



**CONVERSION OF GERMAPHOSPHOLES
WITH TRANSITION METALS**

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Abstract

This report consists of three parts: The first chapter gives an overview of techniques that were acquired during the scholar's stay at the host institute. The second chapter describes the conversion of germaphospholes with transition metals as described in the proposal. The third chapter deals with a newly designed ligand, including background studies, syntheses and characterization of the target molecule.

Zusammenfassung

Der vorliegende Bericht besteht aus drei Teilen: Das erste Kapitel enthält einen Überblick über die wichtigsten Arbeitstechniken, die im Laufe des Forschungsaufenthaltes von der Stipendiatin erlernt wurden. Im folgenden Teil wird die Arbeit am Forschungsthema „Conversion of germaphospholes with transition metals“ dargestellt, das im Proposal beschrieben wurde. Das dritte Kapitel beschreibt Design und Synthese eines neuen Liganden. Die Arbeiten auf diesem Gebiet wurden ebenfalls im Rahmen des Forschungsaufenthaltes durchgeführt.

Acquired techniques

Potassium Mirrors

Solvent purification techniques at the host university require the generation of potassium mirrors in order to dry the organic solvents used for syntheses.

At the home university solvents are mostly used as obtained from a solvent purification system by *Innovative Technologies*. At the host university, an additional drying procedure is performed in addition to the purification by columns: Organic solvents are always stored over potassium mirrors overnight before use.

The scholar not only learned about the generation of the mirrors but also about their controlled destruction. As potassium is extremely reactive when in contact with air, these procedures require especially safe working environments.

This new technique will be used in the laboratories of the home university in future, when very dry solvents are needed. The scholar is going to introduce potassium mirrors to her laboratories colleagues in order to provide them with the possibility to work with even more sensitive materials. New fields of chemical synthesis might be explored by means of this technique.

Alternative Dry Box Techniques

Dry boxes are deployed with different principles by the home and the host working group. At the home university dry boxes are used for storage of chemicals and preparation of NMR samples as well as for preparative procedures. This leads to a very comfortable way of performing reactions with a guaranteed atmosphere of N₂. Contamination of samples and working gadgets is frequently found, which is one of the disadvantages of this system.

In the working group of Prof. Power the dry boxes are only used for the storage of chemicals and products and for the preparation of NMR samples.

This leads to a series of consequences:

- The dry boxes are much cleaner.
- Reactions can only be performed outside the box.
- Reaction flasks have to be perfectly closed because the reactions are performed outside.
- The danger of destroying the sample by air contamination is higher.
- More precise working techniques outside the dry boxes have to be introduced.

To sum up, performing reactions only at Schlenk lines (and not in dry boxes) leads to less contamination of the boxes and the samples but simultaneously decreases the probability of success, when performing very sensitive reactions.

New Schlenk Techniques

As shown in figure 1, Schlenk flasks were used at both universities. Different styles were deployed though, which influenced the handling techniques.



Figure 1: Different Schlenk flasks used at the home university (left) and the host university (right).¹

In addition to the new Schlenk type, different tap fixing techniques were needed. Both handling procedures were useful to acquire for the scholar's future laboratory work.

Mostly a mixture of all these techniques is used in all organometallic laboratories deploying N₂ as reaction atmosphere gas, which makes it very probable for the scholar to be capable of handling various kinds of equipment in different laboratories.

¹ Pictures copied from www.aldrich.com.

Conversion of Germaphospholes with Transition Metals

Introduction

The scientific initial position was the conversion of terphenyl-stabilized tetrylenes with adamantyl-phosphaalkyne.² Variation of the heavier group 14 element (Ge, Sn, Pb) leads to different structures, as shown in figure 2.

