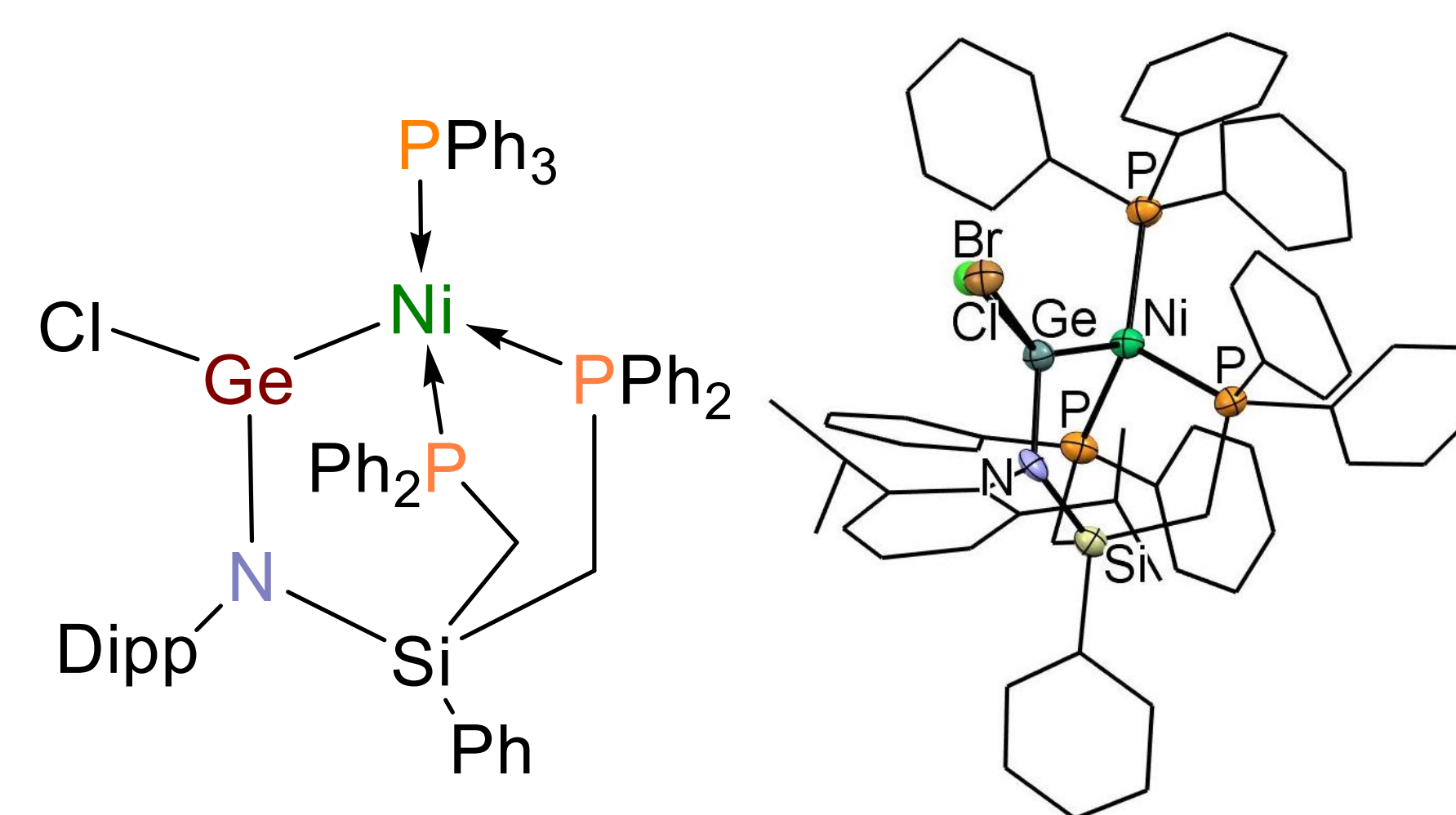


Group 14 element utilization with the goal of small molecule activation

Richard Zell*

Introduction

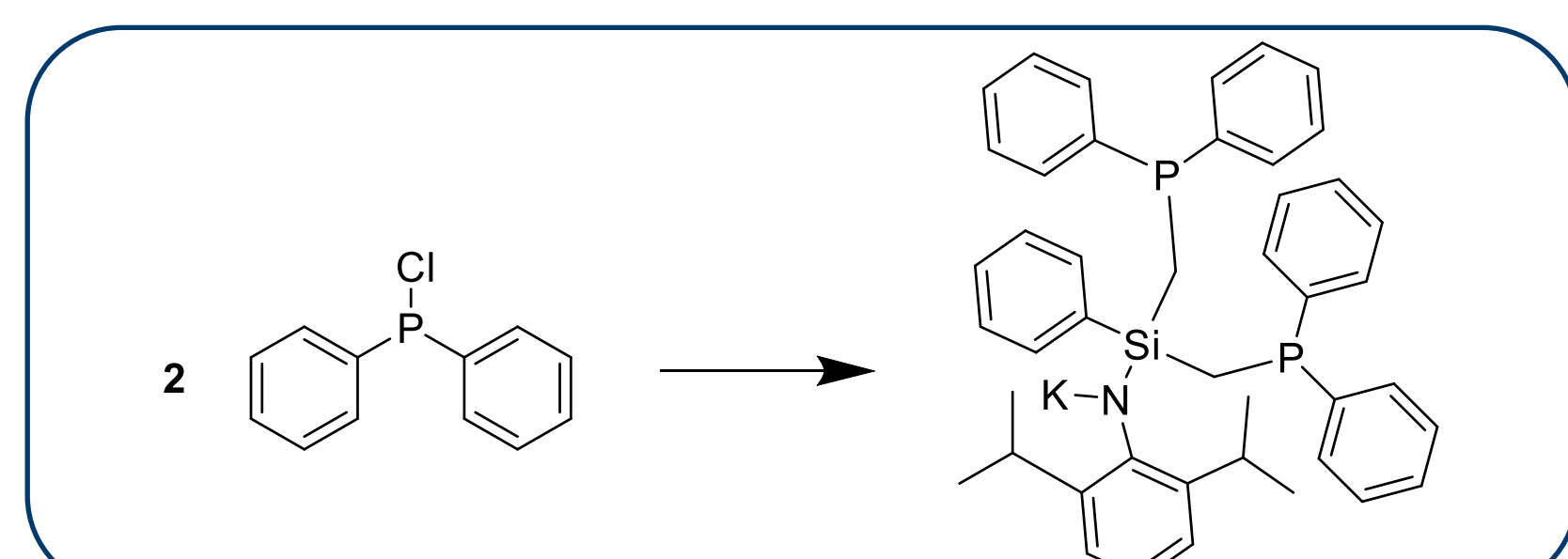
Most metal organic complexes utilize transition metals. Due to their limited deposits and high environmental impact the search for an alternative has gained importance. Low valent group 14 complexes have gained attention in this regard. As most research has been focusing on N-heterocyclic carbenes, this work will focus on utilizing the heavier homologues germynes and stannyls. Using a freshly synthesized phosphine functionalized amid ligand, the synthesis of a germylene nickel⁰ complex was achieved. The synthesis was characterized using ¹H-, ³¹P- and COSY-NMR as well as single crystal X-ray diffraction. After obtaining the germylene ligand system in good purity, the nickel⁰ complex could be obtained. In the final product a mixed chlorinated and bromated complex was obtained. Further experiments to validate the small molecule activation must be performed to validate the activity of this specific complex



