

Final Report

The Application of Magnesium(I) Compounds to Energy Storage Materials - Phase 2

Principal Investigator: Professor Cameron Jones

School of Chemistry

PO Box 23, Monash University

Clayton, Vic, 3800

Australia

Email: cameron.jones@monash.edu

Ph: +61-(0)406476906

Fax: +61-(0)3-99054597

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14. ABSTRACT

This research exploits recent advancements in using stable, very low oxidation state heavier s- and p-block-based compounds as reducing agents in organic transformations under ambient conditions. The central objective of this project was to systematically understand "transition metal-like" properties of main group compounds to 1) develop innovative methodologies to stabilize a range of unprecedented, yet inter-related, low oxidation state/low coordination number p-block compound classes; 2) systematically harness the unique properties of these systems in an exploration of their applicability to synthesis, small molecule activation, catalysis, hydrogen storage and related areas previously dominated by late d-block metal complexes; and 3) pursue replacement of toxic/expensive transition metal complexes by low oxidation state main group systems in technologies derived from the above reactions/applications. This research yielded numerous findings that involved development of monodentate amide ligands with unprecedented bulk that led to a) stabilization of the first example of an amido substituted digermine, which is a germanium alkyne analogue and heavier analogue of as yet unknown 1,2-dicarbene; b) stabilization and full characterization of the first examples of truly one-coordinate group 13 metal amides, monomeric amido-germylenes, c) unprecedented examples of molybdenum amido-germylyne compounds, which possess Mo-Ge triple bonds; and d) the first diketiminate stabilized group 14 element dimer and guanidinate coordinated iron(I) dimer, which possesses a Fe-Fe double bond that is significantly shorter than the more than 6000 other examples of Fe-Fe bonds in the literature. The "transition metal-like" reactivity of low oxidation state p-block digermine systems has been shown to activate dihydrogen at 1 atm. and temperatures as low as -10 °C to yield mixed valence germanium hydrides in solution or the solid state. For larger amide ligands systems, spectroscopic and computational studies revealed that the compounds exist in equilibrium with an unprecedented a 2-coordinate hydrido-germylene. The digermine systems also displayed reactivity towards rapid hydrogermylation of unactivated alkenes under mild conditions at below room temperature to quantitatively yield expected germanium alkyl products. In addition, the digermynes were found to rapidly and quantitatively reduce CO₂ to CO in a matter of seconds at room temperature, and at temperatures as low as -40 °C. Mechanistic studies revealed that the reaction proceeds through an intermediate in which the CO₂ molecule has inserted into the Ge-Ge bond of the digermine. The results of this study are at the very cutting edge of main group chemistry, and represent significant advances to the field.

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Reaction Mechanisms, Chemical Synthesis, Inorganic Chemistry, Low Coordination State, Catalysis, Reducing Agents, Main Group Chemistry

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The Application of Magnesium(I) Compounds to Energy Storage Materials - Phase 2

1. Abstract

This project has been extremely successful and good progress has been made towards all of the originally stated goals. Briefly, (i) a variety of new, extremely bulky monodentate amide ligands have been developed; (ii) these have been utilized to prepare a series of monomeric, low coordinate p-block metal halide precursor complexes; (iii) the precursors have been reduced by magnesium(I) complexes to very low oxidation state/low coordination number p-block complexes, which are of considerable fundamental interest; (iv) the "transition metal-like" reactivity of the low oxidation state complexes has been demonstrated by their use in facile activation of small molecules such as H_2 , CO_2 , N_2O etc.; (v) group 14 hydride complexes resulting from H_2 activations have been utilized for the first sub-room temperature hydrometallations of unactivated alkene substrates, and as the first main group compounds that act as catalysts for the hydroboration of ketones; (vi) a variety of related results, including the preparation of an iron(I) dimer with the shortest Fe-Fe multiple bond, have been achieved. The results of this study are at the very cutting edge of main group chemistry, and represent significant advances to the field. The study as a whole has generated nine papers in the period, with at least another four to be published in the next 12 months. PI Jones has delivered 10 invited or plenary lectures on project results at conferences and institutions in five countries in the period.