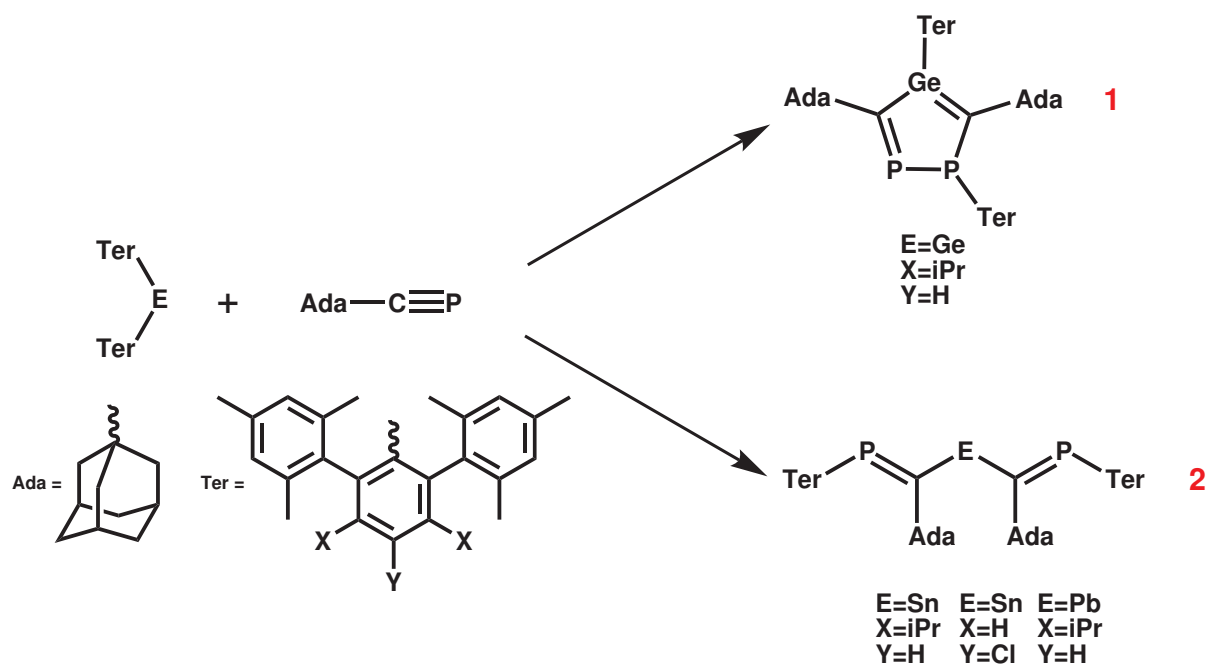


Figure 2: Conversion of terphenyl-stabilized tetrylenes with adamantyl-phosphaalkyne.

These results open up the extremely interesting question if compound **1** and compounds **2** – **4** exist balanced by equilibrium. A similar case was reported by Peng et al. in 2009, when they described the reversibility of distannacyclobutane formation.³ We suppose that compound **1** is formed by cyclization of the linear equivalent as shown in figure 3.

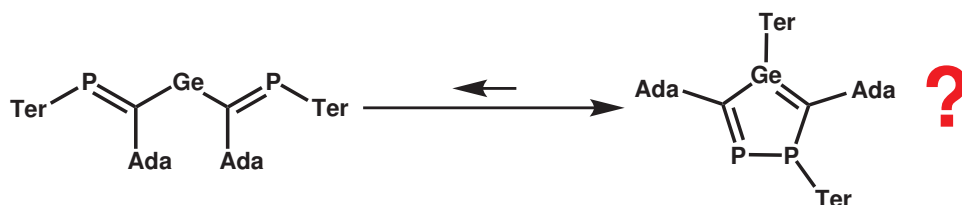


Figure 3: Potential equilibrium of compound **1** and a linear equivalent.

Whether this proposed equilibrium exists or not was planned to be determined at TU Graz before the start of the stay at the host university. Due to starting material problems this fact

² Wilfling, P.; Fischer, R.C. *unpublished results*.

³ Peng, Y.; Ellis, B.D.; Wang, X.; Fettingner, J.C.; Power, P.P. *Science* **2009**, 1668-1670.

could not be proved and is going to be the topic of further investigations at the home university after the end of the scholar's stay at UC Davis.

Although the central ring of compound **1** is not perfectly planar, details in the crystal structure of **1** concerning bonding environment and bond lengths lead to the assumption that this compound is aromatic. The structure is shown in figure 4. Pyykkö et al. published the following calculated bond lengths for Ge-C, C-P and P-P bonds in 2009 (for model substances):^{4,5}

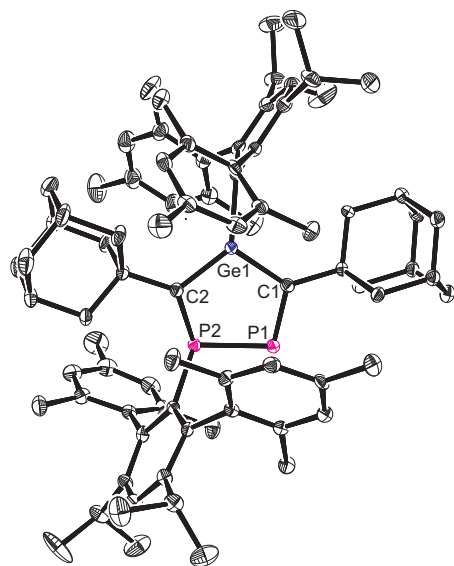


Figure 4: Crystal structure of compound **1**. Selected bond distances /Å and angles /deg: Ge(1)-C(1) 1.9127(1), Ge(1)-C(2) 1.8377(1), C(1)-P(1) 1.7170(1), C(2)-P(2) 1.7591(1), P(1)-P(2) 2.1380(1).

Bond	Bond distance /Å
Ge-C	1.945
Ge=C	1.819
C-P	1.847
C=P	1.66
P-P	2.212
P=P	e.g. 2.051

Table 1: Calculated bond lengths by Pyykkö et al.

As can be seen from table 1, all the bond distances of the central five-membered ring are in the range between single and double bonds, which makes aromaticity a very likely option. Comparing the bond lengths with experimental Ge=C and P=P double bonds known in literature, this trend is confirmed.^{6,7}

The aromaticity of structures related to compound **1** was discussed by Dransfeld et al. in 1998.⁸ They showed that phospholes (as model structures for compound **1**) may feature a

⁴ Pyykkö, P.; Atsumi, M. *Chem. Eur. J.* **2009**, 12770-12779.

