August 6th - August 9th 2017
Georg-August-Universität Göttingen

AGICHEM 2017
Göttingen

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AGICHEM 2017

6th to 9th of August
2017

Anglo-German Inorganic Chemistry Meeting Göttingen

Georg-August-University Göttingen

Imprint

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Design: Alexander N. Paesch

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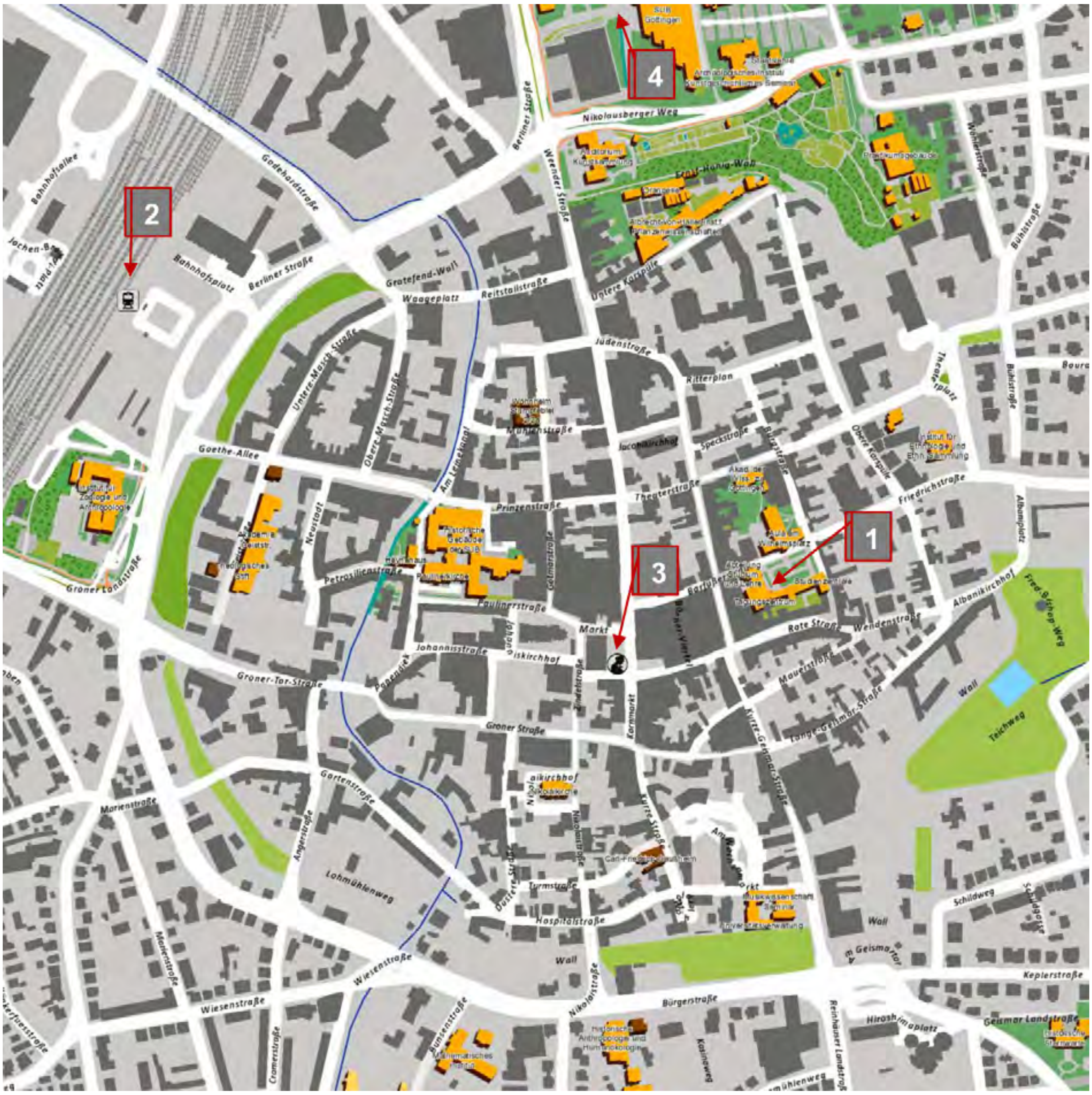
1. Welcome

The AGICHEM 2017 in Göttingen is the 10th conference of the bilateral Anglo-German inorganic chemistry meeting, founded in 1991 by the esteemed colleagues Michael Lappert, Brighton and Heinrich Nöth, München. The conference aims to amalgamate international high-profilers and young scientists in inorganic chemistry to facilitate active exchange of the latest results and promote visibility of our discipline. In times of increasing political segregation, this is particularly important, because chemistry provides general answers to global problems. Accessibility and exchange of scientific value as well as multilateral funding of increasingly expensive challenges are basic conditions to tackle today's trials like sustainable energy, food supply and mobility. In this respect, I am particularly grateful to all British and German colleagues for having accepted the invitation to come to Göttingen and share their latest results. This meeting would not have materialized without the help of the GDCh Wöhler-Vereinigung and the RSC Dalton Division. The Deutsche Forschungsgemeinschaft and der Verband der Chemischen Industrie shared the abovementioned approach and funded the meeting. Various industrial sponsors contributed to facilitate the pleasant atmosphere at the brand-new down-town convention centre "Alte Mensa". Last but not least, I am much obliged to all my staff and students working very hard to make AGICHEM 2017 a successful meeting. My secretary, Frau Heike Tappe, stands for all the others behind the scene taking care of a smooth event.

Göttingen, August 2017 Dietmar Stalke

2. Map of Göttingen



Legend:

1: Conference Hall “Alte Mensa”

2: Central Station

3: Historical Town Hall / “Gänse Liesel”

4: Central Campus

3. Plenary Speakers

Time	Speaker	Monday, August 7th

09:00 Prof. Dr. David Scheschkewitz, Universität des Saarlandes, (SB)

- PhD in chemistry from the Philipps-University of Marburg (1999)
- Postdoctoral stints in the laboratories of Professor Guy Bertrand (Paul Sabatier-University of Toulouse and University of California at Riverside) and Professor Grützmacher (ETH Zürich)
- Habilitation in the laboratories of Prof. Holger Braunschweig at the Julius-Maximilians-University of Würzburg
- Senior Lecturer Imperial College London in 2008
- 2011 Chair of General and Inorganic Chemistry at the Saar-University

His main interests concern 1) the transfer of Si=Si moieties to conjugated organic systems and studies of their chemical, physical and optical properties, 2) unsaturated yet stable small silicon clusters as well as 3) low-valent silicon-based ligands for transition metal complexes.

09:30 Prof. Simon Aldridge, The Queen's College, University of Oxford

- Undergraduate and doctoral degrees in chemistry at Jesus College, Oxford for seven years
- Two years in the USA as a Fulbright Scholar at the University of Notre Dame
- Research fellow at Imperial College London
- First academic post at Cardiff University in 1998
- Returned to Oxford in 2007 to take up current position at Queen's

His research interests are broadly in organometallic chemistry – that is the chemistry of compounds featuring bonds between carbon and a metal. Much of the work of his research group in this area is focussed either on fundamental aspects (such as how to make new types of chemical bond and discover how they react) or on applications of new compounds to real world problems (such as the design of chemical sensors or catalysts).

10:00 Prof. Dr. Berthold Hoge, Universität Bielefeld

- 1994: Diplom, Prof. R. Eujen an der Universität Wuppertal
- 1997: Promotion, Prof. R. Eujen an der Universität Wuppertal
- 1997–1998: Postdoktorandenaufenthalt, Prof. K. O. Christe, University of Southern California
- 1998–2004: Habilitation, Prof. D. Naumann an der Universität zu Köln
- 2004–2009: Privat-Dozent an der Universität zu Köln
- 2010: Professor (W2) für Anorg. Chemie an der Universität Bielefeld

Für Pentafluorethyl-Element-Verbindungen ergibt sich eine vielfältige und einzigartige Synthesechemie, die Stabilisierung Phosphiniger Säuren, elektronisch stabilisierte Stannylene, Silane als äußerst starke Lewis-Säuren.

10:30 Coffee break

11:00 Dr. Mark R. Crimmin, Imperial College London

- 2004: Graduated from Imperial College London and completed a MSc under Prof. Aggarwal
- 2008: Received his PhD in main group chemistry and catalysis from Imperial College London supervised by Prof. Mike Hill and Prof. Tony Barrett
- 2008: Awarded by the Royal Commission for the Exhibition of 1851 research fellowship which he took to UC Berkeley
- 2011: Returned to London as a Royal Society University Research Fellow, initially at UCL and now back at Imperial

His current research interests are centered around developing new organometallic catalysts for the activation of small molecules with a specific interest in compounds of the rare-earth and main group elements.

11:30 **Prof. Dr. Sjoerd Harder, Universität Erlangen-Nürnberg**

- 1990: PhD in Organic Chemistry at the University of Utrecht, Netherlands
- 1998: Private Lecturer, University of Konstanz
- 1999: Habilitation in Inorganic and Organometallic Chemistry at the University of Konstanz
- 2004: Professor of Inorganic Chemistry-C3 at the University of Duisburg-Essen
- 2010: Chair of Inorganic Chemistry at the University of Groningen, Netherlands
- 2012: Chair of Inorganic and Analytical Chemistry at the University of Erlangen-Nürnberg

Alkaline-Earth Metal Chemistry, Calcium in Polymerization, Chemistry and Catalysis, Hydrocarbon-Soluble Calcium Hydride, Hydrogen Storage Materials.

12:00 **Prof. Dr. Michael Whittlesey, University of Bath**

- 1987: BSc at the University of York
- 1991: PhD at the University of York (supervisors Prof Robin Perutz FRS and Dr Roger Mawby): topic was photochemistry of transition metal hydride complexes
- 1991–1993: PDRA at the University of Ottawa (Canada) with Prof Tito Scaiano in organic photochemistry
- 1993–1996: PDRA at the University of York with Prof Robin Perutz FRS – transition metal mediated C-F bond activation
- 1996–1999: Lecturer at the University of East Anglia
- Since 1999: University of Bath, made professor in 2011

Transition metal *N*-heterocyclic carbene complexes for activation / functionalization of small molecules, particularly with ruthenium, nickel and copper.

12:30 **Lunch Break**

14:00 PD Dr. Rajendra Ghadwal, University of Bielefeld

- 2002–2006: PhD, University of Rajasthan, Jaipur (India)
- 2007–2008: Post-Doc, University of Rajasthan, Jaipur (India)
- 2008–2010: Post-Doc, Georg-August-University Göttingen (Germany)
- 2011–2015: Habilitation, Georg-August-University Göttingen (Germany)
- Since 2015: PD at University of Bielefeld (Germany)

His research activities focus on unconventional carbon donor ligands (design and exploration), organometallic catalysis, compounds with a low-valent main-group elements (B, C, Si in particular), small molecules activation, functionalization and molecular materials for chemical energy storage.

14:30 Dr. Adrian B. Chaplin, University of Warwick

- 1998–2002: BSc, University of Massey, (New Zealand)
- 2003–2007: PhD, Docteur ès Sciences, Ecole Polytechnique Fédérale de Lausanne (Switzerland)
- 2007–2009: Junior Research Fellow, Wadham College, Oxford (UK)
- 2009–2011: EPSRC funded postdoctoral research assistant, University of Oxford, (UK)
- Since 2011: Royal Society University Research Fellow, University of Warwick, (UK)

His current research focuses on synthetic and physical chemistry of late transition metal complexes, particularly in connection with their use in small molecule activation and catalysis.

15:00 Prof. Dr. Biprajit Sarkar, Freie University of Berlin

- 2001: MSc at Indian Institute of Technology, Mumbai
- 2001–2005: PhD in Inorganic Chemistry, University of Stuttgart, (Germany)
- 2005–2006: Postdoctoral Researcher at Université Louis Pasteur, Strasbourg, (France)
- 2006–2011: Habilitation in Inorganic Chemistry at University of Stuttgart, (Germany)
- 2010: Substitute at a W2 Professor's position at the Georg-August-University of Göttingen, (Germany)
- Since 2012: Professor at the Freie University of Berlin, (Germany)

His research interests are small molecule activation, electron transfer and optically switchable molecular materials with non-innocent ligands, metal complexes of mesionic/abnormal carbenes and tripodal "click"-triazole-ligands for photochemical bond activation reactions, and magnetically switchable molecular materials.

15:30 Coffee break

16:00 Dr. Michael Ingleson, University of Manchester

- 2001–2004: PhD in organometallic chemistry at the University of Bath (UK)
- 2004–2008: Postdoctoral stays at the University of Indiana (USA) and at the University of Liverpool
- 2008: Awarded a Royal Society Research Fellowship at the University of Manchester, (UK)
- Since 2012: Reader in Chemistry at the University of Manchester, (UK)

Research in the Ingleson Group studies the fundamental and applied properties of boron compounds (particularly borocations), other main group electrophiles (particularly carbocations) and low toxicity, inexpensive transition metal catalysts (Zn, Fe).

16:30 Prof. Dr. Stephan Schulz, University of Edinburgh

- 1992: Diploma at the University of Göttingen
- 1992–1994: PhD. in Inorganic Chemistry at the University of Göttingen
- 1994–1996: Postdoctoral stay at the University of Iowa, (US)
- 1996–2001: Habilitation at the University of Bonn
- 2001–2003: Private-Lecture at University of Bonn
- 2003–2004: C3-Professorship at the University of Cologne
- 2004–2007: C3-Professor at the University of Paderborn
- Since 2007: W3-Professor at the University of Duisburg-Essen

Our preparative research works preferably focuses on organometallic main group element and transition metal compounds, with particular emphasis on the synthesis and reactivity of low-valent organometallic compounds.

17:00	**Coffee Break**

17:30 Prof. Dr. Paul Pringle, University of Bristol

- Diploma Leicester University, (UK) and his PhD at the University of Leeds, (UK)
- Lecturer at University of Warwick, (UK) for 5 years
- Since 1988 he works at the University of Bristol, (UK) and became a professor for inorganic chemistry

The research we do concerns the design and synthesis of new phosphorus(III) ligands for transition metal complexation and homogeneous catalysis.

18:00 Prof. Dr. Jan Weigand, University of Dresden


© AK Weigand

- 2002: Diploma at the University of Munich
- 2005: PhD at the University of Munich
- 2005–2007: Postdoc at the University of Halifax (Canada)
- 2007–2012: Habilitation at the University of Münster, where he became fellow of the Emmy Noether research program and obtained the ERC starting grant
- Since 2013: Professor at the University of Dresden

The research activities are focused on the development of modern and novel concepts in main group chemistry with particular emphases on reactivity studies and sustainable applications. Furthermore another research focus of Weigands group is the development and application of multifunctional ligands in coordination chemistry, solvent extraction and Heterogeneous catalysis for industrial chemistry.

Time	Speaker	Tuesday, August 8th

09:00 Prof. Dr. Stuart Macgregor, Heriot-Watt University Edinburgh

- 1988: BSc at the University of Edinburgh
- 1992: PhD at the University of Edinburgh
- 2006: Reader at the Heriot-Watt University
- Since 2009: Professor at the Heriot-Watt University, leader of the Institute of Chemical Sciences within the School of Engineering and Physical Sciences

His research activity focuses on the use of computational chemistry to model chemical structure and reactivity of transition metal systems, especially those of relevance to homogeneous catalysis and metal-mediated organic synthesis.

09:30 Prof. Dr. Axel Schulz, University of Rostock

- Diploma (1994) and PhD (1995) at the TU Berlin
- Habilitation (2001) at the Ludwig-Maximilians-University of Munich
- Since 2006: Full Professor for Inorganic Chemistry at the University Rostock

His current research focuses on the Molecule-chemistry of the group 14-17 elements, weakly coordinating anions, ionic liquids as well as metal-organic frameworks in catalysis.

10:00 Dr. Alison Parkin, University of York

- MSc (2004) and PhD (2008) at University of Oxford
- 2008–2012: Junior Research Fellow at Merton College, University of Oxford
- Since 2012: Anniversary Research Lecturer, Department of Chemistry at the University of York

Her group specializes in studying and understanding the electrochemical mechanisms which power biological systems, particularly the use of hydrogen as a bacterial fuel. Her group is developing ‘living’ electrochemistry to harness sewage microbes as hydrogen-producing catalysts which are capable of repair and self-replication.

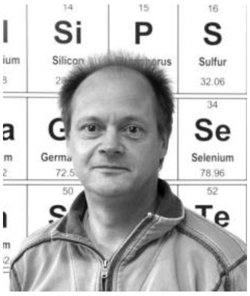
10:30 Coffee break

11:00 Jun.-Prof. Dr. Ann-Christin Pöppler, Julius-Maximilians University of Würzburg

- Diploma (2010) and PhD (2013) at the Georg-August-University of Göttingen
- 2014: Feodor-Lynen Postdoctoral Fellow at the University of Warwick
- 2014: Postdoc, Max Planck Institute for Biophysical Chemistry, Göttingen
- Since 2016: Jun.-Prof. for Organic Structural Chemistry at the University of Würzburg

One of her chemical interests focuses on the identification of structure determining properties by combining experimental solid-state NMR with first principles DFT calculation.

11:30 Dr. Alexander Steiner, University of Liverpool



- Diploma (1991) at the University of Göttingen
- PhD (1994) at the University of Göttingen

His research interests are the synthesis of new multifunctional materials including main group, supramolecular and structural chemistry as well as X-ray crystallography.

12:00 Prof. Dr. Viktoria Däschlein-Gessner, Ruhr-University of Bochum

- 2007: Diploma at the University of Würzburg
- 2009: PhD at the Department of Chemistry, TU Dortmund
- 2015: Habilitation at the University of Würzburg
- Since 2016: Chair of Inorganic Chemistry at the Ruhr-University of Bochum

Her field of activity is the application of unique carbanionic compounds in main group element and transition metal chemistry with focusing on the development of systems that exhibit versatile functionalities and unusual chemical and electronic properties to allow for new transformations and reactivities.

Time	Speaker	Wednesday, August 9th

09:00 Dr. Jennifer A. Garden, University of Edinburgh

- 2010: MSc at the University of Strathclyde
- 2014: PhD at the University of Strathclyde
- 2014–2016: Postdoctoral stay at the Imperial College London
- Since 2016: University of Edinburgh *(Christina Miller Research Fellow)*

Her research activity focuses on the design and synthesis of new homo- and heterometallic complexes, and their application towards real world challenges.

09:30 Prof. Dr. Stefanie Dehnen, Philipps-Universität Marburg

- 1993: Diploma at the University of Karlsruhe (KIT)
- 1996: PhD at the University of Karlsruhe (KIT)
- 2004: Habilitation in Inorganic Chemistry at the University of Karlsruhe (KIT)
- Since 2006: Full Professor for Inorganic Chemistry at the Philipps University of Marburg

Her current research interests comprise synthesis, formation mechanisms, stability and reactivity of binary and ternary chalcogenidometalate anions, organotetrel chalcogenide compounds, binary Zintl anions and ternary intermetalloid clusters.

10:00 Dr. Charles O’Hara, University of Strathclyde, Glasgow

- BSc (2000) and PhD (2004) at University of Strathclyde
- 2005–2006: Postdoctoral stay at University of Bath
- 2006–2011: Lecturer in Inorg. Chem. at the University of Strathclyde
- Since 2011: Senior Lecturer in Inorg. Chem. at the University of Strathclyde *(EPSRC Career Acceleration Fellow)*

His research focuses on the synthesis and structural chemistry of main group organometallic compounds, particularly those that contain two distinct metals.

10:30 Coffee break

11:00 Prof. Dr. Wolfgang Schnick, Ludwig-Maximilians-Universität München

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- 1983: Diploma at University of Hannover
- 1986: PhD at University of Hannover
- 1992: Habilitation in Inorg. Chem. at the University of Bonn
- 1993–1998: Professor for Inorg. Chem. at the University of Bayreuth
- Since 1998: Professor for Inorganic Solid-State Chem. at the University of Munich

His research interests are dedicated to the discovery, development and application of novel functional materials based on nitrides and oxonitrides of group 13–15 elements in combination with alkali, alkaline earth, rare earth metals or hydrogen.

11:30 Prof. Dr. Simon Parsons, University of Edinburgh

- 1987: BSc at the University of Durham
- 1991: PhD at the University of New Brunswick
- 1991–1993: postdoctoral stay at the University of Oxford
- 1993–2007: Postdoctoral stay, Staff Crystallographer, Lecturer then Reader at the University of Edinburgh
- Since 2007: Professor of Crystallography at the University of Edinburgh

His research interests are high pressure crystallography, structural chemistry, X-ray and neutron diffraction, structure of materials, single crystal and powder diffraction, twinning.

12:00 Prof. Dr. Claudia Wickleder, Universität Siegen

- 1989: Diploma at the University of Hannover
- 1995: PhD at the University of Hannover
- 1995–1997: Postdoc at the University of Bern
- 1998–2004: Habilitation in Inorg. Chem. at the University of Cologne
- Since 2004: Professor of Inorg. Chem. at the University of Siegen

Her fields of activity are inorganic solid state and coordination chemistry, research on optical properties of different systems and the development of materials for illuminating technics and photovoltaic.

12:30 Prof. Dr. Claire J. Carmalt, University College London

- 1992: BSc at the University of Newcastle upon Tyne
- 1995: PhD at the University of Newcastle upon Tyne
- 1995–1997: Postdoc at the University of Texas at Austin
- 1997–2002: Lecturer at the University College London (UCL) *(Royal Society Dorothy Hodgkin fellowship)*
- 2002–2004: Senior Lecturer (UCL)
- 2004–2009: Reader (UCL)
- Since 2009: Professor of Inorganic Chemistry (UCL)

Research in developing innovative new routes to inorganic materials within her group includes the synthesis of novel molecular precursors, deposition of films using chemical vapour, spray and atomic layer deposition, formation of superhydrophobic surfaces and deposition of transparent conducting oxide and photocatalytic thin films.

4. Oral Contributions

Functionalisation and stepwise expansion of stable unsaturated silicon clusters (siliconoids)

P. Willmes, K. Abersfelder, Y. Heider, K. Leszczyńska, M. Zimmer, V. Huch,
and D. Scheschkewitz*

Saarland University, Krupp-Chair for General and Inorganic Chemistry,
66123 Saarbrücken, Germany
scheschkewitz@mx.uni-saarland.de

The industrial preparation of bulk silicon is arguably one of the most important scientific developments of the 20th century; the progress in microprocessor performance would be difficult to imagine without silicon as readily available key component. The understanding and the manipulation of silicon surfaces[1] are key aspects of silicon-based technologies.

Stable molecular siliconoids are unsaturated neutral silicon clusters that exhibit typical features of silicon nanoparticles and surfaces, in particular the presence of one or more unsubstituted vertices.[2] Functionalised vertices are a prerequisite for the embedding of siliconoids in extended assemblies. However, only unfunctionalised siliconoids have been reported since very recently, severely limiting further developments in this regard. Conversely, the well-known Zintl anions of silicon are carry several anionic charges (and thus potential functionalisation sites), but suffer from their very high reduction potential as well as the low solubility due to the absence of organic substituents.[3]

Here we report the synthesis and isolation of intermediate species between silicon-based Zintl phases and siliconoids, prepared by the site-selective reductive cleavage of aryl groups. As demonstrated by reactions with electrophiles of Groups 13 to 15, these anionic siliconoids efficiently transfer the Si_6 motif to various substrates, while maintaining the integrity of the unsaturated cluster scaffold. On the other hand, with suitable substrates a targeted preparative expansion of the cluster scaffold can be achieved.

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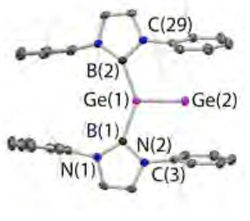
2. (a) D. Scheschkewitz, *Angew. Chem. Int. Ed.* **2005**, *44*, 2954. (b) G. Fischer, V. Huch, P. Mayer, S. K. Vasisht, M. Veith, N. Wiberg, *Angew. Chem. Int. Ed.* **2005**, *44*, 7884. (c) K. Abersfelder, A. J. P. White, H. S. Rzepa, D. Scheschkewitz, *Science* **2010**, *327*, 564. (d) D. Nied, R. Köppe, W. Klopper, H. Schnöckel, F. Breher, *J. Am. Chem. Soc.* **2010**, *132*, 10264. (e) K. Abersfelder, A. J. P. White, R. J. F. Berger, H. S. Rzepa, D. Scheschkewitz, *Angew. Chem. Int. Ed.* **2011**, *50*, 7936. (f) K. Abersfelder, A. Russell, H. S. Rzepa, A. J. P. White, P. R. Haycock, D. Scheschkewitz, *J. Am. Chem. Soc.* **2012**, *134*, 16008. (g) A. Tsurusaki, C. Iizuka, K. Otsuka, S. Kyushin, *J. Am. Chem. Soc.* **2013**, *135*, 16340. (h) A. Tsurusaki, J. Kamiyama, S. Kyushin, *J. Am. Chem. Soc.* **2014**, *136*, 12896. (i) T. Iwamoto, N. Akasaka, S. Ishida, *Nature Comm.* **2014**, *5*, 5353.
3. S. Scharfe, F. Kraus, S. Stegmaier, A. Schier, T. F. Fässler, *Angew. Chem. Int. Ed*. **2011**, *50*, 3630.

Designing Main Group Systems for Small Molecule Activation and Functionalization

Andrey Protchenko, Arnab Rit, Robert Mangan, Matthew Usher, Do Dinh Cao Huan, and Simon Aldridge*
Inorganic Chemistry Laboratory, South Parks Road, Oxford, UK, OX1 3QR
simon.aldridge@chem.ox.ac.uk

Oxidative E-H bond activation processes represent key mechanistic steps in numerous catalytic reactions. Classically such activation is brought about utilizing the readily accessible *n*/*n*+2 redox states of ‘noble’ transition metals. Of late, economic and environmental imperatives have driven the development of alternative systems for small molecule activation. In recent work we have been examining approaches based on Group 13 and 14 metals and present recent results involving the activation and functionalization of H-H, N-H and O-H bonds.[1,2]

Oxidative bond activation at mono-metallic Group 13/14 complexes (e.g. heavier analogues of carbenes) depends critically on the energies of the respective frontier orbitals. With this in mind we have been employing the very strongly σ-donating boryl ligand as a means of elevating the HOMO energy and thereby developing reactive systems with small HOMO-LUMO gaps. We have developed a range of carbene and vinylidene analogues featuring low-valent Si, Ge or Sn centres (e.g. **I**), which activate protic, hydridic and non-polar E-H bonds.[3,4] In the case of the activation of ammonia at tin, N-H oxidative addition can be shown to be followed by reductive elimination to give an N-borylated product. From a mechanistic viewpoint, a non-conventional N-H activation pathway (occurring via a 2-step coordination/proton transfer process) can be shown to be viable through the isolation of potential intermediate species (e.g. **II**, **III**).[3]



I

II

III

1. A.V. Protchenko, K.H. Birjkumar, D. Dange, A.D. Schwarz, D. Vidovic, C. Jones, N. Kaltsoyannis, P. Mountford, S. Aldridge, *J. Am. Chem. Soc.* **2012**, *134*, 6500. 2. (a) J.A.B. Abdalla, I.M. Riddlestone, R. Tirfoin, S. Aldridge, *Angew. Chem. Int. Ed.* **2015**, *54*, 5098; (b) A.V. Protchenko, D. Dange, M.P. Blake, A.D. Schwarz, C. Jones, P. Mountford, S. Aldridge, *J. Am. Chem. Soc.* **2014**, *136*, 10902. 3. A.V. Protchenko, J.I. Bates, L.M. Saleh, M.P. Blake, E.L. Kolychev, A.L. Thompson, C. Jones, P. Mountford, S. Aldridge, *J. Am. Chem. Soc.* **2016**, *138*, 4555. 4. A. Rit, J. Campos, H. Niu, S. Aldridge, *Nature Chem.* **2016**, *8*, 1022.

Perfluoroethylsilanes

Berthold Hoge, N. Schwarze, S. Steinhauer
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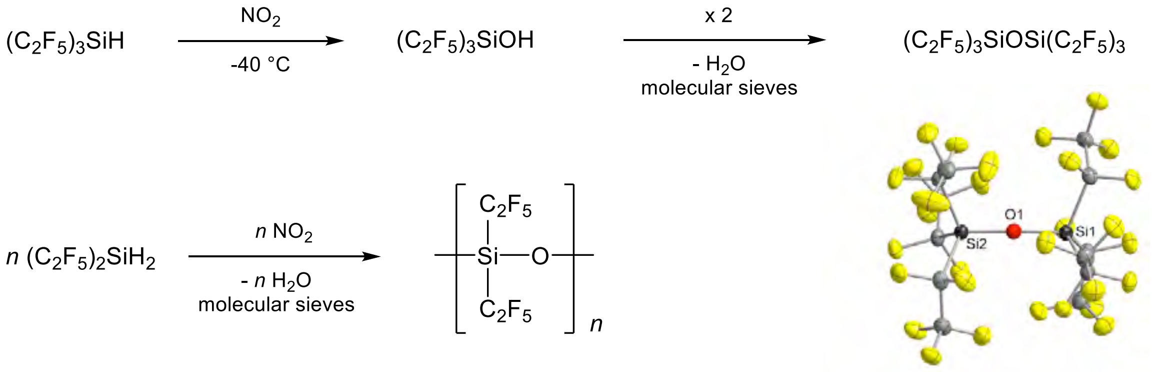
Universitätsstr. 25, 3615 Bielefeld, Germany
b.hoge@uni-bielefeld.de

Recently we reported on the successful synthesis of thermally stable tris- and tetrakis(pentafluoroethyl)silanes and -silicates.[1] The corresponding trifluoromethyl silicon derivatives are barely known, due to the high fluorophilicity of the silicon centre as well as the high stability of difluorocarbene.[2]

Although tris- and tetrakis(pentafluoroethyl)silanes exhibit a remarkable thermal stability, they tend to hydrolyze to Si-OH moieties, which is accompanied by the liberation of pentafluoroethane. Therefore, all attempts to synthesize polymeric bis(pentafluoroethyl)silicone, $[Si(C_2F_5)_2O]_n$, via the treatment of $(C_2F_5)_2SiCl_2$ with water led to a complex reaction mixture due to hydrolysis. Just as well, reaction of $(C_2F_5)_3SiCl$ with water did not yield the desired disiloxane $(C_2F_5)_3SiOSi(C_2F_5)_3$.

Finally, the oxidation of $(C_2F_5)_3SiH$ with NO_2 at low temperatures allows the characterization of $(C_2F_5)_3SiOH$. Due to its high condensation tendency, increased temperatures lead to a decomposition via hydrolysis, caused by the generated H_2O. However, the oxidation of $(C_2F_5)_3SiH$ and $(C_2F_5)_2SiH_2$ in the presence of molecular sieves allows the isolation of $(C_2F_5)_3SiOSi(C_2F_5)_3$ and generation of polymeric bis(pentafluoroethyl)silicone resins, $[Si(C_2F_5)_2O]_n$.



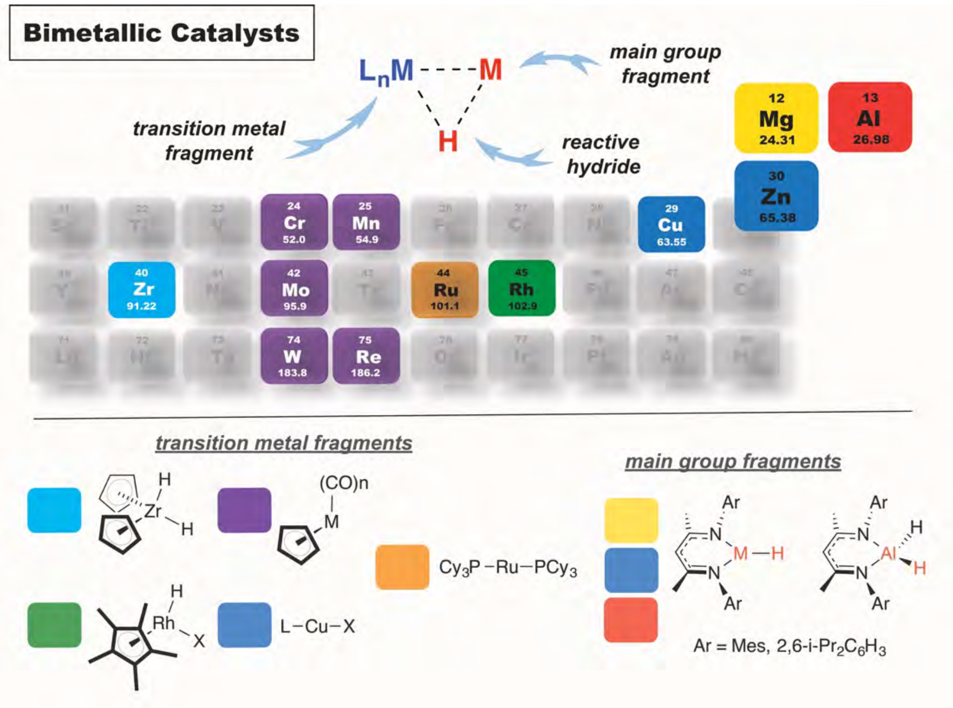
1. a) S. Steinhauer, B. Hoge, B. Neumann, H.-G. Stammler, N. Ignat'ev, *Angew. Chem. Int. Ed.,* **2014**, *53*, 562–564; b) S. Steinhauer, J. Bader, H.-G. Stammler, N. Ignat'ev, B. Hoge, *Angew. Chem. Int. Ed.,* **2014,** *53,* 5206–5209; c) T. Böttcher, S. Steinhauer, B. Neumann, H.-G. Stammler, G.-V. Röschenthaler, B. Hoge*, Chem. Commun.,* **2014,** *50,* 6204–6206; d) S. Steinhauer, T. Böttcher, N. Schwarze, B. Neumann, H.-G. Stammler, B. Hoge, *Angew. Chem. Int. Ed.,* **2014**, *53,* 13269–13272; e) B. Hoge, S. Steinhauer, N. Ignatyev, M. Schulte, *WO **2013**/150448 A1*, BASF SE, Ludwigshafen; f) B. Hoge, S. Steinhauer, N. Ignatyev, M. Schulte, *DE 10 **2012** 006896 A1*, Merck Patent GmbH, Darmstadt.
2. For example: H. Beckers, *PhD Thesis*, Bergische Universität GHS Wuppertal, Wuppertal, **1987**.

Developing Heterobimetallic Hydride Complexes for Catalysis

Olga Ekkert, Michael J. Butler, Mark R. Crimmin

While heterobimetallic complexes have been in-and-out of vogue, there is a growing body of work that suggests they may offer some advantages over their monometallic counterparts in catalysis.

Here we present studies in to the interaction of heavier main group hydrides (M = Al, Zn, Mg) with transition metals. For example, zinc hydrides react non-reversible with a series of transition metal carbonyl complexes, along with coordinatively unsaturated ruthenium complexes bearing phosphine ligands. Some applications of these, and related, complexes will be discussed.



