenes can be used as ligands in organometallic complexes. Recently Hadlington *et al.* reported a Ni^0-complex with a germylene featuring a chloride substituent that is capable of activating ammonia.[2] In this poster, the successful substitution of the chloride with an aryl group at the germylene ligand and their nickel complexes are demonstrated. Therefore, the germylene ligand was reacted with mesityllithium or phenyllithium respectively before the complexation with $Ni(COD)_2$. All compounds were characterised and analysed with ^1H- and ^{31}P-NMR spectroscopy. Moreover, the structures of PhiPDippGePh and PhiPDippGePh-Ni(COD) were confirmed via SC-XRD.



Synthesis of the compounds

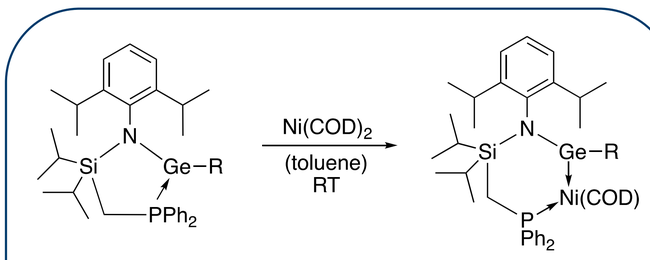
Synthetic access to the Ni-complexes **4** and **5** is provided by a two-step synthesis starting from the germylene ligand PhiPDippGeCl **1**.



1: PhiPDippGeCl

2: R= Mesityl (Mes)
3: R= Phenyl (Ph)

Synthetic access to **2**: PhiPDippGeMes and **3**: PhiPDippGePh; (iP= isopropyl, Dipp= diisopropyl-phenyl).

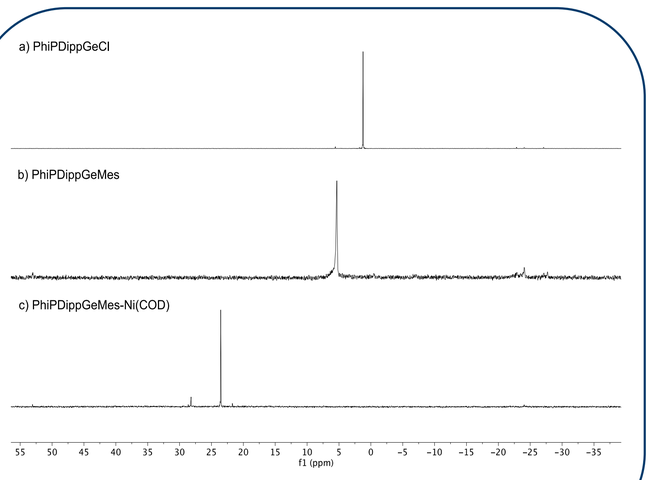


2: R= Mesityl
3: R= Phenyl

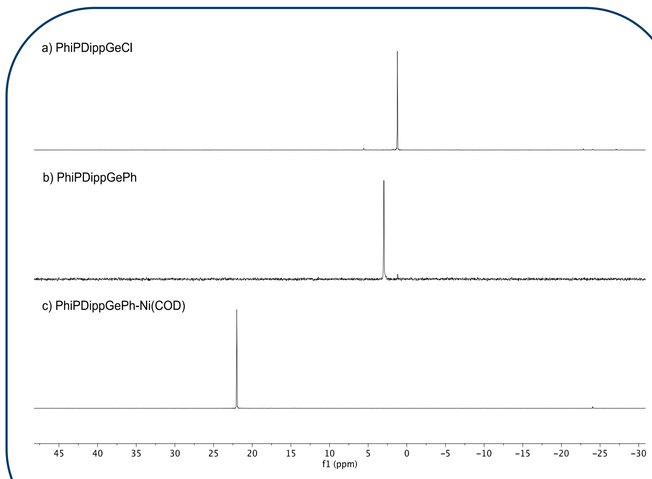
4: R= Mesityl
5: R= Phenyl

Synthesis of **4**: PhiPDippGeMes-Ni(COD) and **5**: PhiPDippGePh-Ni(COD); (COD= 1,5 cyclooctadiene).

Spectroscopy



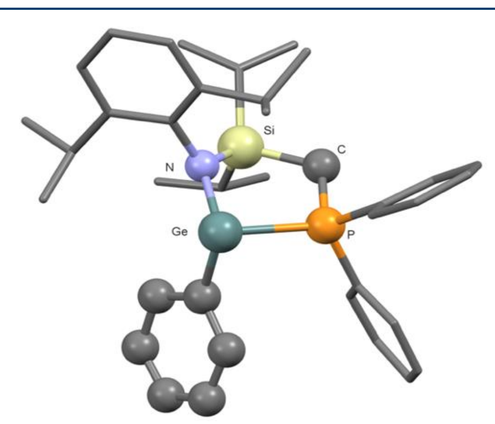
^{31}P-NMR spectra of **1**: a) , **3**: b), **5**: c).



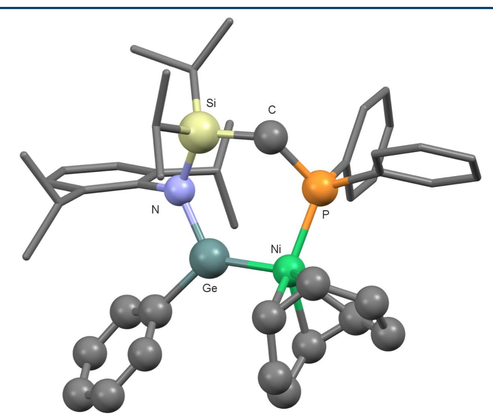
^{31}P-NMR spectra of **1**: a), **2**: b), **4**: c).

Structure

Single Crystal X-Ray Diffraction (SC-XRD)



Crystal structure of PhiPDippGePh **3**, sum of bond angels around Ge: 280°.



Crystal structure of PhiPDippGePh-Ni(COD) **5**, sum of bond angles around Ge: 360°.

Conclusion

The successful syntheses of aryl functionalised germylene ligands and their nickel complexes were demonstrated. Crystals of the compounds PhiPDippGePh **3** and PhiPDippGePh-Ni(COD) **5** were obtained and their structures could be confirmed via SC-XRD. Additional investigations regarding the reactivity of the Ni^0-complex towards small molecules like ammonia require further experimentation since first tests did not lead to positive results. The substitution of the labile COD group at the Ni-centre using different ligands like tricyclohexylphosphane and N-heterocyclic carbenes can be useful to obtain a more reactive 16 valence electron complex to further tune the reactivity of these compounds.

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[1] Y. Mizuhata, T. Sasamori, N. Tokitoh, *Chem. Rev.* **2009**, *109*, 3479-3511.
[2] P. M. Keil, T. Szilvási, T. J. Hadlington, *Chem. Sci.* **2021**, *12*, 5582-5590.