⁵ Pyykkö, P.; Atsumi, M. *Chem. Eur. J.* **2009**, 186-197.

⁶ Power, P.P. *Chem. Rev.*, **1999**, 3463-3504.

⁷ Fischer, R.C.; Power, P.P. *Chem. Rev.*, **2010**, 3877-3923.

⁸ Dransfeld, A.; Nyulázi, L.; von Ragué Schleyer, P. *Inorg. Chem.* **1998**, 4413-4420.

significant level of aromaticity. NICS calculations showing the level of aromaticity of compound **1** have been performed by Flock et al.⁹

Compound	NICS value
“Ge”	- 9.3
“Sn”	- 9.0
Benzene	- 9.2
Cyclohexane	- 1.7

Table 2: NICS values for compound **1** (“Ge”), the hypothetical Sn analogue (“Sn”) and two reference molecules.

Benzene is regarded the standard reference for aromaticity comparisons. Compound **1** seems to show even stronger aromaticity than benzene, the hypothetical Sn analogue lies in the same range. Cyclohexane is shown in table **2** as a not-aromatic species.

Aromaticity leads to analogy of the five-membered ring system with the well-explored cp (cyclopentadienyl, $C_5H_5^-$) ligand system as shown in figure **5**. A similar case was published in 2009 by Yasuda et al., reporting on a trisilacyclopentadienide with significantly aromatic behaviour. A Li derivative of the dienide was obtained and characterized by X-Ray diffraction.¹⁰

Cp is the preliminary model of ligand systems deployed to stabilize sandwich complexes of a great number of metals (metallocenes). The manifold application possibilities of metallocenes in catalysis, in supramolecular chemistry, in nonlinear optics, in medicine and as building blocks for molecular magnets open up a range of potential technological employments for transition metals stabilized by compound **1**.

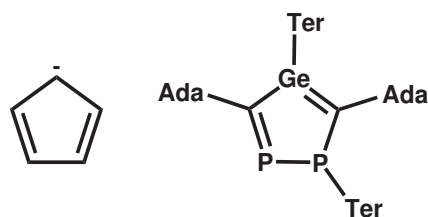


Figure 5: Analogy of cp and compound **1**.

⁹ Flock, M.; Müller, S. *work in progress*.

¹⁰ Yasuda, H.; Lee, V.Y.; Sekiguchi, A. *J. Am. Chem. Soc.* **2009**, 6352-6353.

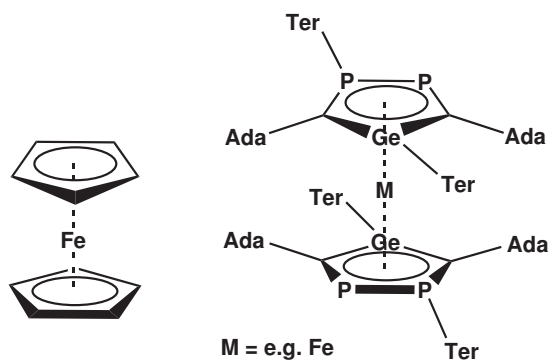


Figure 6: Analogy of ferrocene and potential products stabilized by compound **1**.

Figure **6** shows the analogy of ferrocene, which is an extremely well characterized species, with potential products, when reacting compound **1** with e.g. transition metal halides. A huge range of metallocenes stabilized by cp is known¹¹, which leads to the assumption that a five-membered ring containing Ge will stabilize transition metals as well.

There is a range of possible binding patterns that can be thought of when converting compound **1** with transition metals. Mono- or disubstitution is possible, coordination of the transition metal can occur by two ways, as shown in figure **7**. A wide range of products seems therefore possible for the conversions.

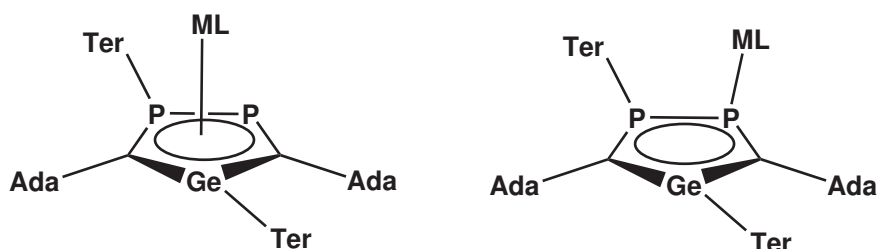


Figure 7: Possible bonding patterns in case of monosubstitution.