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2. A. E. Nako, Qian Wen Tan, A. J. P. White, M. R. Crimmin, *Organometallics* **2014**, *33*, 2685. (*cover article*)
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Early Main Group Metal Hydrides: Synthetic Challenge, Structures and Hydrogen Storage

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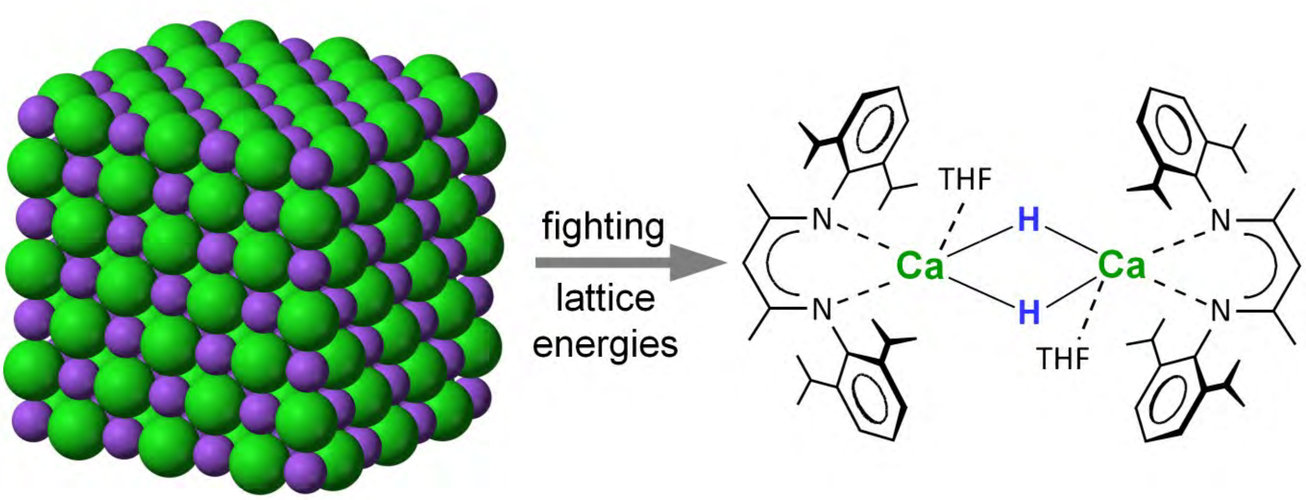
Transition metal hydride complexes boast a long history. They represent key intermediates in crucial industrial processes like catalytic hydrogenation or hydroformylation.

In sharp contrast stands the chemistry of group 1 and 2 metal hydrides that were formerly only known as salt-like compounds of formula $(MH)_\infty$ or $(MH_2)_\infty$. The last decade, however, has seen major developments in the challenging syntheses of their well-defined, hydrocarbon-soluble, metal hydride complexes.[1,2] This sudden change from peculiarity to well-defined compound class is fuelled by the recent development of early main group metal catalysis and a strongly increased interest of polar metal hydrides as hydrogen storage devices. Herein, we discuss our latest developments in this chemistry.



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Bond Activation Reactions by Nucleophilic and Electrophilic Transition Metal Hydride Complexes

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We have recently begun to probe the reactivity of two ruthenium N-heterocyclic carbene (NHC) hydride complexes, $[Ru(IMe_4)_4H_2]$ (IMe_4 = 1,3,4,5-tetramethylimidazol-2-ylidene), and $[Ru(IPr)_2(CO)H][BAr^F_4]$ (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene). As a result of their trans arrangement, the hydride ligands in $[Ru(IMe_4)_4H_2]$ are strongly nucleophilic, leading to unusual C-F[1] and C-O bond activation reactions. In contrast, the cationic IPr complex[2] bears a strongly electrophilic hydride ligand, and has been shown to eliminate ethane upon treatment with $ZnEt_2$ to afford the novel heterobimetallic Ru-Zn complex, $[Ru(IPr)_2(CO)ZnEt][BAr^F_4]$.[3] The reactivity of $[Ru(IPr)_2(CO)H][BAr^F_4]$ and analogues with less bulky NHCs towards a range of ZnR_2 reagents, as well as p-block element alkyl compounds, will be described.

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Carbon-Donor Ligands beyond Classical NHCs in Service of Main Group Chemistry and Organometallic Catalysis

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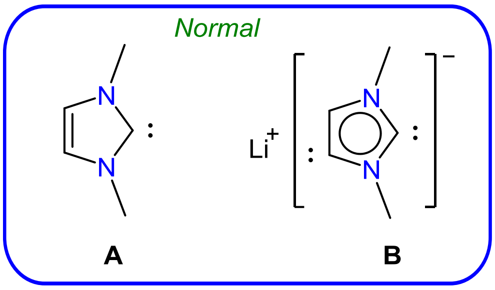
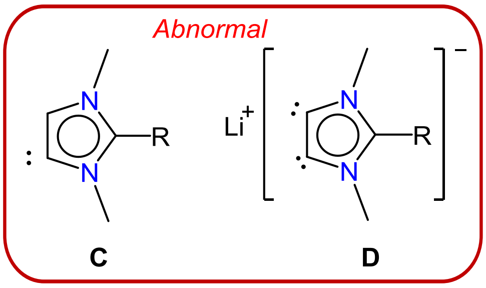
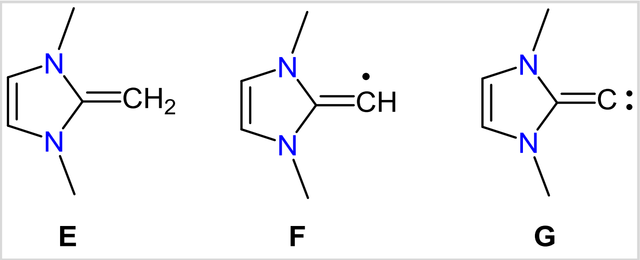




N-Heterocyclic carbenes (NHCs) (**A**) are very versatile carbon-donor neutral ligands that have made significant advances in catalysis and main group chemistry. The success of NHCs further prompted interest in the development of new sets of carbon-donor ligands. Abnormal-NHCs (aNHCs) (**C**)[1] are stronger σ-donors than classical NHCs (**A**) and hence offer substantial promises as ligands.[2] Ditopic carbanionic-NHCs (dc-NHCs) (**B**), provide a unique platform to preparing heteronuclear metal complexes as well as allow indirect access to aNHC-compounds.[3] The coordination sites (1,3-positions) of **B** are however remotely located, and therefore the related complexes exhibit independent or sequential rather than truly synergetic bond activation reactivity. In this context, anionic 1,2-dicarbenes such as dc-aNHC (**D**), albeit very rare entities,[4] are extremely appealing in order to incorporate the cooperativity effect of two metal centers in catalysis.



N-Heterocyclic olefins (**E**), vinlys (**F**), and vinylidenes (**G**) comprise other unconventional carbon-donor ligands that hold enormous promises.[2b] Applications of these ligands in the stabilization of compounds featuring a low-valent main group element will be presented.

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Organometallic chemistry and bond activation reactions employing bioxazoline-derived *N*-heterocyclic carbenes

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Understanding the structure and onward reactivity of coordinatively unsaturated transition metal complexes is of fundamental interest due to the important role these species play in many catalytic reactions. Reflecting the increasing prevalence of NHC ligands in transition metal catalysis,[1] the organometallic chemistry of low-coordinate NHC complexes is a particularly topical area. The ability of unsaturated metal complexes containing NHC ligands to undergo cyclometalation *via* C–H bond activation of alkyl and aryl appendages, however, represents a notable limitation for their isolation and subsequent investigation. Observing that substituent flexibility is key requirement for cyclometalation reactions of NHC ligands, we describe our work exploring the organometallic chemistry of rhodium and iridium complexes of Glorius' conformationally rigid bioxazoline-derived NHC ligand IBioxMe$_4$.[2,3]

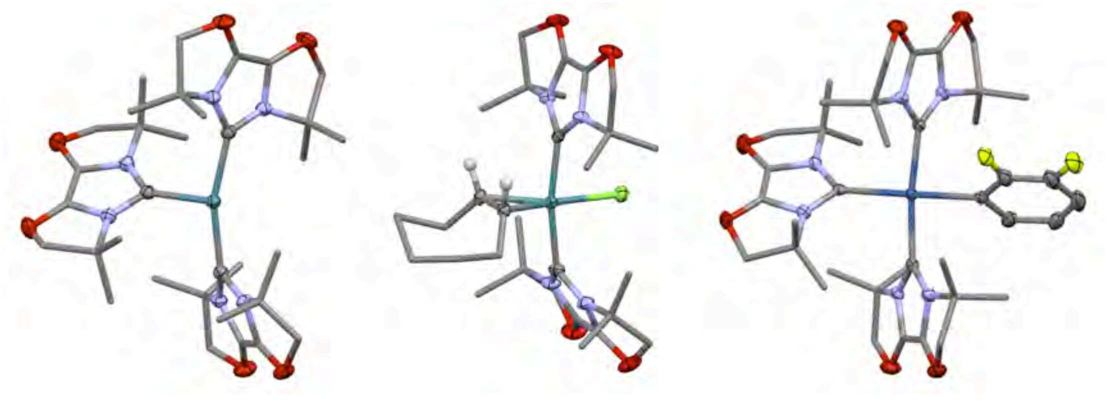

Figure 1. Structures of [Rh(IBioxMe$_4$)$_3$]$^+$, [Rh(IBioxMe$_4$)$_2$(C$_8$H$_{14}$)Cl], [Ir(IBioxMe$_4$)$_3$(H)(C$_6$H$_4$F$_2$)]$^+$.

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Redox-active Mesoionic Carbenes for Redox-Switchable Catalysis

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Mesoionic carbenes are currently hugely popular as ligands in organometallic chemistry and homogeneous catalysis.[1] In this contribution, we will report on a variety of mesoionic carbene ligands of the triazolylidene type that are redox-active.[2] Attempts to determine the donor strengths of these carbenes as a function of their redox-states will be reported. The use of electrochemical and spectroscopic methods for the determination of the aforementioned properties will be discussed. Finally, we will report on redox-switchable catalysis with Au(I) complexes for the synthesis of various heterocycles,[3] electrocatalytic H_2 production at extremely low overpotentials and high turnover frequencies with Co(III) complexes,[4] and the use of Re(I) complexes for electrocatalytic CO_2 reduction.[5] The redox-activity of the mesoionic carbenes, and the influence of the redox properties on the catalytic activity of the metal complexes will be the main focus of this contribution.

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Strong Zinc Electrophiles for Facilitating C-C Bond Formation

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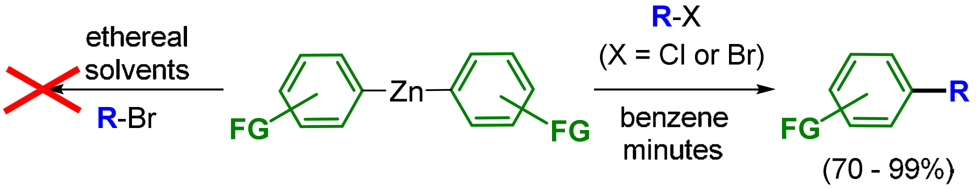
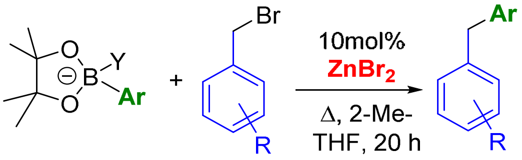
Cross coupling reactions, such as the Suzuki-Miyaura reaction have transformed synthetic chemistry offering facile and reliable methodologies to construct C-C bonds.[1] Historically, cross coupling chemistry has been dominated by Pd and Ni based catalysts, however, both of these metals have significant toxicity issues.[2] The two transition metals with lowest concern from a human exposure perspective are Fe and Zn, and compounds based on the former have received considerable attention and are now established as effective catalysts for cross coupling reactions.[3] However, catalytic in zinc cross coupling methodologies are extremely rare, with only one previous report to the best of our knowledge, a zinc catalysed Kumada coupling.[4] Building on our initial discovery of a zinc mediated C-C cross coupling reaction,[5] we will present our recent studies into developing and understanding a catalytic in zinc Suzuki-Miyaura cross coupling reaction.[6]

Stoichiometric in Zinc.[5]



Using substoichiometric $ZnBr_2$.[6]



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Radicals and Polyanions in Heavy Group 15 Element Chemistry

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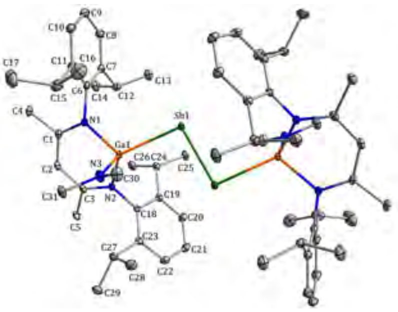
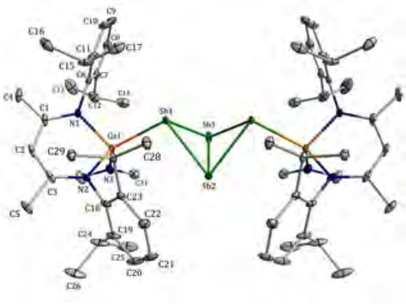
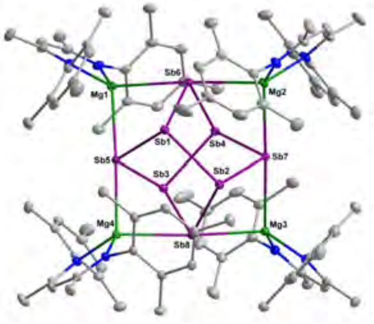
We will report on reduction reactions of metal organic complexes of heavy group 15 elements R_xE (Sb, Bi) with different low-valent main group metal complexes, which serve as one- and two-electron reductants such as RM (M = Al, Ga, In) and R_2Mg_2. The influence of the formal oxidation state of the group 15 reagents (+I, +II, +III) as well as the crucial role of the reductants on the formed reaction products will be summarized and the solid state structures as well as bonding situations of the resulting complexes, which were analyzed by quantum chemical calculations, will be discussed.







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Unconventional Phosphorus Ligands for Catalysis

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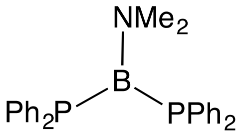
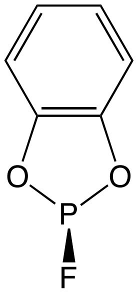
For over half a century, phosphorus(III) ligands containing a combination of P–C, P–O and P–N bonds have been at the heart of landmark developments in organometallic chemistry and homogeneous catalysis.

Here we report ligands containing P–B or P–F bonds (examples shown below) which push the boundaries of P-ligands that can coordinate to transition metals and be applied in homogeneous catalysis. The routes to these exotic ligands often involve P/Si exchange reactions which are simple to carry out, high yielding and remarkably chemoselective. The mechanisms of the P/Si exchange along with the unusual chemistry of the new ligands will be discussed.





***S**yn**P**hos: From Synthesis to Application*

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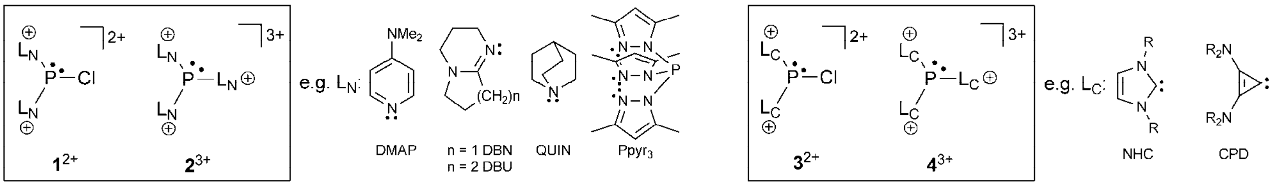
Fundamental research allows us to find new, economically and ecologically attractive ways to meet current challenges. The uncertainty of available phosphorus resources is an urgent concern. Unlike oil, which is lost once used, phosphorus can be recovered and used over and over again or at least transformed into other P-compounds of chemical use. The intention of our research is to contribute to the field of synthetic chemistry both, inorganic and organic, by identifying and developing highly-reactive phosphorus reagents that can be potentially regenerated. In particular, we are interested in *Weiss-type compounds* which are containing N– (**1**$^{2+}$, **2**$^{3+}$) or C–based (**3**$^{2+}$, **4**$^{3+}$) ligands which we call *S*yn*P*hos reagents.



We are entering new avenues of phosphorus chemistry and address fundamental questions to develop new applications which can also be extended to the heavier group 15 congeners. Using those novel and powerful *S*yn*P*hos reagents, new concepts for more efficient, selective and sustainable synthetic procedures are developed. Our research also intends to develop greener and more efficient processes and, whenever possible, to recover the phosphorus after the reaction. Thus, novel phosphorus-based compounds can be used in the recovery of industrial waste by-products such as phosphane oxides and, therefore, have a positive impact on certain chemical industries and the environment.

Acknowledgement: We thank the European Research Council (ERC starting grand, SynPhos - 307616) for financial support.

Modelling Structure and Reactivity of σ-Alkane Complexes in the Solid State

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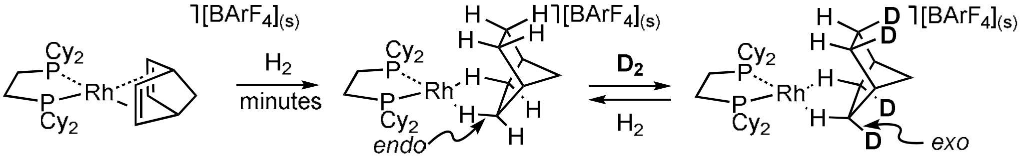
σ-alkane complexes have long been postulated as intermediates on the reaction pathway for C-H activation.[1] Such species are, however, notoriously unstable, making the direct observation of their reactivity extremely challenging. A step change in this area has come from the use of gas-solid reactivity developed by the Weller group as a means to prepare stable σ-alkane complexes.[2] Thus exposure of the alkene precursor $[(Cy_2P(CH_2)_2PCy_2)Rh(NBD)]BAr^F_4$, **1** (NBD = norbornadiene, $Ar^F = 3,5\text{-}(CF_3)_2C_6H_3$)), to H_2 gas effects a crystal-to-crystal transformation to give the corresponding σ-alkane $[(Cy_2PCH_2CH_2PCy_2)Rh(NBA)]BAr^F_4$, **2** (NBA = norbornane). **2** proves to be stable for months allowing for its detailed spectroscopic characterization and reactivity studies.



1 **2** **2-*d₄***

This contribution will detail our use of periodic DFT calculations to model the formation, structure and reactivity of **2**. In particular the observation of reversible H/D exchange in **2** links a σ-alkane complex directly to a C-H bond activation event. Intriguingly, however, this occurs at the *exo*-positions implying significant rearrangement of the NBA ligand within the crystal lattice. The modelling of these process will be described along with parallel experimental studies that elucidate the details of these processes.[3]

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Activation of Small Molecules by Biradicaloids

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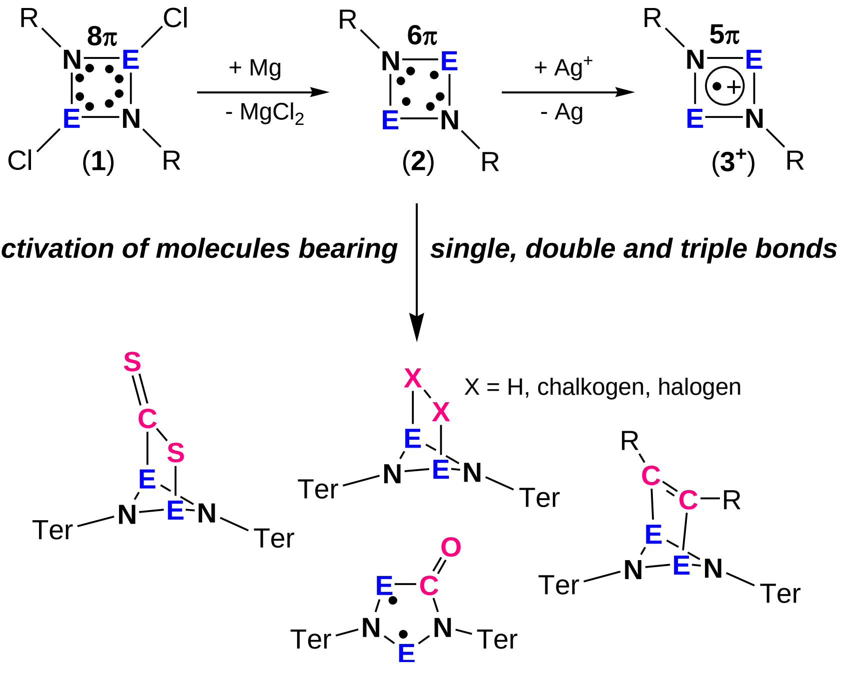
This lectures deals with the synthesis and full characterization of biradicaloids of the type [E(*m*-NTer)]$_2$ (E = element of group 15, Scheme 1 species **2**).[1-3] The reactivity of these biradicaloids **2** was employed to activate small molecules bearing single, double and triple bonds (Scheme 1). Addition of chalcogens (O_2, S_8, Se_x and Te_x) led to the formation of dichalcogen bridged E_2N_2 heterocycles. In formal [2πe+2πe] addition reactions small unsaturated compounds such as ethylene, acetylene, acetone, acetonitrile, tolane, diphenylcarbodiimide, and bis(trimethylsilyl)sulfurdiimide are readily added to the E_2N_2 heterocycle of the biradicaloid **2** yielding novel heteroatom cage compounds. The reaction with CO and isonitriles led to the formation of new cyclic 5-membered heterocycles featuring also biradical character. Oxidation with silver salts gave stable cyclic radical cations (**3**$^+$).



Scheme 1. Activation of small molecules by biradicaloids.

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New Electrochemical Methods for Understanding Biological Redox Chemistry

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Biology produces many inspirational catalysts that ‘activate’ small, inert, molecules such as protons, N_2 and H_2O via redox chemistry catalysed at transition metal active sites. Such enzymes are used in novel clean-energy technologies such as enzyme fuel cells and solar water-splitting devices. The Parkin group is developing protein film Fourier Transform Voltammetry (PF-FTacV) as a tool to study these bio-catalysts in collaboration with Prof Alan Bond (Monash). This talk will showcase recent work carried out on [NiFe]-hydrogenases. Although an “O_2-tolerant” subset of enzymes offer the tantalizing ability to remain catalytically active at oxidizing H_2 in air, they are unfortunately very poor H_2 production (H^+ reduction, $2H^+ + 2e^- \rightarrow H_2$) catalysts. By combining electrochemistry, molecular biology and structural studies we have been able to prove that it is the electron-transfer relay of iron-sulfur centres, not the active site ligands, which play a vital role in controlling O_2 inhibition and catalytic bias. We are now exploring why this happens using PF-FTacV and unpublished results will demonstrate our progress in probing electron transfer centres that are invisible via all previous experiments using electron paramagnetic resonance and “traditional” direct current protein film voltammetry. New advances in electrode surface modifications are also described.[6]

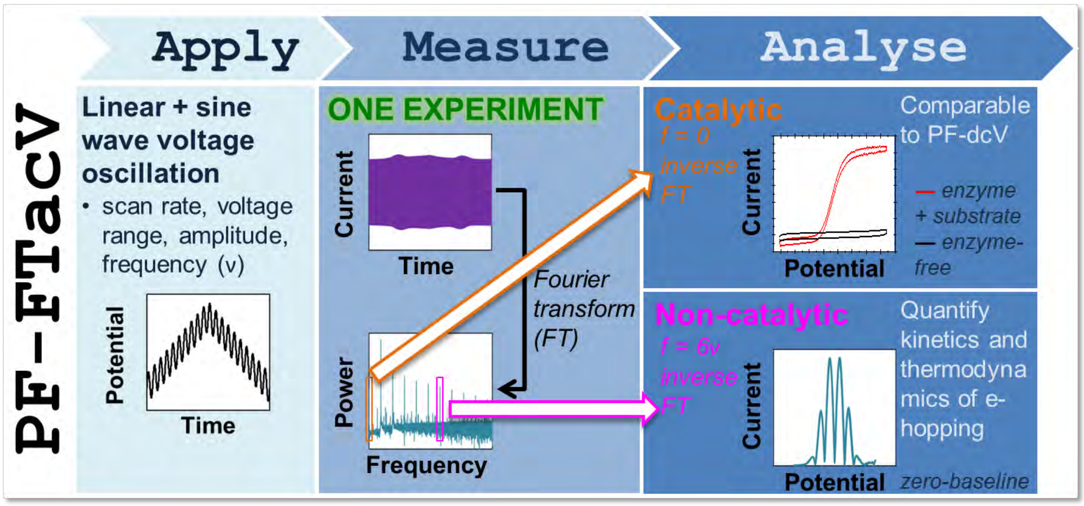

Figure 1 Overview of the technique of protein film Fourier transform alternating current voltammetry, PF-FTacV.

Identification of Structure Determining Properties by NMR Crystallography

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In the field of structure elucidation, NMR crystallography, the combination of experimental solid-state NMR and first principles DFT calculations, is highly complementary to existing diffraction approaches and can be successfully applied to a wide range of different chemical compounds and materials.[1-3]

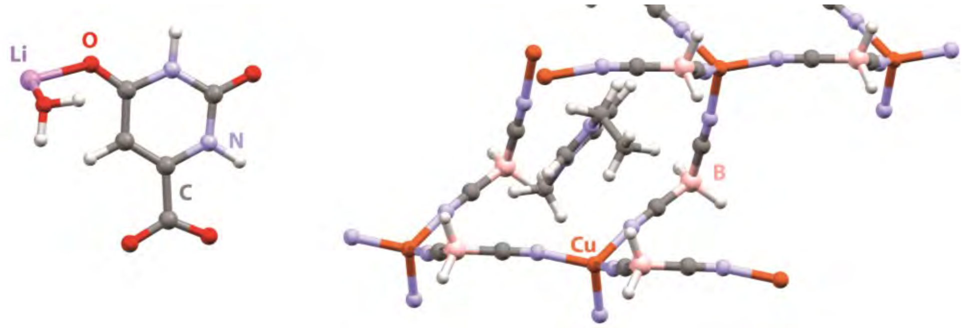

Figure 1: Characterization of structure determining properties of lithium salts (left) and metal organic framework-hybrid materials (right) as well as their intrinsic mobilities.

In the first part, light metal salts and organometallic compounds will be presented, for which an NMR crystallographic study complemented by thermogravimetric and powder X-ray data reveals complexities in structure and dynamics that go beyond the static view of the available crystal structures.

In a second part, this procedure is used to characterize metalorganic framework (MOF)-hybrid materials based on cyanoborate anions[4] by means solid-state NMR and GIPAW (CASTEP)[5-7] calculations with a focus on the mobility of the enclosed organic cations.

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The crystal structures of dimethylzinc and diethylzinc - prototypical organometallic compounds with unusual solid phase behaviour

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The synthesis of dimethylzinc and diethylzinc by Frankland in the mid nineteenth century marks a cornerstone in the history of chemistry.[1] Not only were they among the first organometallic compounds, but studies on their chemical reactions and vapour densities led to the first clear exposition of valency theory. Since then both compounds have found widespread applications in organic and material synthesis. Despite their long history, the solid state structures of these compounds remained elusive. Me_2Zn and Et_2Zn feature the smallest and lightest molecules containing metal atoms in the condensed phase. At standard conditions they exist as volatile, pyrophoric liquids. We have carried out a combined crystallographic and computational study to unravel the solid state structures of these compounds.[2] Dimethylzinc undergoes a solid-solid phase transition at 210 K. The high temperature tetragonal phase exhibits two-dimensional disorder, while the low temperature monoclinic phase is ordered. Both phases contain linearly coordinated zinc atoms. While the methyl groups are staggered in the high temperature phase, they are eclipsed in the low temperature phase. Dimethylcadmium shows a similar phase behaviour.[3] Diethylzinc crystallises in a polar tetragonal arrangement, again with a linear coordination at Zn.

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Metalated Ylides: Unusual Ligands with Unique Donor Properties

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Since the first synthesis of an ylide and their use in Wittig-type reactions these compounds have been applied in a variety of important reactions. In recent years, bisylidic compounds such as carbodiphosphoranes have found renewed interest due to their unique electronic structure and donor properties. While the bonding situation in these compounds is still under debate,[1] their strong donor capacity has been demonstrated such as by the coordination of small molecules or ions or their use in bond activation reactions.[2]

Our group has become interested in the class of metalated ylides. They can be viewed as the anionic congeners of bisylides, formed by replacement of one positively charged onium moiety by a neutral substituent. Comparable to bisylides, metalated ylides possess two pairs of electrons at the central carbon atom and can thus act as monoanionic X,L-type σ- and π-donor ligands (Figure 1). In the past years, we could demonstrate that also metalated ylides are readily isolable ligands with fascinating donor properties.[3] Here, the preparation and electronic structure of metalated ylides as well as synthetic applications will be discussed.

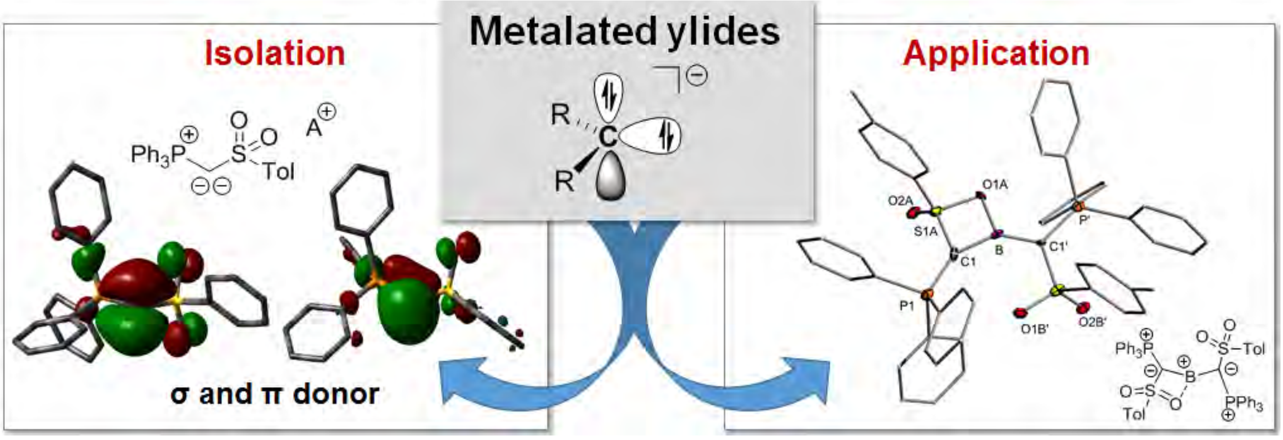

Figure 1. Metalated ylides as unique donor ligands.

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Co-operative Heterodinuclear Catalysts: Applications in CO_2/epoxide Copolymerisation

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The emerging theme of mixed-metal or heterodinuclear cooperativity is an attractive means to enhance catalyst activity and selectivity, particularly when the metals involved are abundant, low toxicity main-group/first-row transition metals. The copolymerisation of CO_2 and epoxides to synthesise polycarbonates (and subsequently polyurethanes) provides a very promising and commercially viable strategy for adding value to captured CO_2. This copolymerisation is critically dependent on the selection of a viable catalyst; some of the most highly active and selective are homodinuclear homogeneous complexes.[1] Detailed kinetic and mechanistic studies have suggested that a heterodinuclear catalyst could exhibit even greater activity, by operating through a cooperative metal-metal mechanism.[2]

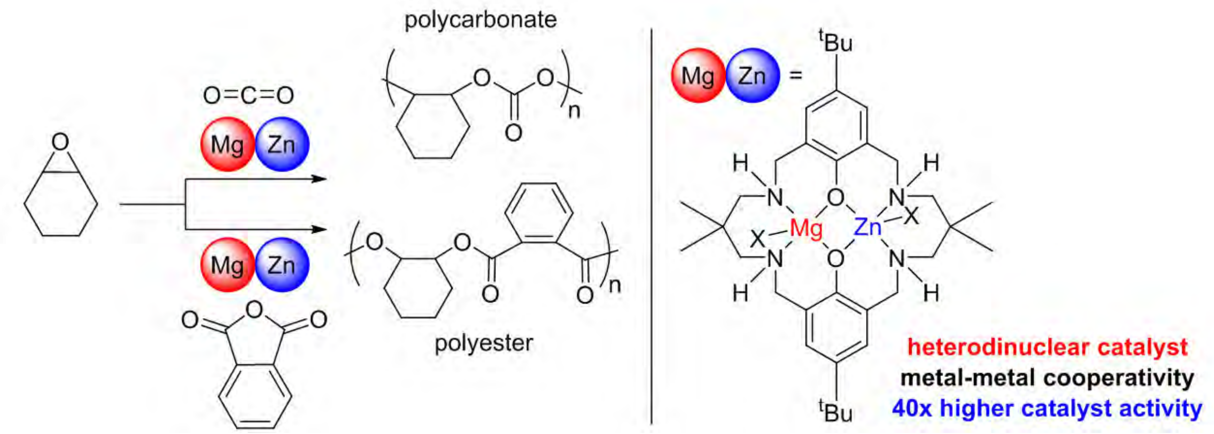

Figure 1 Heterodinuclear catalysts for CO_2/epoxide and epoxide/anhydride copolymerisation

This presentation describes the syntheses, characterisations and catalytic activities of the first heterodinuclear homogeneous catalysts known for CO_2/epoxide copolymerisation (Fig. 1), with a particular focus on magnesium, zinc and titanium systems.[3,4] These catalysts display up to 40 times greater activities than the homodinuclear analogues, either alone or in combination, and operate at low pressure (1 bar of CO_2).

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Spicy Mixtures: Group 14 Atoms as Components of Multinary Clusters

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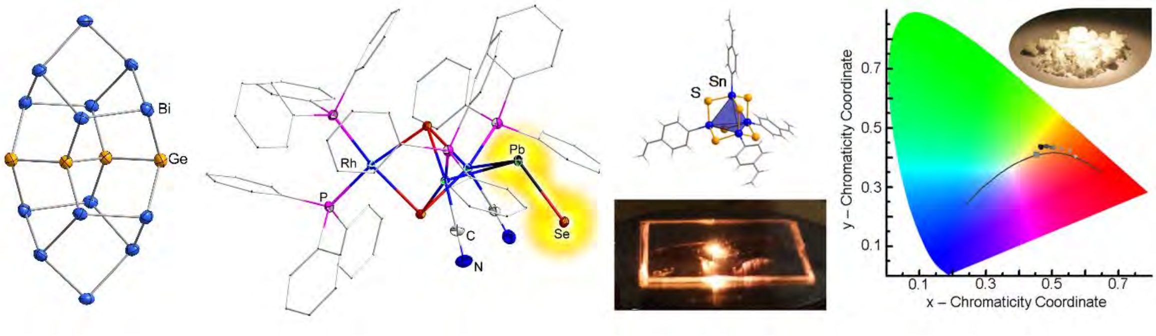
Multinary, non-oxidic metallates as well as metallides have been actively investigated by many research groups over the past decades regarding basic properties as well as their potential use as innovative materials.[1] Recently, binary main group element aggregates proved to be useful synthetic tools for multinary transition metal-main group (semi-)metal clusters.[2-3]

Reactions of chalcogenidoetrelate ions $[E^{14}{}_xE^{16}{}_y]^{q-}$ (E^{14} = Ge, Sn, Pb; E^{16} = S, Se, Te) or the inversely polarized pnictogentrielide/tetrelide ions $[E^{13/14}{}_xE^{15}y]^{q-}$ ($E^{13/14}$ = Ga, In, Tl; Ge, Sn, Pb; E^{15} = As, Sb, Bi) with transition metal (M) compounds lead to the formation of cluster anions like $[Ge_{24}Sn_{36}Se_{132}]^{24-}$, $[Ge_4Bi_{14}]^{4-}$, or $[Rh_3(CN)_2(PPh_3)_4(\mu_3\text{-}Se)_2(\mu\text{-}PbSe)]^{3-}$. These exhibit unusual geometric and electronic structures that position them in between electron precise molecules and superatoms.[5-10] Attachment of organic groups to binary E^{14}/E^{16} units further manipulate their chemical and physical properties, in some cases creating unprecedented non-linear optical properties, such as recently found for $[(4\text{–}(CH_2{=}CH)\text{–}C_6H_4Sn)_4S_6]$.[11]



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Structural and Synthetic Studies Using Templated Magnesiation

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To date the seminal metalation strategy employed in synthesis is undoubtedly Directed *ortho*-Metalation (D*o*M). The first example of D*o*M was reported as long ago as 1938/9,[1,2] and this discovery propelled organometallic compounds from being exotic rarities to indispensable tools in modern synthesis.[3] While there have been a number of reports of metalation at more remote sites, in general these reactions operate in the same way as D*o*M, namely that the position of metalation is controlled by the substituent attached to the aromatic ring. In our template approach, which involves using a sodium magnesiate reagent $[Na_4Mg_2(TMP)_6{}^nBu_2]$ **1** (TMP = 2,2,6,6-tetramethylpiperidide) which can be prepared in a facile manner and be stored for months, it is primarily the positions of the metal centres within the template ring that control the positional metalation reactions. The first section of the presentation will outline our results using **1** to perform metalations of typical D*o*M substrates, culminating in Directed *ortho*-*meta*'- and *meta*-*meta*'-dimetalations.[4] The second part will show our recent reactions of **1** with non-acidic substrates, such as polyarenes, including biphenyl, terphenyls and triphenylbenzenes.