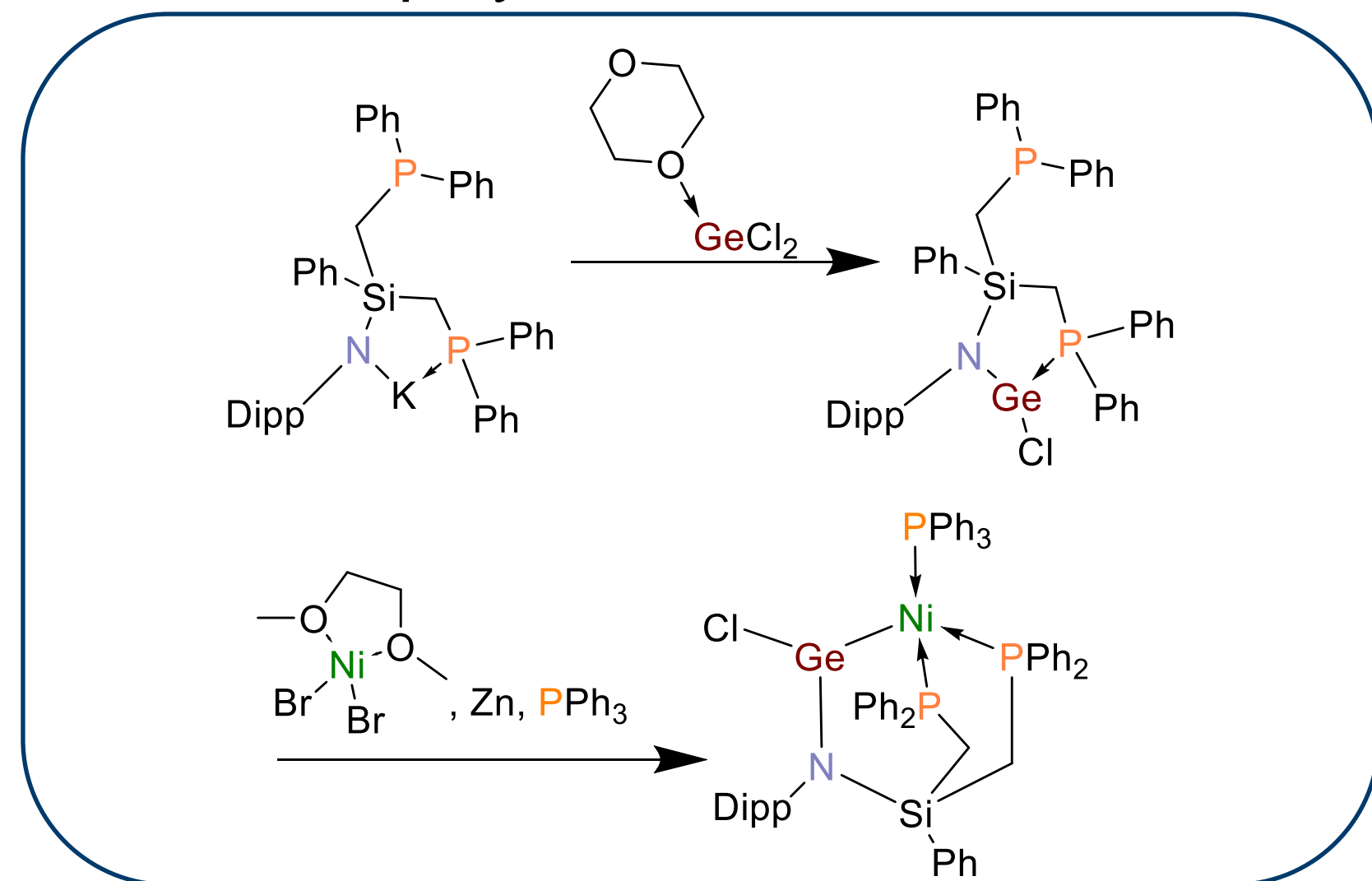
Molecular structures of phenylDippNGeCINiPPh₃ (left) and crystal structure obtained from single crystal diffraction (right).

Synthesis

The tridentate ligand system is obtained in a five-step synthesis from chlorodiphenylphosphane based on the generally applied synthetic route based on [1].

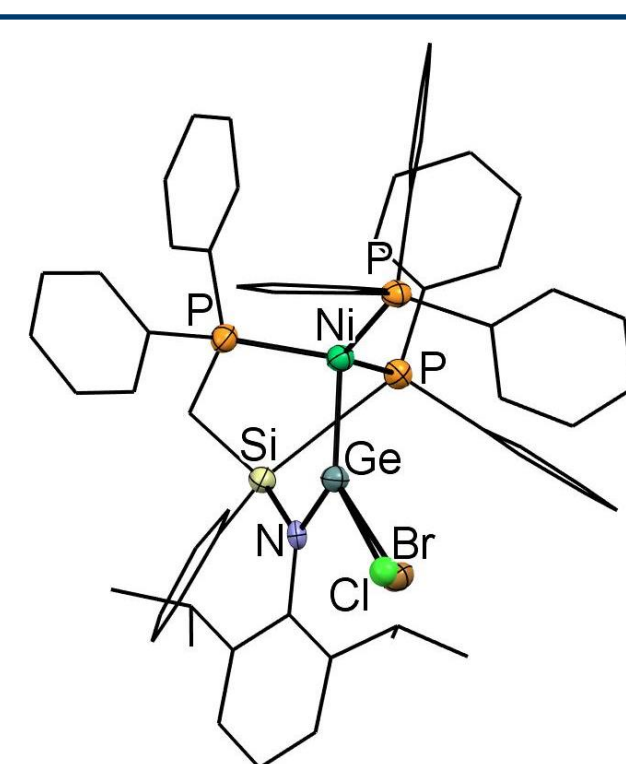


Using the tridentate ligand, the final germanium nickel complex was obtained in a two-step synthesis.