2. Introduction

The explosion of activity that has occurred in main group chemistry over the past two decades has stemmed from the realization that compounds containing heavier s- or p-block elements in very low oxidation states are not incapable of existence under ambient conditions. Indeed, the rapid renaissance that has occurred in this field has given rise to some of the most exciting fundamental breakthroughs in the history of main group chemistry; many of which have drastically altered our perception of structure, bonding and reactivity. However, more than being just chemical curiosities, the high reactivity and increased fundamental understanding of low oxidation state main group compounds has led to them finding an ever expanding array of valuable applications, especially over the last five years. The most exciting developments in this arena derive from the extraordinary recognition that the electronic properties and reactivity of such compounds can, in many cases, be very similar to those of transition metal complexes. It was the central objective of this project to systematically exploit and understand the "transition metal-like" properties of main group compounds with the specific objectives of:

- developing a variety of innovative methodologies to stabilize a range of unprecedented, yet inter-related, low oxidation state/low coordination number p-block compound classes;
- systematically harnessing the unique properties of these systems in an exploration of their applicability to synthesis, small molecule activations, catalysis, hydrogen storage and related areas previously dominated by late d-block metal complexes;
- actively pursuing the replacement of toxic/expensive transition metal complexes by low oxidation state main group systems in technologies derived from the above reactions/applications;

3. Experiment, Results and Discussion

N.B. Much of the work carried out in the period has been published. Accordingly, a brief summary of the most important results will be given here, while further details can be obtained from the cited (see section 4), and attached, papers.

(i) Ligand development

It was a central aim of this study to develop monodentate amide ligands of unprecedented bulk, which would allow the stabilization of low oxidation state main group compounds that have very low coordination numbers. The reasoning was that their resultant electron deficiency, and narrow HOMO-LUMO gaps, would allow them to participate in "transition metal-like" reactivity, a proposal which was borne out by later work. A variety of synthetic techniques (salt metathesis, catalyzed cross couplings, imine hydrogenations etc.) were used to prepare the secondary amine pro-ligands (see Figure 1) which were central to this study.^{2,7-9}

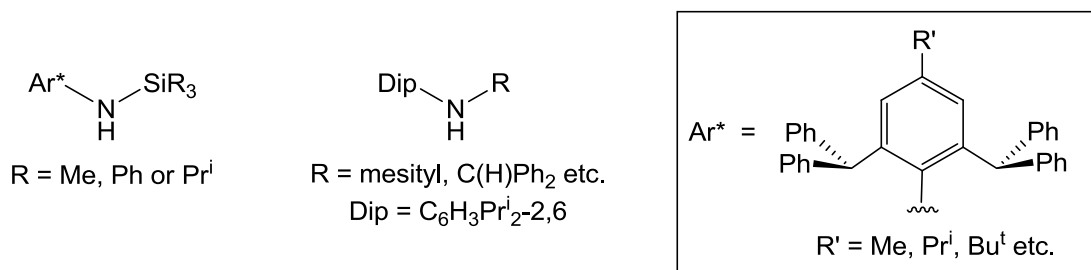


Figure 1. Examples of extremely bulky secondary amine pro-ligands developed in this study

(ii) Stabilization of low oxidation state p-block (and related) complexes

Several routes to the target low oxidation state p-block compounds were used in this study. The most utilized was the reduction of "normal" oxidation state metal halide precursors, LMX_n (L = bulky amide, X = halide), using magnesium(I) dimers, e.g. $[\{(\text{MesNacnac})\text{Mg}\}_2]$ ($\text{MesNacnac} =$

$[(\text{MesNCMe})_2\text{CH}]^-$, Mes = mesityl), that were developed by us in earlier AOARD studies, as specialist reducing agents. This allowed us access to a variety of unprecedented complex types that cannot be accessed by normal reducing agents, e.g. alkali metals, KC_8 etc. It is of note that the unique combination of properties held by the Mg^{I} dimers (solubility, stability, ease of preparation etc.) has led to them finding use by an ever growing number of research groups around the world as specialist reducing agents. Other synthetic routes that have been used are salt elimination reactions between alkali metal amide salts and low oxidation state p-block halides. While some of the heavier p-block examples of the latter are readily available, e.g. MCl , $\text{M} = \text{In}$ or Tl , lighter element examples are not. In this study, a collaboration was commenced with Prof. Hansgeorg Schnöckel of Karlsruhe University, Germany, which led to the construction of a specialist reactor (nick-named the Schnöckelator) at Monash, for the generation of metastable solutions of gallium(I) chloride. These solutions were used in subsequent reactions with alkali metal amides.⁶

Although numerous new low oxidation state amido-metal complex types were generated in this study, a summary of only some of the more important examples is given in Figure 2. These include examples of low oxidation state compounds incorporating bulky bidentate amides (β -diketiminates and guanidinate), that formed an extension of the originally proposed work.