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Advanced Solution Based Syntheses of Functional Nitrides

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Multinary nitrides of main group elements have emerged as intriguing functional materials, e. g. Zn-IV-nitrides (IV = Si, Ge, Sn) as wide bandgap semiconductors or $(Ba,Sr)_2Si_5N_8:Eu^{2+}$ as highly efficient LED-phophor.[1,2] Synthesis of nitrides is often hampered by their limited thermal stability, insolubility or their infusibility. Solution based synthetic techniques are capable to circumvent some of these restrictions. This talk will give an overview about recent progress in solution based techniques employing supercritical ammonia (ammonothermal method) and approaches employing salt melts (metathesis, ion exchange, self flux). Thereby, a number of well crystallized nitrides became accessible, which are either difficult to obtain or have not been accessible by conventional synthesis methods so far, e.g. $Mg_2Si_5N_8$, $CaGaSiN_3$, $ZnSiN_2$, $ZnGeN_2$, and $Li_{47}B_3P_{14}N_{42}$.[2-5]

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Understanding Functional Materials with High Pressure

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In the organic solid state application of high pressure to 10 GPa (100 000 atm) can lead to compression of intermolecular interactions and phase transitions; intramolecular bond distances and angles are generally not greatly affected. The same is not true in coordination complexes, where metal geometry is much more flexible. In view of the importance of coordination complexes as functional materials, this feature makes transition metal complexes particularly attractive subjects for high-pressure studies exploring structure-property relationships. For example, magneto-structural relationships can be studied by applying pressure to modify bond distances and angles at bridging ligands. These structural changes can then be correlated with magnetic property measurements also conducted at high pressure. We have applied this approach in studies of single molecule magnets. The lengths and directions of Jahn-Teller axes strongly influence the magnetic and spectroscopic characteristics of a material, and are particularly sensitive to pressure. More generally, the compression of metal-ligand bonds at high pressure changes crystal field splitting energies leading to colour changes which can be followed by uv-visible spectroscopy (see Figure), providing a direct link between field strength and bond distance. Structure property relationships are conventionally studied using numerous derivatives of a material, looking for specific structural features which correlate with properties of interest, such as coupling or anisotropy in magnetic materials. The advantage of our approach is that all measurements are made on the same material, and there is no need to make the assumption that changes in other parameters which occur on derivatisation are unimportant.

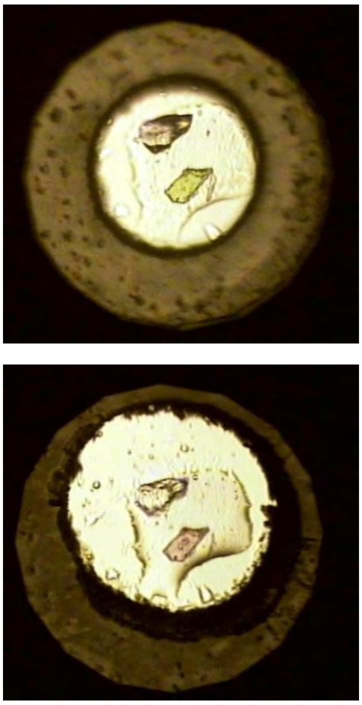

Figure: Piezochromism in a salicyloximato- complex of Ni^{2+} at 6 GPa: the result of tuning the crystal field with pressure.

Less Material-More Energy – Novel Nanostructured Luminescent Materials

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In contradiction to the analogous bulk samples, lanthanide doped luminescent NPs present several advantages as high packing density, low light scattering effects, energy saving synthesis and are easily suspendable in liquid media [1-3]. Due to the small size, nanophosphors are able to build thinner films simply by printing e.g. on the surface LEDs and are less subjected to concentration quenching effects, in comparison to doped micron-sized phosphors. Moreover, core-shell NPs can be functionalized on their surface and are therefore suitable as biological sensors or medical markers [3].

Here, we present several different lanthanide doped NPs. Above all, Eu^{2+} containing NPs are very interesting in this context [4]. However, the common preparation methods using water as solvent in general do not work due to the oxidation behavior of Eu^{2+} ions. Therefore, we developed novel synthesis methods, e.g. in ionic liquids as solvent. By the usage of fluoride containing ionic liquids it is also possible to prepare fluoridic NPs. In detail, we were successful preparing phase pure samples of several materials with small sizes and low size distributions (30-40 nm) with extremely high luminescence quantum yields for the first time. Finally, some applications in biological and medical fields (e.g. medical sensors) and also multifunctional magnetic, afterglow NPs are presented, showing their large benefits compared to common materials due to their higher stability at extremely low toxicity. Especially afterglow nanoparticles overcome the problem of absorption of visible radiation of biological tissue because it can be exited before injection.

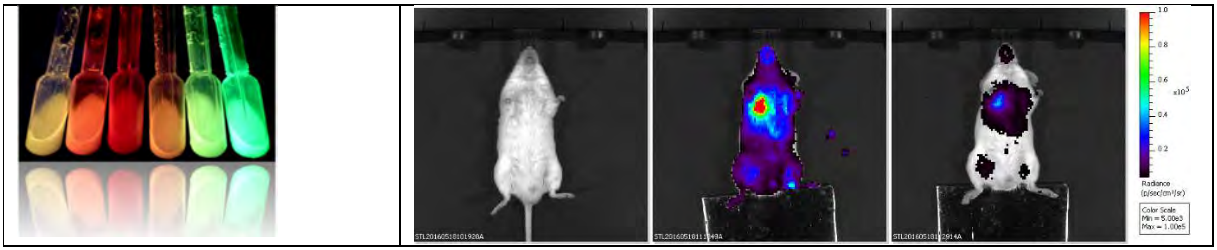

Fig. 1. Left: emission of several Eu^{2+} containing nanoparticles suspended in water, right: afterglow NPs injected in a mouse, middle: after 5 minutes, right: after 10 minutes..

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AACVD of metal oxides: from precursor synthesis to TCOs and photocatalysts

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Current research involves developing processes towards sustainable and inexpensive high quality transparent conducting oxide (TCO) films on float glass. In particular replacement materials for Indium Tin Oxide (ITO) are being developed. These materials are used in low-e window coatings (>£5B pa), computers, phones and photovoltaic devices. Indium is listed as a critical element- available in limited amounts often in unstable geopolitical areas. Tin metal has had the biggest rise in price of any metal consecutively in the last four years (valued at >£30K per ton) and indium is seen as one of the most difficult to source elements. We have been developing sustainable upscaled routes to TCO materials from precursors containing earth abundant elements (titanium, aluminium, zinc) with equivalent or better figures of merit to existing TCOs. Our method uses Aerosol assisted chemical vapour deposition (AACVD) to develop large scale coatings [1].

Compared to conventional CVD, the AACVD method uses aerosol droplets to transport precursors, with the aid of inert carrier gases. Therefore, in AACVD volatility is no longer crucial and this allows for a wider choice of precursors being available for use and can lead to high quality films at low cost [2]. The most basic requirements for precursors of materials are solubility (for solution based CVD, e.g. aerosol-assisted (AA)CVD) and volatility (for low pressure (LP)CVD and atmospheric pressure (AP)CVD). For CVD precursors, besides appropriate volatility, they should exhibit stable vapour pressures, and cleanly decompose to the desired product at useful substrate temperatures. In addition to favourable and stable vapour pressure characteristics, a CVD precursor must also have appropriate reactivity for the desired film growth process. Precursors that satisfy all of these requirements are limited and our research involves the investigation of alternative precursors and deposition technologies in order to improve the functional properties of the resulting films. At present the majority of examples of precursors to metal oxides are alkoxide or β-diketonate complexes. β-ketoimines are a relatively under-investigated and potentially valuable class of ligand for the formation of volatile precursors for the deposition of these oxides. Thermal properties of such complexes can be fine-tuned by thoughtful alteration of the various substituents on the ligand, in particular through functionalisation of the imino residue to incorporate additional donor atoms to occupy coordination sites on the metal centre, preventing oligomerisation of precursor molecules. AACVD is a solution-based method, which alleviates the need for volatile precursors, the main requirement being the solubility of the precursor in the chosen solvent. We describe the synthesis of metal oxide and composite thin films, using a range of precursors, by AACVD - a low cost, tuneable and scalable technique. The synthesis, structures, thermal properties and AACVD application of a range of novel precursors, including zinc, gallium and indium β-ketoiminate and β-ketonate complexes are described. Synthesis of the precursors is possible via various routes, affording products of high purity in good yields [3]. Of particular note is the successful stabilisation of rare gallium hydride and trimeric Zn-O species (Figure 1). CVD studies show the potential for this class of compounds for application in metal oxide thin film deposition. The functional properties of the films have been investigated, including their use as transparent conducting oxides and photocatalysts [4].

The development of a new combinatorial AACVD (cAACVD) rig allowed for the deposition of films with graded composition, which in turn gave a greater degree of control over the resulting stoichiometry of the film afforded. Thin films of graded composition can be achieved by allowing two separate solutions of precursors, e.g. one for Ga and one for In, to enter from opposite sides of the reactor. This creates a gradient in the, for example Ga:In ratio present in the precursor mix horizontally across the substrate and therefore a range of deposition conditions are achieved in a single experiment. These techniques have been extended to photocatalytic SnO_2:TiO_2 and N:Nb:TiO_2 films [5].

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5. Poster Abstracts

Synthesis of Group 13 Element Containing Benzenes

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The chemistry of borabenzenes and boratabenzenes has advanced considerably since 1986.[1] Transition metal-boratabenzene complexes are mostly used as catalysts for olefin polymerization.[2-3]

Since incorporation of nitrogen into polycyclic aromatic frameworks can enhance n-type semiconducting behavior[4], the use of group 13 elements in those structures could be an effective strategy towards feasible p-type materials.[5]

Several methods for the synthesis of borabenzenes have been developed so far, but all are multi step reactions, e.g. via boron cationic species[6] or transmetallations via tin heterocycles.[7-8]

We will show that reduction of $Cp^*BCl_2{\cdot}NHC$ gives NHC-stabilised pentamethylborabenzene in one step. We will give computational insights into a possible mechanistical pathway. Currently, we are extending this new route to prepare the literature unknown, neutral pentamethylaluminabenzene.

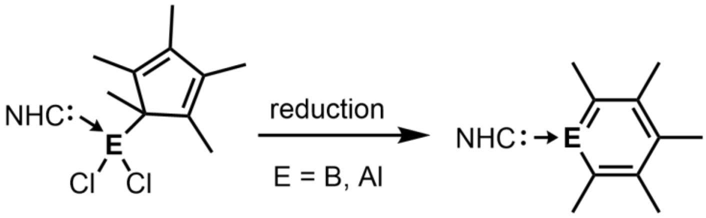

Figure 1 Synthesis of group 13 containing benzenes.

Acknowledgements: This work was supported by the Newton International Fellowship of the Royal Society.

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New and Older Highly Nuclear Metalloid Clusters of Non-Precious Metals

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The first description of a metalloid cluster of a base metal was published 20 years ago: $Al_{77}R_{20}$ (R = $N(SiMe_3)_2$).[1] Before this highlight it seemed to be a dream to trap molecular metal arrangements of this kind of intermediates on the way from AlR_3 to Al metal, because of their thermodynamical favorite decomposition to Al and AlR_3 and because of the extremely high sensitivity for e.g. traces of O_2. In the following decades, we have been succeeded to synthesize further metalloid aluminum and gallium clusters with diameters also on the nanometer scale.[2] Very recently, we could present a highly nuclear magnesium cluster $[Mg_{16}Cp^*_8Br_4K]^-$ that has been detected by mass spectrometry (**Figure 1**).[3] The highly sophisticated disproportionation and trapping method introduced by us about 30 years ago was the key to synthesize such highly reactive intermediates. The topology of metal atoms in many of these clusters reflects that of the metal, or it can be used to give an indication of element modifications yet to be discovered. Therefore, these clusters are snapshots during the very fast processes of the dissolution and the formation of metals.[2] Crystallographically determined metalloid clusters are not also interesting from a theoretical point of view with regard to the bonding aspects but also from a technical perspective of potential interest in e.g. electrochemistry. Herein, we want to present new trends in metalloid cluster chemistry.

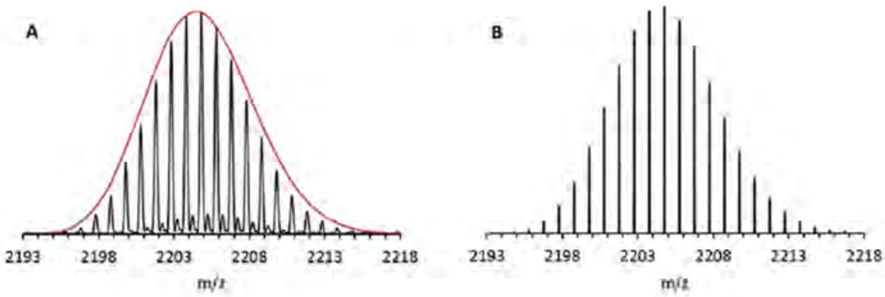

Figure 1 FT-ICR mass spectrum of the metalloid cluster anion $[Mg_{16}Cp^*_8Br_4K]^-$ via the ESI method from THF solution. A: experimental data, the red line represents the shape of the simulated isotopic pattern; B: simulation.[3]

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Azo dye-based colorimetric chemosensor for anions

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Chelating systems that are selective and sensitive to cations and anions are objectives of this work. The structures of receptors that use hydrogen bonding interactions have importance in the design of receptors. The 2-(4-hydroxiazobenzene)benzoic acid (HABA) has two hydrogens groups available for interaction, one is the azo group and the other is the carboxylic acid group, enabling interaction with cations and anions[1]. However, it is known that these ligands have possible tautomeric species according to the media, and can generate undesirable groups[2]. Several titrations of chromophore 2-(4-hydroxiazobenzene)benzoic acid were performed with cations (Mg^{2+}, Hg^{2+}, Pb^{2+}) and anions (Cl^-, F^-, $H_2PO_4^{2-}$, CH_3COO^-, $Cr_2O_7^{2-}$). However, only the interactions with fluoride, acetate, and phosphate were significant, demonstrating the sensitivity of the ligand HABA by these anions, characterized by the displacement of the absorbance bands at 372 nm to 491 nm. The binding constants found to acetate, fluoride, and phosphate were 1.91×10^4, 1.30×10^4 and 1.28×10^4 $mol^{-1}dm^3$ respectively. ^{1}H-NMR titrations confirmed binding constants similar to UV-vis, besides showing evidence of the analyte binding by the hydrogen of the carboxylic acid. The interaction has a 1:1 stoichiometry confirmed by the "Job´s plot"

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FAPESP

Asymmetric Syntheses and Transformations at Stereogenic Silicon Centers

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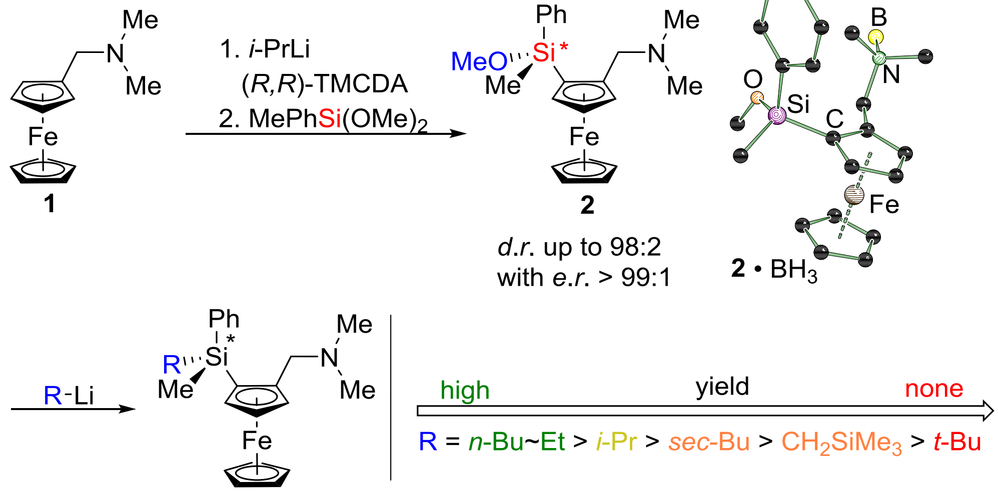
The synthesis of chiral compounds is an important part in academic and industrial chemistry.[1] Within the last years the interest and varity of stereogenic silicon derivatives has grown.[2] The transformation of silicon substrates under maintaining of stereogenic information is one of the central ways to get access to these chiral compounds. The known methods to synthesize defined stereogenic silicon centers are limited und the mechanism of the reaction is less investigated compared to carbon centers.

A new method to build silicon central chirality was found by using planar chiral lithium ferrocene.[3] The stereogenic pathway of this reaction was investigated and diastereomeric ratio up to 98:2 could be observed. The methoxy group also gives possibilities for further transformations.



Substitution reactions were carried out with different lithium organyls and their effects on the yield and the stereochemistry were investigated. Substitutions with *n*-butyllithium show results with complete consumption and conservation of the diasteremeric ratio. In case of enantiomeric pure lithioferrocene one out of the four possible stereoisomers is formed selectively. X-ray analysis and GC/mass-spectroscopy allow the identification and classification of the diastereomers and their relative or absolute configuration.

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Mild and efficient imine hydrogenation with simple calcium amide catalysts

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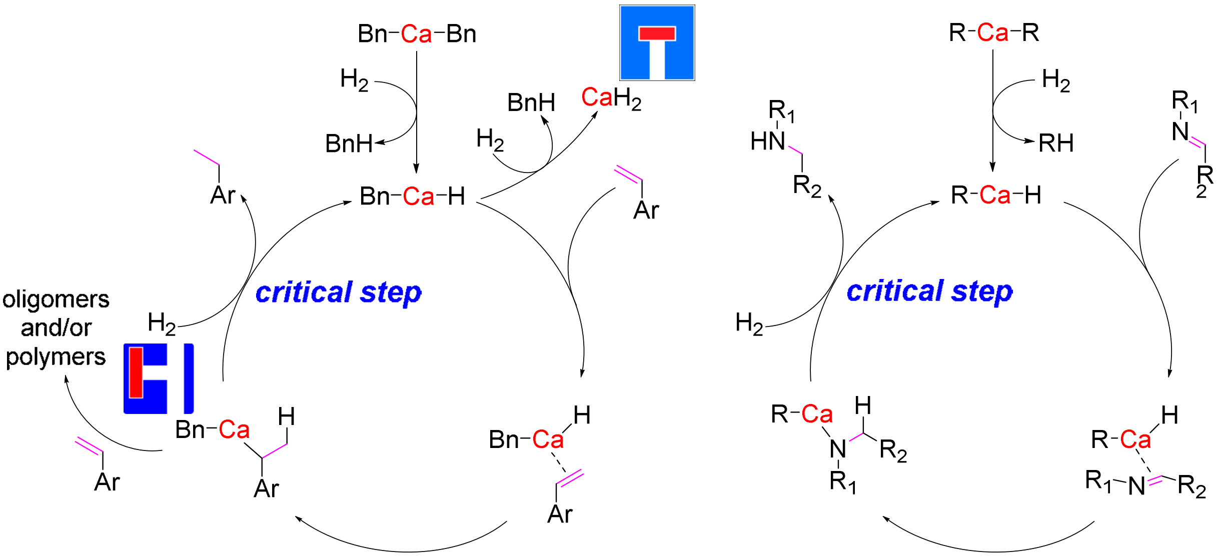
The simple KOtBu represents one of the first non-transition metal catalysts for hydrogenation of ketones, but the conditions are extreme (20 mol% cat, 200 ℃, >100 bar H_2).[1] Harder *et al.* reported simple dibenzylcalcium ($CaBn_2$) that function as catalysts for the hydrogenation of conjugated alkenes under comparatively mild conditions (Scheme 1).[2]



Scheme 1 Catalytic hydrogenation of alkenes (left) and imines (right).

In the case of conjugated alkenes, it was possible to deprotonate H_2 (critical step, pKa = 38) with the benzyl calcium complex, which is a competitive reaction to the polymerization reaction (Scheme 1, left).[2] Our current research focusses on the hydrogenation of imines, in which case deprotonation of H_2 by a calcium amide intermediate is very questionable (Scheme 1, right). Contrary to our expectations, we found that homoleptic alkaline-earth metal amide complexes of the type AeN''_2 (Ae = Mg, Ca, Sr, Ba; N'' = $N(Si(CH_3)_3)_2$) are also able to reduce imines to the corresponding amines with molecular dihydrogen in a catalytic manner under surprisingly mild conditions (60 ℃, 6 bar H_2).

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Structural and functional model systems for the [2Fe-2S] cluster in mitoNEET proteins

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Iron-sulfur clusters are ubiquitous cofactors which exist in a variety of forms and serve a multitude of functions including electron transport, redox reactions and sensing. While the majority of iron-sulfur clusters are ligated by four cysteine residues of the surrounding protein, it has been found that a subset of [2Fe-2S] clusters features different terminal ligands. The most commonly observed of those alternative ligands is histidine but in most cases the role of this alternative ligand is not yet fully understood.[1]

First structural model systems for the special $\{Cys_2\}\{His_2\}$ coordinated [2Fe-2S] cluster of the Rieske protein have recently been reported by our group.[2,3] Proton coupled electron transfer (PCET) was studied in those and related functional model systems, highlighting the importance of the distal nitrogen of the ligand as protonation site.[3,4]

MitoNEET is an outer membrane protein whose exact function remains unclear to date, though a role of this protein in redox and iron sensing as well as in controlling maximum mitochondrial respiratory rates has been discussed.[5] It was shown to contain a redox active and acid labile [2Fe-2S] cluster, which is ligated by one histidine and three cysteine residues.[6] The first structural and functional model complex for this special cluster and its properties in different oxidation and protonation states are presented here. The ability of this cluster and of a related homoleptic system to undergo PCET has been studied, and the corresponding square schemes have been established and compared with the Rieske models.

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Novel Superbasic Mixtures

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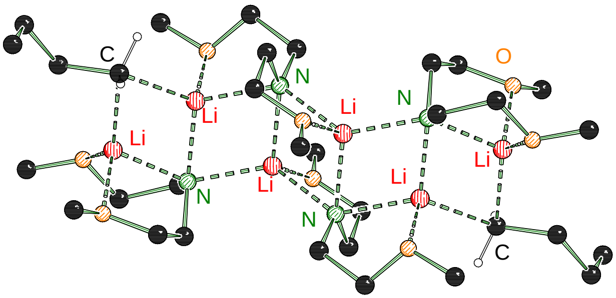
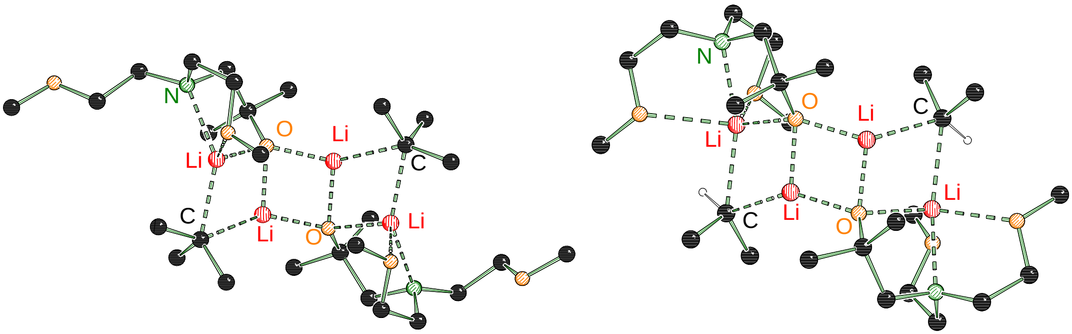
The Lochmann-Schlosser's Base mixture allows the deprotonation of CH-groups with poor acidity at low temperatures. The mechanism behind the reaction involving *n*-BuLi/*t*-BuOK is not known so far and needs to be solved in order to understand the superbasic behavior of this system.[1] The focus of the presented research lies on the identification of novel superbasic mixtures based only on the metal lithium. This research lead to a mixed aggregate forming a six-runged ladder structure including an amide and an organolithium compound.



$[(n\text{-BuLi})_2(C_6H_{14}LiNO_2)_4]$

Figure 1 A mixed aggregate formed by *n*-BuLi and a lithium amide.

Based on these results, similar mixed aggregates formed by lithium aminoalkoxides and organolithium compounds could be isolated. An interesting aspect of the ladder aggregates is the terminal position of the carbanion.



$[(t\text{-BuLi})_2(C_{10}H_{23}LiNO_3)_2]$ $[(i\text{-PrLi})_2(C_{10}H_{23}LiNO_3)_2]$

Figure 2 Obtained ladder structures with terminal organolithiums and lithiumalkoxides.

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Beryllium Phosphine and Amine Compounds

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After decades of neglect due to its alleged high “toxicity”, the coordination chemistry of beryllium has lately seen a little renaissance.[1,2] However the ligand exchange processes at the metal are still little understood and various different ligand exchange mechanisms have been postulated. We recently reported on the synthesis of beryllium phosphine complexes, their characterization and application in the synthesis of beryllium alkyls.[3] During these studies we observed the presence of dynamic equilibria between free and coordinated ligand.

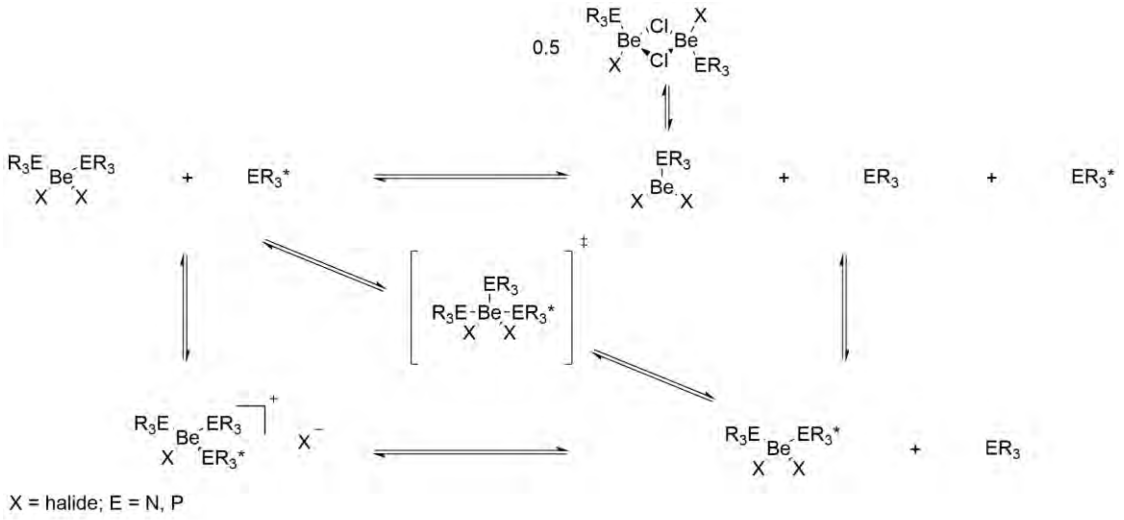

Figure 1 Dynamic phosphine exchange at beryllium halide.

Therefore various additional beryllium coordination compounds of amines and phosphines have been synthesized and characterized, which all exhibit ligand exchange. Utilizing various temperature NMR spectroscopy the thermodynamic parameters for these substitution reactions could be determined. These findings represent the first spectroscopy based data for non-aqueous solvents and are important for a better insight into the reactivity of beryllium regarding ligand substitution. Which is fundamental for a better understanding of the dynamic processes accountable for beryllium associated diseases.

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Zeolites as Catalysts in Hydrocracking, FCC-Cracking and ETH-Process using biogenic and fossil resources

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Raw material change and resource efficiency are major challenges of today´s classical petrochemical processes. Industrial plants use increasing amounts of fracking feeds and renewables to meet the needs of energy supply and mobility in modern society. Meanwhile, restricted local availability in combination with economical and ecological aspects request high flexibility in production concepts.

To meet requirements of new educts, adapted catalyst systems and novel strategies have to be developed. Three examples of zeolite-based research of our group are:

I. Hydrogen-supported cracking of biogenic residues using hierarchical catalysts
II. Production of ZSM-5 -based industrial catalysts from catalyst residues for preferred propene production and stabilization for biogenic co-feeding in FCC process
III. Deactivation behavior of (post-)synthetic modified zeolite catalysts for conversion in Ethanol-to-Hydrocarbons-(ETH) process

Special focus of these three research projects is on (post-)synthesis of materials, recycling, catalytic testing, structure-property-relationships and application of catalyst samples in petrochemical industry. By adjustment of structural and catalytic properties, catalyst samples are designed for mentioned hydrocarbon-pool processes.

Special focus is on:

I. Synthesis conditions to customize hierarchical structure and textural properties of ZSM-5- and Al-MCM-41-containing composite materials for application in hydrogen-supported cracking of various feeds to improve selectivity, durability and regenerability
II. Raw material efficiency by developing modified catalysts or additives as well as recycling of spent FCC catalysts for using biogenic resource technology, directly or as co-feed
III. Combination of post-synthetic treatments to understand and to reduce catalyst deactivation in ETH process

Metal-metal and metal-carbon bond activation reactions of *p*-block compounds using univalent group 13 diyls

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Univalent LM (M = Al, Ga, In) containing the sterically crowded β-diketiminate ligand {L = CH[C(Me)N(2,6-*i*-Pr_2-C_6H_3)]$_2$} adopt monomeric structure in the solid and solution state. They are soluble reductants and are extensively used for activating the bonds in small molecules such as P_4, S_8, O_2, azides, diimines, acetylene and others.[1] Here in we present the reactivity studies of LM with E_2Et_4, ER_3 (E = Sb, Bi; R = alkyl, aryl), *i*-Pr_2Te, Te_2Ph_2 and more. Treatment of LAl with E_2Et_4 produces LAl(EEt_2)$_2$ whereas the analogous reaction of LGa forms a temperature-dependent equilibrium mixture LGa(EEt_2)$_2$, E_2Et_4 and LGa. LIn does not interact with Sb_2Et_4, but formation of LIn($BiEt_2$)$_2$ is observed at low temperatures.[2] LAl and LGa activate the metal-carbon bonds in $BiEt_3$ and *i*-Pr_2Te and afford the insertion compounds LMEt($BiEt_2$) and LM(*i*Pr)Te*i*Pr, respectively.[3,4] The details of synthesis, structures, reactivity studies will be presented.

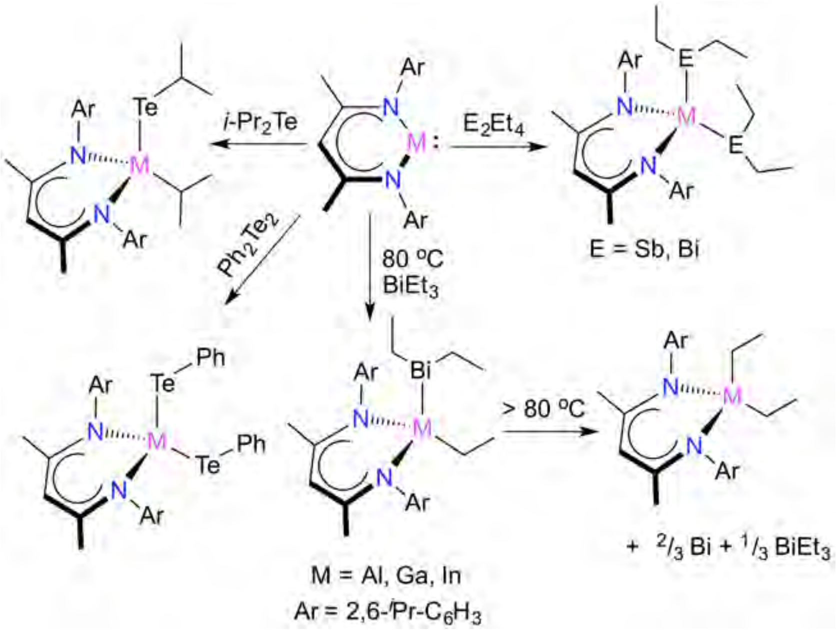

Figure 1 Synthesis of intermetallic compounds.

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Synthesis of a Chiral Carbenoid and its Use in Stereoselective Dehydrocoupling of Phosphines

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Dehydrocoupling is a clean and powerful tool for the formation of a variety of homo- and heteroatomic element-element bonds (E–E and E–E`) with concomitant release of hydrogen. The development of both E–E and E–E´ bond-forming reactions has been triggered by the synthetic potential and the applicability of the obtained products, e.g. inorganic rings, chains and polymers.[1] Originally, transition metal catalysts were required for the E–E bond formation directly from E–H precursors. However, in case of P–P coupling reactions only one transition metal complex, namely the tin complex $Cp^*{}_2SnCl_2$, has been active in P–P bond formation reactions starting directly from phosphines.[2]

Recently, our group reported on lithium chloride carbenoids to be active in selective dehydrocoupling of secondary phosphines. The reaction proceeds *via* dehydrocoupling of the phosphines and simultaneous protonation of the carbenoid. This reaction behavior is unprecedented in carbenoid chemistry. The carbenoid-mediated P–P coupling of secondary phosphines can be performed for a variety of aryl-substituted phosphines and does not require laborious workup, transition metal catalysis, long reaction times or elevated temperature.[1b] Following up this work, we are interested in the possibility of stereoselective dehydrocoupling of secondary phosphines using a chiral carbenoid. In this regard, we want to present the synthesis of a chiral, enantiomerically pure carbenoid and its application in stereoselective P–P bond formation reactions.

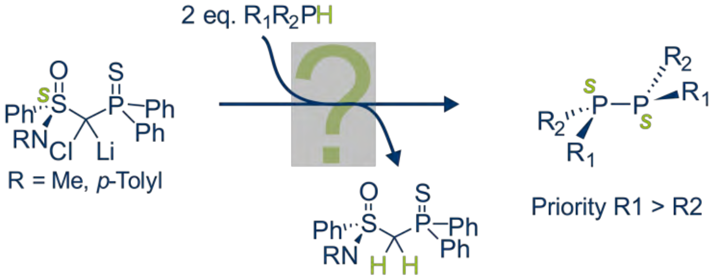

Figure 1. Stereoselective dehydrocoupling of secondary phosphines using a chiral carbenoid.

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Tetrylenes Stablized by Homoconjugation

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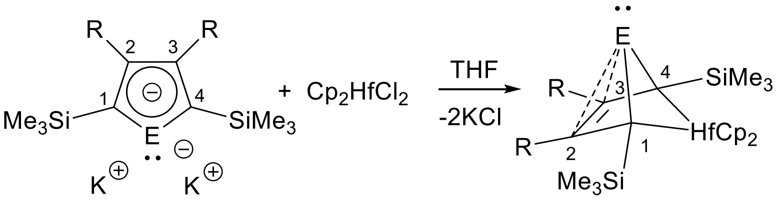
Carbene analogues such as tetrylenes have small HOMO-LUMO gaps and exhibit properties reminiscent to transition metal complexes. Therefore, they can be applied in small molecule activation (H_2, CO_2, NH_3) and bond activation reactions.[1] Against this background, the exploration of new types of tetrylenes has been a hot topic in main group chemistry during recent years. The synthesis of stable tetrylenes is however challenging due to their high inherent reactivity. Here we report on the synthesis of stable silylene **2a** and germylene **2b**[2] by the reaction of dipotassium heterocyclopentadienediides **1** and hafnocene dichloride. The tetrylenes **2a** and **2b** are stabilized by interaction with the remote C^2=C^3 double bond through homoconjugation. The preliminary reactivity studies of tetrylenes **2** revealed their predominant nucleophilic character.



