



The Transition Metal-Like Reactivity of Low Oxidation State s- and p-Block Compounds.

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**10/20/2017
Final Report**

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14. ABSTRACT This was a very successful project that achieved its goal to develop a series of unprecedented two- and three-coordinate magnesium(II) complexes, stabilized by extremely bulky amide ligands. These compounds were used as reagents for catalytic transformation of small molecules. The PI was able to publish 19 papers in international journals and 33 international conference lectures.					
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Summary: This project aimed to develop and stabilize novel, very low oxidation state s- and p-block compounds. While these are highly topical from a fundamental perspective, their high reactivity was to be harnessed for their use as sustainable reagents for the "transition metal-like" stoichiometric and catalytic transformation of small molecules. The project was extremely successful and all of the originally stated goals were achieved. It led to the publication of 19 papers in high profile international journals, including a review in *Nature Reviews Chemistry* which summarizes a good deal of the AOARD funded work. Furthermore, the results of this project were presented at 33 invited institutional or international conference lectures, including a number of Plenary and Keynote presentations. Highlights of the results achieved include:

- (i) the development of a series of unprecedented two- and three-coordinate magnesium(I) complexes, stabilized by extremely bulky amide ligands;
- (ii) these have been applied to the reductive transformation/E-X bond activation of alkenes, dihydrogen, AlH_3 , CO, esters etc., leading to value added products, e.g. the Fischer-Tropsch like conversion of CO to alcohols, the first examples of s-block acyl compounds, and the first example of a compound that undergoes facile and reversible oxidative addition/reductive elimination processes at room temperature, involving a magnesium(I) dimer;
- (iii) Mg^{I} dimers have been utilized as "bespoke" reducing agents to prepare the first Zn-Mg, mixed valence linear Zn_3 , and Zn-Ge^{II} bonded compounds, the latter of which efficiently activates H_2 and other E-H bonded compounds at sub-ambient temperatures;
- (iv) a range of new hydrido tetrylenes ($:\text{E}^{\text{II}}(\text{L})(\text{H})$; E = Ge or Sn, L = bulky amide) have been developed;
- (v) these have been applied as unprecedentedly active reagents for the hydrometallation of unactivated alkenes;
- (vi) similarly, the sometimes reversible activation of a variety of unsaturated small molecules by a project developed digermene, $\text{LGe}=\text{GeL}$, has been achieved;
- (vii) the first use of a low oxidation state main group complex as a catalyst for the highly efficient (more than for any transition metal complex) reduction of carbon dioxide to methanol equivalents.
- (viii) a series of related, and previously inaccessible, low oxidation state compounds, e.g. the first 2-coordinate acyclic diamino silylenes, boryl group 13 metallylenes, (boryl)M: (M = Al or Ga), amido distibenes, $\text{LSb}^{\text{I}}=\text{Sb}^{\text{I}}\text{L}$ and LCo^{I} , have been kinetically stabilized by project developed bulky ligands.

The results of this study have been at the very cutting edge of main group chemistry, and represent significant advances to the field.

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. Our group is internationally leading in this area, and in 2007, we described the first compounds containing magnesium in the +1 oxidation state.¹ Since that time, the further chemistry of these highly reactive systems, and a variety of other low oxidation p-block systems, has been explored under funding from the USAF AOARD. The current project sought to capitalize on the fundamental gains made under those past projects, by systematically investigating the application of low oxidation state magnesium compounds to the activation of small molecules; and the use of low oxidation state p-block compounds as effective catalysts, and stoichiometric reagents for processes previously only viable with expensive and toxic noble d-block metal complexes.² Both areas ultimately led to new routes for the conversion of abundant and cheap starting materials to "value added" chemical products, and lie within the broader realm of sustainable chemical synthesis. The originally state goals of this project were:

- the preparation of a second generation of "text book" low oxidation state magnesium complexes and clusters, the properties of which will be readily tailored to specific reactivity requirements
- the development of Mg-Mg bonded compounds as cheap, non-toxic alternatives to low valent f- and early d-block metal systems (e.g. U^{III} and Sm^{II}) for the reductive activation of small molecules (e.g. H₂, CO₂, CO, N₂, C₂H₄ and mixtures thereof).
- the development of low oxidation state group 14 compounds as replacements for expensive and toxic late transition metal complexes in catalytic processes involving the addition of E-H bonds (E = H, B, Si, P etc.) to unsaturated substrates.
- and, the acquirement of a thorough fundamental understanding of the mechanisms of the above mentioned, unprecedented reaction types using an battery of experimental and computational techniques

Results and Discussion: The project has been extremely successful and all of the originally stated goals were fulfilled. Highlight achievements are mentioned below.