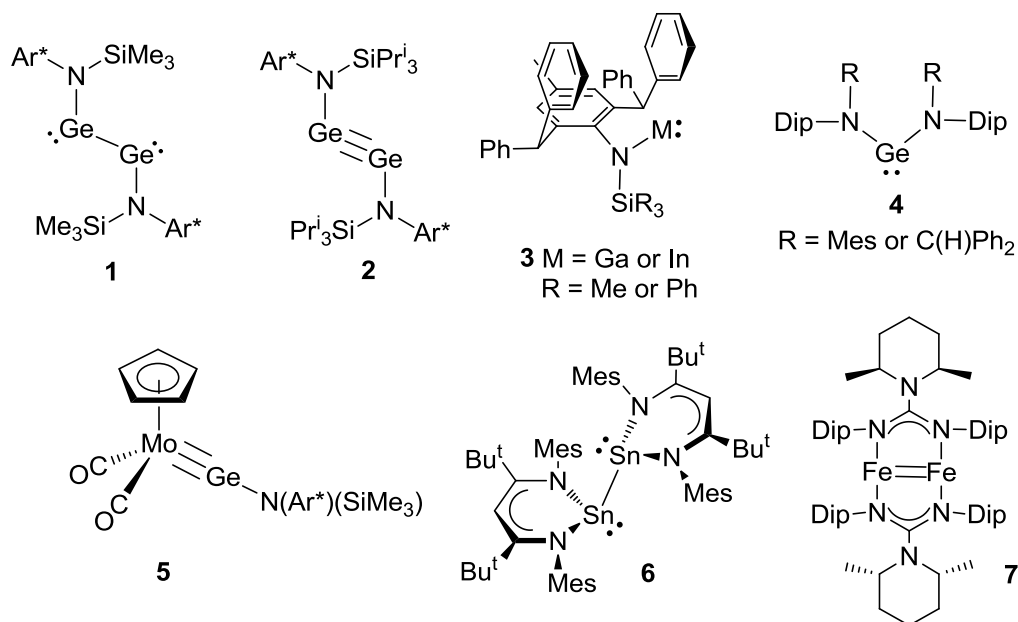


Figure 2. Examples of very low oxidation state compounds generated in this study.

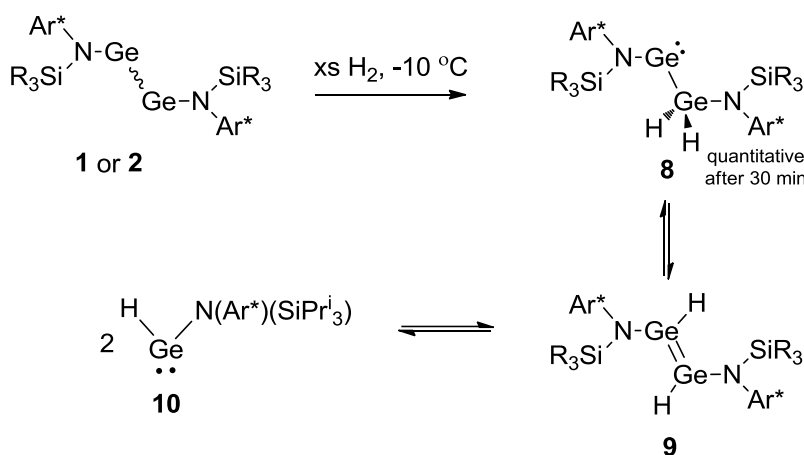
The extreme bulk of the monodendate amides developed in this study allowed the stabilization of the first example of an amido substituted digermine, **1**, which is a germanium analogue of alkynes.² However, unlike linear, triply bonded alkynes, it possesses a *trans*-bent structure ($\text{N-Ge-Ge} \approx 100^\circ$)