1

2

1a: E = Si, R = Ph
1b: E = Ge, R = Me

2a: E = Si, R = Ph
2b: E = Ge, R = Me

Scheme 1. Synthesis of homoconjugated tetrylenes **2**.

Acknowledgements: This work was supported by the Carl von Ossietzky University Oldenburg. Z.W. Dong thanks the Ministry of Science and Culture (MWK) of the Lower Saxony State for a Georg-Lichtenberg scholarship and the University Society Oldenburg e.V. for a congress scholarship.

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Binary and Ternary Organotetrel Sulfide Clusters

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Tetrelchalcogenide clusters featuring organic ligands have attracted increasing attention during recent years due to their intriguing chemical and physical properties.[1] The organic ligands influence their optical properties as well as their reactivity towards molecules and surfaces.[2] Recent investigations on organotetrel sulfide clusters $[(RSn)_4S_6]$ featuring an adamantane-like topology have demonstrated extreme optical nonlinearity, allowing for either strong second harmonic generation or white-light emission when driven by an IR laser diode.[3]

Reactions of binary organotin chalcogenide clusters with coinage metal complexes yield ternary clusters that allow for fine-tuning of the optoelectronic properties by extension of the inorganic core.[4] The reaction of $[(PhSn)_4S_6]$ with AuCl and excess PMe_3, for instance, yields an adamantane-type cluster with one phenyl moiety being replaced by an $[Au(PMe_3)_3]$ fragment, thus under formation of a tin-gold bond.

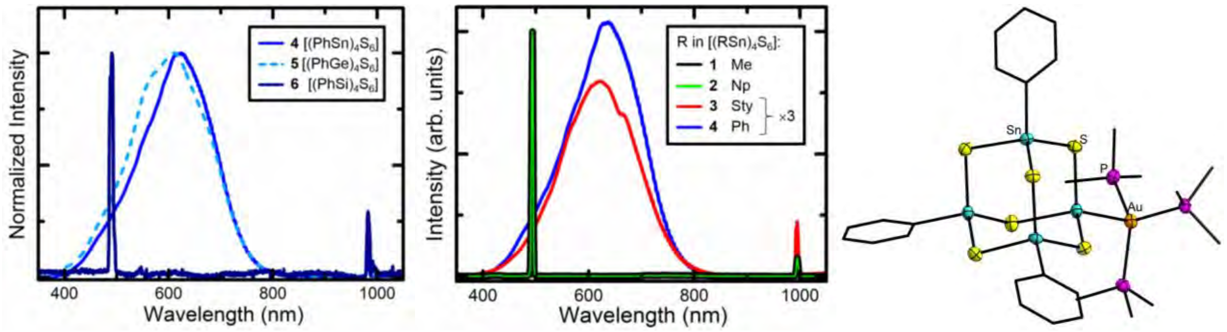

Figure 1 Left and center: Emission spectra of $[(RT)_4S_6]$ for an excitation wavelength of 980 nm. Right: Molecular structure of $[(PhSn)_3(\{Me_3P\}_3AuSn)S_6]$.

Future studies aim at the variation of the organic substituents as well as the chalcogen atoms in the inorganic core to elucidate the influence of the cluster composition on the optical properties. The deposition of the molecules on surfaces will be subject to further investigations.

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Oxidation of the Tetrahedral Molybdenum Complexes $[\{Cp^RMo(CO)_2\}_2(\mu,\eta^2:\eta^2\text{-}EE')]$ (E, E´= P, As, Sb, Bi)

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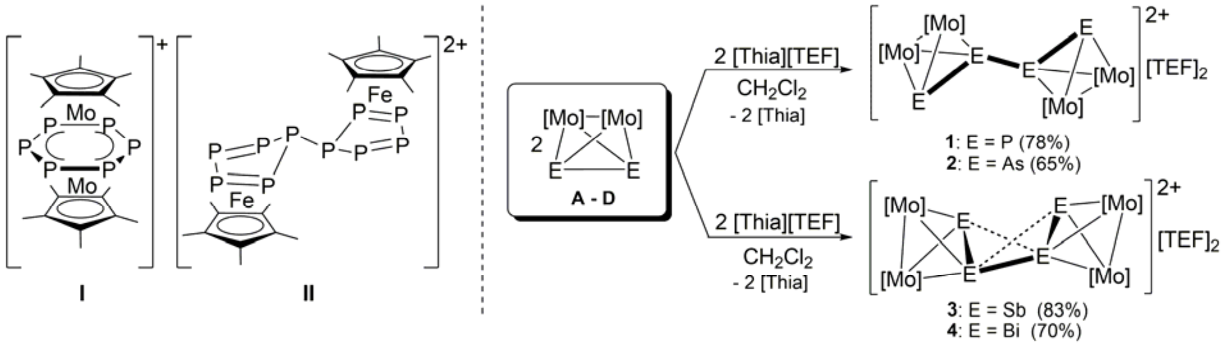
The oxidation chemistry of transition metal complexes bearing “naked” polypnictogen ligands can lead to a variety of reaction pathways. For example, the oxidation of $[(Cp^*Mo)_2(\mu,\eta^6:\eta^6\text{-}P_6)]$ results in a bis-allylic distortion of the P_6 ring (**I**, Scheme 1, left).[1] Otherwise, oxidation of $[Cp^*Fe(\eta^5\text{-}P_5)]$ causes a dimerization via P-P-bond formation (**II**, Scheme 1, left).[2] The first substituent-free polyphosphorus cation, namely $[P_9]^+$, was obtained by *Krossing et al.* by oxidation of P_4 with $[NO]^+$.[3] This prompted us to investigate the oxidation chemistry of $[\{CpMo(CO)_2\}_2(\mu,\eta^2:\eta^2\text{-}E_2)]$ (E = P (**A**), As (**B**), Sb (**C**), Bi (**D**)) due to their isolobal relation to P_4. If the complexes **A**-**D** are reacted with the strong one-electron oxidant $[C_{12}H_8S_2]^+$ containing the WCA $[Al\{OC(CF_3)_3\}_4]^-$ (= [TEF]), a dimerization occurs yielding the dicationic E_4 complexes $[\{CpMo(CO)_2\}_4(\mu_4,\eta^2:\eta^2:\eta^2:\eta^2\text{-}E_4)]^{2+}$ (E = P (**1**), As (**2**), Sb (**3**), Bi (**4**)) selectively (Scheme 1, right). These complexes bear the first unsubstituted dicationic E_4 chains stabilized by four $[CpMo(CO)_2]$ transition metal fragments. Hereby, **1** and **2** show a zigzag chain with an unexpected gauche conformation. In contrast, the compounds **3** and **4** reveal a cluster-like structural motif with rather short E-E contacts leading to a distorted “butterfly” geometry. Furthermore, the influence of the counterion and the Cp substituent was investigated, as well as the reactivity of the analogous tetrahedral molybdenum complexes containing two different pnictogen atoms.



Scheme 1 Different P_n oxidation products (left). Oxidation of the complexes **A**-**D** (right).

[1] M. Fleischmann, F. Dielmann, L. J. Gregoriades, E. V. Peresypkina, A. V. Virovets, S. Huber, A. Y. Timoshkin, G. Balázs, M. Scheer, *Angew. Chem. Int. Ed.* **2015**, *54*, 13110-13115.

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Chemistry of Dichloro-Cycloazatriphosphane

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Ring systems based on group 15 elements (pnictogens) have been in the focus of chemical research for almost 150 years.[1] Especially four-membered N_2P_2 and P_4 ring systems have been thoroughly investigated, *inter alia* as precursors to low-coordinate phosphenium ions or biradicaloid species.[2] Yet, little is known about four-membered NP_3 ring systems, which is why we set out to investigate this class of compounds as a systematic addition to NP chemistry.

Following our well-established approach to functionalize small inorganic ring systems by introducing halogen substituents as leaving groups,[3] we developed a multi-step synthesis towards [Mes*P(μ-PCl)$_2$NMes*] (**3**, Figure 1) *via* highly reactive diphosphene intermediates (**1**, **2**).

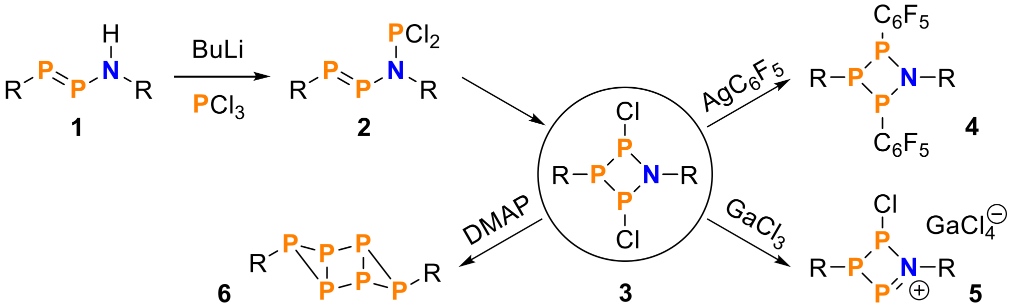

Figure 1. Synthesis and reactivity of compound **3** (R = Mes* = 2,4,6-tri-*tert*-butylpheny).

Recently, we have been investigating the stability and reactivity of **2** and **3** towards Lewis acids, bases, and reducing agents. For example, the reaction of **3** with $GaCl_3$ yielded a cyclophosphenium salt (**5**) at low temperatures, whereas treatment of **3** with the Lewis base DMAP led to formal [2+2] cycloreversion and subsequent formation of the unusual tricyclohexaphosphane Mes*P_6Mes* (**6**).[4]

[1] H. Köhler, A. Michaelis, *Ber. Dtsch. Chem. Ges.* **1877**, *10*, 807.
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[3] J. Bresien, K. Faust, A. Schulz, A. Villinger, *Angew. Chem. Int. Ed.* **2015**, *54*, 6926.
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Mechanistic Insight into the Hydrosilylation of Alkenes Using Early Main-Group Metal Catalysts

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The key to developing highly efficient catalysts is to fully comprehend the reaction mechanism. Computational chemistry allows us to model the reactions and possible alternatives. We here present density functional calculations for the hydrosilylation of conjugated alkenes using Ca and K-based catalysts introduced by Harder *et al.* [1]. The Markovnikov or anti-Markovnikov regiochemistry strongly depends on the catalyst and on the reaction medium. We compare the results of gas-phase and PCM solvent model calculations for the full catalytic system and model systems thereof. Our mechanistic insights are discussed within the framework of the growing number of early main group metal catalysts for alkene hydrosilylation [2].

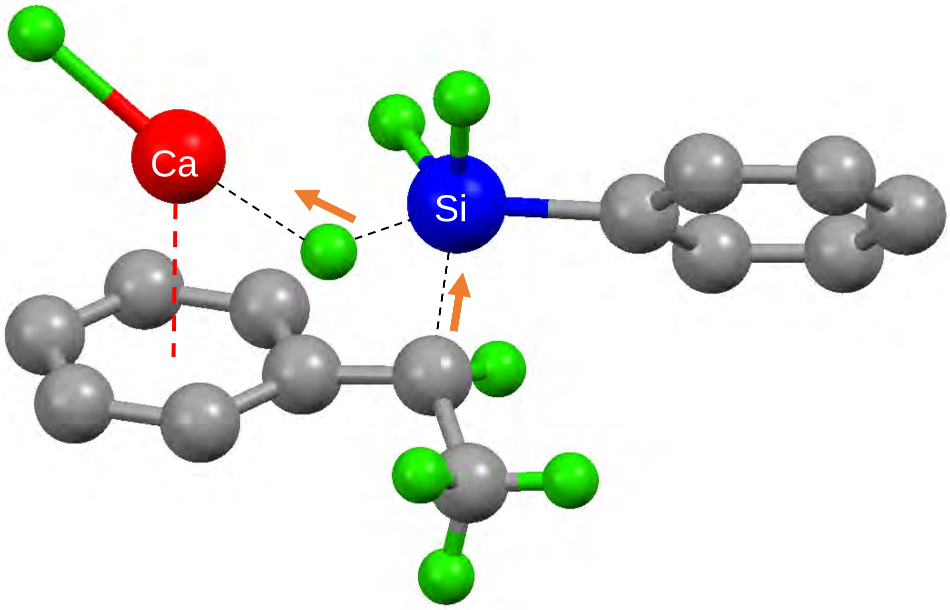

Figure 1. Transition state for the silicon-carbon bond formation with concerted hydride transfer (arrows representative of movement during the transition state)

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Intermetalloid clusters of group 15 elements

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Intermetalloid clusters are model systems to investigate intermetallic interactions, electronic transitions, bonding or size evolution of electronic properties on the molecular level.

Binary Zintl-anions have proven to be good starting materials for the synthesis of such molecules. A particularly interesting case is the elemental combination of Ga/Bi. The tetrahedral species, $(GaBi_3)^{2-}$, tends to release Ga^0 under formation of polybismuthide species like Bi_{11}^{3-}.[1] A reaction of $(GaBi_3)^{2-}$ with $[U(C_5Me_4H)_3]$ yielded $[U@Bi_{12}]^{3-}$, a doughnut-shaped array of three connected Bi_4 units surround a central U atom. Magnetic properties indicate antiferromagnetic coupling of the central U^{4+} ion with a radical Bi_{12}^{7-} shell.[2]

To get a more complete understanding of main group metallide chemistry, the transition to lighter homologues is desirable. Investigation of the system K-Ge-As resulted in the synthesis of the phase $K_2Ge_3As_3$ which can be made in high yield using conventional solid-state methods. The anionic moiety is electron-precise and made of two noradamantane units which are interlinked and form infinite, 1-dimensional strands. Still, expanding the chemistry of pnictide-based intermetalloid cages to arsenic is not an easy endeavor, since a prevalence of seven-atom cages exists for the elements P – Sb.[3]

Another approach is the extraction of ternary K-As-M mixtures. The intermetalloid cluster $[Nb@As_{11}]^{3-}$ was crystallized as its $[K(crypt\text{-}222)]^+$ salt from extracts of crude melts of K, As, and Nb. It represents a new type of polyarsenide cage adopting a unique structure that complements the family of endohedral group 5@main group metal cluster anions with non-deltahedral shells.

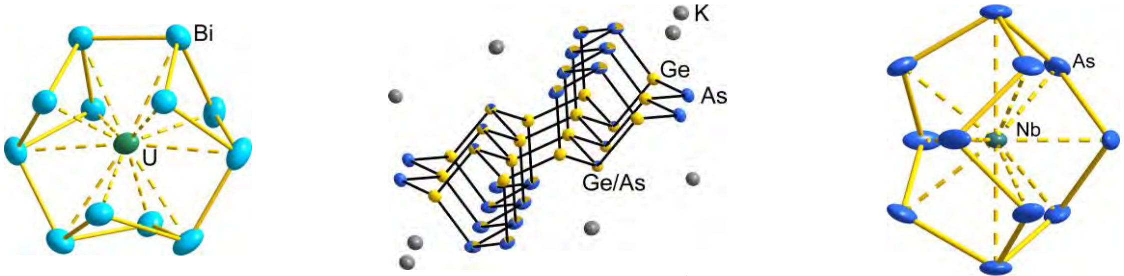

Figure 1: sections of crystal structures of: left: $[U@Bi_{12}]^{3-}$, middle: $K_2Ge_3As_3$, right: $[Nb@As_{11}]^{3-}$.

[1] B. Weinert, A. R. Eulenstein, R. Ababei, S. Dehnen, *Angew. Chem*. **2014**, *126*, 4792.
[2] N. Lichtenberger, R. J. Wilson, A. R. Eulenstein, W. Massa, R. Clérac, F. Weigend, S. Dehnen, *J. Am. Chem. Soc.* **2016**, *138*, 9033.
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An Iminiophosphoryl-Substituted, Methandiide-Derived Carbene Complex in Cooperative Bond Activation Reactions

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Transition metal carbene complexes have been used in a wide variety of different applications in synthesis and catalysis. The reactivity of the carbene complex M=CR$_2$ is hereby significantly influenced by the sterical and electronic properties of the substituents R. In the last few years, carbene complexes derived from methandiides have received increasing attention as they represent a formally new type of complexes which does not fit in the typical Fisher and Schrock classification pattern[1] Nevertheless, the number of methandiides suitable for the synthesis of carbene complexes is still scarce.

Our research group has focused on the synthesis and application of new methandiides, especially on the influence of different stabilizing functional groups on the reactivity of the corresponding carbene complexes. Thus, we were able to synthesize a sulfonyl- and thiophosphoryl-stabilized methandiide and applied it as ligand in a ruthenium carbene complex which showed versatile applicability in bond activation and transfer reactions.[2] Based on these results, we were interested to further modify the dimetalated system and to examine the effects on the corresponding carbene complexes. Here we present the synthesis of a new methandiide-derived ruthenium carbene complex and its application in the activation of a series of E–H bonds.[3]

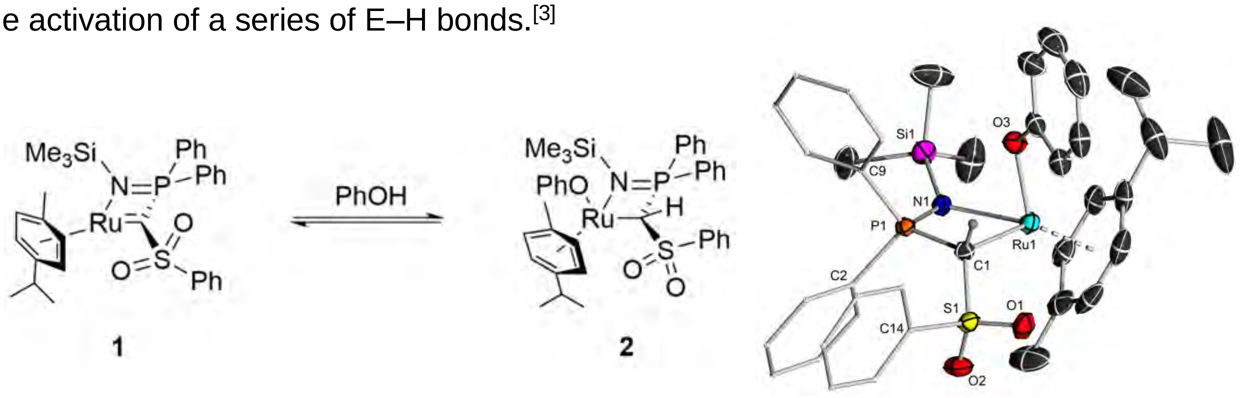

Figure 1. Bond activation reaction of phenol with carbene complex **1**.

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Cooperative Activation and Redox Transformation of Nitric Oxide and Nitrosobenzene at a Dinickel(II) Dihydride Complex

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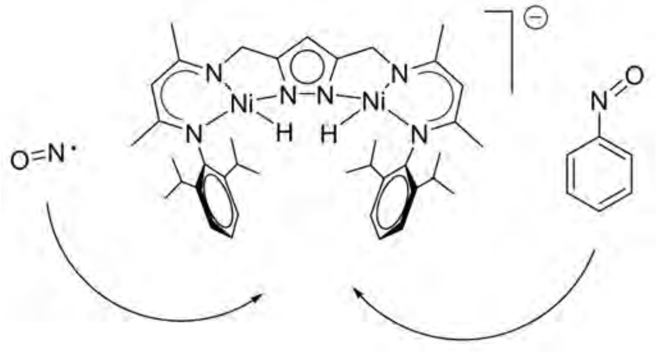
Nitric oxide (NO) and organic nitroso compounds such as nitrosobenzene (PhNO) have an intimately connected biochemistry. In fact, these organic products are implicated as reactive intermediates in biological systems and can have similar effects, acting as cellular signaling molecules or vasodilators.[1] Moreover, PhNO can be considered a stable analogue of nitroxyl (HNO) which has been suggested to be a probable intermediate of a variety of biotransformations involving nitrogen-containing compounds.[2] Therefore, it is of no surprise that over the last century, studies regarding the mechanisms by which metalloenzymes can act as carrier molecules and "store" these substrates have been intensified. In this regard, employing nickel and copper β-diketiminates as models for these metalloenzyme active sites led to interesting findings.[3] In our group, we recently developed a new ligand that has a pyrazole spanning two β-diketiminate subunits, and we synthesized a novel dinickel dihydride complex which turned out to be highly versatile and features striking reactivity towards small molecules.[4] Here we present the reactivity of this dinickel dihydride complex towards nitric oxide and nitrosoarenes (see Figure). The results provide new insights into the transformations of these important substrates at cooperative bimetallic sites, which may be relevant for the biochemistry of nitric oxide and related compounds.



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Determination of the electronic and steric properties of *sym*-dimethyltetraphenylcarbodiphosphorane

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sym-dimethyltetraphenylcarbodiphosphorane $C(PMePh_2)_2$ (**A**) was first described in 1976 by Schmidbaur *et. al*.[1] In contrast to the more prominent hexaphenylcarbodiphosphorane $C(PPh_3)_2$ (**B**), the follow-up chemistry of **A** is not well determined until now. Our previous studies of **A** show diverse and distinct differences in comparison to **B**.

In our group we want to determine these differences, especially focusing on the electronic and steric properties. To achieve proper information, we are using several spectroscopic methods and X-ray crystallography.

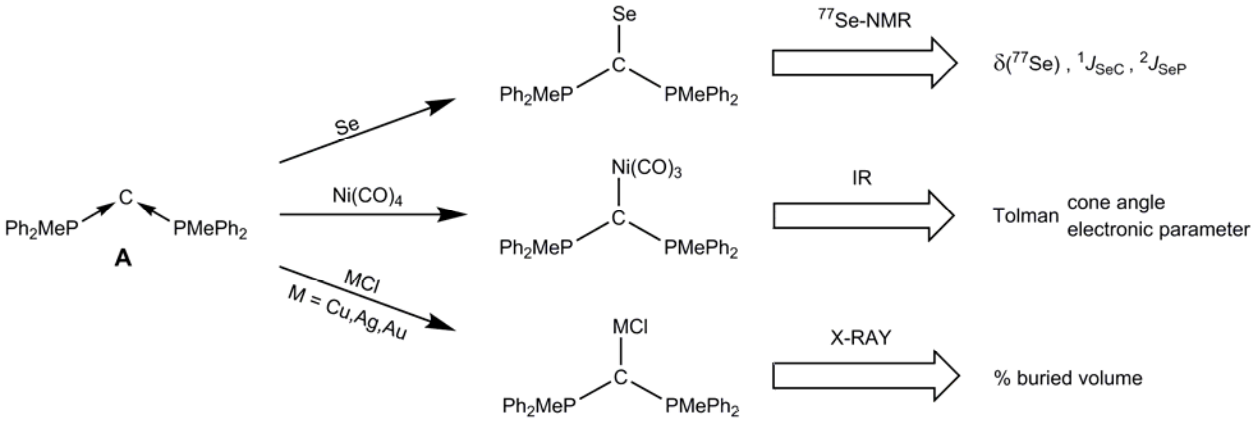

Figure 1 Syntheses of different complexes of **B** and corresponding spectroscopic examinations.

In this work, we will present the results of our spectroscopic examinations (Tolman cone angle[2], percent buried volume[3] and ^{77}Se NMR parameters[4]) and discuss the electronic and steric properties of **A**.

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3 H. Clavier, S. P. Nolan, *Chem. Comm.*, **2010**, *46*, 841.
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Aromatic and organometallic functionalization of Sn/S Clusters

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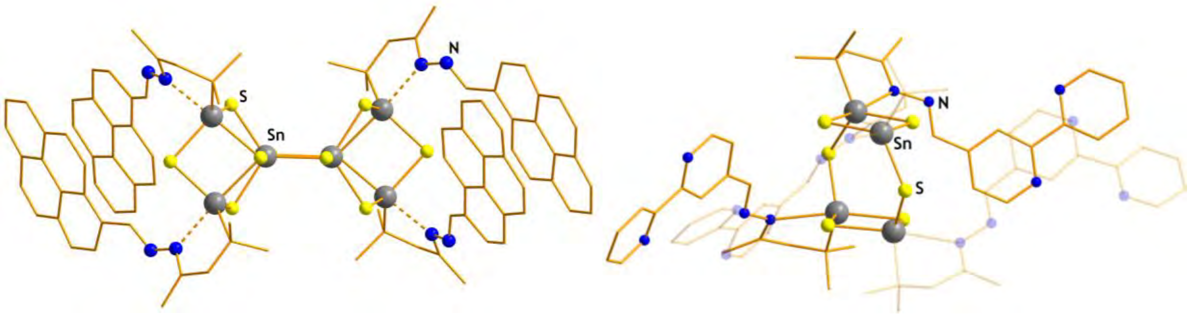
A large variety of organotin sulfide clusters were recently synthesized and investigated with regard to their characteristics.[1] Directed derivatization of the organic ligands that are attached to the cluster allows the introduction of further functionalities that affect the physical properties of the cluster and their reactivity towards complementarily functionalized molecules. By reaction of functional binary clusters with organic molecules of complementary reactivity, hetero- and polyaromatic ligands that lead to interesting optical properties can be attached.[2] Recent work led to the attachment of polyaromatic and heteropolyaromatic ligands by utilizing their hydrazine derivatives.[3] Ferrocenyl and ruthenocenyl ligands were introduced in the same manner, which resulted in different electrochemical responses.[4]



Molecular structures of pyrene-functionalized (left) or 4-(hydrazonomethyl)-2,2`-bipyridine-terminated (right) Sn/S clusters with [Sn_6S_{10}] or [Sn_4S_6] scaffolds, respectively.

Recent investigations aim at (a) the attachment of chelating ligands and (b) (poly)aromatic groups to the binary clusters. The first may serve to trap transition metal atoms or complex fragments. The π-aromatic system of aromatic ligands have shown to significantly influence the optoelectronic properties of the compounds.[5] Moreover, the attachment of polyaromatic ligands will allow for interaction of the compounds with solid, in particular with metal or semimetal surfaces.[6]

References:
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Structural & Magnetic Properties of Low Valent Cobalt-Silylamido-Complexes

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Low-coordinate silyl-amido-complexes of first row transition metals were first discovered by Bürger and Wannagat in the 1960's.[1] In recent years these complexes attracted attention due to their magnetic properties. A large zero-field splitting D as expression of large magnetic anisotropy leads to a possible use as single-molecule magnet (SSM).[2,3] Here, we present a series of new three-coordinate cobalt-silylamido complexes bearing phosphine ligands (**1-5**). The dependence of D on variation of phosphine and amido ligands was examined and will be discussed.

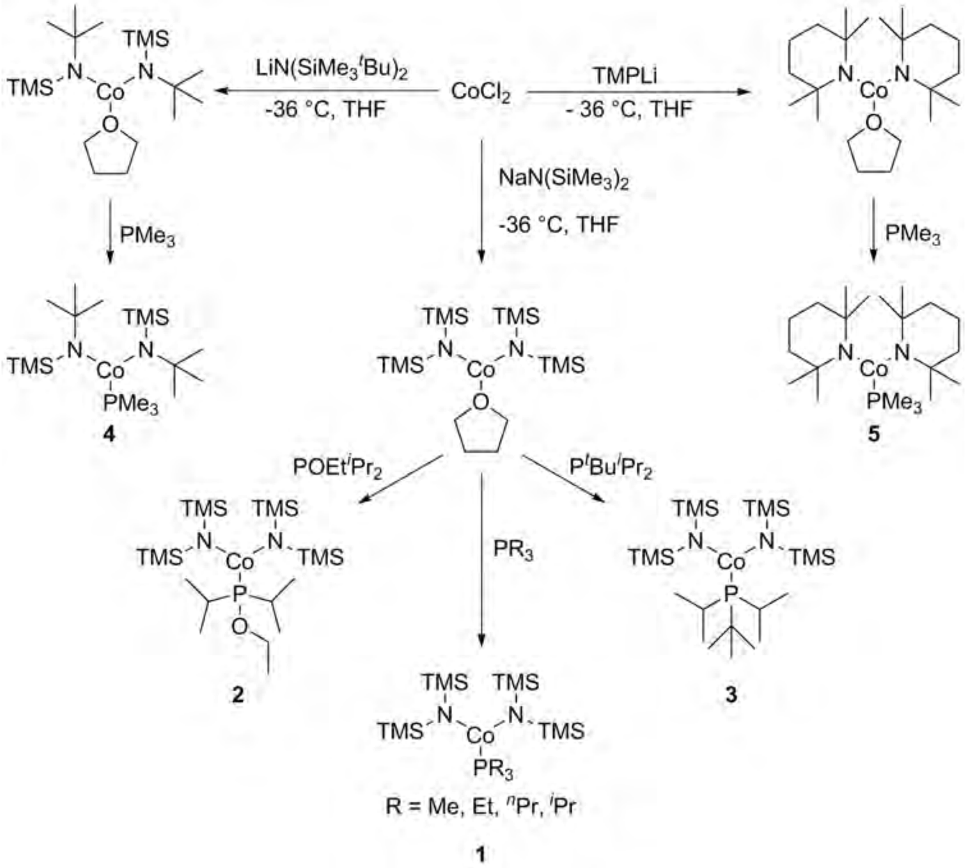

Figure 1 Synthesis of new Cobalt-Amido-Complexes.

1 H. Bürger and U. Wanngat, *Monatsh. Chem.*, **1963**, 1007-1012.
2 A. M. Bryan, G. J. Long, F. Grandjean and P. P. Power, *Inorg. Chem.*, **2013**, *52*, 12152−12160.
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$[Ga_4(\mathit{t}BunC)_8]^{4+}$, $[Ga_2(phen)_4]^{4+}$ and $Ga_5(DMAP)_{10}]^{5+}$ highly charged cations supported by the WCA $[Al(OC(CF_3)_3)_4]^-$

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Early approaches to stabilise Ga^{I} paved the way to today's low valent gallium chemistry, but also behold some backdraws: Ga[GaX$_4$] does contain a Ga^{I} ion that can be solvated in aromatic solvents, unfortunately its Ga^{I} cation is not available for further chemistry without redox reactions, involving the anion $[GaX_4]^-$.[1] $[Ga_2Cp^*]^+[B(C_6F_5)_4]^-$ was the first reported $[GaX_4]^-$ free Ga^{I} starting material by Fischer et al.,[2] still having the disadvantage of creating on equivalent of GaCp*-sideproduct. By using perfluoroalkoxy-aluminate type salts like Ga(PhF)$_2$*[PF]* (*[PF]*$^-$ = $[Al(OC(CF_3)_3)_4]^-$)[3] the weakly coordinated anion (WCA), provides pseudo gas phase conditions, which allows sensitive Ga$^+$ compounds to be introduced to various ligands and form new and interesting multicore complexes, by representing an atom economic Ga^{I}-source.

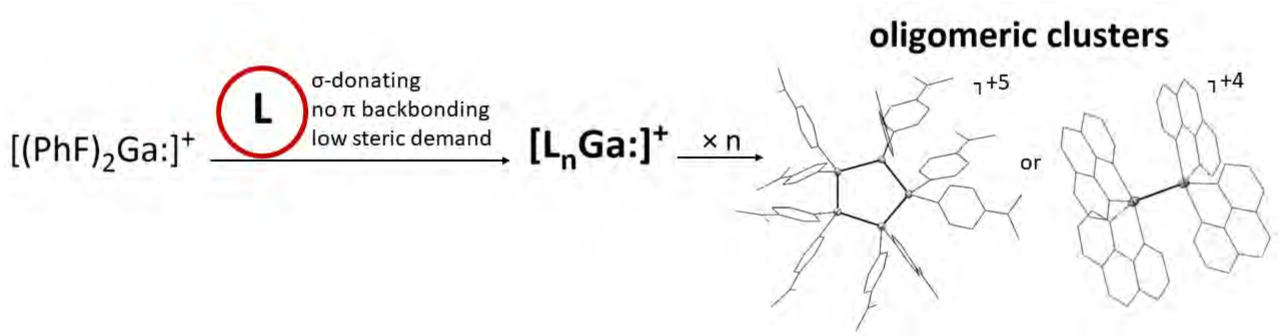

Figure 1 Simplified reaction scheme for the formation of highly charged cationic Ga-cluster.

Besides the WCA the properties of the ligand play an important role in stabilising these highly charged cations. These compounds are also solely a solid state phenomenon, can not be detected in solution and only as fragments via MS. Following the cluster chemistry of Indium[4] different ligands like phenanthroline (phen), *tert*-butyl-isocyanide (*t*BuNC) and 4-(dimethylamino)pyridin (dmap) were used and lead to two fourfold and one fivefold postive charged ion with the last one presenting a whole new arrangement of ions in the crystal lattice.

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Amino-Ferrocenyl-Based Chiral Siloxide Ligands

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The heavier homologs of carbinols, the silanols, are drawing increasingly more interest to themselves as siloxide ligands in catalysis and as building blocks for silica based hybrid materials.[1,2] However, only few examples of siloxide ligands bearing an additional non-Si-O donor are investigated so far. The first amino-siloxides appeared in the early 90s, without being further pursued.[3] Here, we wish to present our recent work on amino-ferrocenyl-siloxides of zinc. The use of ferrocene as backbone has several advantages. It is sterically demanding and thus allows better controllability in terms of self-condensation. Moreover, the stereoselective *ortho*-lithiation of aminoferrocene is well developed in our group, opening the field of chiral siloxide ligands.[4] The emphasis of this presentation will lie on the synthesis and structural characterization of dimeric zinc silanolates, as well as some selected examples of zinc silandiolates and siloxandiolates.[5]

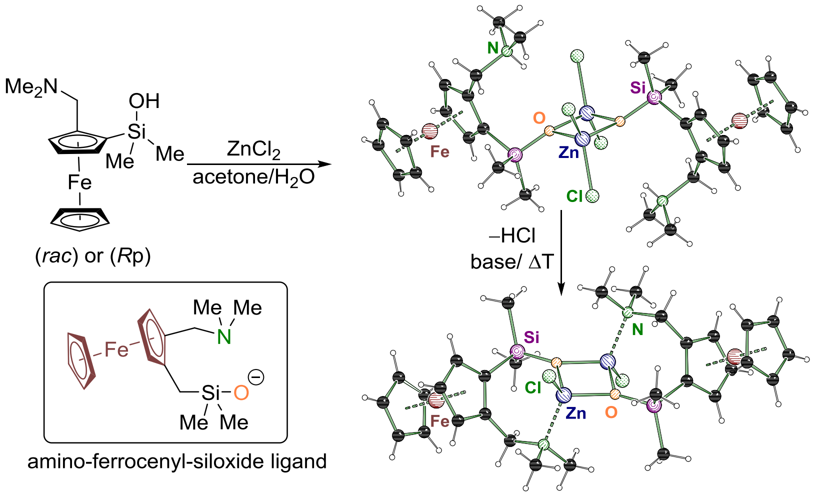

Figure 1. Aminosiloxides of zinc derived from ferrocenyl aminosilanols.

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Borazinylphosphines

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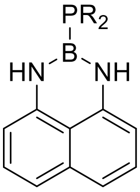
Borylphosphines, which contain P–B bonds (e.g. **1**), have been studied to far less than their P–C, P–O and P–N bonded counterparts.[1,2] As a result, the range of accessible P–B bonded structures is underdeveloped and little is known of the potential applications of these molecules. We are interested in P–B bonded borazinylphosphines (**2**) which are isoelectronic with phenyl phosphines. Recently, we have exploited the mild halosilane elimination route (eq. 1) to form novel borylphosphines in quantitative yields.[3]



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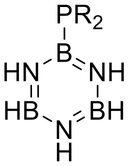
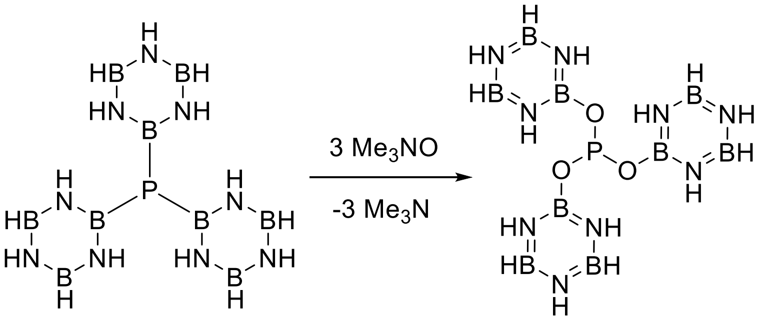


2

$$R_2PSiMe_3 + ClBR'_2 \xrightarrow{-ClSiMe_3} R_2PBR'_2$$ **eq. 1**

Here, we present the synthesis of a series of borazinylphosphines from the reactions of various silylphosphines and chloroborazines. Notably, the triborazinylphosphine (**3**), an inorganic analogue of PPh_3 has been obtained and structurally characterised.