(i) Development of the first two-coordinate Mg^I dimers. To date, all Mg^I dimers developed are three- or higher coordinate, and have required the incorporation of bulky N,N'-chelating ligands for the purpose of kinetic stabilization.³ Indeed, theoretical studies have suggested that two-coordinate Mg^I dimers are incapable of ambient existence.⁴ This view has been dispelled in this study with the use of extremely bulky amide ligands, developed in this project, for the stabilization of a series of linear, two-coordinate Mg^I dimers, **1** (Figure 1).⁵ While very thermally stable, the low-coordinate nature of these compounds makes them significantly more reactive than their 3-coordinate counterparts. This has been manifested by the fact that the compounds have been shown to activate H₂ (at 40 atm.), and to cleanly and selectively activate strong C-F bonds of perfluoroarenes, e.g. C₆F₆, C₆H₄F₂ etc (unpublished results). The synthetic possibilities of these results are wide, and will explored post-project.

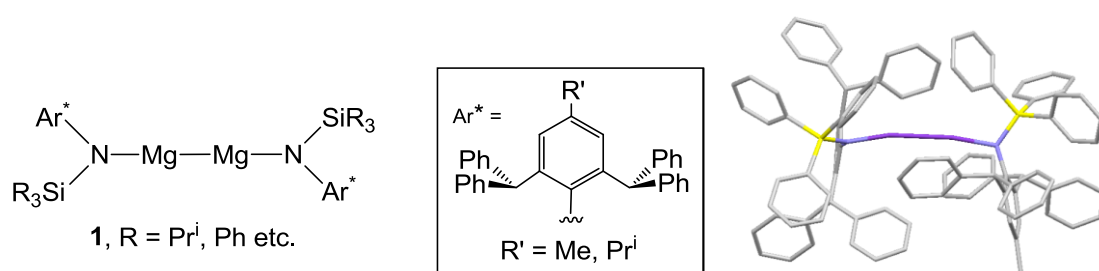
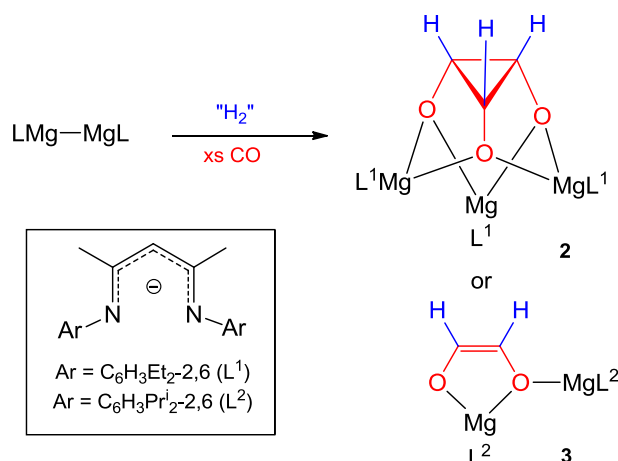


Figure 1. Two-coordinate Mg^{I} dimers

(ii) Three-coordinate Mg^{I} dimers (and related compounds) as powerful reagents for reductive transformations.

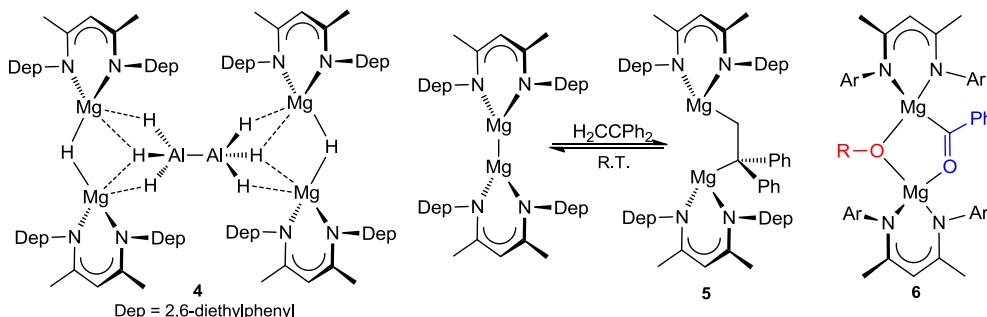
One of the most ambitious of the originally proposed goals was to utilize Mg^{I} dimers for the transformation of commodity gasses to value added products. In one of the highest profile results of the study, this has been achieved by the sequential reaction of β -diketiminato coordinated Mg^{I} dimers with a source of H_2 (i.e. 1,3-cyclohexadiene), then CO to give an enolate complex **2**, or an unprecedented cyclopropane-triolate complex **3**, depending on the bulk of the β -diketiminato ligand (Scheme 1).⁶ These complexes can be quenched to give the corresponding alcohols, and the chemistry represents the first Fischer-Tropsch like reactivity for a main group compound. It will be further developed post-project, especially with a view to using **1** as more reactive species for such transformations, perhaps even in catalytic regimes.