While another type of reaction including W was studied by the scholar in May 2010 in the group of Prof. Streubel (Bonn, Germany), research at the Institute of Inorganic Chemistry in Graz is basically focused on the chemistry of main group elements, especially on elements of group 14. Hence, reactions deploying W as the metal centre of the aimed product are performed in Graz and another model reaction with Cr as metal centre had been already performed at the Institute of Inorganic Chemistry before the scholar went to UC Davis. Further characterization by NMR and X-Ray diffraction is still in progress. As cp_2Cr is a highly air-sensitive compound and versatile reagent for ligand exchange, substitution of cp by compound **1** will lead to further stabilization of the metallated species.

¹¹ Elschenbroich, C. *Organometallics*, 3rd ed.; WILEY-VCH Verlag GmbH & Co. KGaA: Weinheim, 2006.

The Power group started working on transition metals deploying a range of different ligand systems some years ago. Prof. Power also published research data dealing with the correlation of transition metals and heavier main group elements concerning chemical behaviour. He showed that characteristics of heavier main-group elements and transition metals are much more similar than those of lighter main-group elements compared to their heavier congeners.¹² Working with Zn, Cd, Hg¹³, Cr¹⁴, Mn^{15,16}, Co¹⁷, Fe¹⁸ and others, the working group has extensive experience in the chemistry of a huge range of transition metals.

Furthermore, the collaboration between the two working groups already lasts for years (see e.g. ^{19, 20, 21, 22, 23}) and further publications will contribute to the benefits of the successful cooperation.

Experiments and Results

A series of conversions was performed with elemental metals. The reaction conditions for the samples:

- C₆D₆ as solvent
- inert atmosphere (mostly dry box)
- NMR scale

Studies showed that conversions with these reagents lead to conservation of the starting material.

As a consequence a series of conversions with metal halides was conducted. Some of the reactions performed are shown in figure 8. The reaction conditions stayed the same as described above.

¹² Power, P. P. *Nature* **2010**, 463, 171-177.

¹³ Zhu, Z.; Brynda, M.; Wright, R.J.; Fischer, R.C.; Merrill, W.A.; Rivard, E.; Wolf, R.; Fetting, J.C.; Olmstead, M.M.; Power, P.P. *J. Am. Chem. Soc.* **2007**, 10847-10857.

¹⁴ Wolf, R.; Ni, C.; Nguyen, T.; Brynda, M.; Long, G.J.; Sutton, A.D.; Fischer, R.C.; Fetting, J.C.; Hellman, M.; Pu, L.; Power, P.P. *J. Inorg. Chem.* **2007**, 11277-11290.

¹⁵ Ni, C.; Rekken, B.; Fetting, J.C.; Long, G.J.; Power, P.P. *Dalton Transactions* **2009**, 8349-8355.

¹⁶ Ni, C.; Lei, H.; Power, P.P. *Organometallics* **2010**, 1988-1991.

¹⁷ Ni, C.; Stich, T.A.; Long, G.J.; Power, P.P. *Chem. Comm.* **2010**, 4466-4468.

¹⁸ Lei, H.; Guo, J.; Fetting, J.C.; Nagase, S.; Power, P.P. *J. Am. Chem. Soc.* **2010**, 17399-17401.

¹⁹ Fischer, R.C.; Pu, L.; Fetting, J.C.; Brynda, M.A.; Power, P.P. *J. Am. Chem. Soc.* **2006**, 11366-11367.

²⁰ Rivard, E.; Fischer, R.; Wolf, R.; Peng, Y.; Merrill, W.A.; Schley, N.; Zhu, Z.; Pu, L.; Fetting, J.C.; Teat, S.J.; Nowik, I.; Herber, R.H.; Takagi, N.; Nagase, S.; Power, P.P. *J. Am. Chem. Soc.* **2007**, 16197-16208.

²¹ Wolf, R.; Fischer, J.; Fischer, R.C.; Fetting, J.C.; Power, P.P. *Europ. J. Inorg. Chem.* **2008**, 2515-2521.

²² Zhu, Z.; Fischer, R.C.; Ellis, B.D.; Rivard, E.; Merrill, W.A.; Olmstead, M.M.; Power, P.P.; Guo, J.D.; Nagase, S.; Pu, L. *Chem. Eur. J.* **2009**, 5263-5272.

²³ Fischer, R.C.; Power P.P. *Chem. Rev.* **2010**, 3877-923.

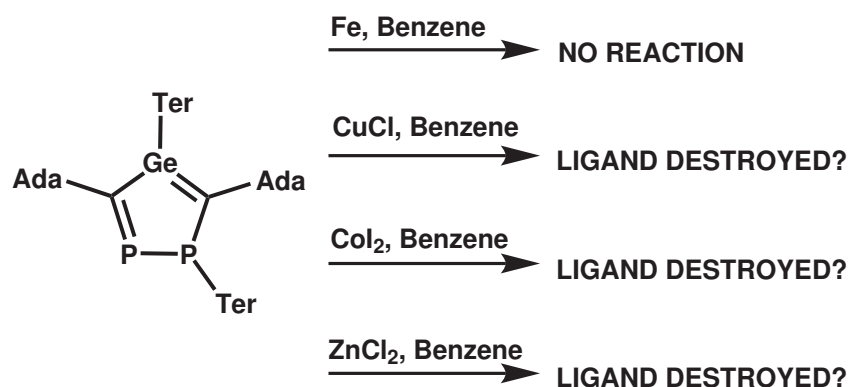


Figure 8: Examples for the conversion of compound **1** with metals and metal halides.