and an extremely long Ge-Ge single bond (ca. 2.71 Å). As such it can be considered as a 1,2-digermene, i.e a heavier analogue of as yet unknown 1,2-dicarbenes. Remarkably, when an even bulkier amide ligand was employed, a product, **2**, containing a Ge-Ge bond (ca. 2.35 Å) more than 0.35 Å shorter than that in **1** was formed.¹⁰ Theoretical studies suggest this has a bond order between 2 and 3, no Ge lone pairs, and significant singlet biradicaloid character. The differences here are due to the greater ligand bulk in **2** preventing planarity of each R₂NGeGe fragment, thus disallowing N-lone pair overlap with the empty p-orbital at Ge, and thereby allowing Ge-Ge multiple bond formation. The extremely reactive nature of **1** and **2** has proved them to be highly effective in a number of "transition metal-like" synthetic processes (see below).

The unique nature of the amide ligands developed in this study has also led to the stabilization and full characterization of the first examples of truly one-coordinate group 13 metal amides, **3**,⁶ monomeric amido-germylenes, **4**,⁸ and unprecedented examples of molybdenum amido-germylyne compounds, e.g. **5**, which possess MoαGe triple bonds.⁷ The further reactivity of these species that derives from their low-coordinate p-block metal centers is currently under development. Considering the success had in this arm of the study, it was extended to the use of bidentate β-diketimate or guanidinate ligands to stabilize very low oxidation state systems. Two high profile results from these investigations were the synthesis, using our Mg^I reagents, of the first β-diketimate stabilized group 14 element dimer, **6**,³ and the guanidinate coordinated iron(I) dimer, **7**, which possesses an Fe-Fe double bond which is significantly shorter than the more than 6000 other examples of Fe-Fe bonds in the literature.⁴ This low-coordinate compound is currently being investigated as a highly reducing reagent for the activation of dinitrogen.

(iii) The "transition metal-like" reactivity of low oxidation state p-block systems

Much progress has been made towards developing the application of low oxidation state compounds from this study (mainly **1** and **2**) to processes normally associated with expensive and toxic transition metal complexes/catalysts. For example, both **1** and **2** have been shown to activate dihydrogen at 1 atm. and temperatures as low as -10 °C to yield mixed valence germanium hydrides, **8**, which in solution exist in equilibrium with the hydrido-digermenes, **9** (Scheme 1).^{2,10} Remarkably, these reactions also occur in the solid state, which has led to **1** and **2** to be examined as soluble models for the reversible hydrogenation of Ge containing materials. When the larger amide ligand is incorporated in **9**, we have found through spectroscopic and computational studies that the compound exists in equilibrium with an unprecedented 2-coordinate hydrido-germylene, **10**.¹⁰

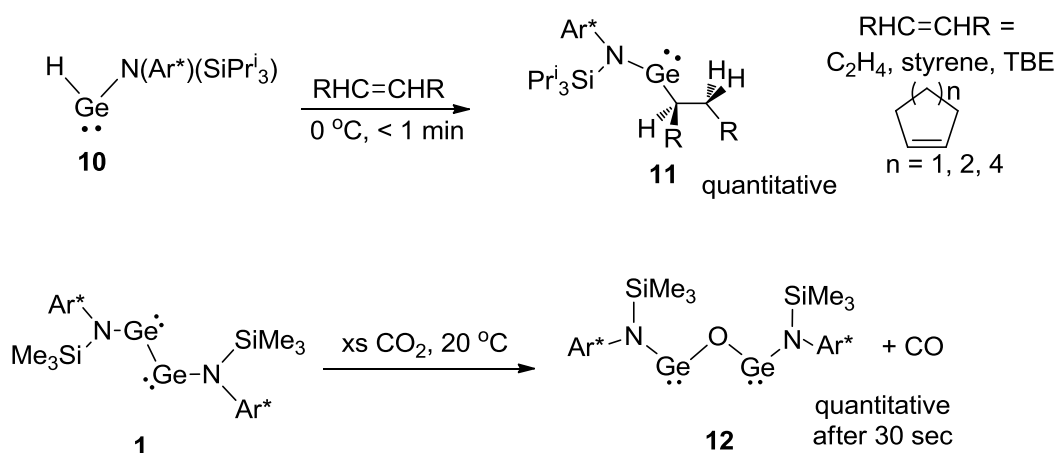


Scheme 1. The facile activation of H₂ using amido-digermynes.