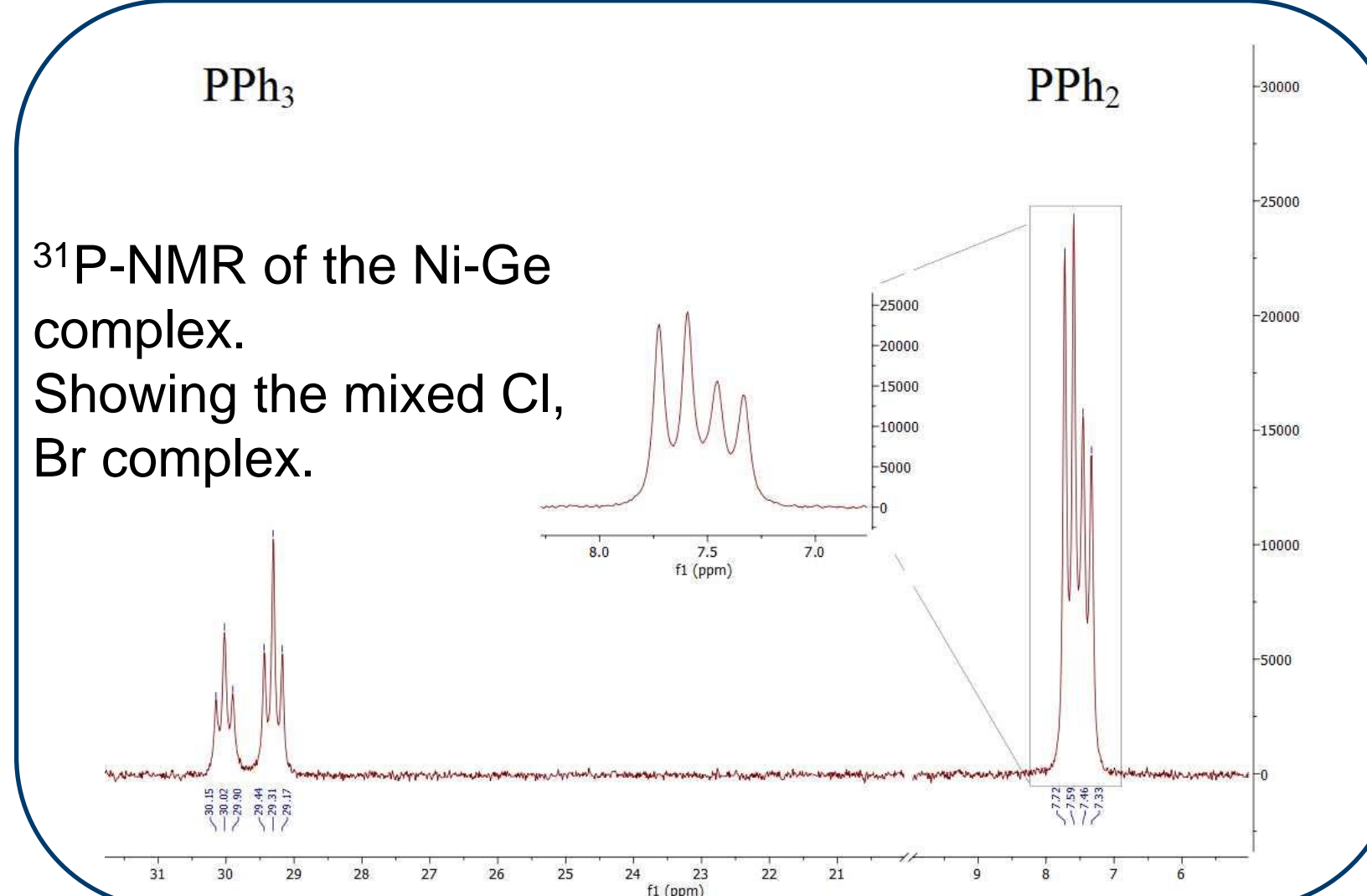


Structure and Spectroscopy

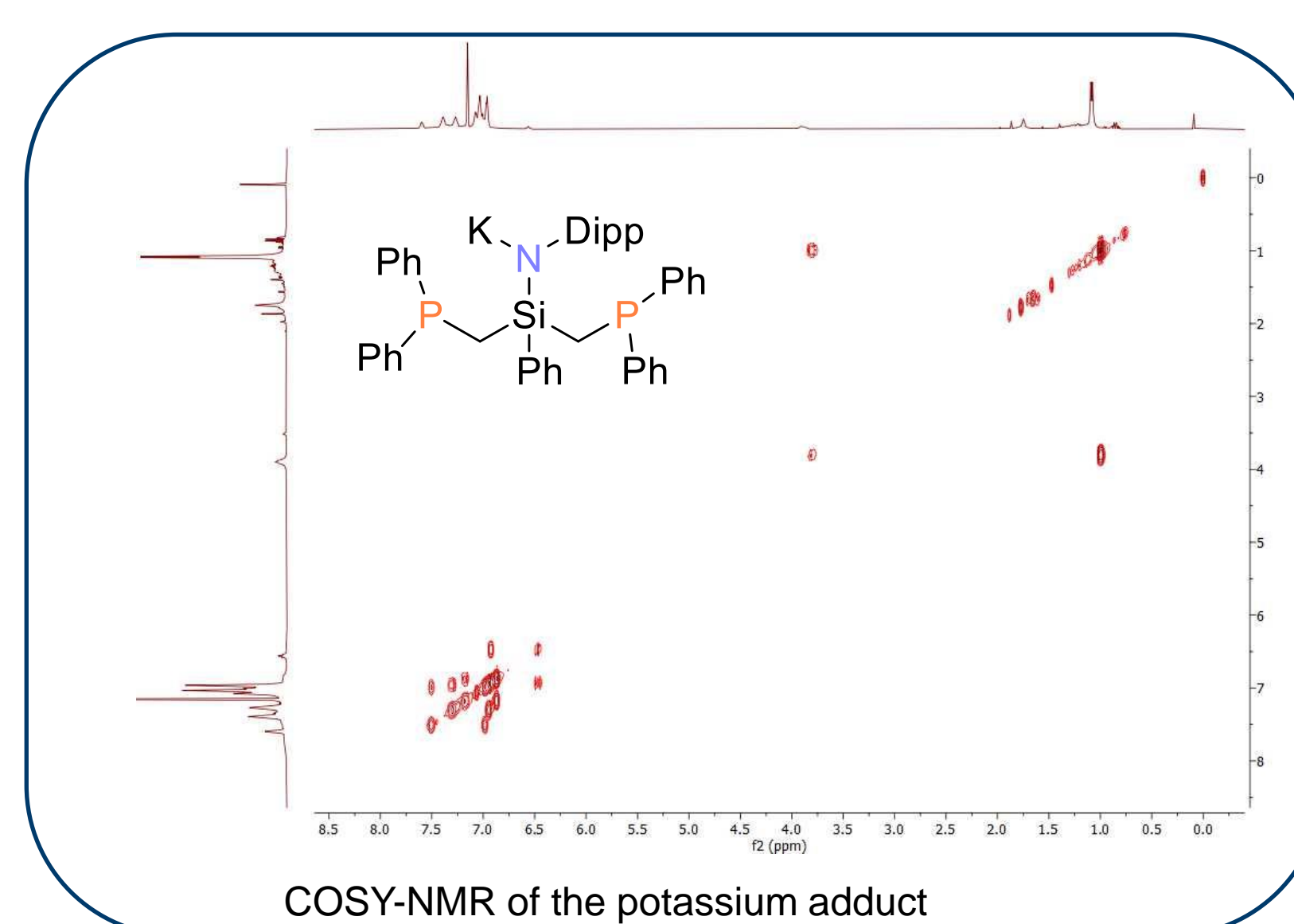