Variation of reaction conditions (e.g. 80 °C, longer reaction times) did not lead to changing reaction behaviour. In every reaction with metal halides the ligand system was destroyed by the harsh conditions. ^{31}P NMR showed partial destruction of the ligand system. ^{31}P NMR studies were chosen to be the perfect means for reaction process controlling because of the high abundance of ^{31}P and the subsequent easiness of detecting this NMR nucleus. Measurements could be performed very fast (e.g. 5 minutes).

Consequently the use of metal carbonyls was the next step to moderate the reaction conditions. At first $\text{Mo}(\text{CO})_6$ was deployed in order to obtain coordination products.

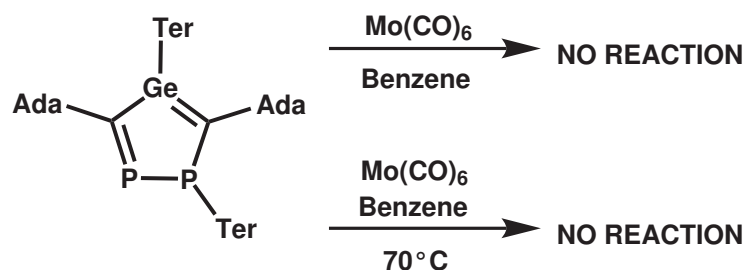


Figure 9: Conversion of compound **1** with $\text{Mo}(\text{CO})_6$.

NMR measurements proved that this reagent did not lead to any reaction. As a further consequence, $\text{Ni}(\text{CO})_4$ was proposed as another starting material, more reactive than $\text{Mo}(\text{CO})_6$ but not as harsh as the metal halides. In contrast to $\text{Mo}(\text{CO})_6$, this reagent is very toxic, which is one of the reasons why it was not used earlier. In addition, $\text{Ni}(\text{CO})_4$ is carcinogen and the vapours may auto ignite. The handling of $\text{Ni}(\text{CO})_4$ was one of the handling techniques acquired by the scholar during the stay. $\text{Ni}(\text{CO})_4$ is not used at the home university and the scholar had never handled it before.

Reactions with $\text{Ni}(\text{CO})_4$ were performed very successfully, ^{31}P NMR showed that the ligand system remains stable and the two ^{31}P -peaks are shifted significantly. As a consequence,

$\text{Ni}(\text{CO})_4$ is going to be achieved at the home university for further investigations of these reactions. Further characterization of the final product will be performed in Graz too.

Discussion

Reactions of the ligand starting material (compound **1**) with a series of metals and metal halides were performed unsuccessfully and showed either no reaction or destruction of the ligand.

Consequently, a series of reactions deploying metal carbonyls was performed following the processes by ^{31}P NMR. While conversion with $\text{Mo}(\text{CO})_6$ under varying conditions did not lead to any reaction, $\text{Ni}(\text{CO})_4$ seems to be the perfect reagent for obtaining coordination products. The significant NMR signals were shifted as expected and the colour of the solution changed accordingly.

Further work will include the up-scaling of the reaction (reactions were performed on NMR scale only). In addition other characterization methods (X-ray, UV-Vis, etc.) have to be applied in order to fully characterize the product. Depending on the real structure of the molecule, further reactions using the product as a starting material may be possible. These reactions will point out the similarities and differences between the product and ferrocene.

Ligand Synthesis

Introduction

The Power group has worked on the topic of amido complexes for several years. In 2009 their work on the conversion of terphenyl-substituted amido ligands with $\text{Fe}\{\text{N}(\text{SiMe}_3)_2\}_2$ was published and led to huge interest in the unusual magnetic behaviour of the products of this publication.²⁴

The synthesis of the terphenyl-based amido ligands, though, is very time-consuming and is only possible in relatively bad yields. Therefore an alternative to terphenyl-substitution was needed.

During the scholar's stay with the working group a new ligand was developed, which is shown in figure 10. The new ligand combines less steps of synthesis – in comparison to the terphenyl analogue – with the sterical hindrance required for the stabilization of the further target compounds.

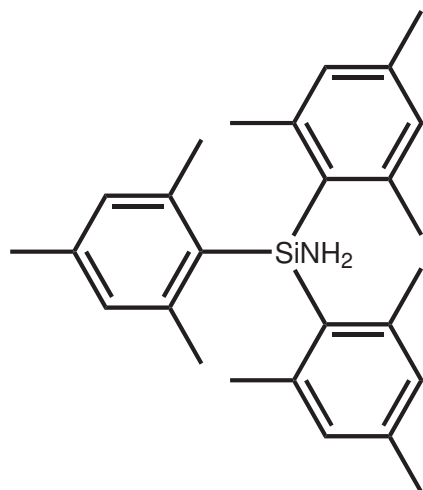


Figure 10: The target molecule: a mesityl-substituted silylamido ligand.