Given that the hydrido-germylene, **10**, is extremely electron deficient, and that it may well exhibit ambiphilic reactivity through its Ge lone pair, its reactivity towards the hydrogermylation of unsaturated substrates was investigated. As test substrates, it was decided to employ unactivated alkenes which can normally only undergo hydrogermylation reactions under forcing conditions and in the presence of a catalyst. However, a variety of alkenes were shown to undergo rapid hydrogermylation at below room temperature to quantitatively yield the expected germanium alkyl products, **11** (Scheme 2). This highlights the potential compounds such as **10** have for, not only stoichiometric transformations, but also catalytic processes (unpublished results). We are currently exploring the possible reductive elimination of alkane products from **11** under an H₂ atmosphere, to concomitantly regenerate **10**. If this is achievable, compound **10**, would represent the first example of a low oxidation state main group compound to act as an alkene hydrogenation catalyst. Similarly we are currently exploring the use of **10** as a catalyst for a number of other processes, e.g. the selective hydroboration of ketone, aldehydes and nitriles. Very promising results have recently been achieved in that work (unpublished results).

The reduction of the green-house gas, CO₂, to useful chemicals and fuels is an area of great interest. However, almost all of the progress that has been made in this field derives from the use of transition metal complexes as reagents and catalysts. We have shown that the digermine, **1**, will rapidly and quantitatively reduce CO₂ to the useful C₁ feedstock, CO, in a matter of seconds at room temperature (Scheme 2).⁵ Indeed, this reaction is so facile that it proceeds at temperatures as low as -40 °C. We have explored the mechanism of this remarkable reaction and found that it proceeds through an intermediate in which the CO₂ molecule has inserted into the Ge-Ge bond of **1**. We are currently exploring the possibility of making the reaction catalytic in digermine. In a similar vein, we have

shown that a β -diketiminato coordinated germanium(II) hydride compound rapidly reacts with CO_2 to yield a formate complex which can be quenched to yield formic acid.¹ The same germanium hydride has also been shown to hydrogermylate a phosphalkyne, $\text{P}\alpha\text{CBu}^\dagger$, at room temperature. Remarkably, this process has been shown to be reversible by simply heating the hydrogermylated product to ca. 50 °C.



Scheme 2. Hydrogermylation of alkenes and the reduction of CO_2 by low oxidation state germanium compounds

4. List of publications, collaborations, etc. resulting from this work.

(a) Publications

The following publications resulted from the project and acknowledge AFOSR/AOARD support (see attached reprints):

1. Synthesis, Characterization and Reactivity of an N-Heterocyclic Germanium(II) Hydride: Reversible Hydrogermylation of a Phosphalkyne, S.L. Choong, W.D. Woodul, C. Schenk, A. Stasch, A.F. Richards and C. Jones, *Organometallics*, **2011**, 30, 5543-5550.
2. A Digermene with a Ge-Ge Single Bond that Activates Dihydrogen in the Solid State, J. Li, C. Schenk, C. Goedecke, G. Frenking and C. Jones, *J. Am. Chem. Soc.*, **2011**, 133, 18622-18625.
3. Contrasting Reductions of Group 14 Metal(II) Chloride Complexes: Synthesis of the First β -Diketiminato Tin(I) Dimer, S.L. Choong, C. Schenk, A. Stasch, D. Dange and C. Jones, *Chem. Commun.*, **2012**, 48, 2504-2506.
4. Low-Coordinate Iron(I) and Manganese(I) Dimers: Kinetic Stabilization of an Exceptionally Short Fe-Fe Multiple Bond, L. Fohlmeister, S. Liu, C. Schulten, B. Moubaraki, A. Stasch, J.D. Cashion, K.S. Murray, L. Gagliardi and C. Jones, *Angew. Chem. Int. Ed.*, **2012**, 51, 8294-8298.