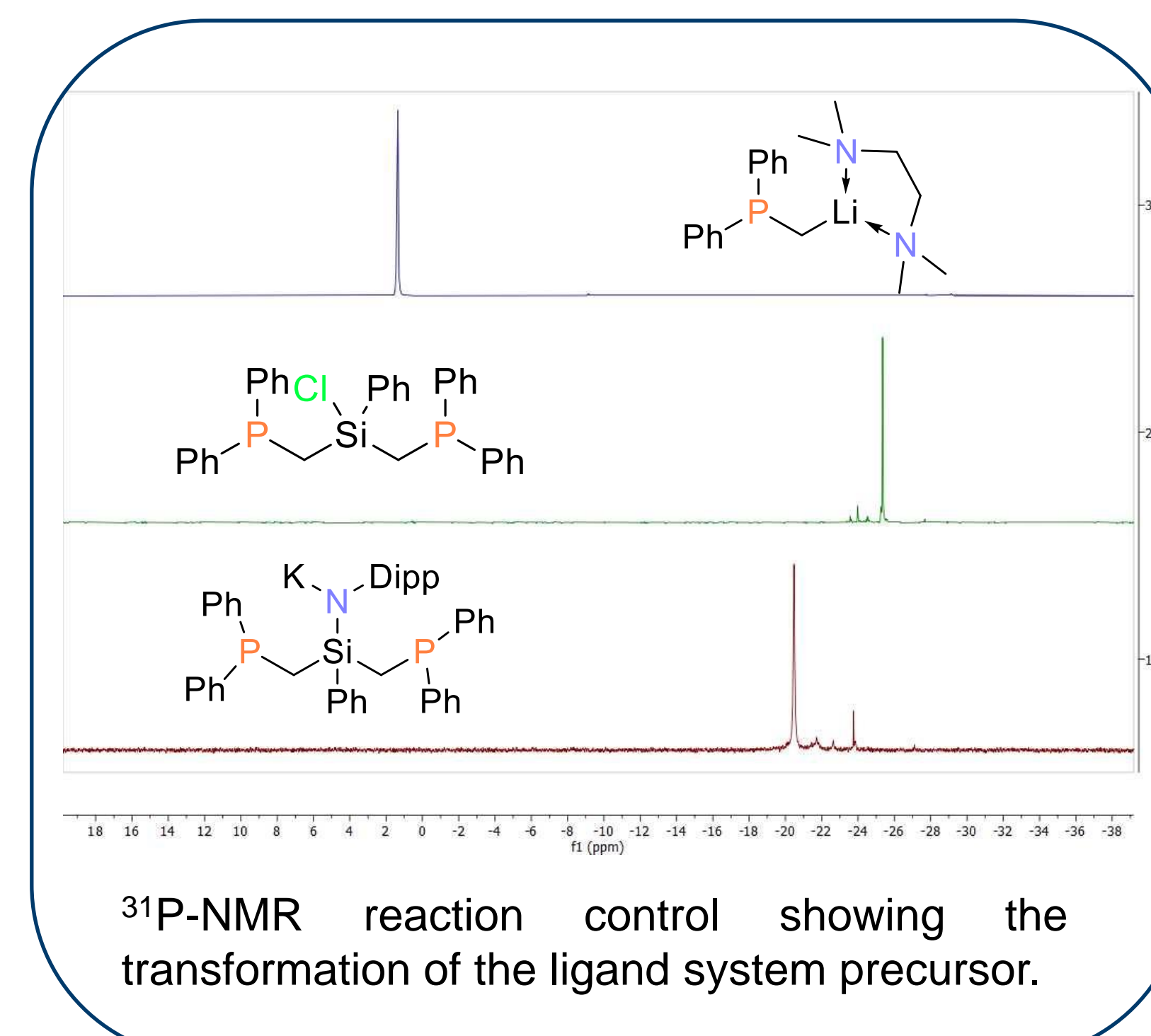
X-Ray structure of the Ni-Ge complex. Data verified with similar complexes.[2]