Literature research showed that attempts to obtain parts of the target molecule had been undertaken before. In addition, a wide range of publications on analogue structures is available. Studying these papers led to a scheme of potential reactions that were the base of the synthesis of this new ligand.

²⁴ Merrill, W.A.; Stich, T.A.; Brynda, M.; Yeagle, G.J.; Fettingner, J.C.; De Hont, R.; Reiff, W.M.; Schulz, C.E.; Britt, R.D.; Power, P.P. *J.Am.Chem.Soc.* **2009**, 12693 – 12702.

Experiments and Results

First attempts to obtain the ligand system are shown in figures 11 and 12.

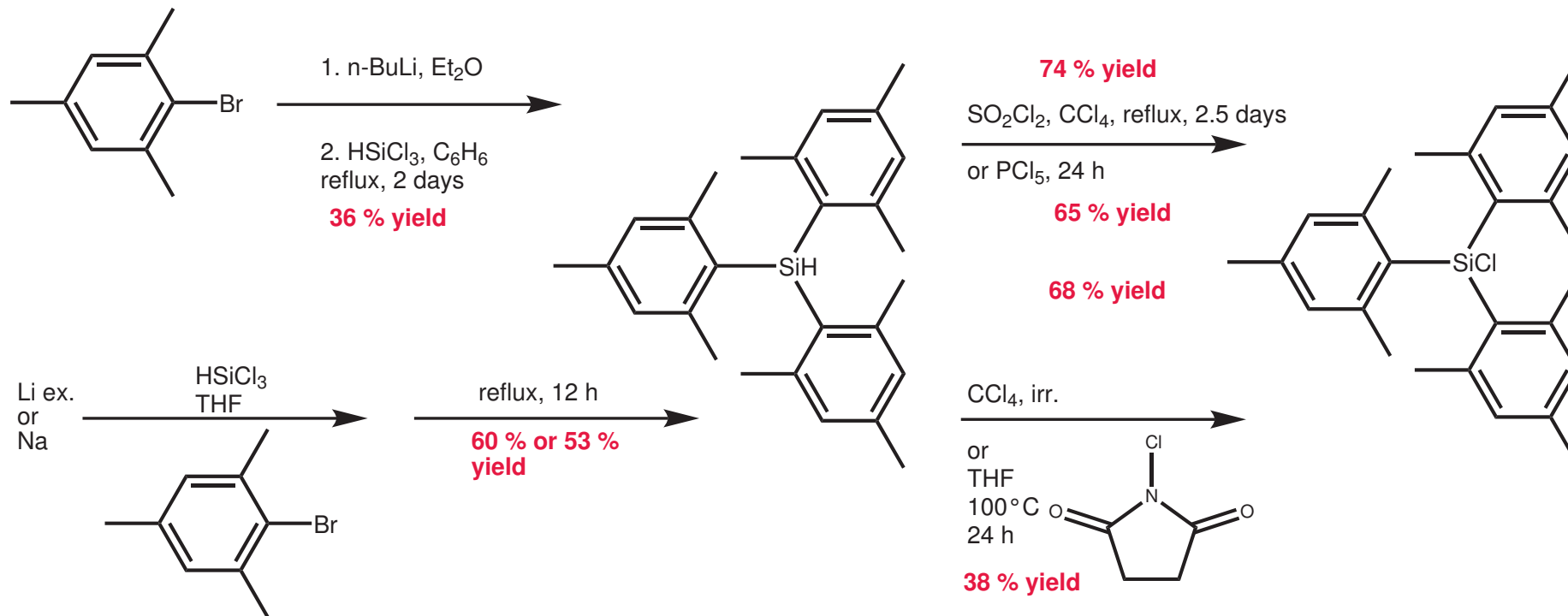


Figure 11: First reaction strategy to obtain the parent molecule Mes_3SiCl .^{25,26,27,28}

²⁵ Gynane, M.J.S.; Lappert, M.F.; Riley, P.I.; Riviere, P.; Riviere-Baudet, M. *J. Organomet. Chem.* **1980**, 5 -12.

²⁶ Turnblom, E.W.; Boettcher, R.J.; Mislow, K. *J. Am. Chem. Soc.* **1975**, 1766 – 1772.

²⁷ Lambert, J.B.; Stern, C.L.; Zhao, Y.; Tse, W.C.; Shawl, C.E.; Lentz, K.T.; Kania, L. *J. Organomet. Chem.* **1998**, 21 – 31.

²⁸ Zigler, S.S.; Johnson, L.M.; West, R. *J. Organomet. Chem.* **1988**, 187 – 198.