5. The Facile Reduction of CO₂ to CO with an Amido-Digermine, J. Li, M. Hermann, G. Frenking, C. Jones, *Angew. Chem. Int. Ed.*, **2012**, 51, 8611-8614.
6. Monomeric Group 13 Metal(I) Amides: Enforcing One-Coordination Through Extreme Ligand Steric Bulk, D. Dange, J. Li, C. Schenk, H. Schnöckel and C. Jones, *Inorg. Chem.*, **2012**, 51, 13050-13059.
7. Utilizing Steric Bulk to Stabilize Molybdenum Aminogermine and Aminogermine Complexes, J. Hicks, T.J. Hadlington, C. Schenk, J. Li and C. Jones, *Organometallics*, **2013**, 32, 323-329.
8. Synthesis and crystal structures of two bulky bis(amido)germylenes, E.W.Y. Wong, T.J. Hadlington and C. Jones, *Main Group Met. Chem.*, **2013**, in press, DOI: 10.1515/mgmc-2013-0015.
9. Extremely Bulky Amido and Amidinato Complexes of Boron and Aluminium Halides: Synthesis and Reduction Studies, E.W.Y. Wong, D. Dange, L. Fohlmeister, T.J. Hadlington, C. Jones, *Aust. J. Chem.*, **2013**, in press, DOI: 10.1071/CH13175.

The following paper has been submitted for publication:

10. Activation of H₂ by a Multiply Bonded Amido-Digermine, L[†]GeGeL[†]: Evidence for the Formation of a Hydrido-Germine, :Ge(H)(L[†]), T.J. Hadlington, M. Hermann, J. Li, G. Frenking and C. Jones, *Angew. Chem. Int. Ed.*, submitted.

(b) Invited conference and institution presentations

1. "Molecular Magnesium(I) Compounds: "Bespoke" Reducing Agents for the Synthetic Chemist", Department of Chemistry, Würzburg University, Germany, October, 2011.
2. "Molecular Magnesium(I) Compounds: "Bespoke" Reducing Agents for the Synthetic Chemist", Department of Chemistry, Marburg University, Germany, October, 2011.
3. "Molecular Magnesium(I) Compounds: "Bespoke" Reducing Agents for the Synthetic Chemist", Department of Chemistry, Heidelberg University, Germany, October, 2011.
4. "Modern Main Group Chemistry: From Fundamental Advances to Functional Molecules" RACI Burrows Award Lecture, IC11, University of Western Australia, December, 2011.
5. "Molecular Magnesium(I) Compounds: "Bespoke" Reducing Agents for the Synthetic Chemist", Invited Plenary Lecture, RSC Dalton Division Joint Interest Group Conference, Warwick University, April, 2012.
6. "Accessing the Inaccessible: Magnesium(I) Compounds as Specialist Reducing Agents for the Synthetic Chemist", Invited Plenary Lecture, IRIS13, Victoria, British Columbia, Canada, August, 2012.

7. "Accessing the Inaccessible: Magnesium(I) Compounds as Specialist Reducing Agents for the Synthetic Chemist", Chemistry Department, University of Alberta, Edmonton, Canada, August, 2012.
8. "Accessing the Inaccessible: Magnesium(I) Compounds as Specialist Reducing Agents for the Synthetic Chemist", Chemistry Department, University of Calgary, Canada, August, 2012.
9. "Accessing the Inaccessible: Magnesium(I) Compounds as Specialist Reducing Agents for the Organometallic Chemist", Invited Keynote Lecture, ICOMC, Lisbon, Portugal, September, 2012.
10. "Accessing the Inaccessible: Magnesium(I) Compounds as Specialist Reducing Agents for the Organometallic Chemist", Invited Plenary Lecture, RSC Main Group Interest Group Meeting, London, UK, September, 2012.

(c) Collaborations resulting from this work

1. **Professor Hansgeorg Schnöckel** (Karlsruhe Institute of Technology, Germany): Main group metal clusters; group 13 metal(I) and magnesium(I) halides.
2. **Professor Gernot Frenking** (Marburg University, Germany): Computational chemistry and its application to the understanding of the unusual structure and bonding in low oxidation state main group complexes.