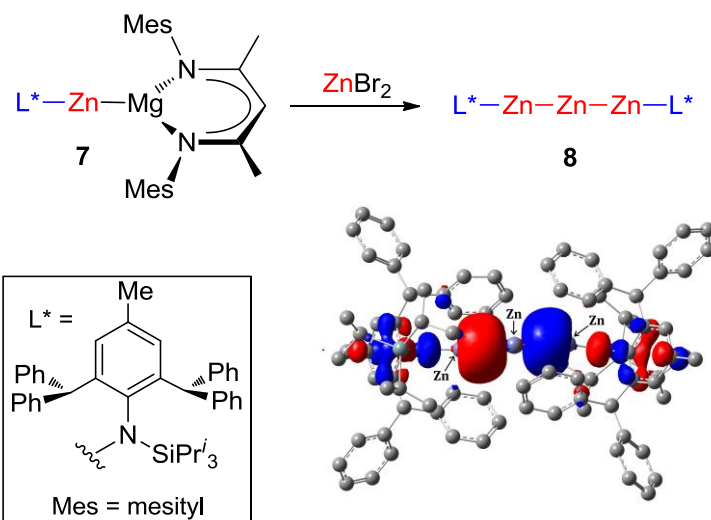
Scheme 1. Fischer-Tropsch like reactivity of Mg^{I} dimers.

In an extension to this remarkable Fischer/Tropsch like reactivity, the versatility of Mg^{I} dimers as "bespoke" reducing agents was further demonstrated. For example, their reaction with aluminum hydride complexes led to the first example of a binary, low oxidation state aluminum hydride species, **4**, that is stable at ambient temperature.⁷ The unprecedented $[\text{Al}_2\text{H}_6]^{2-}$ anion in **4** is a valence isoelectronic analogue of ethylene, and holds significant potential for the study of Al/Mg metallic mixtures as hydride storage materials. In an example of reactivity towards unsaturated small molecules, Mg^{I} dimers have been shown to cleanly undergo a 1,2-addition to alkenes, to give, for example, **5**. Such reactivity is unprecedented for s-block compounds and remarkably, these addition reactions were shown to be reversible at room temperature.⁸ Thus, compound **5** represents the first example of a system that undergoes a facile and reversible oxidative addition/reductive elimination processes at room temperature, involving a magnesium(I) dimer. This gives hope for the future use of magnesium(I) systems in oxidative

addition/reductive elimination based processes. Another interesting result involved the use of magnesium(I) dimers for the facile two-electron reductive cleavage of a variety of esters to give the first examples of s-block acyl compounds, **6**.⁹ These hold significant synthetic potential as "umpolung" sources of nucleophilic anionic acyl fragments in organic protocols.

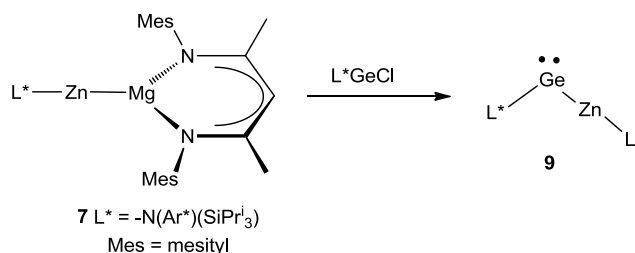


Given how valuable Mg^I dimers have proven as "bespoke" reducing agents in both organic and inorganic syntheses,³ we have further explored their utility in the formation of novel metal-metal bonded compounds. In this respect, the reduction of group 12 metal halide complexes, incorporating project developed mono-dentate amides, with Mg^I complexes, has given the first examples of two-coordinate amido-metal(I) dimers, L^*MML^* ($M = Zn, Cd$ or Hg). The first compounds possessing unsupported $Zn-Mg$ bonds, e.g. **7**, and the first linear two-coordinate mixed valence tri-zinc complex, **8** (Scheme 2).¹⁰ The latter compound type was predicted by a prior theoretical study to not exist at room temperature. The publication describing this work was highlighted in *Nature Chemistry*.¹¹



Scheme 2. Zinc(0) and mixed valence zinc (0/+1) compounds stabilized by extremely bulky monodentate amide ligands.