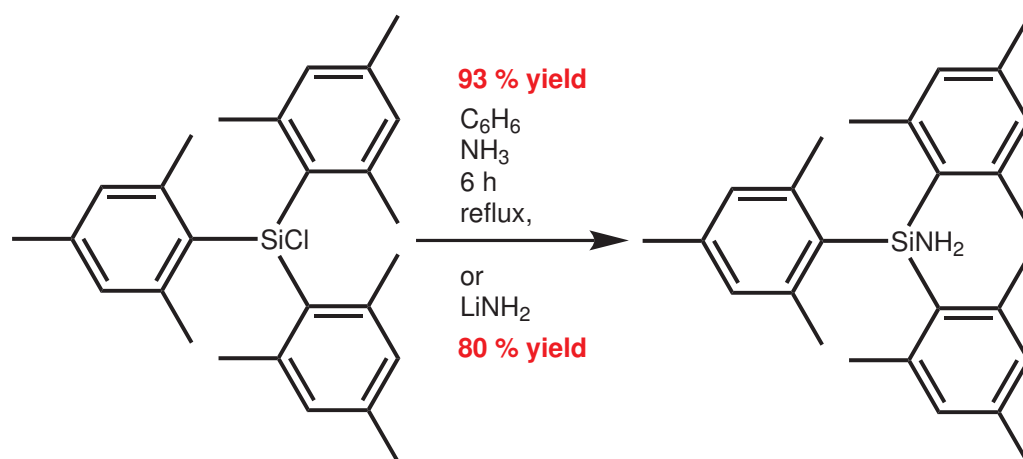


Figure 12: Planned reaction for converting the parent molecule into the target molecule.^{29,30}

While the first step of the reaction – the synthesis of the silane derivative – was performed successfully and by the reactions shown in figure 11, the synthesis of the halide derivative could not be performed with success. References found for this type of reaction had always been applied to smaller systems, e.g. Ph_3SiCl . The sterical hindrance in the target molecule of this work seems to partially prevent the reaction in the planned way.

The halide derivative was only obtained in very low yields and could not be cleaned to a degree good enough for further reactions. Therefore, the final step of the reaction (shown in figure 12) could never be performed and a new reaction pathway towards the target molecule had to be found.

In the end a better reaction pathway was found by avoiding the halide step and converting the silane directly into the amine. Further optimization will be needed to improve purity and crystal quality of the product.

²⁹ Al-Rafia, S.M.I.; Lummis, P.A.; Ferguson, M.J.; McDonald, R.; Rivard, E. *Inorg. Chem.* **2010**, 9709 – 9717.

³⁰ Lee, Banerjee, Odom, *Organometallics* **2005**.

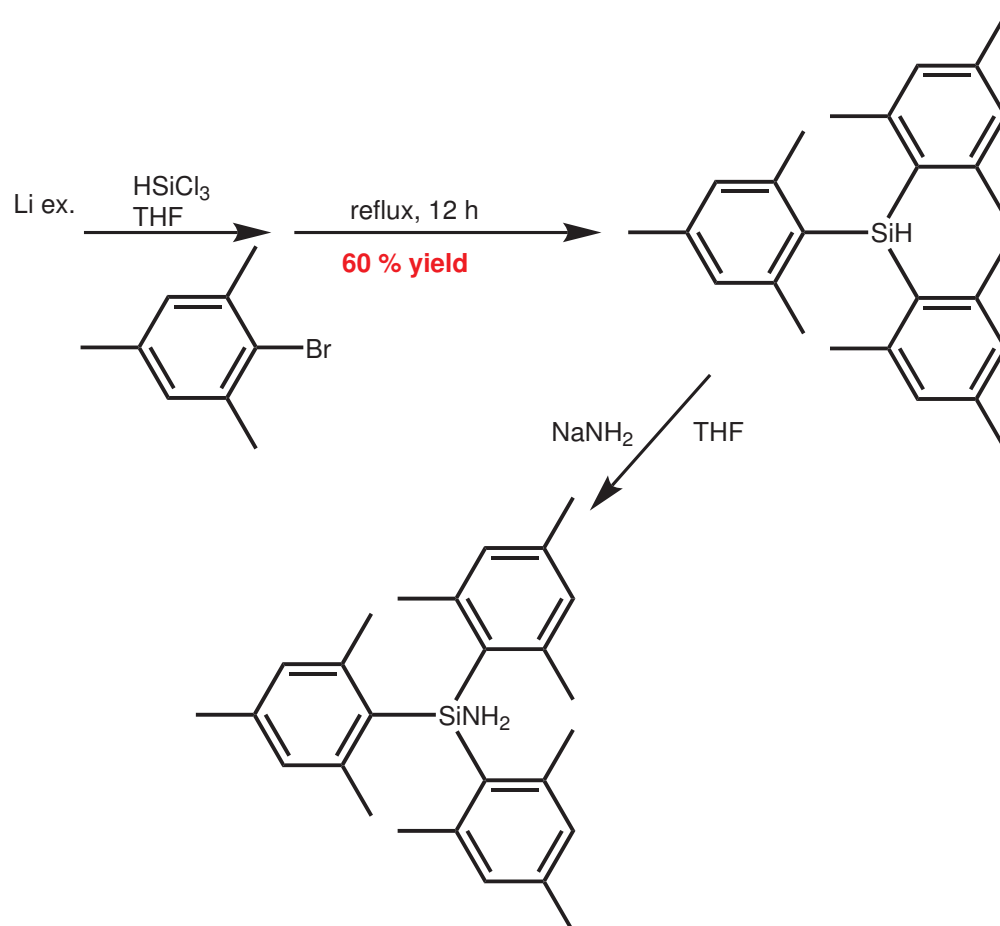


Figure 13: Final and successful reaction pathway to obtain the target molecule.^{25,31}

The reactions shown in figure 13 provide clean NMR data and yield X-Ray quality crystals. Further reactions are going to be performed by R. Alan Gamage, working at the host university.