3 **4**

Treatment of borazinylphosphines with trimethylamine N-oxide (TMAO) leads to insertion of an oxygen atom into the P–B bond to give P–O–B species (e.g. $R_2POB_3N_3H_5$). For example, triborazinylphosphite (**4**) was formed upon reaction of **3** with TMAO.

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Cooperative Substrate Activation by Dinuclear Nickel Complexes of the “*Two-In-One*” Pincer Scaffold

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Bringing two metal ions in close proximity offers interesting perspectives for the cooperative activation and catalytic transformation of substrates. Ditopic pyrazolate-based bridging ligands are known to represent valuable ligand scaffolds in this regard.[1] These studies on bimetallic systems featuring metal-metal cooperativity (MMC) are often inspired by multimetallic sites found in the active centers of metalloenyzmes.[2]

In recent work our group presented a new binucleating pyrazolate ligand that can be viewed as composed of two {PNN} pincer-like compartments (see **Figure 1**); a diiron(II) complex of that “two-in-one” pincer ligand was shown to undergo reversible spin state switching in solution through ligand exchange processes.[3] As pincer ligands are known to support metal-ligand cooperativity (MLC) involving (de)protonation events at the ligand backbone,[4] we surmised that the “two-in-one” pincer system might enable favourable dual cooperativity combining MMC and MLC. Here we present some dinickel complexes of the “two-in-one” pincer ligand, including a unique dinickel dihydride, that exploit such dual cooperativity effects in the activation of small molecule substrates.

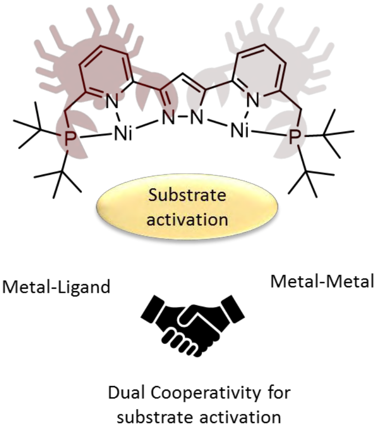

Figure 1

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Reactions of $SiBr_2(CAAC^{Me})$ with Nucleophiles

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Abstract: N-heterocyclic carbenes (NHCs) and cyclic alkyl(amino)carbenes (CAACs) play an eminent role in the stabilization of highly reactive low-valent silicon compounds.[1,2] Their structures and reactivities are strong influenced by the different electronic properties of NHCs and CAAC's.[3]

In the present work we describe the diverse reactivity of $SiBr_2(CAAC^{Me})$ (**1**) with nucleophiles. Compound **1** was obtained by 2e-reduction of $SiBr_4(CAAC^{Me})$ with KC_8. It reacts with C-, N- or P-centered nucleophiles to afford novel Si(II) bromides of the general formula $SiBr(Nu)(CAAC^{Me})$ (Nu= $\{P(Mes)_2\}$ (**2**), Mes (**3**), $\{N(SiMe_3)_2\}$ (**4**)), which were fully characterized (*Figure 1*). A comparison of the structural parameters reveals a dramatic shortening of the Si-$C^{carbene}$ bond lengths in **2** and **4** (d(Si-C_{carb}) = 186.6(2) pm (**2**), 185.6(4) pm (**4**)), compared with **1** (d(Si-C_{carb}) = 201.7 pm), as well as a reduced pyramidalization at Si (Σ°Si = 289.9° (**1**), 328.8° (**2**), 334.9° (**4**)). The structural parameters suggest increased Si-C_{carb} π-bonding in **2** and **4** leading to silene-type structures.

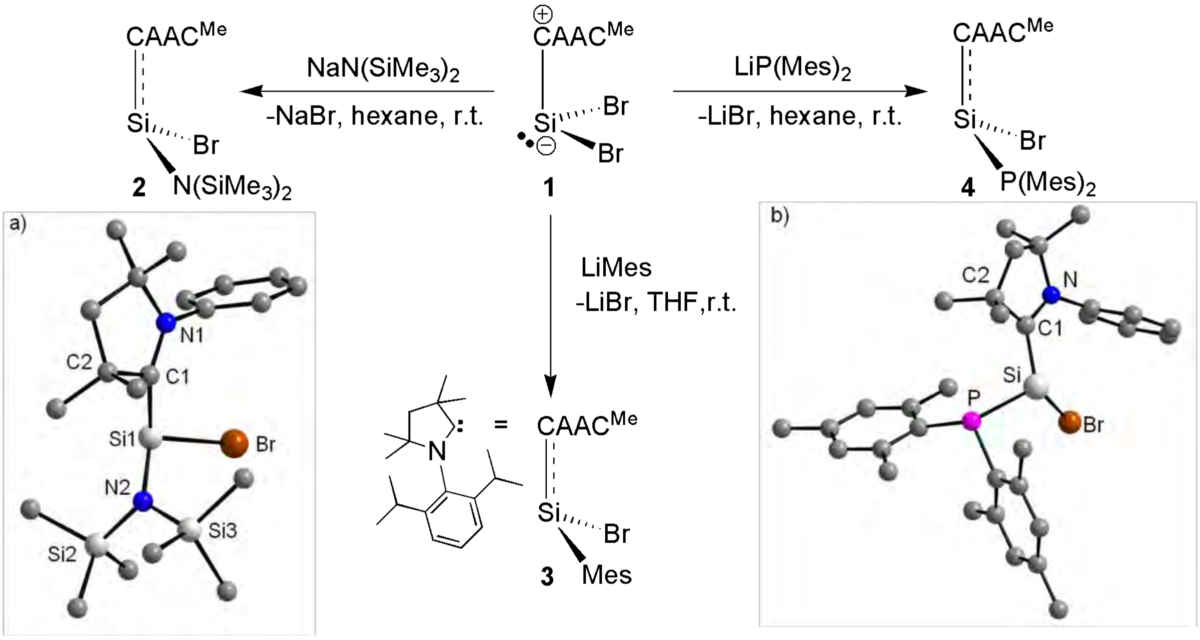

Figure 1. Reactions of $SiBr_2(caac^{Me})$ (**1**) with various nucleophiles; a) molecular structure of $SiBr\{N(SiMe_3)_2\}(CAAC^{Me})$ (**2**) ; b) molecular structure of $SiBr\{P(Mes)_2\}(CAAC^{Me})$ (**4**).

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Computational Studies on Binary Tetrahedral Zintl Anions – Reactivities and Functionalization

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As a contribution to contemporary Zintl anion chemistry,[1-5] we performed extensive and systematic computational studies on the reactivities and possible functionalization of binary, tetrahedral group 13/14, 13/15, and 14/15 clusters. We therefor applied density functional theory (DFT) methods[6,7] to simultaneously optimize the geometric and electronic structures of the afore mentioned anions.

The focus of this part of the study are attachment of protons, silyl groups and (metal)organic substituents, respectively, to the Zintl clusters (s. Figure 1). To date, this has not been realized experimentally for the quoted tetrahedral anions.

The overall goal of this study is the reduction of the high anionic charges in order to modify the anions' chemical and physical surface properties, and thus their further behavior and reactivity in common organic solvents. The results will be part of a library of binary tetrahedral Zintl anions, which should help inorganic chemists plan their syntheses.

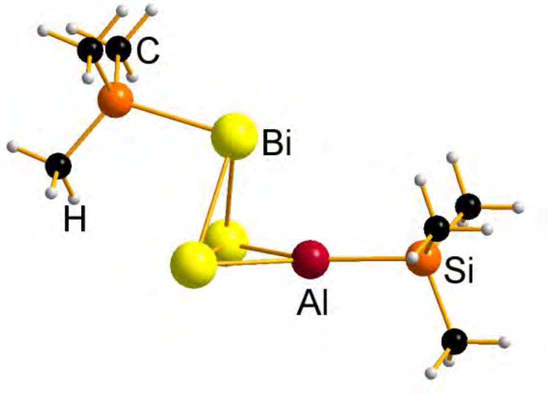

Figure 1 Optimized structure of the hypothetical disilylated species [$AlBi_3(SiMe_3)_2$].

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New type of plumbylene dimerisation
-Ferrocene-based diaminoplumbylenes-

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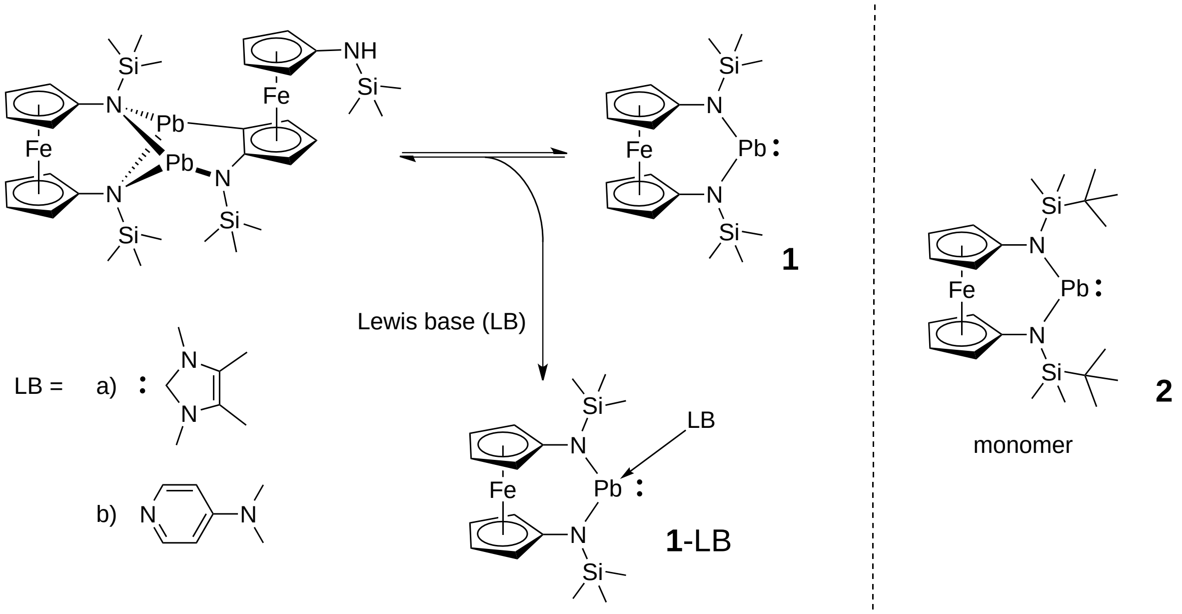
The isolation of the first stable N-heterocyclic carbene (NHC) by Arduengo et al. in 1991 was followed by a tremendous development of NHC chemistry.[1] The heavier homologs of NHCs (N-heterocyclic tetrylenes, NHTs) have experienced a similarly rapid progress.[2] Soon after Siemeling et al. obtained the first stable NHCs with a 1,1'-ferrocenediyl backbone,[3] efforts were made to synthesize and isolate the heavier homologs.[4]

Investigations of the synthesis of corresponding N-heterocyclic plumbylenes (NHPbs) suggest the trimethylsilyl (TMS) substituent as a good choice for obtaining an isolable NHPb. Interestingly, the TMS-substituted plumbylene **1** shows an unprecedented type of plumbylene dimerisation involving a C–H activation at a cyclopentadienyl ring. It proved possible to isolate this plumbylene as monomeric Lewis acid–base adducts **1**-LB (see Figure).[4] Further investigations show that the bulky SiMe$_2$*t*Bu substituent allows the isolation of the monomeric plumbylene **2** as a black solid in excellent yield. A systematic study performed with other substituents of the type SiMe$_2$R (R = Et, *i*Pr, Ph, Mes, Fc) has revealed that the proportion of monomeric plumbylene in the equilibrium mixture correlates with the steric bulk of the substituents.



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Unsymmetrical sp^2-sp^3–diboranes as precursors for the formation of B-B–chains

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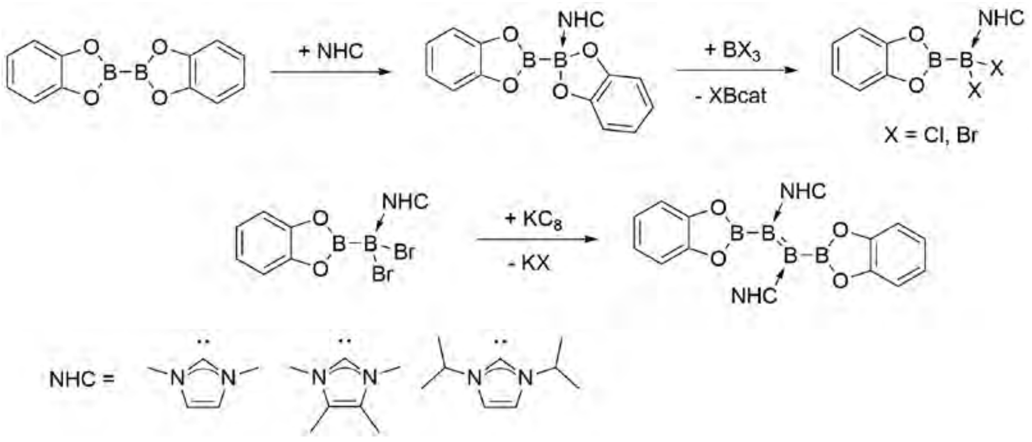
ABSTRACT

Ever since the unexpected synthesis of an unsymmetrical NHC-stabilized 1,1-dihalodiborane(4), our group has been interested in the reduction chemistry of this class of compounds.[1,2] To avoid C-H–activation, we synthezised suitable precursors by treating B_2Cat_2 with NHCs to give the monoadducts.[3] Subsequent reaction with BX_3 forms new 1,1-dihalodiborane(4)–adducts, which were then reduced to generate the first examples of boryl-substituted diborenes with *π*-conjugated boron-atoms.



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Reactivity of a Cp* substituted Halogen Dialane

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Although homonuclear bonds between most elements in groups 13 to 15 are well studied, the synthesis of dialanes is still challenging. Since the first dialane was synthesized by Uhl *et al.* in 1988 only a few other examples have been reported.[1] In contrast to diboranes, whose chemistry is well studied and established[2], the reactivity of 1,2-dihalogenated dialanes in particular has received little attention.[1b,c] In this contribution, we have synthesized a new dialane, $(Cp^*AlBr)_2$, and tested its reactivity towards several Lewis bases, alkynes and azides. With most Lewis bases a disproportionation is induced, which leads to Cp^*AlBr_2 Lewis base adducts, as well as $(Cp^*Al)_4$ (Figure 1, top). Furthermore, the insertion of electron rich molecules like alkynes and azides into the Al-Al bond was successfully achieved. In the case of alkynes, a dialuminated olefin was isolated (Figure 1, middle). The reaction with azides leads to loss of N_2 and to the formal insertion of a nitrene into the Al-Al bond (Figure 1, bottom).

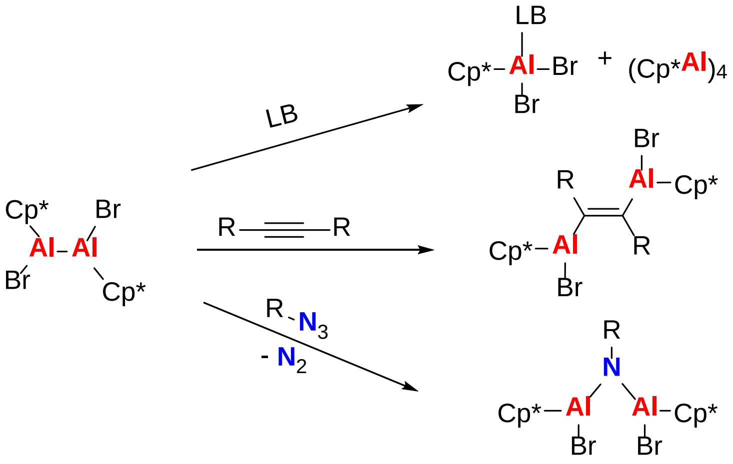

Figure 1 Reactivity of $(Cp^*AlBr)_2$ towards Lewis bases, alkynes and azides.

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Alkoxysilane-terminated Phosphazenes as Precursors for an Artificial Solid-Electrolyte Interphase on Silicon Materials

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We present a new approach for the functionalisation of silicon surfaces with (poly)phosphazenes by the synthesis of the respective triethoxysilane-terminated species. Phosphazenes have been known to be versatile inorganic-organic hybrid polymers that can provide beneficial properties to lithium ion batteries.[1,2] Due to their high elasticity and ion-conductivity, depending on the side groups, polyphosphazene coatings may increase the cycle life of cells employing silicon as an anode material.

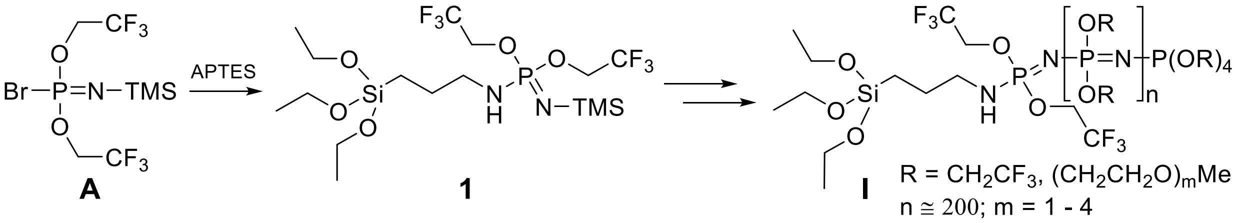

Figure 1 Synthesis of aminopropyltriethoxysilane (APTES) functionalised phopshazene-monomer **1** and suggested polymerisation product **I** for coating purposes.

The synthetic pathway begins with the synthesis of a bromo-phosphazene monomer **A** followed by substitution with APTES or derivative.[3] Polymer growth[4] may be achieved from **1** either in solution or grafted onto a silicon substrate. The results are studied by NMR and electron microscopy to gain insight into coating behavior, layer thickness and morphology. Furthermore, this approach is deployed on different silicon materials in lithium ion cells to identify the benefits and limitations of the system.

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Reactivity Studies of a NHC-stabilized Disilavinylidene

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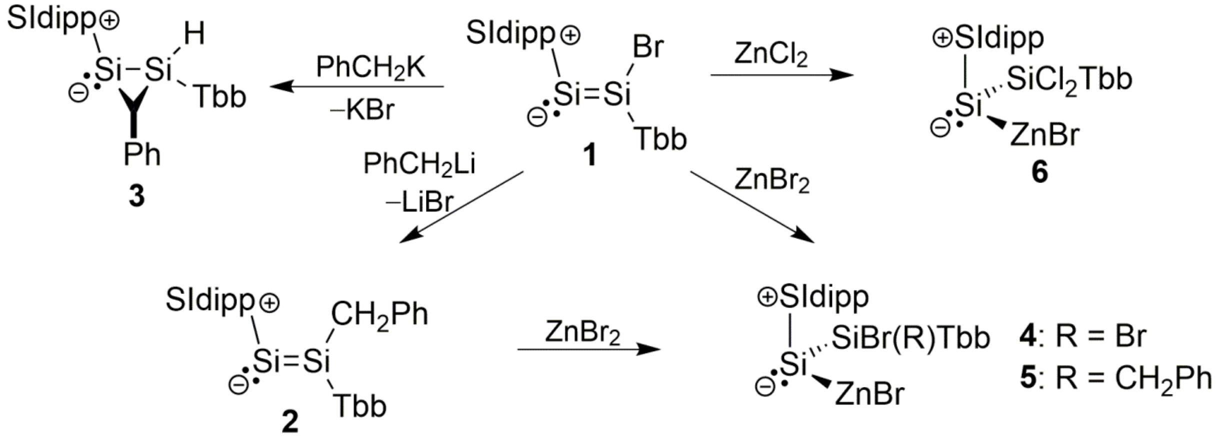
The chemistry of disilynes (RSi≡SiR) has flourished since the isolation of a room-temperature stable derivative some years ago.[1] In comparison, disilavinylidenes (:Si=SiR$_2$), which are valence-isomers of the disilynes, could not be isolated so far. The parent compound (:Si=SiH$_2$) was recently formed in the gas-phase reaction of ground-state atomic silicon (Si) with SiH$_4$.[2] We have been interested in developing valuable sources for these extremely reactive species, that could be used in molecular silicon chemistry, and recently succeeded in the isolation of the first NHC-stabilized disilavinylidene (SIdipp)Si=Si(Br)Tbb (**1**), (SIdipp = C[N(C$_6$H$_3$-2,6-*i*Pr$_2$)CH$_2$]$_2$, Tbb = C$_6$H$_2$-2,6-((CH(SiMe$_3$)$_2$)$_2$-4-*t*Bu).[3]

Herein, we report on the reactions of **1** with carbanions and Lewis acids providing access to new classes of hypo-valent Si compounds (*Scheme 1*). Treatment of **1** with PhCH$_2$M (M = Li, Na, K) afforded either the disilavinylidene substitution product **2** or the NHC-stabilized disilacyclopropylidene **3** depending on the alkali metal. Compounds **1** and **2** react selectively with ZnX$_2$ to yield unprecedented NHC-stabilized zinco-silylenes (**4** – **6**). All compounds were fully characterized. The present reactivity studies highlight the ambiphilic character and the high synthetic potential of **1**.



Scheme 1 Reactivity studies of the NHC-stabilized disilavinylidene Tbb(Br)Si=Si(SIdipp) (**1**).

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Modelling Disorder with DSR in ShelXle and Olex2

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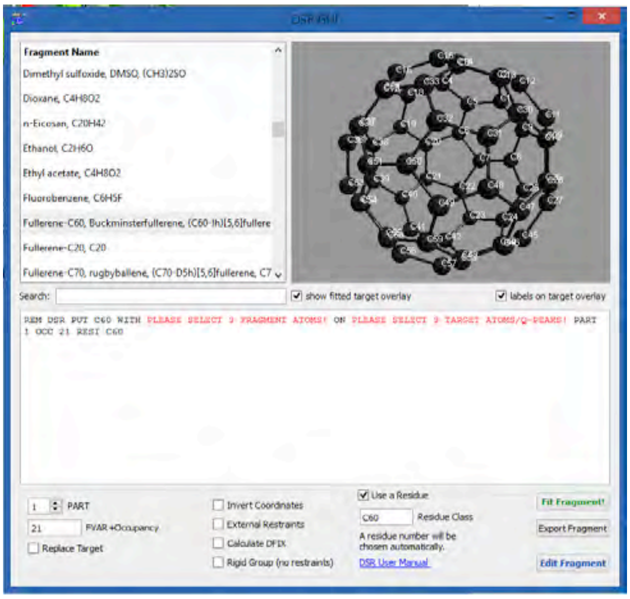
One of the remaining challenges in single-crystal structure refinement is the proper description of disorder in crystal structures. DSR[1] performs semi-automatic modelling of disordered moieties using SHELXL[2]. It contains a database with 120 molecular fragments and their corresponding stereochemical restraints and a fitting procedure to place these fragments on the desired position in the unit cell. The program is also suitable for speeding up model building of well-ordered crystal structures. Writing a special DSR command into the SHELXL .res file of the target structure instructs DSR on where to place and how to orient a molecular fragment from the fragment database in the unit cell.

Recent features to DSR such as the Graphical user interfaces (GUIs) for DSR in ShelXle[3] (figure 1) and Olex2[4] are presented. With the new GUI, the user has full control over every aspect of the model building while keeping the procedure as simple as possible. Also additional checks were added to keep restraints in the database consistent and to avoid erroneous refinement models or brainless automation.

The software can be downloaded at [5].



Dimethyl sulfoxide, DMSO, (CH3)2SO
Dioxane, C4H8O2
n-Eicosan, C20H42
Ethanol, C2H6O
Ethyl acetate, C4H8O2
Fluorobenzene, C6H5F
Fullerene-C60, Buckminsterfullerene, (C60-Ih)[5,6]fullere
Fullerene-C20, C20
Fullerene-C70, rugbyballene, (C70-D5h)[5,6]fullerene, C7

Search:
☑ show fitted target overlay
☑ labels on target overlay

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REM DSR PUT C60 WITH PLEASE SELECT 3 FRAGMENT ATOMS! ON PLEASE SELECT 3 TARGET ATOMS/Q-PEAKS! PART
1 OCC 21 RESI C60
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1 PART
21 FVAR+Occupancy
☐ Replace Target
☐ Invert Coordinates
☐ External Restraints
☐ Calculate DFIX
☐ Rigid Group (no restraints)
☑ Use a Residue
C60 Residue Class
A residue number will be chosen automatically.

Figure 1 Graphical user interface for DSR in ShelXle.

Strain-Promoted Azide-Alkyne Cycloaddition at Tin Sulfide Clusters

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In agreement with the fact that most known organotin(IV) compounds are very toxic, they show high biological and antitumor activity; in a few cases they are even more effective than cisplatin. With sterically demanding substituents, like those in trialkyltin(IV) and triaryltin(IV) compounds, the toxicity decreases.[1,2] However, so far only few organotin(IV) compounds have been investigated in regard of their biological activity and pharmaceutical relevance.[3] Recently, we successfully coupled different Boc-protected amino acids or peptides to precursor clusters $[(R^1Sn)_4S_6]$ (**A**) or $[(R^1Sn)_3S_4Cl]$ (**B**) (R^1 = $CMe_2CH_2C(O)Me$) and characterized them by NMR spectroscopy and mass spectrometry.[4] Now, we achieved the first postfunctionalization of a tin sulfide cluster by a strain-promoted azide-alkyne 1,3-cycloaddition (SPAAC) of an azido-adamantane, that was previously attached by condensation to organo-functionalized cluster **B**. According to this proof of concept, we are now able to attach a wide diversity of functional groups to the cluster, allowing the tuning of properties such as solubility, hydrolytic stability, and reactivity.[5]

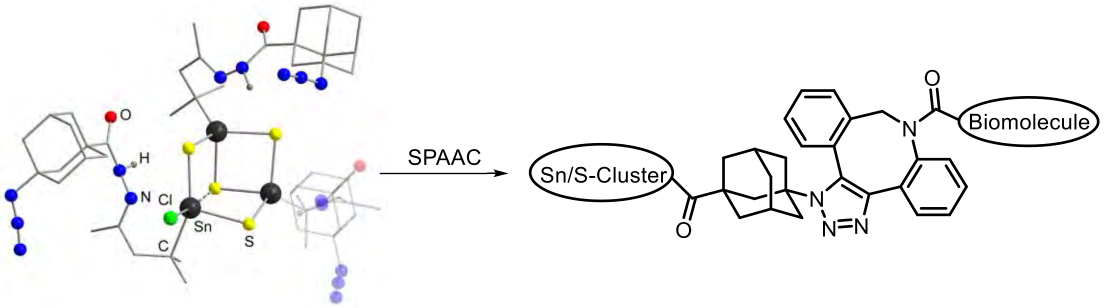

Figure 1 Cluster B with azido-adamantane substituents and postfunctionalization.

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Synthesis and Properties of Hydridosilyl Sulfonium Ions

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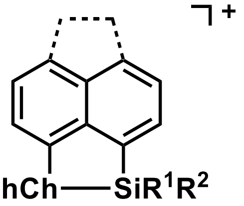
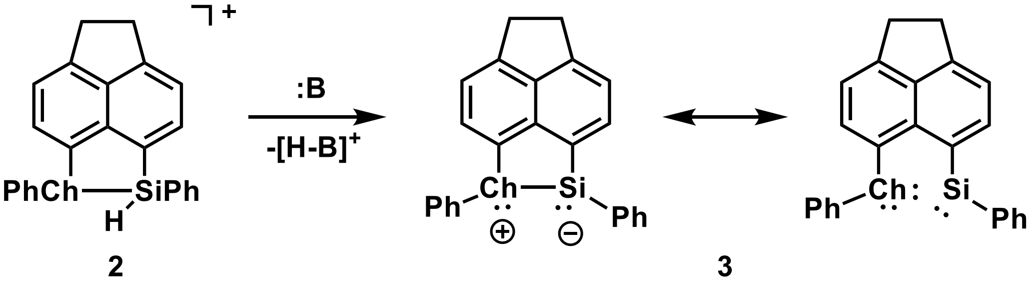
Recently, we presented the synthesis, structure and first applications of a series of silyl chalconium ions **1**.[1] The naphthyl- or acenaphthyl framework as backbone enforces the intramolecular interaction between the silicon center and the chalcogenyl substituent. First investigations on the reactivity of silylated chalconium ions **1** showed catalytic behavior in hydrodefluorination reactions, Diels Alder reactions and Si-H bond activation.



1

Ch = O, S, Se, Te
R^1 = Me, R^2 = Me, ^{t}Bu, Ph

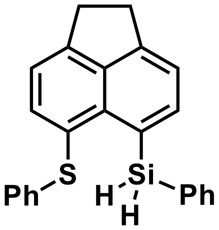
Based on this experience, we planned the synthesis of Si-H substituted chalconium ions **2**. Species **2** show promise to be an active hydrosilylation reagent. In addition, it can be considered as a protonated silylene **3** (Scheme 1), which opens the perspective for new applications of these compounds.[2]



Ch = O (a), S (b), Se (c), Te (d)

Scheme 1 Formation of stabilized silylene **3** from chalconium ion **2**.

Sulfonium ion **2b** was obtained by the hydride transfer reaction of silane **4** with tritylborate $[Ph_3C][B(C_6F_5)_4]$. The properties of the resulting borate **4b**$[B(C_6F_5)_4]$ will be discussed in this contribution.



4

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A Question of Electron (De)localization: Binary and Ternary Zintl Clusters with Ru(*cod*)$^{2+}$ units

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The synthesis of binary and ternary intermetalloid clusters from reactions of homo- and heteroatomic Zintl anions with transition metal complexes is an active field of research that has significantly contributed to the general understanding of cluster formation, structures, and bonding.[1]

While there is a large variety of elemental combinations represented in these ternary clusters, not a single report has been published on the reactivity of binary group13/15 anions towards d-bloc transition metal complexes.

Herein we present the results from reactions of $(\text{TlBi}_3)^{2-}$ with $[\text{Ru}(\textit{cod})(\text{Me-allyl})_2]$ that yield the first ternary cluster of this elemental combination alongside the binary cluster $[\text{Bi}_9\{\text{Ru}(\textit{cod})\}_2]^{3-}$.[2] Unprecedented for Zintl clusters, electron-precise bonding and delocalized 2e3c bonds coincide within one molecule. Quantum chemical studies are presented that are crucial to understand the unique bonding situation.

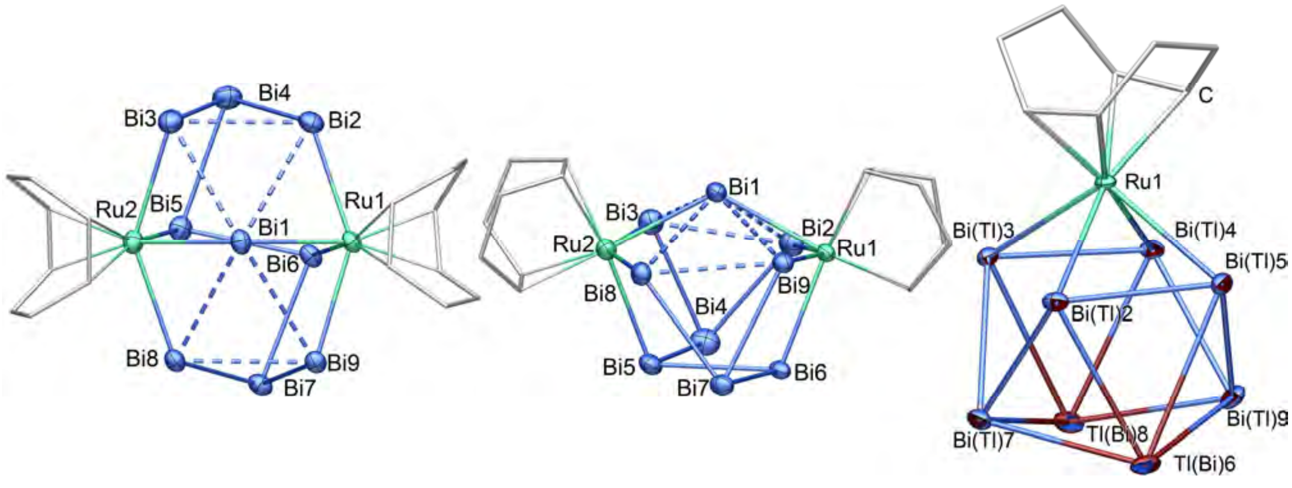

Figure 1 Single crystal structures of $[\text{Bi}_9\{\text{Ru}(\textit{cod})\}_2]^{3-}$ (left, center) and $(\text{Tl}_2\text{Bi}_6\{\text{Ru}(\textit{cod})\})^{2-}$ (right).

[1] a) S. Mitzinger, L. Broeckaert, W. Massa, F. Weigend, S. Dehnen, *Nat. Commun.* **2016**, *7*, 10480; b) S. Scharfe, F. Kraus, S. Stegmaier, A. Schier, T. F. Fässler, *Angew. Chem. Int. Ed.* **2011**, *50*, 3630; c) B. Weinert, S. Dehnen, in *Clusters – Contemporary Insight in Structure and Bonding* (Ed.: S. Dehnen), Springer International Publishing, **2017**, 99.
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Aminotroponiminates: Coordination and Reductive Dimerisation

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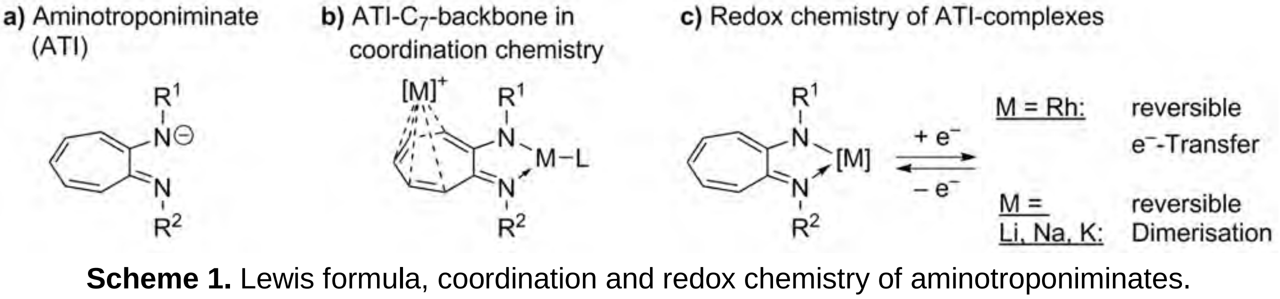
Aminotroponiminates (ATIs) are established as monoanionic, bidentate *N*,*N*-chelating ligands (Scheme 1a). They have found application in the stabilisation of low-valent main group species and in homogeneous catalysis.[1] Here we show that the C_7 backbone of ATIs can play an active role in the coordination and redox chemistry of this class of ligands.