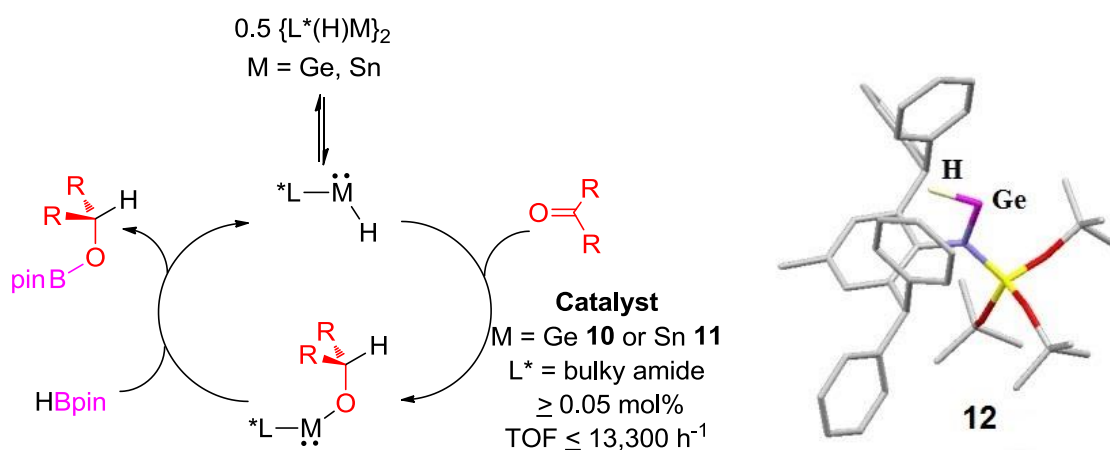
In chemistry related to Mg^I reactivity, the $Mg-Zn$ bonded complex **7**, acts as an "inorganic Grignard reagent" in its reaction with an amido-germanium(II) halide. The remarkable product, **9**, is the first example of a compound bearing a $Zn-Ge^{II}$ bond (Scheme 3).¹² It is essentially a rare example of a metallogermylene, which DFT studies (collaboration with Frenking, Marburg) show has an extremely narrow HOMO-LUMO gap. This is the source of its high reactivity (see below).



Scheme 3. Synthesis of a highly reactive zinca-germylene

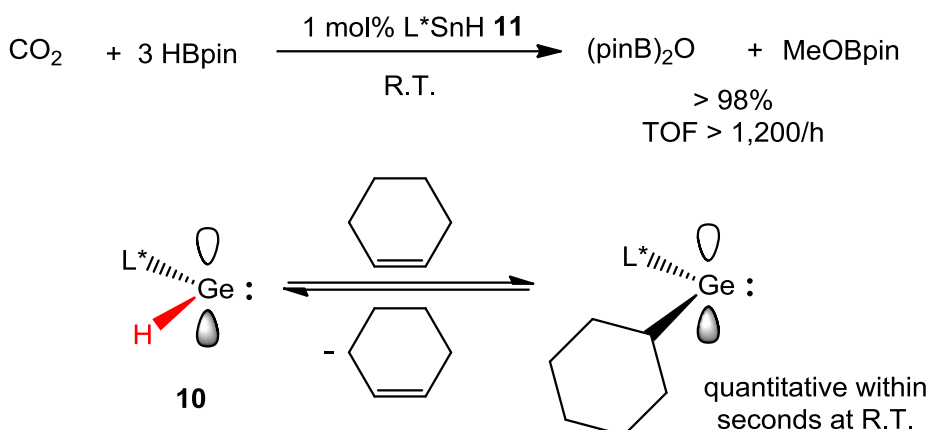
(iii) *The stabilization and catalytic/stoichiometric reactivity of low oxidation state group 14 complexes toward small molecules.* As part of the USAF/AOARD funded study (FA2386-11-1-4110) that preceded this work, the first examples of monomeric, two-coordinate hydrido tetrylenes, $:E(L)(H)$ ($E = Ge$ or Sn), were shown to exist in equilibrium in solution with dihydrido-ditetrelenes, $(L)(H)EE(L)(H)$.¹³ Considering that $:E(L)(H)$, are extremely electron deficient, having 6-valence electrons, and an empty p-orbital, it was proposed that they would be highly active towards the hydrometallation of a range of unsaturated substrates (*cf.* boranes and transition metal (TM) hydrides), including carbonyl compounds, unactivated alkenes etc. This has been amply demonstrated in the project.

For example, compounds **10** and **11** (*cf.* **12** also prepared in this project¹⁴) have been demonstrated as the first low oxidation state main group compounds to act as catalysts in organic transformations. That is, they have been utilized in loadings of as low as 0.05 mol% for the quantitative catalytic hydroboration of aldehydes and ketones with turn over numbers that can exceed 13,000/hr (Scheme 4).¹⁵ This activity rivals that for all TM based catalysts used for such transformations.



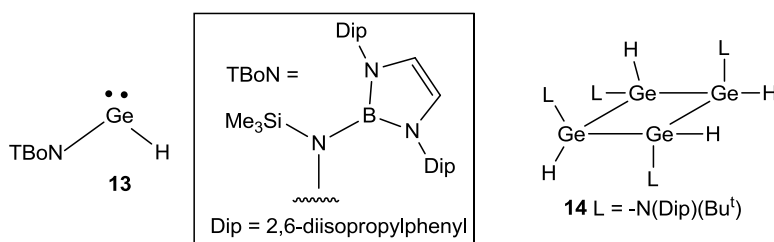
Scheme 4. Efficient hydroboration of carbonyl compounds catalyzed by hydridotetrylenes, and the monomeric, two-coordinate Ge^{II} hydride complex, **12**.