One sample reaction, that will be the model for further research is shown in figure 14. Depending on whether or not this reaction is conducted successfully, it will pioneer a new field of ligands for both working groups.

³¹Rofouei, M.K.; Lawless, G.A.; Morsali, A.; Hitchcock, P.B. *Inorganica Chimica Acta* **2006**, 3815 - 3123.

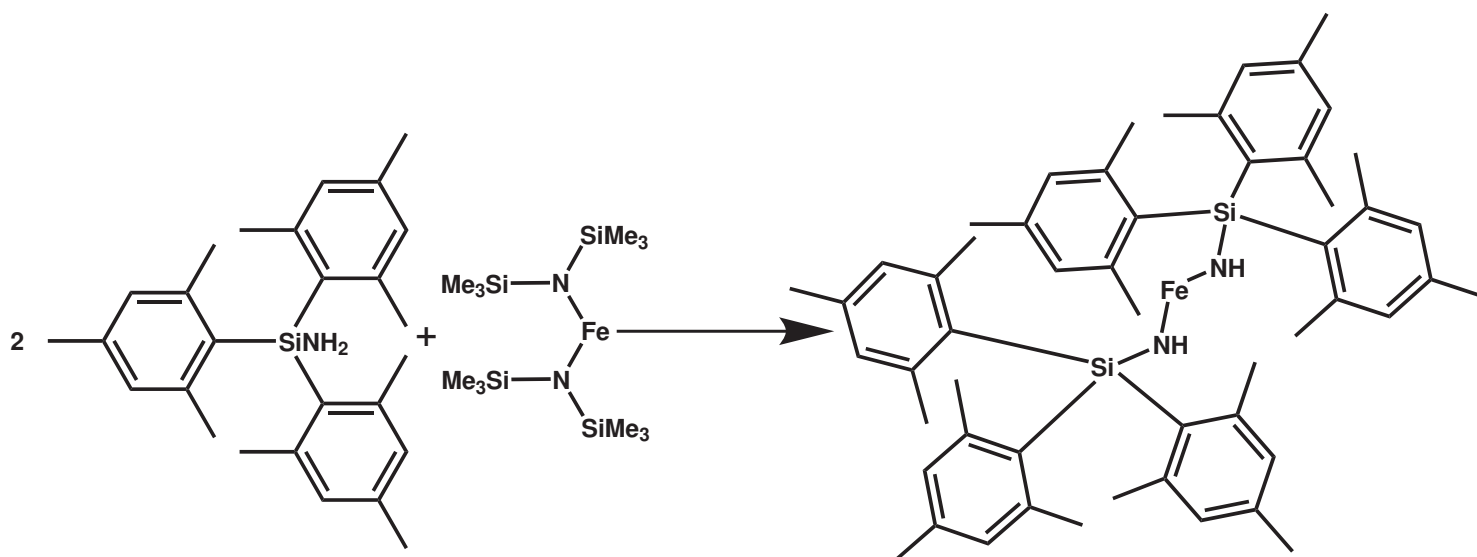


Figure 14: Future deployment of the new ligand, which is going to be performed at UC Davis.

Discussion

The new ligand Me₃SiNH₂ was successfully designed and synthesized. Further optimization of the synthesis will be performed by members of the Power group. This new ligand is the first step towards conversions of Fe{N(SiMe₃)₂}₂ with amido ligands with less synthetic effort (and therefore by deploying cheaper starting materials) than necessary for the terphenyl-based molecules. In addition further work will compare the characteristics of the two ligand systems and show differences between carbon- and silicon- substitution.

Summary

In total, the scholar's stay with the host working group was successful first of all in means of transfer of good laboratory practices. She acquired new handling techniques and gained lots of insights into transition metal chemistry, which is a field that is not being investigated at the Graz University of Technology.

In addition, the proposed reaction of the Ge containing ring system with Ni(CO)₄ was proven to be successful. Further investigations will be continued at the home university. A series of metals, metal halides and other metal carbonyls was proven to either be too reactive (destroyed the ring system) or too little reactive (did not lead to any reaction at all.)

A new ligand system replacing terphenyl groups by trimethylsilyl groups was designed and synthesized. This makes the way to Fe(II) stabilizing compounds much easier.

Furthermore the stay led to collaboration on a new paper, which is going to be published soon. This publication contains data of both working groups and has been scientifically discussed intensely during the stay. New ideas on further chemistry have been created and first steps to convert these to concrete reactions have already been undertaken.

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