In sodium-ATI-compounds, for instance, $C_7(\pi)\rightarrow M$ bonding interactions are realised (Schema 1b).[2] Cyclic voltammetry of a range of ATI complexes shows that the redox chemistry of ATIs can be controlled by choice of the central atom. Whereas reversible electron transfer at strongly negative potentials is observed for Rh compounds, alkali metal complexes undergo chemically reversible, reductive dimerisation with selective C–C bond formation (Scheme 1c).[3] The reductive dimerisation was found to be a general reactivity pattern for alkali metal ATIs. Its selectivity can be controlled by choice of the central atom and by the substitution pattern of the ATI ligand. These findings show that ATIs have to be included into the growing family of redox-active ligands. Preliminary catalytic studies suggest possible applications of ATIs as electron transfer catalysts in C–C coupling reactions.



Scheme 1. Lewis formula, coordination and redox chemistry of aminotroponiminates.

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Synthesis and Characterization of a Stable Tetrasilatetraamide

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The objective of this work is to study the formation mechanisms of strained geometry group 14 element clusters whose structures resemble the surface of the group 14 element [1]. In particular siliconoid clusters [2] are the focus of this work. The clusters will be investigated in reactions such as H_2 addition, ethylene absorption, addition of other small molecules, and redox processes.

For this purpose trihalogenosilanes [3] were synthesized and reduced with different reducing agents based on alkali and alkaline earth metals. With this approach a bicyclo[1.1.0]tetrasilatetraamide (see Figure) with two three- and two four-coordinate silicon atoms was obtained. The synthesis, characterization, and reactivity of this compound will be presented in this poster.

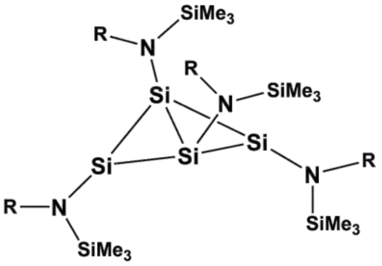

Figure 1. Structure of the Bicyclo[1.1.0]tetrasilatetraamide (R = 2,6-Diisopropylphenyl).

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Mechanistic Studies of a Highly Active Molecular Diruthenium Water Oxidation Catalyst

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Water oxidation constitutes the bottleneck in exploiting the sun's energy for generating solar fuels. Consequently, in the past decades, significant efforts have been devoted to the development of efficient water oxidation catalysts (WOCs), both heterogeneous and homogenous. Molecular complexes are particularly useful due to their convenient tunability and the possibility of obtaining detailed mechanistic insight.

Following this approach, our groups established a series of rugged dinuclear ruthenium complexes for water oxidation based on highly organized pyrazolate-based ligand scaffolds, such as **1**$^-$.[1,2] For further elaboration of these dinuclear ruthenium WOCs, anionic carboxylate groups were incorporated in the ligand framework in order to significantly lower the redox potentials. This resulted in complex **2**$^+$, which exhibits an exceedingly high water oxidation activity.[3]

Herein we present the new complexes **3**$^{3-}$ and **4**$^{3-}$, which are derivatives of **2**$^+$ with improved water solubility. Both complexes were thoroughly characterized and investigated in regard to their chemical and photochemical water oxidation activity.

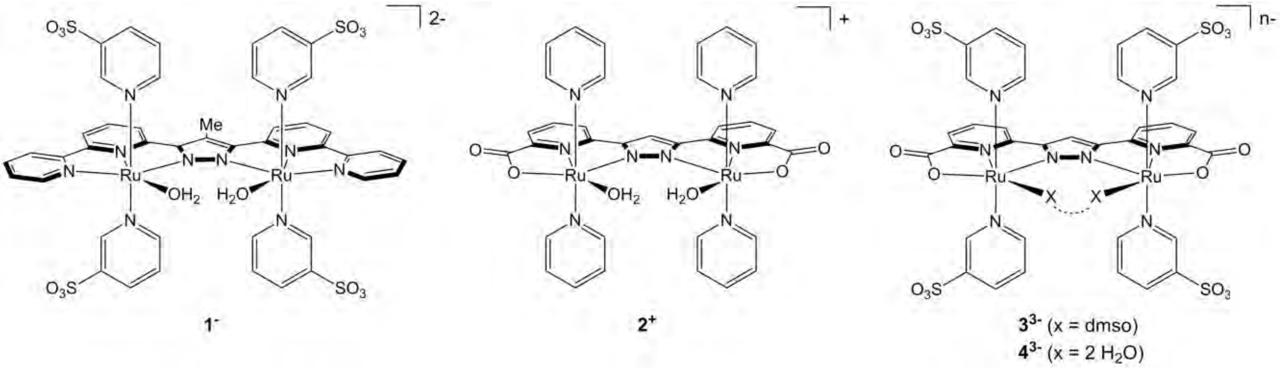

Figure 1 Schematic representation of the complexes **1**$^-$, **2**$^+$. **3**$^{3-}$ and **4**$^{3-}$.

1 S. Neudeck, S. Maji, I. López, S. Meyer, F. Meyer, F. A. Llobet, *J. Am. Chem. Soc.*, **2014**, *136*, 24.

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Low valent germanium cations for small molecule activation

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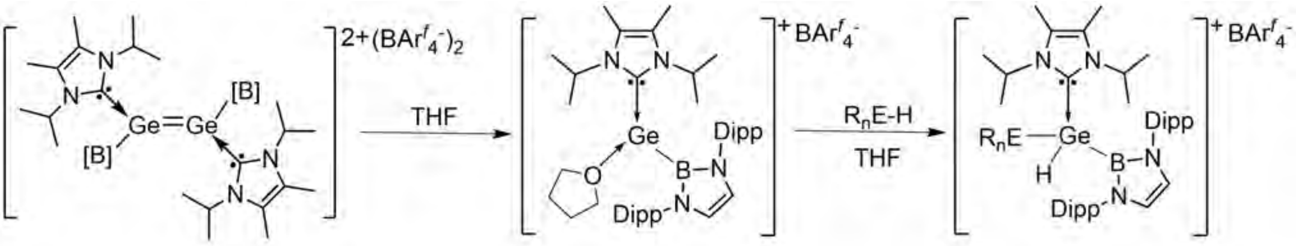
In recent years, a range of main group systems have demonstrated the capability for oxidative addition of small molecules.[1] However, subsequent further reactivity, including reductive elimination, is much rarer.[2] Research from our group and others has probed the consequences of incorporating a net positive charge in carbene-type systems. Germylenes of the type $[R(L)Ge]^+$, for example, show a greater propensity for oxidative addition, disincentivised aggregation of Ge=E bonds,[3] and in one case reversible E-H bond activation.[4]

Herein, novel low-coordinate germanium cations are described, featuring an N-heterocyclic carbene and a strong anionic donor. Oxidative addition of a range of E-H bonds has been demonstrated, with evidence for onward reactivity. Sterically unprotected Ge=N and Ge=C moieties have been synthesised, and novel two-centre E-H addition reactivity also achieved across the latter.



$[B] = B(NDippCH)_2$; Dipp = 2,6-$iPr_2C_6H_3$; $Ar^f = 3,5\text{-}(CF_3)_2C_6H_3$

Figure 1 Reactivity of a boryl substituted germanium cation

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2 A. V. Protchenko, J. I. Bates, L. M. A. Saleh, M. P. Blake, A. D. Schwarz, E. L. Kolychev, A. L. Thompson, C. Jones, P. Mountford, S. Aldridge, *J. Am. Chem. Soc.*, **2016**, *138*, 4555.
3 A. Rit, R. Tirfoin, S. Aldridge, *Angew. Chem., Int. Ed.*, **2016**, *55*, 378.
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Synthesis and Application of 1,2,4-Triazolium-based Chiral, Cationic Phosphonites

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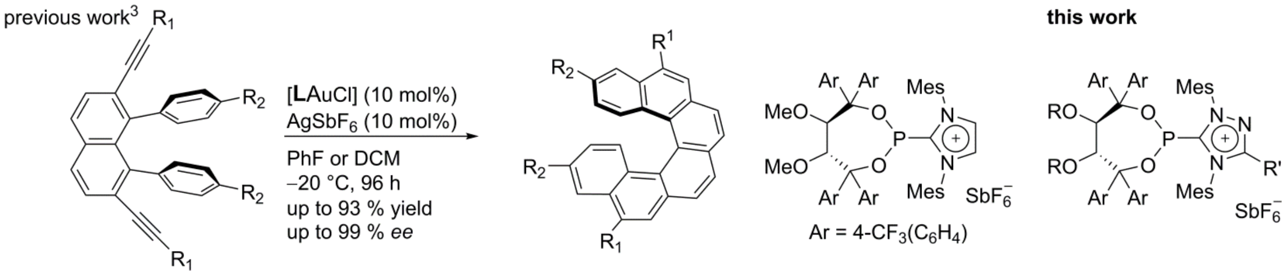
Phosphorus-based ligands have a tremendous impact on todays organometallic chemistry, most likely due to their readily tailorable steric and electronic properties.[1] Introduction of a positively-charged substituent directly attached to the phosphorus atom reduces its *σ*–donor character and enhances its *π*–accepting nature.[2] Hence cationic phosphorus-based ligands enable the development of electron-poor transition metal catalysts.[2] Recently, our group was able to prepare various substituted [6]carbohelicenes in high optical purities, using a gold-catalyst based on a TADDOL-derived cationic phosphonite ligand (figure 1).[3]

To obtain even more *π*–acidic Au(I) complexes, a second generation of chiral, cationic phosphonite ligands containing 1,2,4-triazolium substituents was investigated. Synthesis of these cationic phosphonites and the corresponding Au(I) complexes are the topic of this presentation. Recent results of the application of these chiral, cationic phosphonites in the enantioselective synthesis of [6]carbohelicenes will also be presented.



1 **2** **L** **L**^{triaz}

Figure 1 Au(I)-catalyzed enantioselective synthesis of [6]carbohelicenes using chiral, cationic phosphonite **L** and the second generation of chiral, cationic phosphonites containing a 1,2,4-triazolium substituent **L**^{triaz}.

[1] For selected examples, see: (a) C. A. Tolman, *Chem. Rev.*, **1977**, *77*, 313. (b) J. Carreras, G. Gopakumar, L. Gu, A. Gimeno, P. Linowski, J. Petuškova, W. Thiel, M. Alcarazo, *J. Am. Chem. Soc.*, **2013**, *135*, 18815. (c) G. Mehler, P. Linowski, J. Carreras, A. Zanardi, J. W. Dube, M. Alcarazo, *Chem. Eur. J.*, **2016**, *22*, 15320. (d) H. Tinnermann, C. Wille, M. Alcarazo, *Angew. Chem. Int. Ed.*, **2014**, *53*, 8732. (e) Á. Kozma, T. Deden, J. Carreras, C. Wille, J. Petuškova, J. Rust, M. Alcarazo, *Chem. Eur. J.*, **2014**, *20*, 2208.

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Halogen Stabilised Silyl Cations

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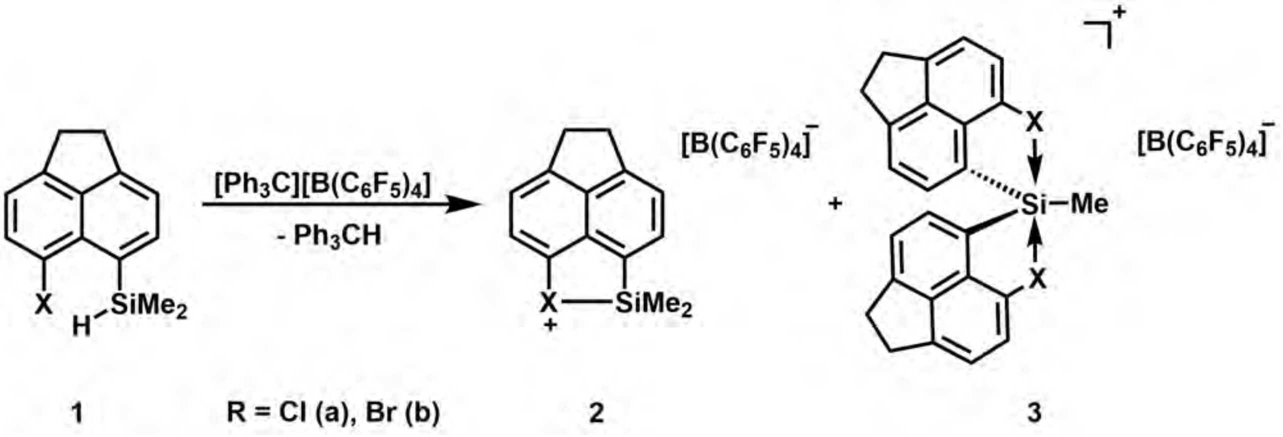
Silyl cations are strong Lewis Acids and found beneficial applications in catalysis and in bond activation reactions. Therefore the Lewis acidity can be influenced by an electron donating group and as a consequence the reactivity of the silyl cations can be tuned.[1] Here we report the syntheses of two silyl borates **2**,**3** $[B(C_6F_5)_4]$, where the positive charged silicon atoms are intramolecularly stabilised by electron donation from halogen substituents.



Scheme 1 Hydride transfer reaction of silanes **1** with trityl borate.

We noticed a different reactivity between both halonium ions **2**. In addition we found that the halonium ions **2** undergo an intermolecular aryl-alkyl exchange reaction to form the siliconium ions **3**.[2,3]

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Is crystal structure determination a routine method?

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At the 2001 DGK meeting in Bayreuth, Roland Boese asked the question “is crystal structure determination a routine method?” and answered “in principle yes, but only in routine cases!” Even though what is considered a routine case may have shifted over the past 16 years, Roland Boese’s answer is still largely correct. This poster presents a crystal structure that looked like a routine case at first but turned out to require rather more love and care than the average service structure.

TriazaphospholeniumTetrafluoroborate: The First Phosphorus Derivative of a Mesoionic Carbene

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Since the pioneering work of Bertrand and Arduengo III, heteroatom-stabilized carbenes have emerged to an important and versatile class of compounds during the last decades.[1] Particularly imidazolylidenes of type **A** (Figure 1) have turned into very popular ligands in transition metal chemistry and metal-mediated synthesis. Originating from the highly versatile and flexible copper-catalyzed [3+2] cycloaddition of acetylenes with organic azides ("click-reaction"), 1,2,3-triazolylidenes of type **B** have recently been developed as a new class of abnormal carbenes.[2] As a matter of fact, these mesoionic compounds (MICs) currently play a significant role in carbene-chemistry, due to their modular synthesis and flexibility of metal insertion.

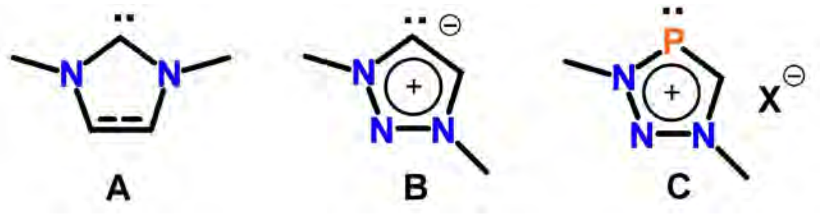

Figure 1 Imidazolylidene (**A**), 1,2,3-triazolylidene (**B**) and 1,2,3,4-triazaphospholenium salt (**C**).

As an extension of our previous work on low-coordinate phosphorus heterocycles and inspired by the obvious valence isoelectronicity between 1,2,3-triazolylidenes and 1,2,3,4-triazaphospholenium salts (**C**), we now started a program to investigate hitherto unknown phosphorus derivatives of mesoionic carbenes and report here on our first results concerning their synthesis, reactivity and coordination chemistry.

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Hexaphenylcarbodiphosphorane complexes of metal(I/II) bis(trimethylsilyl)amides

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The class of the carbodiphosphoranes was first described in 1961 by Ramirez *et al.*[1] Carbodiphosphoranes are characterized by their central carbon atom in the formal oxidation state of zero.[2] Therefore carbodiphosphoranes are capable of σ- and π-donation. The most prominent compound of this class is hexaphenylcarbodiphosphorane $C(PPh_3)_2$ (**1**).

There are many complexes of **1** described in the literature.[3] In this work we describe the syntheses of metal bis(trimethylsilyl)amides complexes of **1**, as shown below.

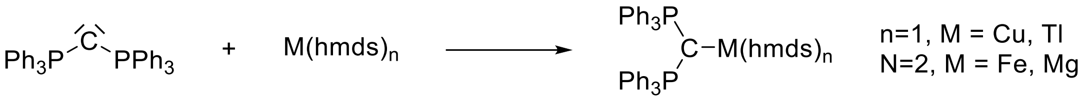

Figure 1 Reaction scheme of **1** with bis(trimethylsilyl)amides.

The spectroscopic, electronic (and magnetic) properties of the complexes will be discussed alongside with first reactivity studies. Also, results of DFT calculations concerning the bonding situation in these complexes will be presented.

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Reactivity of B_2X_4 and Ga_2X_4 towards Platinum Complexes

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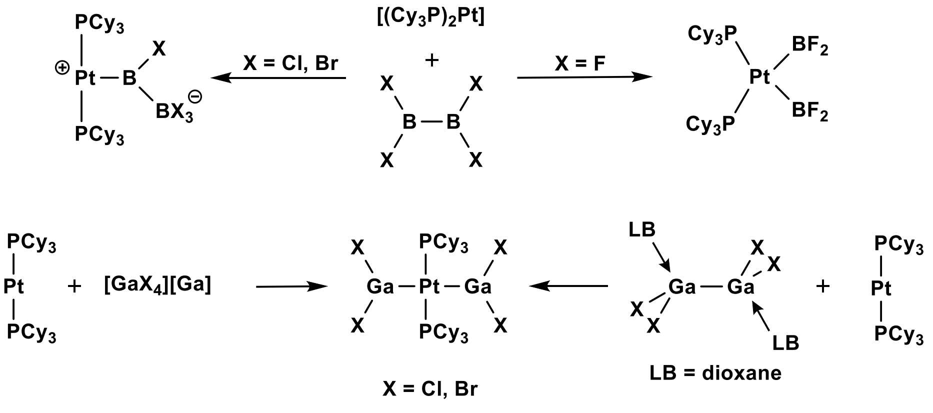
Our general interest in transition metal boryl compounds led us to investigate the chemistry of B_2X_4[1] with the well-established[2] transition metal Lewis base $[(PCy_3)_2Pt]$, leading to an unusual outcome. While B_2F_4 is known to undergo oxidative addition of the B–B bond resulting in bisboryl complexes (as earlier shown by *Norman* and *Marder* with various transition metals[3]), the combination of equimolar amounts of B_2Cl_4 or B_2Br_4 with $[Pt(PCy_3)_2]$ provides highly unusual zwitterionic borylborato complexes with a positive charge at Pt and a σ-bound $–B(X)BX_3^-$ (X = Cl, Br) ligand. The analogous reactions with $[Ga][GaX_4]$ or $Ga_2X_4\cdot 2$dioxane (X = Cl, Br) effects in an oxidative addition of the Ga–Ga bond to the platinum center, which bears two gallyl ligands trans to each other.



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A Homoleptic Beryllium Azide

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In this work we present the synthesis and structure of the first homoleptic beryllium azide **1** $(Ph_4P)_2Be(N_3)_4$. The compound is analyzed by heteronuclear NMR-spectroscopy (^{9}Be and ^{14}N) and investigated with the help of quantum mechanical methods including NBO-, ELF- and LOL analysis as well as with calculated NMR-shifts (GIAO).

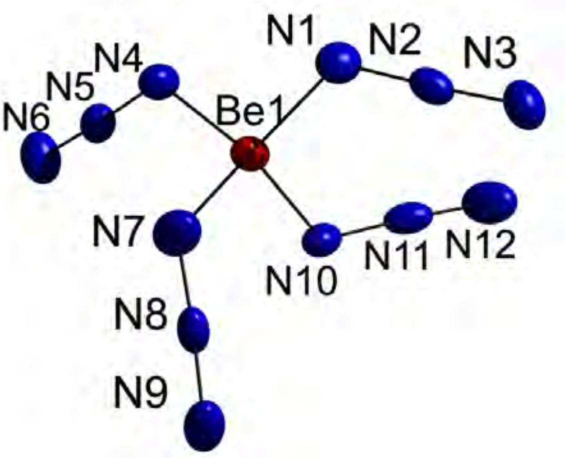

Figure 1 molecular structure of $Be(N_3)_4^{2-}$

$Be(N_3)_2$ was in situ synthesized by the reaction of $BeCl_2$ with an excess of Me_3SiN_3 under reflux conditions for seven days and then reacted with two equivalents of Ph_4PN_3, yielding **1** as large colorless crystals after workup which didn't show any shock or temperature sensitivity.

$$BeCl_2 + \text{xs } Me_3SiN_3 \xrightarrow[\text{7 days}]{\text{reflux}} Be(N_3)_2 \xrightarrow[CH_2Cl_2]{2\ Ph_4PN_3} (Ph_4P)_2Be(N_3)_4$$

Figure 2 synthesis of $(Ph_4P)_2Be(N_3)_4$

The quantum mechanical analysis indicate, that the Be-N-bonds are highly ionic with the values (Be +1.59, N_α −0.68, N_β +0.21, N_γ −0.42) from NBO-analysis with few covalent contributions as one can see in the ELF- and LOL-plots. The ^{9}Be-NMR shift (0.04 ppm) underline that the tetrahedral coordination mode is also present in solution and the ^{14}N NMR shifts (−310 (s, N_α, $\nu_{1/2}$ = 18 Hz), −246 (s, N_γ, $\nu_{1/2}$ = 95 Hz), −132 (s, N_β, $\nu_{1/2}$ = 44 Hz) support the assumption that the azide (N_3^-) is highly ionic.

1 D. Naglav, B. Tobey, B. Lyhs, D. Bläser, C. Wölper, G. Jansen, and S. Schulz *manuscript submitted*

A Copper Complex as a Redox Catalyst in the Hydrogen Evolution Reaction

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The electrochemical or photochemical proton reduction is an important means of converting electric or light energy into chemical energy, i.e. hydrogen. The energy can be regenerated by burning H_2 in a fuel cell.[1] Platinum is the most efficient catalyst for the HER[2] but it is very expensive and therefore complexes based on earth abundant metal ions such as cobalt, nickel or molybdenum have been investigated in the last decades as HER catalysts. The majority of these complexes has been studied in organic solvents with organic acids as proton sources, a few in water, while examples of earth-abundant metal ion complexes operating in seawater are rare.

We utilised a mononuclear copper complex, **1**, in the electrochemical-driven HER in buffered Millipore water and standardised seawater.[3] Complex solutions of **1** are active at solution's pH of 4 to 8, yet, the active species is different depending on the reaction medium. In acidic and neutral phosphate buffered water, the initially formed $[Cu^{I}H_2L^{1}]^{3+}$ species decomposes and the high activity originates from the decomposition products and from soluble species. In artificial seawater the catalytic activity was much lower, virtually no decomposition was observed, and likely the complex represents the active species.[3]

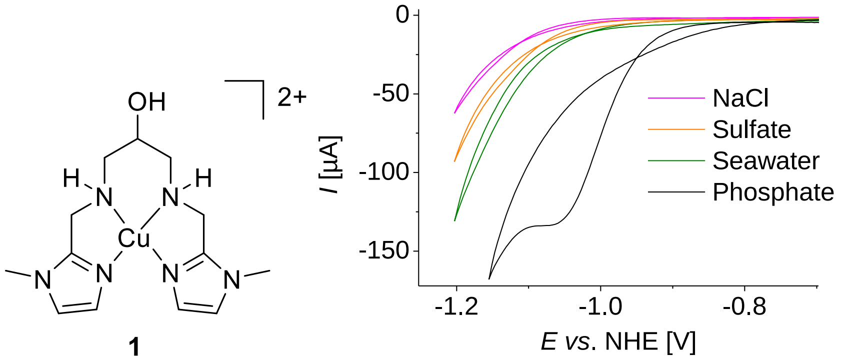

Figure 1. Left : Copper complex, which was utilised in the study. Right : CV of the catalytic wave in dependence of the conducting salt at pH = 8, I = 0.1 M, v = 0.1 Vs^{-1}, [**1**] ≈ 1 mM.

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Wagner-Meerwein Type Rearrangements in Oligosilanes

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Oligosilanes exhibit a high preference to rearrange via methyl or trimethylsilyl shifts into more branched isomers after treatment with a Lewis acid.[1,2] These rearrangements were found to proceed via silyl cationic species.[3]

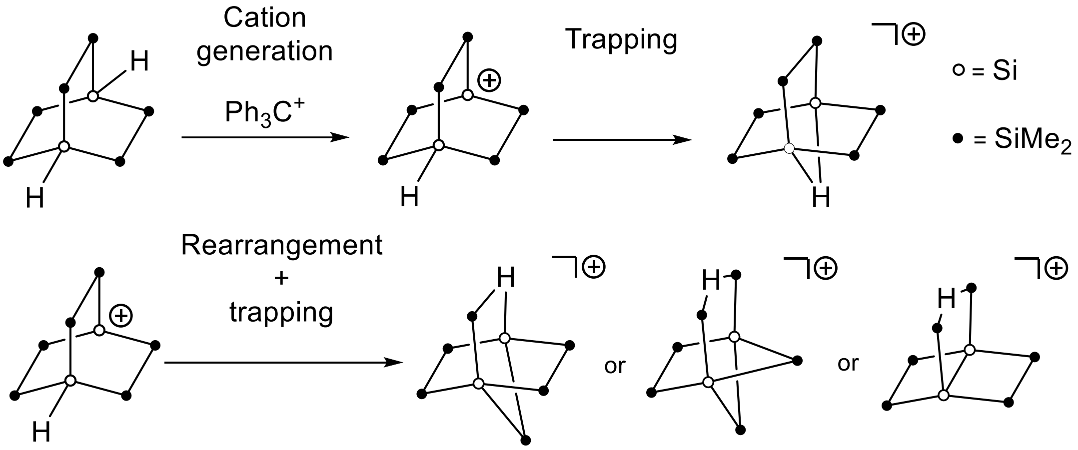

Figure 1. Formation of Si-H-Si bridged silyl cations

Introduction of Si-H functionalities in the oligosilane framework facilitates the selective generation of cationic centers by hydride transfer reaction and also offers the possibility to trap intermediates in the rearrangement reaction by formation of intramolecular 2e3c Si-H-Si bridges by the so called hydrogen trick.[4]

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Coordination Chemistry of the Main Group Elements with Bulky Anionic Guanidinato Ligands

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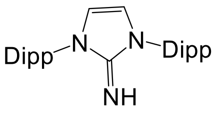
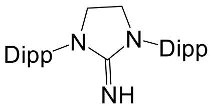
Ligands of the guanidinate family have been pioneered by Tamm, Inoue and Rivard, proved to be highly effective at stabilising transition metal, f-metal and main group systems.[1-3] On top of previous work we have synthesized two novel ligands to further extend the guanidinato family, **1c** and 1d, which are the ring expanded analogues of **1a**[1] and **1b**[4] reported previously. With DFT calculation we have reveal their electronic properties such as σ- and π- donation, showing stronger donor strength from guanidinato ligands with expanded ring. In further study, we have investigated the coordination chemistry of main group element, for example, on group 14, with guanidinato substituents. This includes a range of unsymmetrical and symmetrical group 14 compounds such as $Sn(N(SiMe_3)_2)(n\text{-}DippN)$, where n= 5, 6, and 7 (**2a**). These compounds have been characterised by *in situ* ^1H, ^{13}C and ^{119}Sn NMR spectroscopy and in the case of n=7 **(2b)** by X-ray crystallography. In the case of Pb chemistry after the formation of labile intermediate $Pb((N(SiMe_3)_2)(IDippN)$, it readily begins to convert into plumbylenoid **2c** at room temperature. This conversion serves as a very rare example of C-H activation by a bimetallic group 14 system. Future study will be on group 13 elements such as boron, where we will attempt to stabilize boron cation (**2d**), an electron deficient system, with these strong donors.



1a



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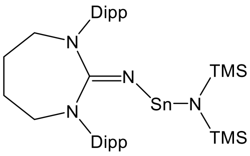
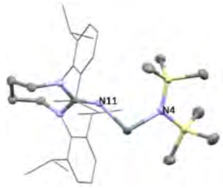


2a



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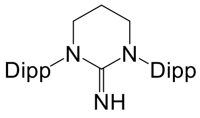
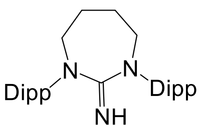
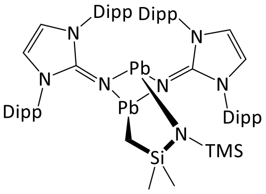


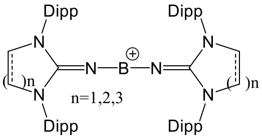
1c



1d



2c



2d

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Preparation of novel ternary selenidocadmates

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The electronic properties of II-VI semiconducting materials, for example of CdSe or HgSe, could be affected by formally introducing K_2Se into these structures.[1,2] This resulted in anionic structures with different dimensionalities, which showed a blue-shift of their band gaps and new photo-conducting and luminescent properties.[3] Deconstructing the 3D network structure of $K_2Sn_2Se_5$ is possible by ionothermal treatment in the presence of an amine through a 2D layered phase to a 1D chain structure back to a 3D network.[4] We now intend to prepare ternary phases of $K_xCd_ySe_z$ to use them as starting materials, based on the structural diversity of the analogous solid phases containing Hg.[5-7]

Recently it was possible to prepare two ternary K/Cd/Se phases by reacting K_2Se with CdSe at the ratios 1:3 and 3:1 followed by solvothermal extractions in *en*. We obtained the first single-crystal structure determination of $K_2Cd_3Se_4$. Furthermore, we succeeded in the synthesis of the novel compound K_6CdSe_4, which is isostructural with K_6HgSe_4.[8] As the yields and purities are moderate we are now improving the solvothermal extractions of the solid phases to obtain crystals in higher yields and purities in order to use them as starting materials in the build-up or deconstruction of 3D networks in ionic liquids.

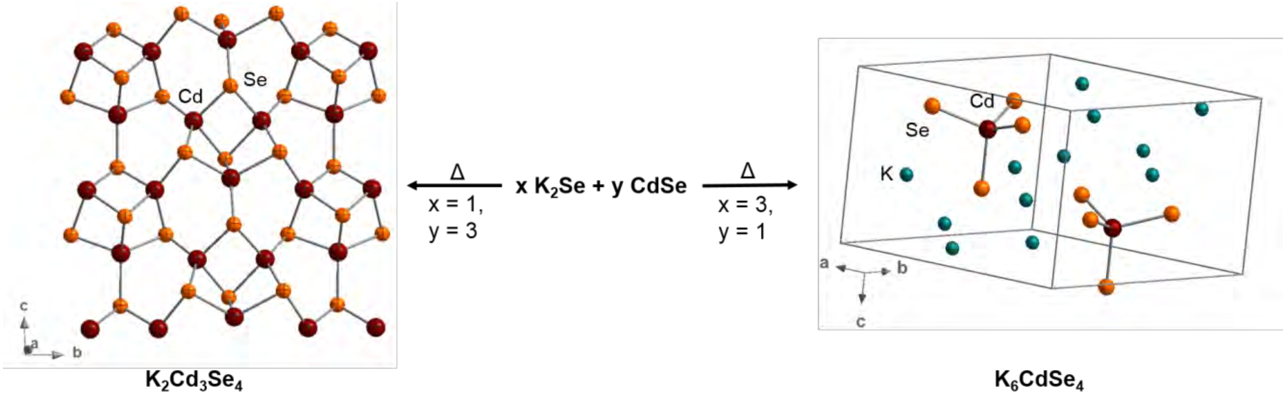

Figure 1 Synthesis of two novel selenidocadmates.

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The $B(C_6F_5)_3$-Catalyzed Tandem Meinwald Rearrangement-Reductive Amination

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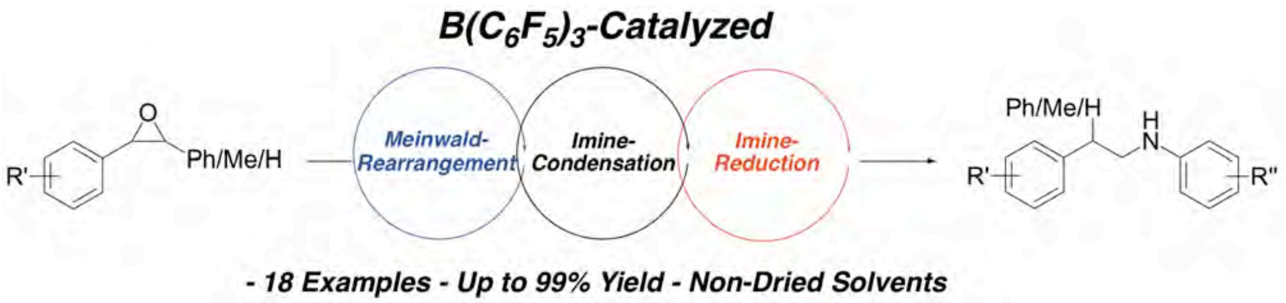
Tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) is a powerful reagent that found in recent years many applications as catalyst for Frustrated Lewis pair type (FLP) transformations. Examples include its use as catalyst for hydrogenation[1] and hydrosilylation[2] reactions. Recently, the $B(C_6F_5)_3$-catalyzed reductive amination of aldehydes that uses hydrosilanes as reducing agents has been reported.[3] As $B(C_6F_5)_3$ is also capable of catalyzing the Meinwald-rearrangement,[4] it was of interest if both reactions could be performed in a one-pot tandem procedure.

Here, a system of three coupled catalytic cycles enabling the one-pot transformation of epoxides to amines via Meinwald-rearrangement, imine condensation and imine reduction is presented (Figure 1).[5] This assisted tandem catalysis is catalyzed by $B(C_6F_5)_3$ resulting in the first tandem Meinwald rearrangement-reductive amination protocol. The reaction proceeds in nondried solvents and yields β–functionalized amines. In particular, β–diarylamines are obtained in high yields. The protocol has been tested for the scope of epoxides and amines, and is a complementary strategy to the classic Lewis-acid mediated synthesis of amino alcohols from amines and epoxides.

Figure 1 The $B(C_6F_5)_3$-catalyzed transformation of epoxides to amines via tandem Meinwald rearrangement-reductive amination.



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Synthesis of Novel *N*-Heterocyclic Silylenes

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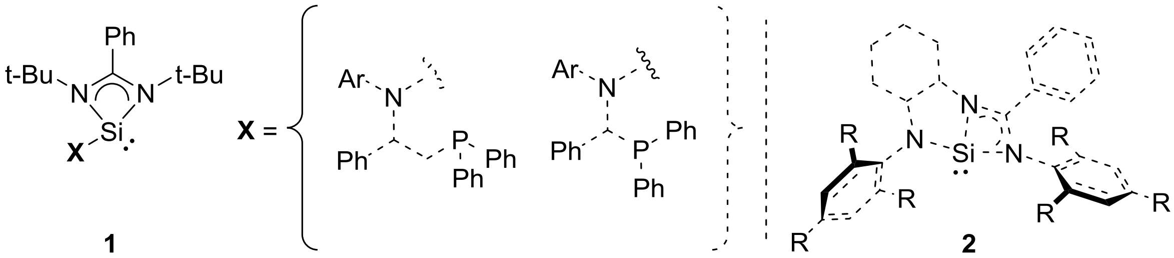

Scheme 1: Examples of the synthesis of novel 4-membered *N*-heterocyclic silylenes.

Since *West* and *Denk* reported the first isolable *N*-heterocyclic silylene (NHSi) in 1994 transition metal complexes now enjoy an enormous attention. But in comparison to the ubiquitous reports of *N*-heterocyclic carbene (NHC) complexes, NHSi complexes are still comparatively rare.[1] Nevertheless they can perform interesting stoichiometric transformations. Since 2012 publications of catalytically active NHSi transition metal complexes are remarkably increasing with a broad range of applications (e.g. C-H bond borylation of arenes, cycloaddition reactions, etc.).[2-4]

The main target is to synthesize and isolate suitable stable *N*-heterocyclic silylene ligands for the complexation of group 11 metals (Cu, Ag and Au) on the basis of the 4-membered *N*-heterocyclic silylene **1** (**Scheme 1**). There are just a few group 11 NHSi complexes known so far but the various catalytically applications of their NHC analogues illustrate the huge potential of such compounds.[5-6] Therefore the first step is to provide new silylenes containing additional donor-sites for enhanced coordination of transition metal centres. Ongoing research will also investigate the synthesis of sterical demanding silylenes (**2**) with a very similar binding motif to **1** by providing an intern donor-function.