More recently, the high activity of **10** and **11** toward small molecule activation has been further developed. For example, the compounds have been revealed as the most efficient main group catalysts employed for the reduction of the greenhouse gas CO_2 to a methanol equivalent (e.g. Scheme 5),¹⁶ and the most active group 14 metal hydrides used for the, sometimes reversible, hydrometallation of unactivated alkenes (e.g. Scheme 4).¹⁷ All of these results highlight the potential such systems have for replacing TM based reagents in organic synthetic transformations.



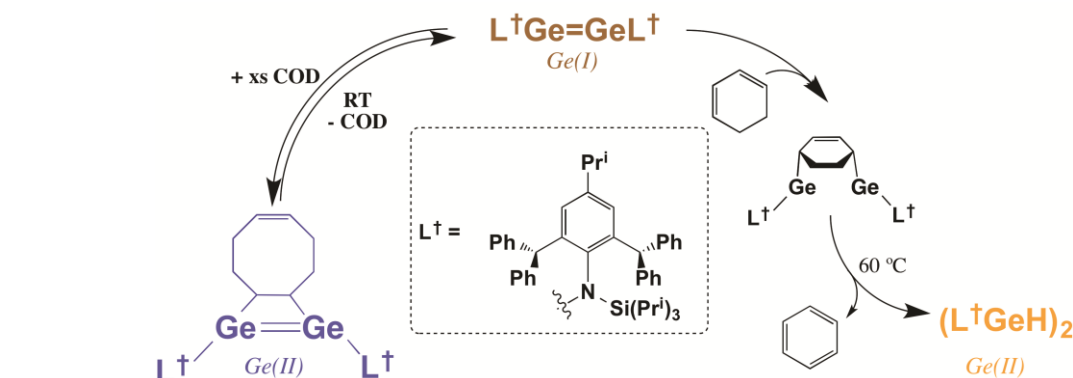
Scheme 5. The catalytic reduction of CO₂ to a methanol equivalent, and the facile hydrogermylation of cyclohexene, using **10** or **11**.

A range of other :E(L)(H) systems have been prepared, and their reactivity found to be readily controlled by altering the electronics and steric bulk of the amide ligand, e.g. as in the boryl substituted system, **13**. Similarly, novel higher nuclearity systems, e.g. **14**, can be prepared when smaller amide ligands are employed (unpublished results). The stoichiometric and catalytic reactivity of all of these systems towards unsaturated substrates will continue to be explored post-project.



A related and remarkable study has looked at the reactivity of the Zn-Ge bonded compound, **7**, towards E-H bonds. This was found to oxidatively add H-H, N-H, B-H, Si-H bonds quantitatively to the Ge^{II} centre of the compound.¹² Such single site reactivity is scarce for group 14 compounds, and results from the aforementioned extremely narrow HOMO-LUMO gap in **7**.

Another important result that has come from this work is the use of digermynes, developed in prior AOARD funded studies, as reagents for the facile reduction, C-H activation and reversible cycloaddition of a variety of alkenes, alkynes etc.¹⁸ In some cases these processes have, for the first time, been shown to be reversible at room temperature (for example, see Scheme 6). The facile transfer hydrogenation of digermynes was also demonstrated.



Scheme 6. The reversible addition of 1,5-cyclooctadiene to an amido-digermyne, and its facile transfer hydrogenation.

(iv) *The stabilization of other very low oxidation state metal systems.* Considering the significant utility the extremely bulky amides, and other ligands, developed in this study hold for the stabilization of novel, low oxidation state Mg and group 14 metal compounds, it was decided to broaden their use to the stabilization of complexes containing metals from other groups of the periodic table.

This approach proved successful, and two examples which illustrate this can be found in Figure 2. Firstly, highly reactive low coordinate amido-cobalt(I) complexes, e.g. **15**, have been prepared and their further chemistry studied.¹⁹ Moreover, in collaboration with Prof. Simon Aldridge (Oxford University), the first amido-distibene, **16** (an antimony(I) compound), has been prepared by reduction of the antimony(III) precursor, LSbCl₂, using an anionic boron(I) heterocycle. The study also gave rise to the first boryl substituted dibismuthene, **17**.²⁰

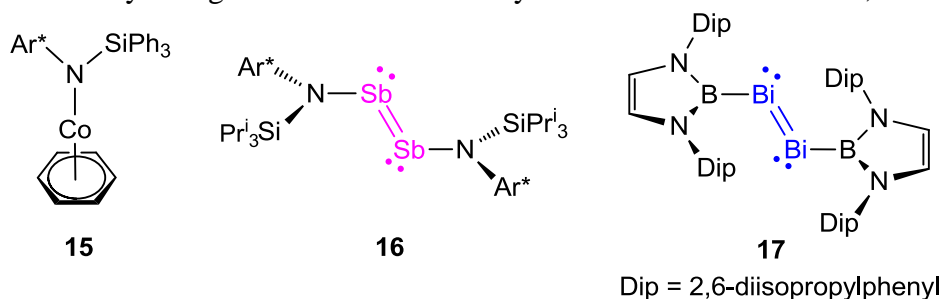


Figure 2. Metal(I) complexes stabilized by bulky amide or boryl ligands.