Distances	[Å]	Angles	
N-Ge	1.88(1)	X _{Hal.} -Ge-N	100.2(0)°
Ni-Ge	2.19(9)	X _{Hal.} -Ge-Ni	142.6(2)°
Ni-P _L	2.17(0); 2.19(6)	PPh ₃ -Ni-PL	118.5(3)°; 122.8(4)°
Ni-PPh ₃	2.20(9)	PPh ₃ -Ni-Ge	114.6(6)°



Reaction control



Conclusion

The germylene nickel⁰ complex could be obtained and verified, using ¹H-, ³¹P- and COSY-NMR as well as single crystal diffraction. The data revealed a nearly tetrahedral environment around the nickel centre with all phosphines bound to the nickel. Only slight deflection by the steric size of the tridentate ligand of the triphenylphosphine was observed. Because both chloride and bromide salts were deployed, a halide exchange took place, resulting in a mixture of the chloride and bromide complex. This effect is shown throughout all measurements resulting in two sets of NMR peaks. While the reactions were successful, side reactions could not be avoided resulting in impurities in the product.

* This work was performed under the supervision of Philip Keil in the Group of Dr. Hadlington at the Chair of Inorganic Chemistry with Focus on New Materials at TUM.

[1] Keil P. M.; Szilvási T.; Hadlington T. J. *Chem. Sci.* **2021**.

[2] Feng Z.; Jiang Y.; Ruan H.; Zhao Y.; Tan G.; Zhang L.; Wang X. *Dalton Trans.* **2019**, *48*, 14975–14978.