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Unprecedented coordination behavior of a highly Lewis-acidic cationic Mg β-diketiminate complex

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Cationic complexes of group 3 and 4 metals are well known as models for the active species in olefin polymerization.[1] By contrast, applications of cationic alkaline-earth metal complexes remain scarce[2,3] The field of cationic β-diketiminate complexes is largely untouched and hitherto their existence heavily relies on stabilization by coordinating solvents such as pyridine and THF.[3]

Abstraction of a butyl group from DIPPNacnacMgBu in presence of a neutral alkyne or arene affords a cationic Mg complex coordinated by the respective substrate (Figure 1). These represent rare examples of structurally characterized alkaline-earth metal complexes coordinated by neutral unsupported π-systems.[4] Such complexes are highly interesting model systems for catalyst-substrate interactions in the rapidly growing field of early main group catalysis.[5]

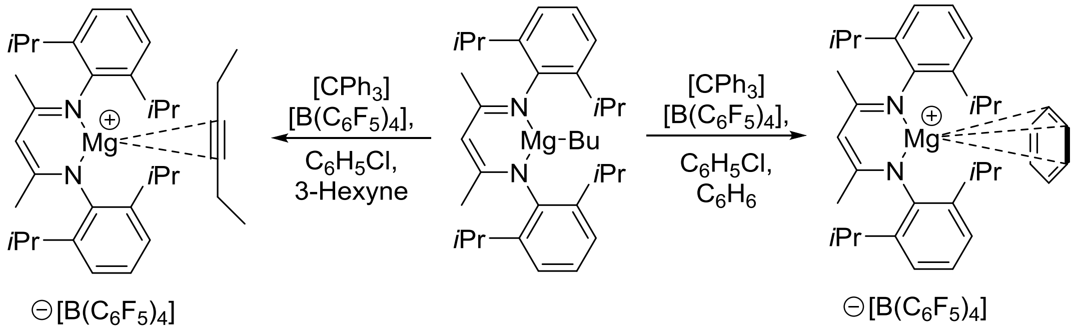

Figure 1. Formation of cationic Mg β-diketiminate complexes in presence of neutral π-ligands

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Yes we Scandium - Sc(η^5-C_5H_5)(η^8-C_8H_8) revisited

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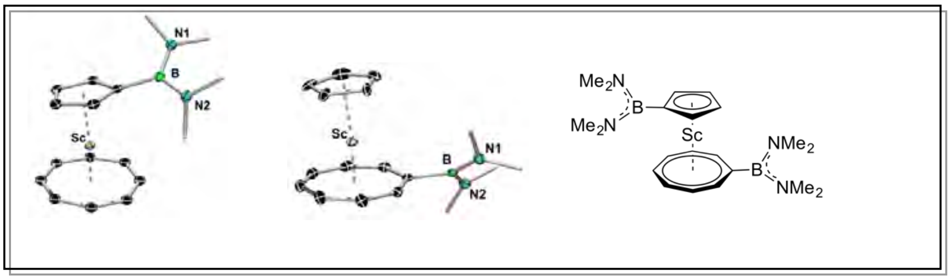
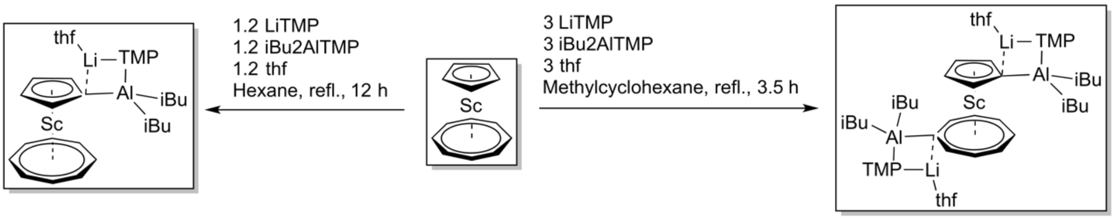
Our working group has a longlasting interest in the chemistry of differently substituted *sandwich complexes*, especially boron-containig complexes and the so called *ansa*- or [*n*]-Metallocenophanes ([*n*]-Metalloarenophanes, respectively) which feature *n* elements bridging the two ring-shaped ligands. The synthesis of the heteroleptic compound Sc(η^5-C_5H_5)(η^8-C_8H_8) (**1**) was recently improved in our working group and the use of boron-substituted ligands allowed for the isolation of the first ring-substituted derivates of **1**.



Scheme 1: Ring-substituted heteroleptic Sc(III)-sandwich compounds.

Attempts of our working group to apply the established metallation-protocols to **1** by using a variety of deprotonating agents and reaction conditions did not lead to the desired deprotonated species. In collaboration with Dr. Antonio Martínez-Martínez and Prof. R. Mulvey from the University of Strathclyde, Glasgow, the metalation could be achieved applying a *trans-metal-trapping* reaction-protocol, recently developed in their group.[1] The reactivity of the metallated systems are subject of current studies in our lab.



Scheme 2: Reaction conditions for the succesful metallation of 1 by Mulvey et al.

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Synthesis of Novel Sulfidostannate Compounds

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Syntheses of chalkogenidometalates have been subject to multifaceted research over the last decades. Chalcogenidometalates exhibit a broad spectrum of chemical and physical properties, including ion conductivity,[1] photocatalytic activity,[2] and ion exchange.[3] The structural motifs vary in their dimensionalities. In our group, we have used ionothermal syntheses for building-up selenidometalate frameworks from smaller units (bottom-up), or for the intentional decomposition of corresponding networks into fragment structures (top-down).[4,5] However, no according studies were undertaken to date with analog sulfide reactants, in spite of their better availability and lower toxicity.

$E_4SnS_4 \cdot 14H_2O$ (E = Li, Na) was used as starting material in the bottom-up approach. The two thiostannates were treated in an ionothermal way with different ratios of two ionic liquids (ILs) at different temperatures, and under addition of the auxiliary amines *en*, DMMP and TMEDA in different amounts. We obtained, among other compounds, a salt of the known $[Sn_{10}S_{20}O_4]^{8-}$ cluster anion,[7,8] however with ionic liquid counterions and an unprecedented assembly of the supertetrahedra (Fig. 1). We achieved the isolation of the clean product from the IL and the characterization via single crystal Raman spectroscopy.

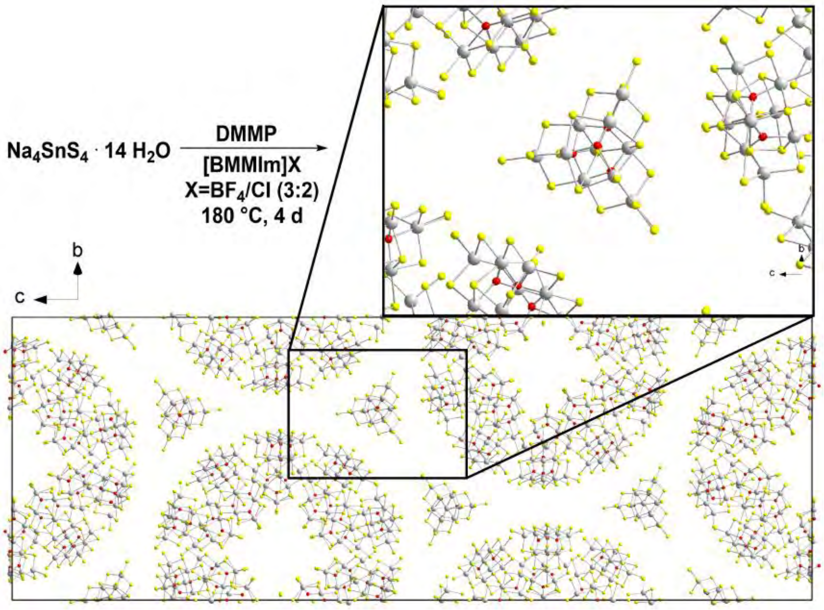

Figure 1: Reaction pathway and unit cell of the novel oxosulfidostannate salt comprising $[Sn_{10}S_{20}O_4]^{8-}$ anions beside ionic liquid cations.

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Investigation of the reactivity of $[Cp'''Co(\eta^4\text{-}P_4)]$

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There are only very few examples known for organometallic compounds containing a *cyclo*-P_4 ligand as an end deck. Beside the complexes $[Cp^RM(CO)_2(\eta^4\text{-}P_4)]$ (M = Nb, Cp^R = Cp*,[1] M = Ta, Cp^R = Cp'', Cp''',[2-3] M = V, Cp^R = Cp*[4]) $[Cp'''Co(\eta^4\text{-}P_4)]$ (**1**)[5] is the first carbonyl free compound of this type.[6] It could be synthesized by the reaction of white phosphorus with the reactive triple deck compound $[(Cp'''Co)_2(\eta^4{:}\eta^4\text{-}C_7H_8)]$ under mild conditions.[5] It shows a high tendency to dimerize irreversibly in solution to form $[(Cp'''Co)_2(\mu_2\text{-}\eta^4{:}\eta^2{:}\eta^1\text{-}P_8)]$ (**2**).[5] The reactivity of **1** towards silver (I) salts, nucleophiles und reduction agents was investigated. The reaction of **1** with Ag[TEF] ([TEF] = $Al\{OC(CF_3)_3\}_4$) leads to the one dimensional polymer $[(Cp'''Co(\mu_3\text{-}\eta^4{:}\eta^1{:}\eta^1\text{-}P_4)Ag]_n^{n+}$ (**3**). The reaction of **1** with NaOH yields $[Cp'''Co(\eta^3\text{-}P_4O(H))]^-$ (**4**). Using $LiCH_2SiMe_3$ as a nucleophile the analogous product $[Cp'''Co(\eta^3\text{-}P_4CH_2SiMe_3)]^-$ (**I-5**) could not be isolated. Instead, it acts as an intermediate (**I-5**) and reacts as a nucleophile with **1** to form $[(Cp'''Co)_2(\mu_2\text{-}\eta^3{:}\eta^3\text{-}P_8CH_2SiMe_3)]^-$ (**5**). Compound **1** can be reduced by $K[CpFe(CO)_2]$ to the dianionic complex $[(Cp'''Co)_2(\mu_2\text{-}\eta^3{:}\eta^3\text{-}P_8)]^{2-}$ (**6**). The reactions are summarized in Figure 1.

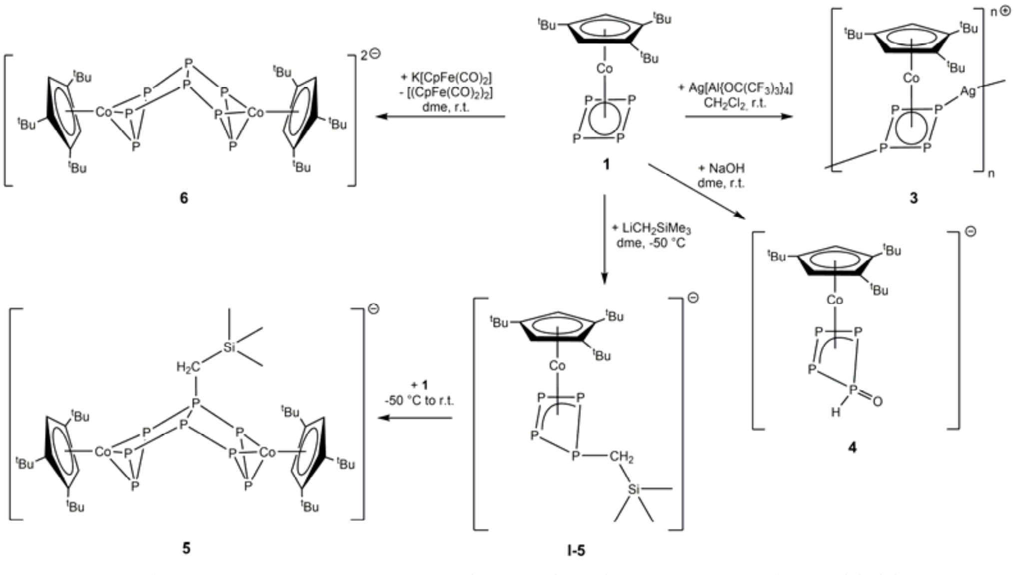

Figure 1: Reactivity of **1** towards Ag[TEF], NaOH, $LiCH_2SiMe_3$ and $K[CpFe(CO)_2]$. Anions and cations, respectively, are omitted.

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A T-Shaped α-Cationic Phosphine with Carbodiphosphorane Backbone

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Inspired by recent work on α-cationic phosphines,[1-3] and geometrically constrained phosphorous(III),[4] we developed a synthetic route to a molecule in which both concepts are combined: the cationic, T-shaped phosphine with carbodiphosphorane backbone, [k^3-C{P(C_6H_4)Ph_2}$_2$]Cl ([CDPP]Cl, Figure 1).

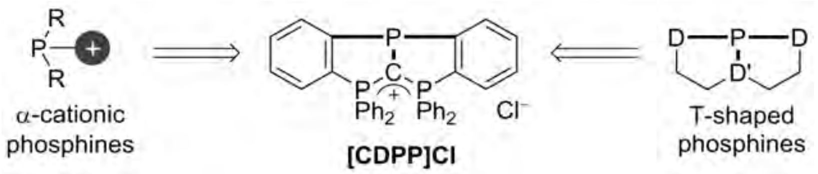

Figure 1 **Amalgamation of two concepts in the cationic T-shaped phosphine [CDPPCl].**

On the trail of its model compounds performed reactivity studies disclosed interesting and, with regards to homogenous catalysis, promising properties of [CDPP]Cl. For example, reaction of [CDPP]Cl with gold(I) precursors provide the appropriate monocationic complexes [CDPPAuCl]X; as indicated by the bond parameters present in the molecular structure (with X = [$AuCl_2$]$^-$ as non-coordinating counter ion), the positive charge is distributed through the carbodiphosphorane moiety. A unique assembly of three types of organophosphorous compounds – phosphine, phosphonium, and pentavalent phosphorane – is present in the neutral T-shaped phosphine k^3-C{P(C_6H_4)Ph_2}{P(C_6H_4)Ph_2Me}, which is obtained by simple reaction of [CDPP]Cl with methyllithium. Just like its starting compound, it readily reacts with gold(I)chloride. Further screening on the search for possible applications of the isolated substances, e. g. in Au(I) catalyzed transformations, are currently under investigation.

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New Lithium Aluminium Hydride Complexes: Synthesis, Structural Characterisation and Applications in Catalysis

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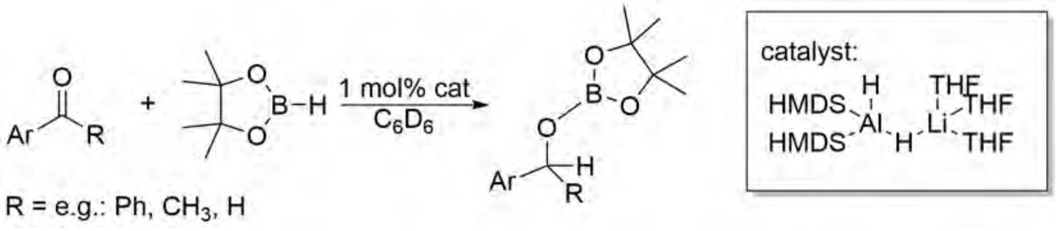
For sustainability purposes, there is growing interest in advancing the catalytic uses of earth abundant main group metals, such as aluminium. While $LiAlH_4$ has long been used for the reduction of unsaturated substrates, recently the groups of Roesky and Nembenna have reported aluminium hydride complexes capable of catalysing hydroboration reactions of alkynes as well as carbonyl compounds.[1]

As reported here, in our work we have prepared a range of heteroleptic lithium aluminium hydride complexes incorporating bulky hexamethyldisilazide [HMDS, $(Me_3Si)_2N^-$] and different donor ligands including THF, *N,N,N',N'*-tetramethylethylenediamine (TMEDA) and *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA). These complexes have been characterised in the solid state by single crystal X-ray diffraction and IR spectroscopy, and in the solution phase using multinuclear NMR spectroscopy. Interestingly, these compounds find application as pre-catalysts for the hydroboration of carbonyl compounds.



Scheme 1: Hydroboration of carbonyl substrates using HBPin

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Stable Co(II) Hydride Pincer Complexes: Isolation and Hydrogenation Catalysis

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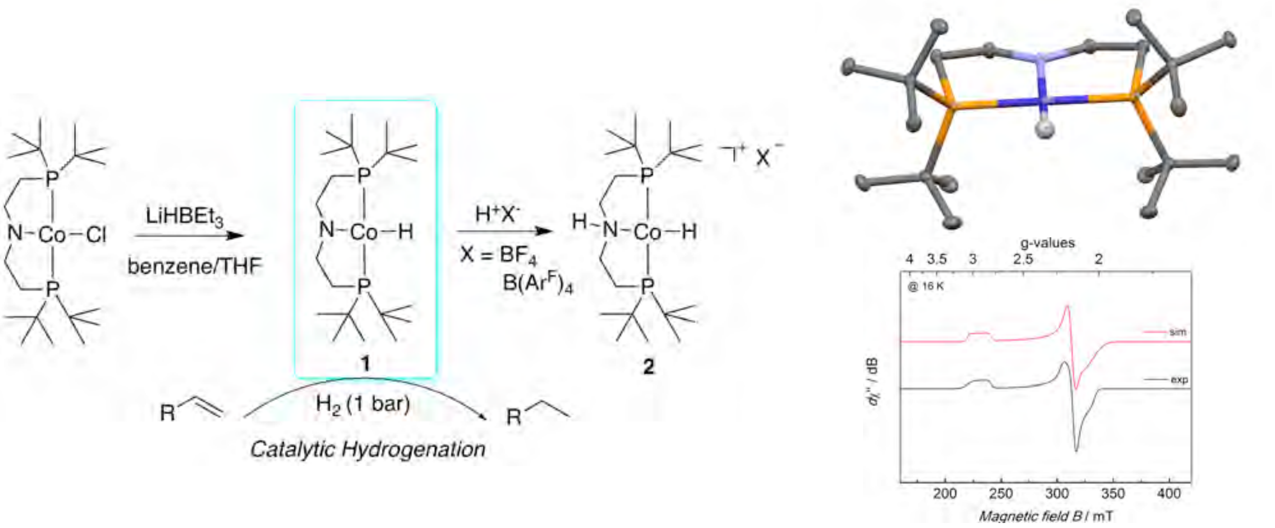
Recently, PNP pincer ligated base metal complexes of Fe, Co, Ni have attracted much attention in homogeneous catalysis.[1] Cobalt(II) PNP pincer complexes were efficient as pre-catalyst for the hydrogenation of olefins as well as C=N and C=O bonds under mild conditions.[2,3] Based on computational data, cobalt(II) hydrides were proposed as key intermediates[4] but their experimental identification and mechanistic relevance remain to be clarified.

Here we present the synthesis and complete characterization of the cobalt(II) hydrides complexes $(PNP^{tBu})Co^{II}H$ and $[(PNP^{tBu})Co^{II}H]^+X^-$ ($HPNP^{tBu}$ = $HN(CH_2CH_2(PtBu_2)_2$; X = BF_4, $B(Ar^F)_4$) (Figure 1). Their use as pre-catalyst and their mechanistic role in olefin hydrogenation at 1 bar H_2 are discussed.



X-ray structure & EPR spectrum of ***1***

Figure 1 Synthesis and Characterization of Pincer Co(II)H complexes.

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A Telluryl Stabilised Silyl Cation

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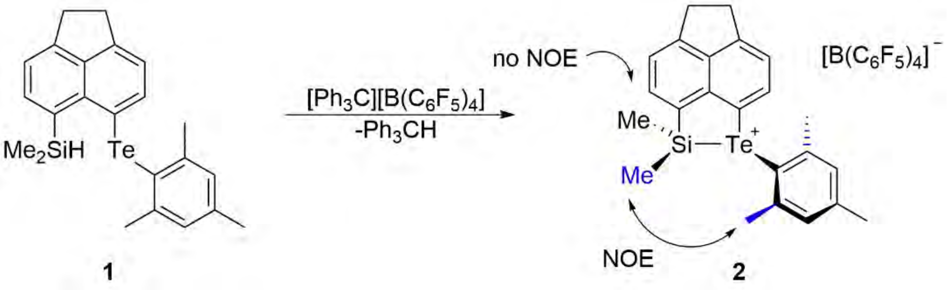
Silyl cations show an exceptional reactivity, due to their electron deficiency associated with a high Lewis acidity. This indicates that these species can be used in bond activation reactions, which was already shown by several groups.[1-3] To control the reactivity, the Lewis acidity at the silicon atom needs to be influenced, for example by employing Lewis basic groups. In this study a telluryl group was introduced. The cation **2** was formed by a hydrogen transfer reaction with a trityl borate (Scheme 1). The coordination environment of the tellurium atom in cation **2** is trigonal pyramidal, which is supported by a NOESY NMR experiment.



Scheme 1: Synthesis of the telluryl stabilised silyl cation **2**.

An EXSY NMR experiment shows that the configuration at the tellurium atom is not stable. Quantum chemical calculations suggest that the chalcogen atom undergoes an inversion process. The inversion is visualised in Figure 1, showing that the telluryl group moves in and out of the plain of the carbon skeleton. The activation barrier for this process was calculated to be $\Delta E = 109\ \mathrm{kJ \cdot mol^{-1}}$.

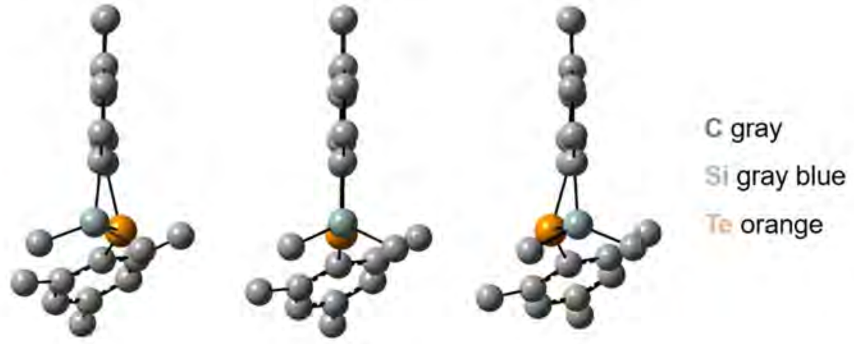


Figure 1: Inversion process at the tellurium atom of the silyl cation **2** (M06-2X/def2-tzvp, hydrogen atoms are omitted for clarity).

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Synthesis of Boryldiazenido Complexes

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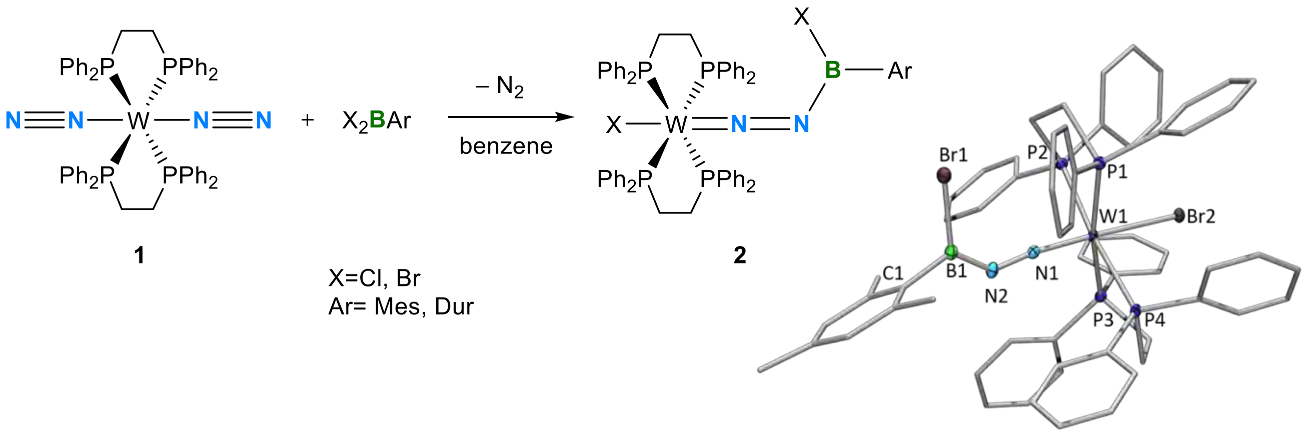
Our research group has a longstanding interest in the formation of boryl and borylene complexes. Platinum boryl complexes are formed *via* oxidative addition of B–Hal bonds from aryl(dihalo)boranes to [Pt(PR$_3$)$_2$].[1] The abstraction of halide ligands from such a boryl complex forms a cationic boryl complex, which in some cases can convert to an arylborylene complex.[2] Filippou *et al*. used bis(dinitrogen) complexes to form complexes containing a triple bond between the metal center (W or Mo) and a group 14 element (Ge-Pb).[3,4] Based on this precedence, we were interested in a new strategy for the formation of group VI boryl complexes by reacting a bis(dinitrogen) complex with haloboranes, which could possibly react further to borylene complexes. Interestingly, the bis(dinitrogen) complex [W(N$_2$)$_2$(dppe)$_2$] (**1**) reacts with aryl(dihalo)boranes or trihaloboranes with addition of a B–X bond across the WNN unit and loss of only one N$_2$ moiety, to form boryldiazenido complexes (**2**).



X=Cl, Br
Ar= Mes, Dur

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Hydrosulfido, Sulfido and Persulfido Interconversions at a Preorganized Dinickel Site

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Cooperative effects in di- and multinuclear metal systems play a key role in many enzymatic reactions.[1] Such cooperative effects can lead to more efficient and selective transformations, conformational control of substrates, higher local reagent concentration at the metal centers and stabilization of reactive species and complex intermediates.[2] The combination of nickel and *S*-based ligands is of particular current interest, due to its relevance in various biological systems.[3]

We have been working on the development of highly preorganized dinuclear metal complexes of metal···metal-bridging compartmental pyrazolate ligands, many of which mediate the bioinspired transformation of small substrates.[4,5] Here we present a series of hydrosulfido, sulfido and persulfido nickel(II) complexes based on a new compartmental pyrazolate/NHC hybrid ligand.

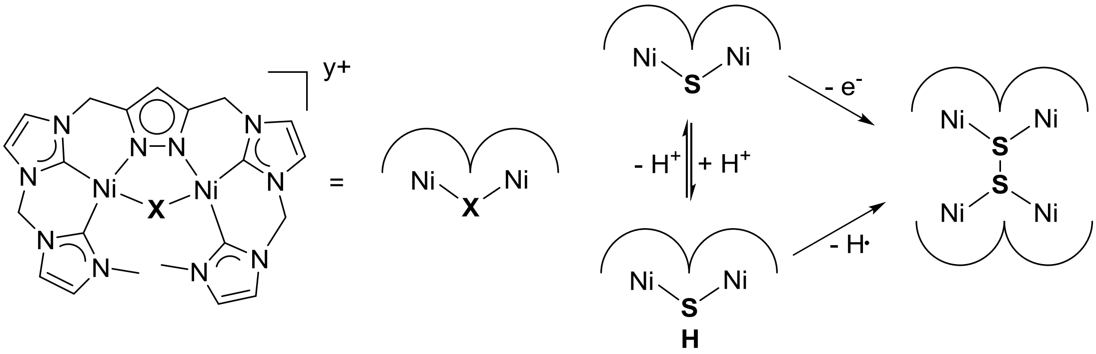

Figure 1 Series of hydrosulfido, sulfido and persulfido nickel(II) complexes.

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Hydrolysis Of Amino Acid-Functionalized Organotin Sulfide Clusters

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Hybrid compounds featuring biomolecules attached to inorganic clusters or nanoparticles have gained significant research interest in recent years due to the combination of the optoelectronic properties of the inorganic cores with the reactivity and/or bioactivity of the organic decoration.[1]

Research in our group has focused on organotetrel chalcogenide clusters, in particular the reactivity of the compounds $[(R^1Sn_3)S_4Cl]$ and $[(R^1Sn_4)S_6]$ (R^1= $CMe_2CH_2C(O)Me$).[2] Their carbonyl groups can be used to attach biomolecules to the clusters, thus increasing the biocompatibility and bioactivity.[3] By bringing the polar tin sulfide groups into cells, an application as enzyme inhibitor or cytotoxic agent would be possible.[3]

Current studies focus on the reactivity of amino acid- and peptide-functionalized organotin sulfide clusters towards acids in order to probe the clusters' stability and to identify decomposition products with potential biological relevance.

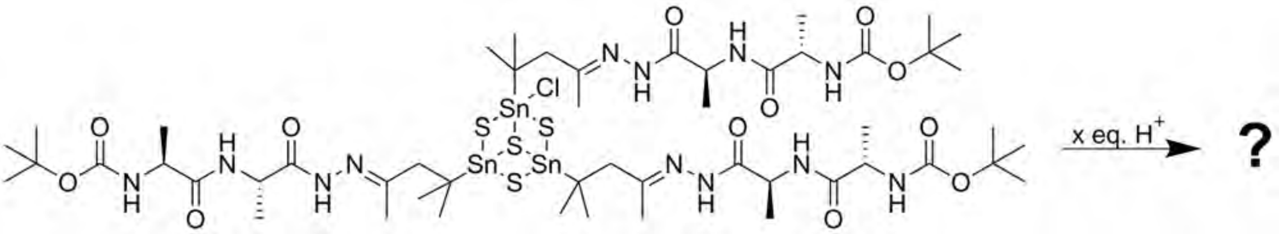

Figure 1 Protolysis of $[(R^2Sn)_3S_4Cl]$ (R^2= $CMe_2CH_2C(NNH\text{-}Ala\text{-}Ala\text{-}Boc)Me$)

It is to be expected that the addition of hydrochloric acid leads to a decomposition of the cluster and release of H_2S, thus causing the desired cytotoxic effect. This has already been observed qualitatively for tin sulfide clusters with ferrocenyl groups, but the hydrolysis of biomolecule-functionalized organotin sulfide clusters has not been explored.[4]

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Unusual Electronic Behavior Through the Unification of Two Classic Organoiron Centers

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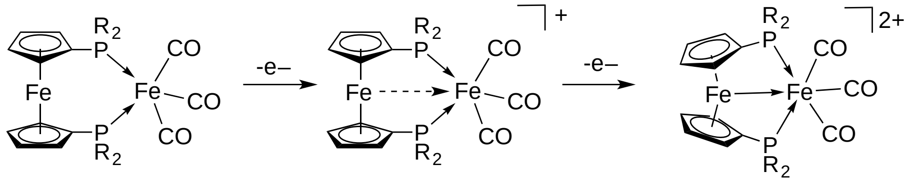
Transition metal complexes of 1,1'-bis(diorganylphosphino)ferrocene (dRpf) are almost ubiquitous,[1] and coordination flexibility of dpRf is well established, however it is generally assumed that the ferrocene moiety is redox innocent despite such a feature being potentially useful in many catalytic systems.[2]

Herein we present prototypical bis(diorganylphosphino)ferrocene tricarbonyliron to probe unique interactions between two classic organoiron centers. These complexes show two oxidations in the cyclic voltammogram (CV), in contrast to (1,n-bis(diorganylphosphino)alkane)tricarbonyliron, e.g. $Fe(CO)_3$dppp (1,3-bis(diphenylphosphino)propane), which exhibits only a single oxidation wave.

Using IR- and UV-Vis-NIR-spectroelectrochemistry along with EPR and Mössbauer spectroscopy we were able to probe the exact nature of the two oxidations observed in the CV. Crystallographic analysis and DFT calculations help to elucidate the nature of the Fe-Fe interactions. The ferrocene backbone opens to help stabilize some of the spin density from the unpaired electron on the tricarbonyliron(I) (Scheme 1).

Remarkable is the formation of the ferrous species, $[Fe(CO)_3dRpf](OTf)_2$, the first example of such a ferrous complex. The ferrous state is stable because of the formation of a Fe-Fe bond.[3]



Scheme 1. Oxidation induced metal-metal interaction

References:

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Metalated ylides and their applications in main group chemistry as stabilizing ligands

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Bisylides (**A** in Figure 1) have received great attention over the past years due to their unique reactivity and electronic structure.[1] The structurally closely related methandiides (**B** in Figure 1) can be viewed as their dianionic congeners.[2] A link between bis-ylides and methandiides would be a monoanionic yldiide, such as compound **1**. Such compounds are supposed to be strong σ- and π-donors and are of considerable interest as ligands, but examples of isolated and structurally characterized yldiides are rare.[3]

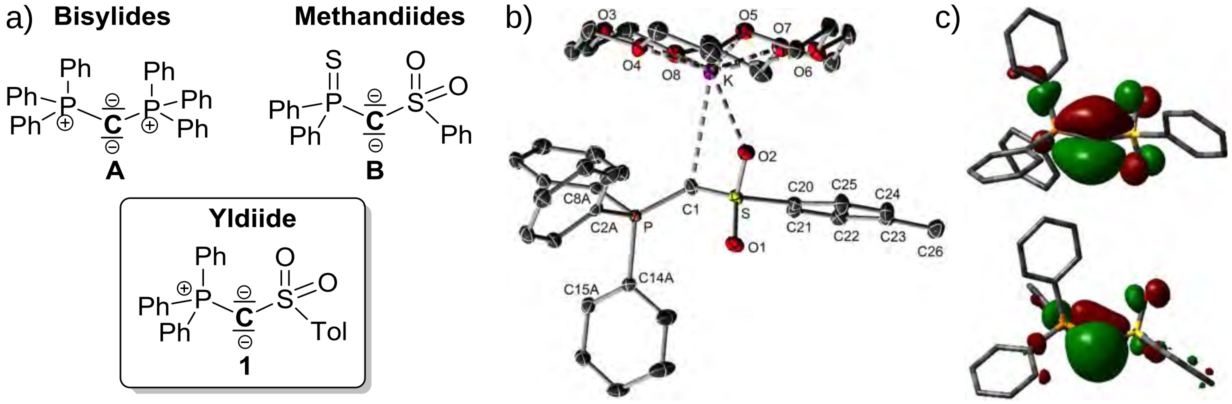

Figure 1 a) Comparison of bis-ylides, methandiides and yldiides; b) Molecular structure of yldiide **1**; c) Kohn-Sham orbitals of **1** (HOMO (top) and HOMO-1 (bottom)).

Here we report the synthesis of yldiide **1** directly from its protonated precursor by deprotonation with strong bases. The electronic structure of this compound is elucidated through X-ray analysis of its potassium and sodium salts as well as DFT studies. Comparison with bisylides and methandiides confirmed the similarities between these compounds. Reactivity studies demonstrate the unique reactivity of the yldiide which can be explained by its capability to act as σ- and π-donor. For example its ability to stabilize borenium cations as well as their synthesis, structure and reactivity are discussed. [4]

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Nitrosylation of Biomimetic [2Fe2S] Clusters

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The Rieske center is a [2Fe2S] cluster first discovered in 1964.[1] However, structural and functional synthetic analogues that emulate its heteroleptic coordination sphere have been reported only recently.[2-4] After isolating and characterizing the complexes in their diferric, mixed valent and protonated states, we were now interested in exploring their reactivity towards nitric oxide (NO). NO is a neurotransmitter and plays an important role in cardiovascular regulation.[5] On the other hand, its release can also lead to cytotoxicity. Studies on biological and synthetic iron-sulfur clusters suggest that NO triggers the degradation of the iron-sulfur core and formation of dinitrosyl iron complexes (DNICs).[6,7] The results of studies on the reactivity of the Rieske models and of a first model of the redox-active [2Fe2S] cluster of the integral membrane protein mitoNEET[8] which features a {His$_3$Cys} ligation will be presented, together with insight into the electronic structure of the DNICs obtained from DFT calculations.