Other successes from this phase of the study can be found below. That is, the only example of an acyclic two-coordinate diamino silylene, **18**, has been developed (Figure 3) and its reactivity towards O₂ and C-H activation explored.²¹ Interestingly, Sn, Ge and Pb analogues of this compound were reported as long ago as 1974, while the first carbene analogue was described in 1996. Such compounds have been "holy grails" of silicon chemists for decades. That work was carried out in collaboration with Aldridge, Oxford, as was the use of a bulky and highly nucleophilic boryl ligand in the stabilisation of the first examples of boryl group 13 metallocenes, **19** and **20**, which were isolated as iron carbonyl complexes.²² Finally the preparation of the first example of a two-coordinate Zn hydride, **21**, has been achieved, and it has been shown to be active as a catalyst for the hydroboration of carbonyl compounds.²³

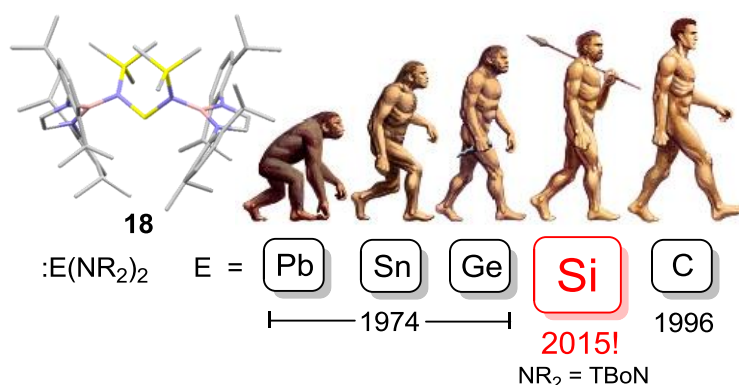
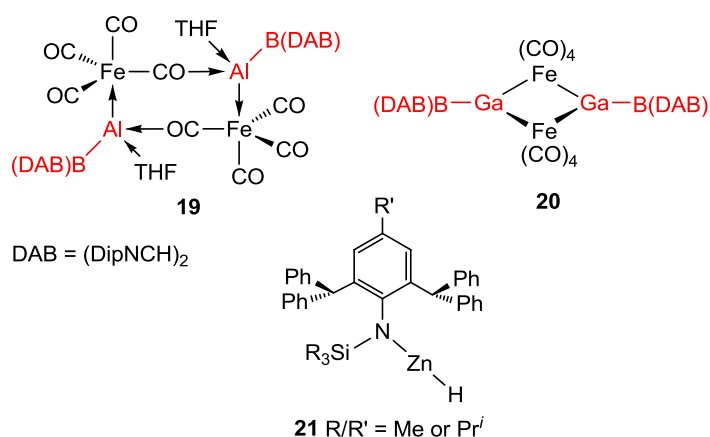


Figure 3. The first diaminosilylene



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List of Publications and Significant Collaborations that resulted from your AOARD supported project (see attachments):