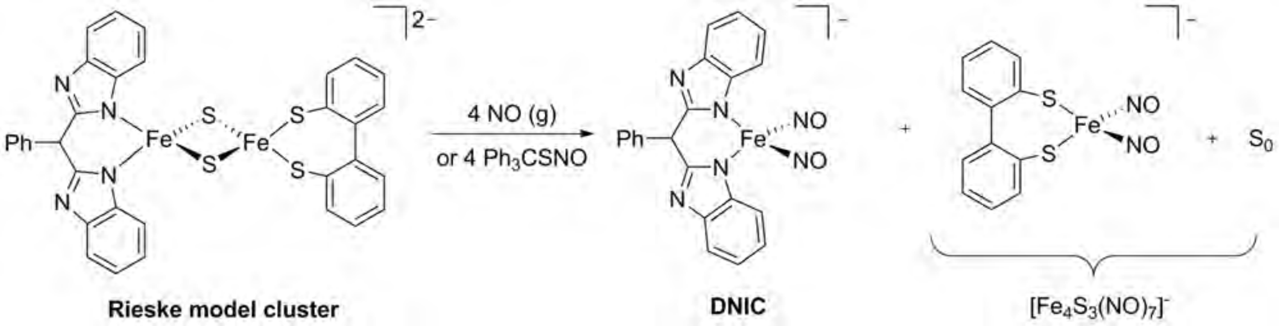

Figure 1 Nitrosylation of a Rieske model cluster.

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Abnormal CO_2 Insertion by a Transition Metal Hydride

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Hydrogen transfer from transition metal hydride (TMH) complexes is pivotal as elementary reaction in many catalytic chemical and biochemical transformations. Combination of formal proton and electron transfer can result in net proton, hydrogen atom or hydride transfer.[1] While ground state hydrogen transfer reactions are well examined, photochemical reactivity of group 10 TMH complexes is rare.[2] Herein we report the synthesis of Nickel(II) hydride **1** with an aliphatic unsaturated PNP (PNP = $N(CHCHP\textit{t}Bu_2)_2$) pincer.[3] While thermal CO_2 insertion yields formate **2**, photochemical CO_2 activation of **1** gives hydroxycarbonyl **3** via unprecedented abnormal CO_2 insertion.

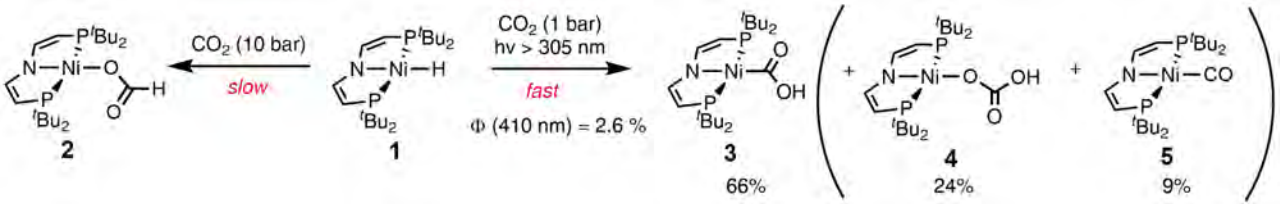

Figure 1 Thermal and photochemical reactivity of Nickel(II) hydride 1.

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Diazaphospholium salts for a bottom-up approach towards Phosphorus substituted Polycyclic Aromatic Hydrocarbons

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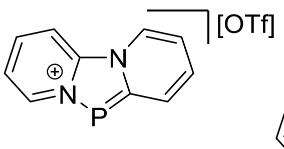
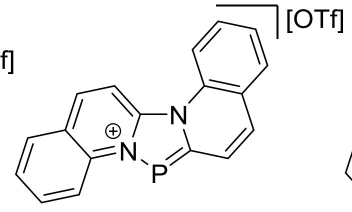
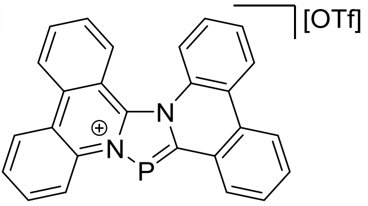
Phospholes are a well investigated substance class, however, only very few examples of diazaphospholium cations are described in literature.[1,2] We developed a facile protocol for the synthesis of cationic, annulated diazaphospholium triflates **1-3**[OTf] starting from readily accessible dichlorophosphanyl substituted pyridine derivatives.



1[OTf]

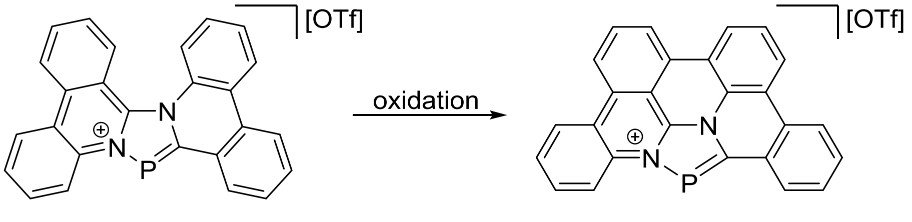


2[OTf]



3[OTf]

Diazaphospholium cations are feasible building blocks for the bottom-up synthesis of N,P-doped graphene-type materials, a substance class of which interesting electronic properties are expected.[3]



3[OTf] **4**[OTf]

3[OTf] is readily oxidized in a Scholl-type reaction to **4**[OTf]. Currently, polycyclic phospholium triflates **1-4**[OTf] are investigated with respect to their electronical and optical properties.

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Acknowledgement: We thank the European Research Council (ERC starting grand, SynPhos - 307616) for financial support.

Preparative Electrosyntheses and *in situ* Spectroelectrochemistry of Phosphorus-containing Bipyridinium radicals

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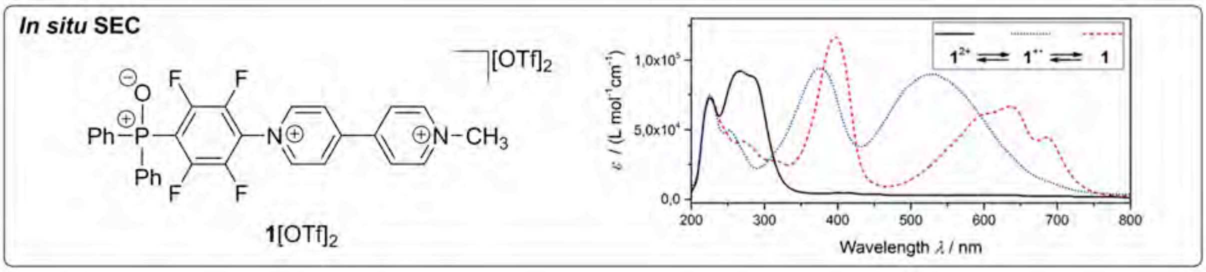
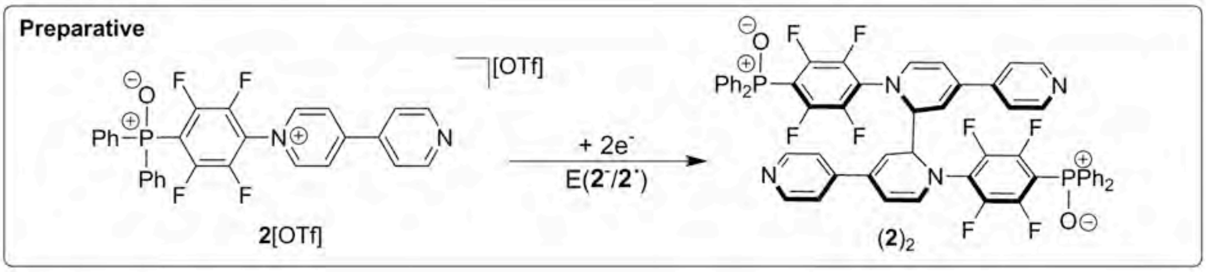
Spectroelectrochemistry (SEC) is a powerful tool for the *in situ* characterization of electrochemically generated reactive species like phosphorus-centered radicals.[1] In our investigation towards stable and reversible redox active phosphorus compounds we synthesized the bipyridinium derivatives **1**[OTf]$_2$ and **2**[OTf] by *onio*-substitution.[2] This contribution is focused on the preparative electrosynthesis of the stable and strongly colored reduction products of dication $\mathbf{1}^{2+}$ and of cation $\mathbf{2}^{+}$. *In situ* UV-VIS-NIR spectroelectrochemical cyclic voltammetry in a novel thin-layer flow cell of dication $\mathbf{1}^{2+}$ is used to elucidate its reversible ($\mathbf{1}^{2+} \rightleftharpoons \mathbf{1}^{+\bullet} \rightleftharpoons \mathbf{1}$) two-stage (deep blue & red) electrochromic behavior.[3]





Subsequential preparative electrochemical reduction of cation $\mathbf{2}^{+}$ to the stable radical $\mathbf{2}^{\bullet}$ and anion $\mathbf{2}^{-}$ results in the formation of an unusual dimer $(\mathbf{2})_2$ by synproportionation. Introducing cationic charges by protonation leads to a C–C bond cleavage to the stable radical cation $[\mathbf{2}\mathrm{H}]^{+\bullet}$.

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Acknowledgement: We thank the European Research Council (ERC starting grand, SynPhos 307616) for financial support.

Highly Active and Readily Accessible Dizinc Catalyst for CO2/Epoxide Copolymerization

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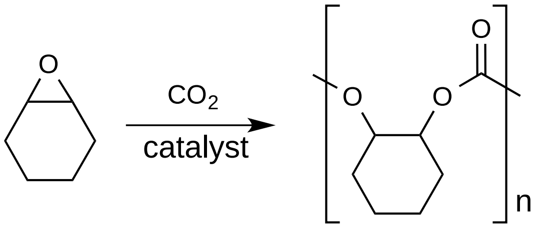

In the pursuit of CO_2-based materials, we seek to develop efficient catalysts for the copolymerization of CO_2 and epoxides to give polycarbonates. Desirable attributes for such catalysts are high copolymerization activity at low CO_2-pressure, as well as chemo- and stereo-control over the formed polymer. Some great progress has been made in the field of CO_2 / epoxides copolymerization during in the last decade.[1]

Here we report a novel chiral zinc catalyst, that can be isolated in 97 % yield from commercial sources, and that produces polycarbonates selectively from neat cyclohexene oxide under 1 bar of CO_2 at temperatures above 50 °C. At 80 °C reaction temperature, TONs of 1684 and TOFs up to 149 h^{-1} were measured, while producing an isotactic-enriched polycarbonate with a probability P_m of 65 % for the formation of a meso diad. Some mechanistic insight as well as structural characterization of the precatalyst have been obtained.

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Cycloaddition Reactions of Azides and a Polarized, Cationic Diphosphene

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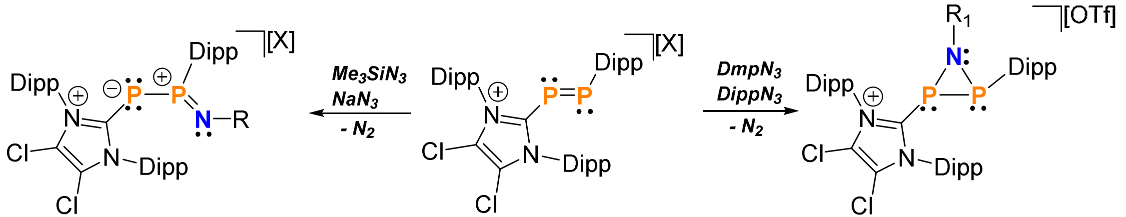
The Huisgen Cycloaddition is a classical organic reaction of dipolarophiles with 1,3-dipolar compounds, which lead to the formation of organic, five-membered (hetero)cycles.[1] Only a very small number of inorganic, binary, five-membered ring derivatives containing only the group 15 elements phosphorus and nitrogen are known.[2] These compounds tend to be very thermolabile and, thus, decompose under the release of N_2. In this respect, we have studied the reactivity of the polarized, cationic diphosphene **1**$^{+[3]}$ towards various azides.[4]



3[OTf] (R_1 = Me_3Si)
4 (R_1 = $GaCl_3^-$)

1[X]

2a[OTf] (R_1 = Dmp)
2b[OTf] (R_1 = Dipp)

Dipp = 2,6-di-isopropylphenyl,
Dmp = 2,5-dimethylphenyl

For azides featuring aromatic substituents (*i.e.* Dipp, Dmp) the selective formation of azadiphosphiridine cations **2a,b**$^+$ is observed. The reaction of **1**[X] (X = OTf, $GaCl_4$) with the electron rich azides Me_3SiN_3 and NaN_3 give the unusual diphosphenimine derivatives **3**[OTf] and **4**, respectively, featuring an acyclic P_2N moiety. In depth theoretical calculations provide insights into the reaction mechanisms to the cyclic and acyclic forms.

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Acknowledgement: We thank the Graduate Academy TU Dresden and the German Science Foundation (DFG, grant number WE421/3-1) for financial support.

Axially Chiral Dianionic Calcium Complexes as Catalysts in the Asymmetric Alkene Hydroamination

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The catalytic intramolecular alkene hydroamination is a highly atom-efficient, waste-free synthetic pathway towards *N*-heterocycles. Routes to these key building blocks in pharmaceuticals[1] are predominated by rare earth metal catalysts. As calcium shows similar chemical behavior but is biocompatible, cheap and world-wide available, application in catalytic hydroamination is highly rewarding.[2] Unfortunately, asymmetric catalytic protocols are plagued by the Schlenk Equilibrium, a facile ligand redistribution reaction, causing catalyst degradation and enantioselectivities that are often well below 50%.[2,3]

Herein, we overcome the Schlenk Equilibrium by introducing the concept of dianionic non-innocent ligands that do not just play a spectator role but also activate the substrate. Based on the axial chiral 1,1´-binaphthyl-2,2´-diamine (BINAM) backbone, bearing various bulky residues, chiral dianionic calcium compounds are designed (Figure 1). Subsequently, their coordination chemistry, catalytic reactivity and enantioselectivity in the intramolecular alkene hydroamination are discussed.

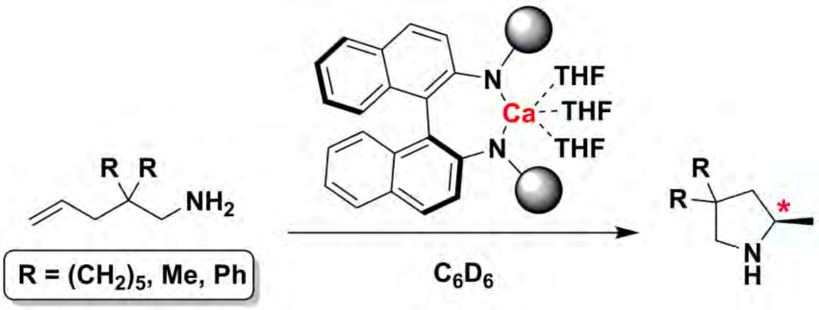

Figure 1: Asymmetric calcium catalysed hydroamination.

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Synthesis of heteroleptic ketoiminate zinc complexes and their application in lactide polymerization

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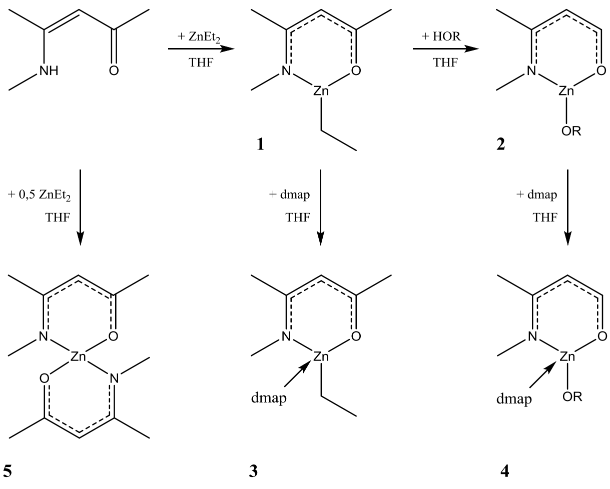
Since our first steps in lactid polymerization,[1] we began to explore ketoimiate zinc compounds with a intramolecular donor, where various substituents on the metal center were tested towards their capability to produce polylactid.[2-3] Herein we report the synthesis and characterization of heteroleptic zinc ketoiminate complexes LZnR (L = MeNacac = MeNC(Me)CHC(Me)O; R = Et (**1**), O-2,6-Me_2-Ph (**2**)) containing the sterically less demanding MeNacac ligand as well as their dmap adducts dmap-Zn(L)R (dmap = 4-dimethylamino pyridine; R = Et (**3**), O-2,6-Me_2-Ph (**4**)) and the homoleptic complex L_2Zn (**5**). Their technical application as catalyst in ring-opening polymerization (ROP) of *rac*-lactide in CD_2Cl_2 solution at ambient temperature was investigated. While all complexes were active in lactide polymerization, **2** and **3** showed the highest activities and were found to polymerize *rac*-lactide (90% conversion) within 140 (**3**) and 180 minutes (**2**), respectively.



HOR: HO-2,6-Me_2-C_6-H_3, dmap: 4-Me_2-NC_5-H_4-N

Figure 1 Synthesis of **1-5**.

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A N_4Bi_4-Heterocubane

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In the literature, little is known about heterocubanes containing only nitrogen and the heaviest pnictogens antimony and bismuth within the heterocubane structure. For example, the group of *Latscha* presented the first heterocubane only containing nitrogen and antimony(V).[1] A heterocubane comprising chloride substituted Sb(III) was synthesized by *Dehnicke* et al. in 1994.[2] A heterocubane containing only nitrogen and bismuth is unknown; however, the group of *Wright* published a heterocubane with a $N_4Bi_2Li_2$ core.[3]

We observed the formation of a heterocubane with a binary N-Bi core during our investigations on tetrazenides. After a reaction protocol following the route of *Trogler* et al.[4] utilizing 3,5-bis(trifluoromethyl)aniline as amine source and quenching of the reaction mixture with $BiCl_3$ yellow crystals of the heterocubane **1** (Fig. 1) where obtained.

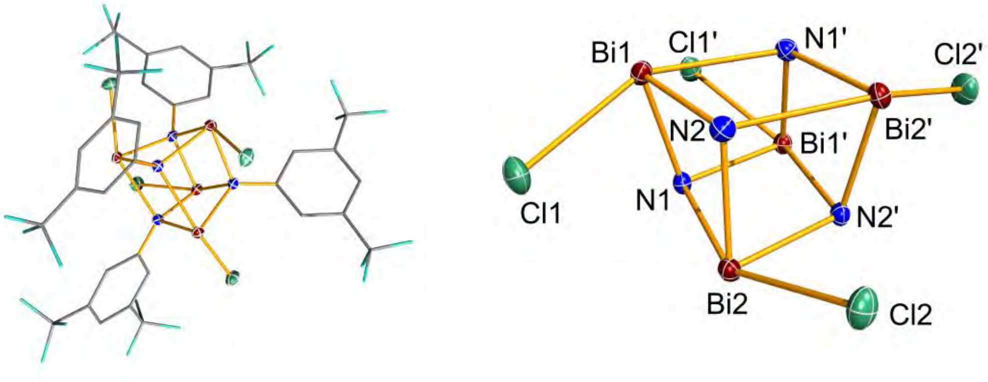

Figure 1: Left: Crystal structure of **1** (solvate molecules and H atoms omitted). Right: $N_4Bi_4Cl_4$ core of **1**.

Compound **1** was presumably formed by the reaction of the dilithium salt of 3,5-bis(trifluoromethyl)aniline with $BiCl_3$ forming the *cyclo*-dibismadiazane in the first step, which then dimerized to form **1**.

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Rhodium Catalyzed Meinwald Rearrangement of Terminal Epoxides to Ketones

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Catalysts for the rearrangement of terminal epoxides are less common compared to the rearrangement of internal epoxides. Only several catalysts are known to selectively convert terminal epoxides into methylketones, e.g. $Pd(OAc)_2$,[1,2] MnI_2 or $Co_2(CO)_8$.[3] Rhodium-pincer complex **1**, which has two electron-donating N-heterocyclic carbene moieties, has been proved to be a highly active catalyst for the Meinwald rearrangement of terminal epoxides to methylketones (**Figure 1**).[4] To further extend the substrate scope of this reaction, we synthesized a number of functionalised terminal epoxides[5,6] and scanned the selectivity and substrate tolerance of catalyst **1**. As a result, moderate to high yields can be obtained and a range of functional groups is compatible. Side reactions will also be discussed.

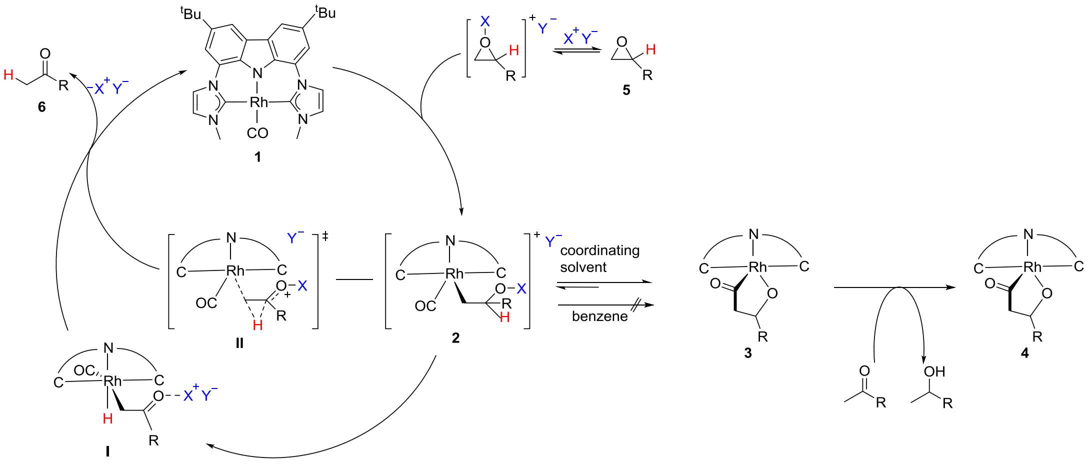

Figure 1 Proposed reaction mechanism for Rh catalyzed Meinwald rearrangement

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First steps towards Heptacarbonylcations of Niobium and Tantalum

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Our objectives are the syntheses of Heptacarbonylcations of the 4d and 5d transition metals Niobium and Tantalum in the condensed phase, which could be proved by MS in the gas phase already. These **G**as **P**hase **C**ations (**GPCs**) observed by *Ricks et al.*[1,2] are promising molecules in the group of **GPCs**, as they follow the 18VE rule interrelated with a high postulated stability. To enable condensed phase access to **GPC** salts, **W**eakly **C**oordinating **A**nions (**WCAs**), such as the perfluoro-tert-butoxy aluminate $[Al(OR^F)_4]^-$, inducing **P**seudo **G**as **P**hase **C**onditions are used.[3]

Our aim is to take inspiration from the wealth of experience from the **GPCs** known from advanced MS methods and harvest the application potential of stable **GPC** salts from mechanistic studies up to small molecule activation and catalysis.

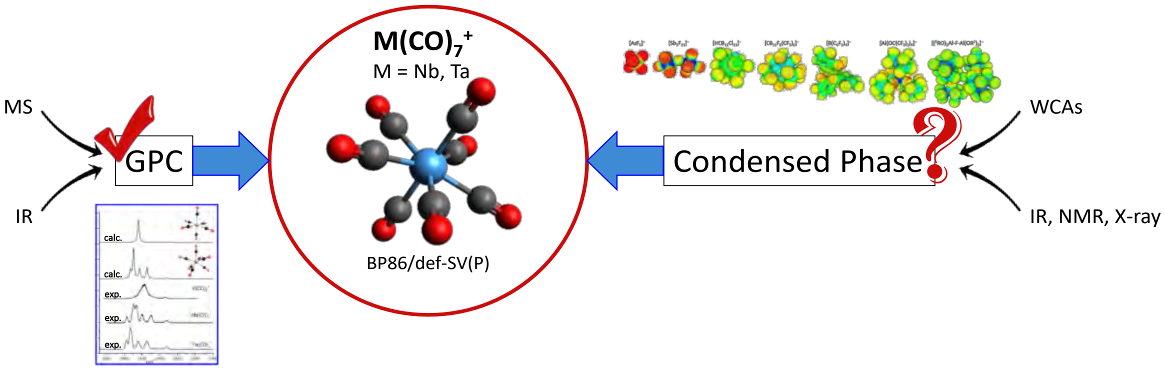

Figure 1 In the gas phase existing Heptacarbonylcations should be synthesised and analysed in the condensed phase with the help of WCAs.

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Aluminium Mediated C=C Coupling of an Isonitrile

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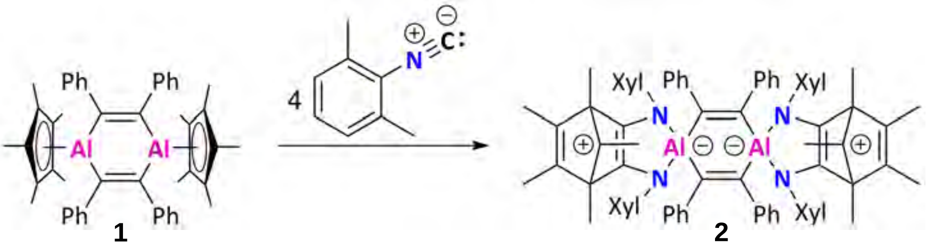
Developing the reactivity of low valent group 13 compounds is necessary to expand this challenging chemistry beyond a few isolated examples. Currently, the chemistry of β-diketiminate supported aluminium(I) complexes is well studied,[1] with cycloaddition[2] and oxidative addition[3] reactions being documented. The reactivity of (Cp*Al)$_4$ with unsaturated organic molecules is not yet reported.

Having already considered the mechanism[4] of the reported reductive elimination of a C-H bond from (Cp*Al)$_4$,[5] we now examine the reactivity of unsaturated bonds to this metal centre. The reaction of diphenylacetylene, which is a proposed cycloaddition, leads to the formation of **1**, a compound with a central Al_2C_4 framework. The solid state structure of this product shows a boat conformation of the 1,4-dialuminacyclohexadiene moiety, and the coordination mode of the Cp* ring remains η^5.



1 **2**

Scheme 1 Insertion and coupling of an aryl isonitrile into the Al-C bonds of a novel 1,4-dialuminacylcohexadiene derivative to form a bis-zwitterion

Exploring the reactivity of **1**, we find that the addition of 2,6-dimethylphenyl isonitrile leads to the unexpected insertion and coupling of the terminal isonitrile carbon to form a new C=C bond and a stable neo-classical carbocation, **2**. This is confirmed by the solid state structure and supported by DFT calculations.

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A Simple Approach to Alkaline-Earth Metal Hydride Complexes

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The synthesis of heavy alkaline-earth metal hydride complexes (Ae = Ca, Sr, Ba) is highly challenging. This is due to their kinetic instability which is triggered by the Schlenk equilibrium to form the thermodynamically stable $(AeH_2)_\infty$. However, the first successful synthesis of a calcium hydride complex in 2006 (Figure 1)[1] has been rewarded with unique reactivity and application in several catalytic or stoichiometric hydrogenation reactions.[2] The choice of the anionic spectator ligand, which should be multidentate and bulky, has been thought to be crucial for success. Indeed, only two other ligand types are known to stabilize calcium hydride complexes. Recent work by our group showed that not only the anionic spectator ligand but also the nature of the neutral (co)solvent is essential.[3]

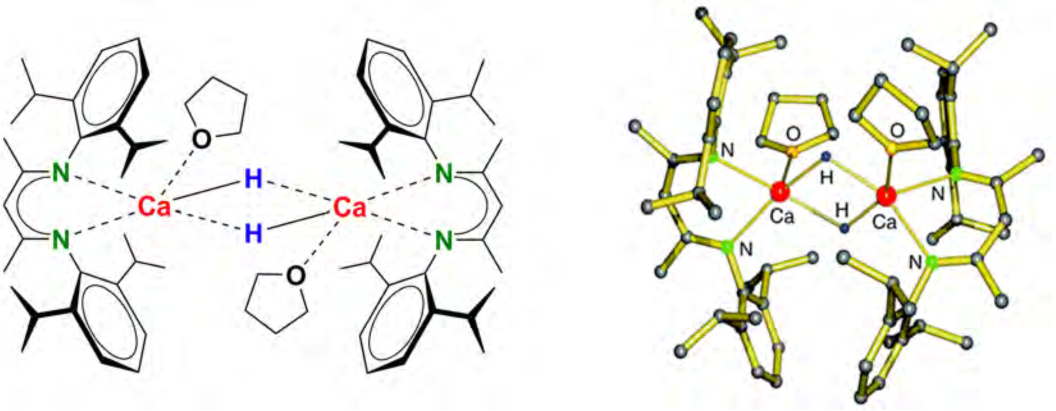

Figure 1. Crystal structure of $[(DIPPnacnac)CaHTHF]_2$.

Herein we present a comprehensive study in which we show that a very simple spectator ligand in combination with various (co)solvents can successfully stabilize a large series of alkaline-earth metal hydride clusters.[4] Considering the simplicity and the success of the synthetic strategy towards these new cluster systems, broad application possibilities are proposed.

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Dinuclear Rhenium Complex with a Proton Responsive Ligand as a Redox Catalyst in the CO_2 Reduction Reaction

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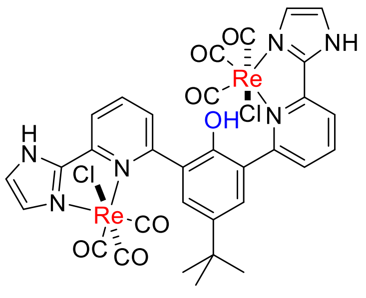
The electrochemical reduction of CO_2 has been investigated intensively in the last decades. It represents a key step towards the use of CO_2 as a powerful and cheap fuel source or as chemical feedstock.[1] The multielectron reduced products of CO_2 are very similar in energy, thus, its reduction necessitates catalysts that are selective in the formation of one of the multiple products. Additionally, the catalyst must bypass the high-energy radical $CO_2^{\cdot-}$. One of the best explored catalyst families in this respect are the group 7 tricarbonyl-diimine complexes.[2]

We utilised a dinuclear α-diimine rhenium complex, **1**, $[Re_2(L)(CO)_6Cl_2]$, with a proton responsive ligand as catalyst in the electrochemical CO_2 reduction catalysis. The complex has a phenol group in close proximity to the active centre, which may act as a proton relay during catalysis, and pyridine-NH-imidazole units as α-diimine donors. The complex is an active catalyst and CO is the main product. The complex exhibits higher activities than $[Re(L^{NN})(CO)_3Cl]$ in MeCN/water mixtures, L^{NN} = bpy, ^{t}Bu-bpy. A detailed spectro-electrochemical and theoretical investigations revealed a comprehensive picture of the reduction chemistry of **1** under catalytic and non-catalytic conditions and these results will be presented.[3]



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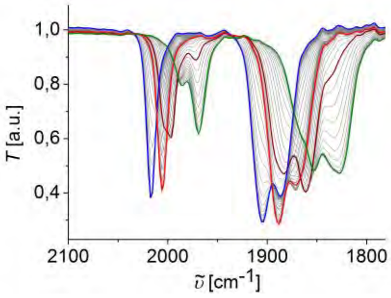

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Hetero-Cyclopentane-1,3-diyls as Molecular Switches

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Biradicaloids, *i.e.* species with two radical centers that interact considerably, are an intriguing class of compounds with an unusual electronic structure and interesting properties.[1] Whilst carbon-based, four-membered biradical(oid) ring systems are often fleeting intermediates in bond breaking and bond formation processes, species incorporating heteroatoms such as group 15 elements (pnictogens) are often much more stable and can be isolated.[2]

Recently, we reported on the synthesis of hetero-cyclopentanediyls (**2**) by insertion of isonitriles into cyclodiphosphadiazanediyl (**1**, Figure 1).[3] Detailed studies of compound **2Dmp** revealed a highly selective photochemical switching process triggered by irradiation with red light (λ_{max} = 650 nm), which afforded the housane **2'Dmp**. The thermal reverse reaction occurred quickly at ambient temperature ($t_{½}$ ≈ 7 min, 298 K), but slowly at temperatures below 0 °C ($t_{½}$ ≈ 342 min, 268 K). The reaction was studied by means of variable temperature NMR as well as UV/Vis spectroscopy and complemented by computations. The complete process was found to be fully reversible; hence the system can be regarded as a molecular switch.[4]

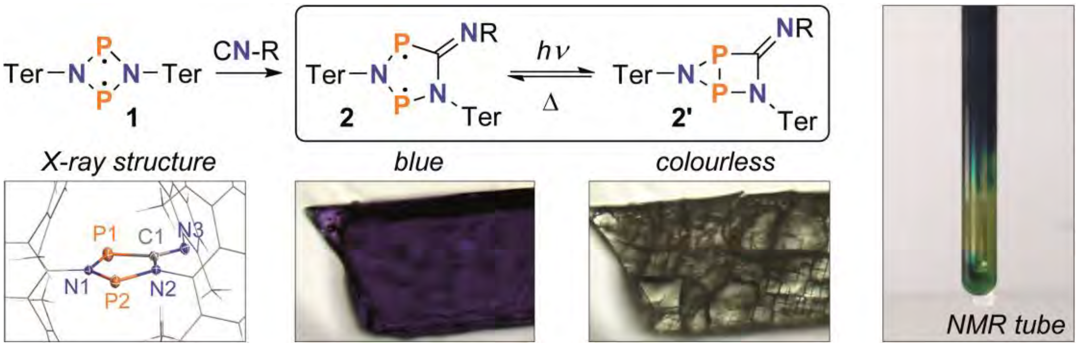

Figure 1. Under irradiation with red light, the biradicaloid **2Dmp** isomerized to housane **2'Dmp** (Ter = 2,6-dimesitylphenyl, Dmp = 2,6-dimethylpheny).

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SCHEDULE: AGIChem 2017, Göttingen, August 06th – August 09th, 2017

Hour / Time	Sunday, August 6th	Monday, August 7th	Tuesday, August 8th	Wednesday, August 9th
08:30		*Opening Remarks*		
09:00		David Scheschkewitz, Saarbrücken	Stuart Macgregor, Heriot Watt	Jennifer Garden, Edinburgh
09:30		Simon Aldridge, Oxford	Axel Schulz, Rostock	Stefanie Dehnen, Marburg
10:00		Berthold Hoge, Bielefeld	Alison Parkin, York	Charles O'Hara, Strathclyde
10:30		*Coffee break*	*Coffee break*	*Coffee break*
11:00		Mark R. Crimmin, IC London	Ann-Christin Pöppler, Würzburg	Wolfgang Schnick, LMU
11:30		Sjoerd Harder, Erlangen	Alexander Steiner, Liverpool	Simon Parsons, Edinburgh
12:00		Michael Whittlesey, Bath	Viktoria Däschlein-Gessner, Bochum	Claudia Wickleder, Siegen
12:30		*Lunch break*	*Lunch Break*	Claire Carmalt, UC London
13:00				*Closing Remarks and farewell*
14:00		Rajendra Ghadwal, Bielefeld	*Postersession II ****	
14:30		Adrian Chaplin, Warwick		
15:00		Biprajit Sarkar, FU Berlin		
15:30		*Coffee break*		
16:00	*Registration, Alte Mensa*	Michael Ingleson, Manchester	*Social program*	
16:30		Stephan Schulz, Duisburg-Essen		
17:00		*Coffee break*		
17:30		Paul Pringle, Bristol		
18:00	*Welcome Mixer, Alte Mensa (ends at 21:30)*	Jan Weigand, Dresden	*Conference Dinner; Poster Prices Alte Mensa (ends at 22:00)*	
18:30		*Postersession I (ends at 21:30) ****		

*** Postersession I (Monday) Odd Numbers: 18:30 - 20:00 / Even Numbers: 20:00 - 21:30; Postersession II (Tuesday) Even Numbers: 14:00 - 15:00 / Odd Numbers: 15:00 - 16:00