a) papers published in, or submitted to, peer-reviewed journals

1. Low Coordinate Germanium(II) and Tin(II) Hydride Complexes: Efficient Catalysts for the Hydroboration of Carbonyl Compounds, T.J. Hadlington, M. Hermann, G. Frenking, C. Jones, *J. Am. Chem. Soc.*, **2014**, 136, 3028-3031.
2. Two-Coordinate Hydrido-Germylenes, T.J. Hadlington, B. Schwarze, E.I. Izgorodina, C. Jones, *Chem. Commun.*, **2015**, 51, 6854-6857.
3. Utilisation of a Lithium Boryl as a Reducing Agent in Low Oxidation State Group 15 Chemistry: Synthesis and Characterisation of an Amido-Distibene and a Boryl-Dibismuthene, D. Dange, A. Davey, J.A.B. Abdalla, S. Aldridge, C. Jones, *Chem. Commun.*, **2015**, 51, 7128-7131.
4. Low Coordinate Cobalt(I) Complexes Stabilised by an Extremely Bulky Amide Ligand, J. Hicks, C. Jones, *Organometallics*, **2015**, 34, 2118-2121.
5. The Reactivity of Amido-Digermynes, LGeGeL (L = Bulky Amide), Towards Olefins and Related Molecules: Facile Reduction, C-H Activation and Reversible Cycloaddition of Unsaturated Substrates, T.J. Hadlington, J. Li, M. Hermann, A. Davey, G. Frenking, C. Jones, *Organometallics*, **2015**, 34, 3175-3185.
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9. Stabilization of a Two-Coordinate, Acyclic Diaminosilylene (ADASi): The Missing Link in the :E(NR₂)₂ Series (E = Group 14 Element), T.J. Hadlington, J.A.B. Abdalla, R. Tirfoin, S. Aldridge, C. Jones, *Chem. Commun.*, **2016**, 52, 1717-1720.
10. Two-Coordinate Magnesium(I) Dimers Stabilized by Super Bulky Amido Ligands, A. J. Boutland, D. Dange, A. Stasch, L. Maron, C. Jones, *Angew. Chem. Int. Ed.*, **2016**, 55, 9239-9243.
11. Two-Coordinate Terminal Zinc Hydride Complexes: Synthesis, Structure and Preliminary Reactivity Studies, M. J. C. Dawkins, E. Middleton, C. E. Kefalidis, D. Dange, M. M. Juckel, L. Maron, C. Jones, *Chem. Commun.*, **2016**, 52, 10490-10492. N.B. All acknowledgements, including to AOARD were omitted in the editorial stage of this publication. It was too late to fix this error of the journal when it was noticed by the authors.
12. Synthesis, Characterisation and Computational Analysis of the Dialanate Dianion, [H₃Al–AlH₃]²⁻: A Valence Isoelectronic Analogue of Ethane, S.J. Bonyhady, N. Holzmann, G. Frenking, A. Stasch, C. Jones, *Angew. Chem. Int. Ed.* **2017**, 56, 8527-8531.
13. Boryl Substituted Group 13 Metallylenes: Complexes with an Iron Carbonyl Fragment, D. Dange, C.P. Sindlinger, S. Aldridge, C. Jones, *Chem. Commun.*, **2017**, 53, 149-152.
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17. An Acyclic Zincagermylene: Rapid Activation of Dihydrogen at Sub-Ambient Temperature, M. M. Juckel, L. Zhao, J. Hicks, G. Frenking, C. Jones, *Chem. Commun.*, **2017**, in press.
18. Reversible Oxidative insertion of a C=C Bond into Magnesium(I) Dimers: Generation of Highly Active 1,2-Dimagnesioethane Compounds, A.J. Boutland, A. Carroll, C.A. Lamsfus, A. Stasch, L. Maron, C. Jones, *J. Am. Chem. Soc.*, **2017**, submitted.

19. Dimeric Magnesium(I) β -Diketiminates: A New Class of Quasi-Universal Reducing Agent, C. Jones, *Nature Rev. Chem.*, 2017, **1**, 0059. Review article covering partially AOARD funded work, and acknowledging AOARD.

b) conference and institution presentations

1. "The Stabilization and Transition Metal-Like Reactivity of Low Oxidation State Group 14 Metal Complexes", Invited Lecture, International Conference on Coordination Chemistry, Singapore, July, 2014.
2. "New Routes to Low Oxidation State Si/Ge/Sn Compounds: Useful Reagents for Chemical Synthesis". Invited Lecture 17th International Symposium on Silicon Chemistry, Berlin, August, 2014.
3. "Super Bulky Amides: New Ligands for the Stabilisation of Low-Valent Main Group Complexes", RSC Frankland Award Lecture, Mike Lappert Memorial Symposium, Burlington House, London, April, 2015.
4. "Super Bulky Amides: New Ligands for the Stabilisation of Low-Valent Main Group Complexes", RSC Frankland Award Lecture, Edinburgh University, April, 2015.
5. "Super Bulky Amides: New Ligands for the Stabilisation of Low-Valent Main Group Complexes", RSC Frankland Award Lecture, University of Sussex, April, 2015.
6. "Super Bulky Amides: New Ligands for the Stabilisation of Low-Valent Main Group Complexes", RSC Frankland Award Lecture, Nottingham University, April, 2015.
7. "Super Bulky Amides: New Ligands for the Stabilisation of Low-Valent Main Group Complexes", Invited Keynote Lecture, IRIS-14 conference, Regensburg, Germany, July, 2015.
8. "Super Bulky Amides: New Ligands for the Stabilisation of Low-Valent Main Group Complexes", Chinese University of Hong Kong, Hong Kong, October, 2015.
9. "New Routes to Low Oxidation State Silicon Compounds: Useful Reagents for Chemical Synthesis". Invited Keynote Lecture, ASIS-5 conference, Jeju, South Korea, October, 2015.
10. "The Stabilization and Transition Metal-Like Reactivity of Low Oxidation State/Low Coordination Number p-Block Complexes", Invited Session Lecture, Pacifichem, Honolulu, USA, December 2015.
11. "Magnesium(I) Compounds: Bespoke Reagents for the Synthesis of Low-Coordinate Metal-Metal Bonded Complexes", Invited Session Lecture, Pacifichem, Honolulu, USA, December 2015.

12. "The Stabilization and Transition Metal-Like Reactivity of Low Oxidation State/Low Coordination Number s- and p-Block Complexes", Invited Session Lecture, Cotton Award Symposium in Honour of Francois Gabbai, ACS National Meeting, San Diego, USA, March 2016.
13. "The Stabilization and Transition Metal-Like Reactivity of Low Oxidation State/Low Coordination Number s- and p-Block Complexes", Invited Lecture, 2nd International Small Molecule Activation Conference, Cancun, Mexico, May 2016.
14. "The Stabilization and Transition Metal-Like Reactivity of Low Oxidation State/Low Coordination Number Group 14 Complexes", Invited Lecture, ICOMC, Melbourne, July, 2016.
15. "The Stabilization and Transition Metal-Like Reactivity of Low Oxidation State/Low Coordination Main Group Complexes", RSC Australasian Lectureship, University of Melbourne, August, 2016.
16. "The Stabilization and Transition Metal-Like Reactivity of Low Oxidation State/Low Coordination Group 14 Complexes", Invited Plenary Lecture, International Conference on Germanium, Tin and Lead, Pardubice, Czech Republic, August, 2016.
17. "The Stabilization and Transition Metal-Like Reactivity of Low Oxidation State/Low Coordination Main Group Complexes", ETH, Zurich, Switzerland, September, 2016.
18. "The Stabilization and Transition Metal-Like Reactivity of Low Oxidation State/Low Coordination Main Group Complexes", Oxford University, UK, September, 2016.
19. "The Stabilization and Transition Metal-Like Reactivity of Low Oxidation State/Low Coordination Main Group Complexes", RSC Australasian Lectureship, University of Tasmania, October, 2016.
20. "The Stabilization and Transition Metal-Like Reactivity of Low Oxidation State/Low Coordination Main Group Complexes", RSC Australasian Lectureship, University of Auckland, NZ, December, 2016.
21. "The Stabilization and Transition Metal-Like Reactivity of Low Oxidation State/Low Coordination Main Group Complexes", RSC Australasian Lectureship, Victoria University, Wellington, NZ, December, 2016.
22. "The Stabilization and Transition Metal-Like Reactivity of Low Oxidation State/Low Coordination Main Group Complexes", RSC Australasian Lectureship, Canterbury University, Christchurch, NZ, December, 2016.

23. "The Stabilization and Transition Metal-Like Reactivity of Low Oxidation State/Low Coordination Main Group Complexes", RSC Australasian Lectureship, Otago University, Dunedin, NZ, December, 2016.
24. "The Stabilization and Transition Metal-Like Reactivity of Low Oxidation State/Low Coordination Main Group Complexes", RSC Australasian Lectureship, Macquarie University, Sydney, March, 2017.
25. "The Stabilization and Transition Metal-Like Reactivity of Low Oxidation State/Low Coordination Main Group Complexes", RSC Australasian Lectureship, Curtin University, Perth, March, 2017.
26. "The Stabilization and Transition Metal-Like Reactivity of Low Oxidation State/Low Coordination Main Group Complexes", RSC Australasian Lectureship, University of Western Australia, Perth, March, 2017.
27. "The Stabilization and Transition Metal-Like Reactivity of Low Oxidation State/Low Coordination Main Group Complexes", RSC Australasian Lectureship, Griffith University, Gold Coast, March, 2017.
28. "The Stabilization and Transition Metal-Like Reactivity of Low Oxidation State/Low Coordination Main Group Complexes", RSC Australasian Lectureship, University of Adelaide, March, 2017.
29. "Super Bulky Amides: New Ligands for the Stabilisation of Synthetically Applicable Low-Valent Main Group Complexes", Plenary Lecture, RSC ISACS: Challenges in Inorganic Chemistry, Conference, University of Manchester, April, 2017.
30. "Super Bulky Amides: New Ligands for the Stabilisation of Synthetically Applicable Low-Valent Main Group Complexes" Acceptance lecture for the RL Martin Distinguished Chair in Chemistry, Monash University, April, 2017.
31. "Modern Main Group Chemistry: From Fundamental Advances to Functional Molecules" Acceptance lecture for Fellowship of the Australian Academy of Science, Shine Dome, ANU, Canberra, May, 2017.

32. "Super Bulky Amides: New Ligands for the Stabilisation of Synthetically Applicable Low-Valent Main Group Complexes", Plenary Lecture, ICHAC-12 Conference, University of British Columbia, Vancouver, Canada, June, 2017.
33. "Modern Main Group Chemistry: From Fundamental Advances to Functional Molecules" invited lecture for the Victorian division of the Australian Academy of Science, University of Melbourne, July, 2017.

c) provide a list any interactions with industry or with Air Force Research Laboratory scientists or significant collaborations that resulted from this work.

The whole period of the project involved on-going collaborations with Prof. Gernot Frenking (Marburg University, Germany), Prof. Simon Aldridge (Oxford University, UK), and Prof. Laurent Maron (Toulouse University, France). All collaborations are greatly beneficial to the project, and all resulted in publications.